

TECHNICAL NOTE

Date: 2019-09-19

SSM registration number: 2019-2484

Activity number: 3030016-01

**Review of SKB:s
Supplementary
Information on copper
canister integrity issues**

Authors: P. Szakálos^{a,b} and C. Leygraf^b

a) Szakálos Materials Science AB

b) Royal Institute of Technology, KTH

Contents

Introduction	3
1. Discussion and conclusions concerning the five corrosions issues pointed out by The Land and Environmental Court	4
2. Salt enrichment in the deposition holes, the Sauna effect	6
2.1. Short summary	6
2.2. The Sauna effect- introduction	6
2.3. Background data and information taken from different SKB-reports	7
2.4. SKB reports concerning the Sauna effect	10
2.4.1. Detailed comments on TR-15-09 and TR-17-07, concerning tests 1-9 of the Sauna effect.....	11
2.5. Detailed analysis and consequences of salt enrichment in a Forsmark repository (Sauna effect)	14
3. Stress corrosion cracking and hydrogen embrittlement in unalloyed copper (CuOFP)	16
3.1. Short summary	16
3.2. Introduction SCC and HE	17
3.3. Slow strain rate testing of copper performed at Japan Atomic Energy Agency (JAEA).....	17
3.4. Slow strain rate testing of copper at Studsvik AB	18
3.4.1. Hydrogen measurement on SSRT-exposed samples.....	22
3.5. Hydrogen charging of bulk metal and welds due to copper corrosion	23
3.6. Hydrogen and hydroxide uptake of canister copper exposed 7 years in SKB prototype repository in the Äspö Hard rock laboratory.	25
3.7. Precracked CT-specimens under constant load exposed in sulphide containing groundwater at room temperature	27
3.8. Retrieval and post-test examination of packages 4 and 5 of the MiniCan field experiment.	28
3.9. A study of hydrogen effects on creep ductility.....	29
3.10. Microbial influence on corrosion of copper in the repository environment, Aalto University.....	30
3.11. Discussion and conclusions regarding SCC and hydrogen embrittlement (HE) and hydrogen sickness (HS) of unalloyed copper (CuOFP) in a deep repository environment.....	30
4. General corrosion and pitting corrosion	33
4.1. Short summary	33
4.2. General- and pitting corrosion- introduction	33
4.3. General copper corrosion in pure oxygen gas free water	34
4.4. Increased general copper corrosion in contact with bentonite....	36
4.5. Microbial induced “corrosion” degradation of the bentonite buffer	37
4.6. Pitting corrosion in the repository environment	39
4.6.1. FEBEX, 18-year long term study in a repository environment.	39
4.6.2. A 15-year exposure in pure anoxic water and observed pitting corrosion in the SKB-project Alternative Buffer Material (ABM).....	41
4.6.3. Pitting corrosion of copper in anoxic groundwater environment in the presence and absence of sulphate reducing bacteria (SRB)	42

4.7. Discussion regarding pitting corrosion in a repository environment	43
5. The effect of radioactive radiation.	43
5.1. Summary.....	43
5.2. More detailed report.....	44
5.2.1. The difference between separate and combined effects of radiation and water exposure	44
5.2.2. High-energy synchrotron x-ray diffraction (HEXRD)	45
5.2.3. Discussion.....	47
6. Summary	48
7. References.....	50
APPENDIX 1	54

Introduction

The Land and Environmental Court in Nacka, Sweden, announced January 23, 2018, that:

The Swedish method for long-term storage of the Swedish nuclear waste (KBS-3) is permissible if:

1. Svensk Kärnbränslehantering AB (SKB) produces evidence that the repository in the long-term will meet the requirements of the Environmental Code, despite remaining uncertainties regarding how the protective capability of the canister may be affected by:

- a.** Corrosion due to reaction in oxygen-free water
- b.** Pitting corrosion due to reaction with sulphides, including the so-called sauna effect on pitting corrosion
- c.** Stress corrosion cracking due to reaction with sulphides, including the so-called sauna effect on stress corrosion cracking
- d.** Hydrogen embrittlement
- e.** Influence of radioactive radiation on pitting corrosion, stress corrosion cracking and hydrogen embrittlement.

2. The long-term responsibility for the final repository according to the Environmental Code has been clearly assigned.

SKB has submitted supplementary information and some few new studies on canister integrity issues, especially regarding copper corrosion as required by the Land and Environmental Court.

This technical report concerns the review of that material. With reference to the remaining uncertainties (a-e above) raised by the Environmental Code and addressed by SKB in the Supplementary Information this Technical Reports is divided into the following four Chapters.

2. Salt enrichment in the deposition holes, the Sauna effect (issues b and c)
3. Stress corrosion cracking & hydrogen embrittlement in unalloyed copper (c and d)
4. General corrosion and pitting corrosion (a and b)
5. The effect of radioactive radiation (e)

Additionally, condensed discussions and conclusions concerning the five corrosion issues pointed out by The Land and Environmental Court have been summarized in Chapter 1. More detailed information on these issues is presented in Chapters 2 o 5.

1. Discussion and conclusions concerning the five corrosion issues pointed out by The Land and Environmental Court

According to The Land and Environmental Court in Nacka, Sweden, SKB should produce evidence, i.e. supplementary information, showing that the repository in the long-term will meet the requirements of the Environmental Code, concerning the following issues:

- a. Corrosion due to reaction in oxygen-free water
- b. Pitting corrosion due to reaction with sulphides, including the so-called Sauna effect on pitting corrosion
- c. Stress corrosion cracking (SCC) due to reaction with sulphides, including the so-called Sauna effect on stress corrosion cracking
- d. Hydrogen embrittlement (HE)
- e. Influence of radioactive radiation on pitting corrosion, stress corrosion cracking and hydrogen embrittlement.

Issue (a). Corrosion in pure oxygen-free water is discussed in detail in section 4.3. It is concluded that copper corrosion by pure water has a much higher equilibrium hydrogen pressure than that of pure and dry Cu_2O since at least two more strictly anoxic corrosion products exist, CuOH and a hydrogen containing and somewhat distorted Cu_2O -crystal, see Figure 4.2. It is confirmed by Ab-initio calculations that the hydrogen equilibrium pressure is around 1 mbar for CuOH /Belonoshko A.B. and Rosengren A. 2012/. Since issue (a) also includes oxygen-free water corrosion in general it should be added that internal corrosion is found to take place as hydroxide formation (CuOH) inside the copper metal when exposed to anoxic ground water, as shown in section 3.6. This internal corrosion process with CuOH is also confirmed by Ab-initio calculations /Korzavyi P. and Sandström R. 2014/. SKB has not incorporated these anoxic corrosion processes in the safety analysis. In the Supplementary information it is discarded as negligible which is obviously not true, since the internal corrosion by hydroxide formation can penetrate the copper canister within some few hundred years, as shown in Figure 3.13.

Issue (b). Pitting corrosion due to reaction with sulphides are described in sections 4.6.1 (FEBEX-project, Switzerland), 4.6.2 (ABM-project, Sweden) and 4.6.3(VTT SRB-project, Finland). All three projects detected pitting corrosion on unalloyed copper in different anoxic environments containing various sulphide-concentrations. The natural groundwater sulphide content was used in both the Swiss FEBEX-project and the Swedish ABM-project, i.e. possibly up to 10^{-4}M . The Finnish VTT-project used synthetic ground water with sulphate which during anoxic conditions will be in equilibrium with sulphide, possibly up to 10^{-3}M . The important conclusion is that unalloyed SKB-copper is susceptible to pitting corrosion when exposed to repository conditions and that the sulphur/sulphide content and natural SRB content has a clear impact on the pitting corrosion rate. A pitting corrosion rate of $175\mu\text{m}$ was measured with the somewhat higher sulphur content and the presence of natural SRB, at only 12°C , in the Finnish project. Knowing that the Sauna effect with sulphur (and chloride) salt enrichment will be operating for more than 1000 years, see Chapter 2, it is obvious that several localised corrosion processes such as sulphide/SRB induced pitting corrosion will occur. SKB has made the conclusion in the Supplementary information that pitting corrosion “seems unlikely”, see section 4.7. This conclusion is obviously incorrect.

Issue (c) and (d). Stress corrosion cracking and hydrogen embrittlement. In reality, it is virtually impossible to distinguish between SCC and HE cracks in unalloyed copper when exposed to an anoxic environment containing hydrogen sulphide ions (HS⁻), such as in a deep repository environment. It is stated in the handbook entitled “Stress Corrosion Cracking Theory and Practice” /Raja V.S. and Shoji T. 2012/ that “SCC in some materials can involve generation and ingress of hydrogen at crack tips, and characteristics and mechanisms of SCC and HE have a lot in common.” With this scientific background it is logical to incorporate issue (c) and (d) together since these are entangled and not possibly to fully separate in the case of copper in a repository environment. SCC and HE in a repository environment are described in sections 3.1 to 3.11, in which section 3.5, 3.6 and 3.9 are more focused on HE, including hydrogen sickness (HS). SKB seems not to believe in the new compelling results from the latest years which are compiled in the mentioned sections concerning SCC and HE/HS. SKB tries to explain the extensive crack formation in these studies by “manufacturing defects” and that “SCC has questionable scientific support”, the latter speculation could have been correct with the limited scientific knowledge before 2008, but not anymore. In case of a Forsmark repository with the prevailing Sauna effect (salt enrichment), it can be concluded that these issues (c) and (d) will be responsible for all early canister failures, i.e. up to 40% already within 100-200 years as discussed in section 3.11. More specifically, failures due to HE a HS will dominate since these degradation processes operate without any applied load, in contrast to SCC.

Issue (e). Influence of radioactive radiation on pitting corrosion, stress corrosion cracking and hydrogen embrittlement. The effect of radiation is discussed in detail in Chapter 5. It can be concluded that SKB has not performed any study on;

- radiation and pitting corrosion
- radiation and stress corrosion cracking
- radiation and hydrogen embrittlement

in a relevant repository environment (groundwater) or any multi-combination of these issues.

This implies that the uncertainties remain regarding the influence of radioactive radiation on pitting corrosion, stress corrosion cracking and hydrogen embrittlement. SKB:s supplementary information as a response to the Swedish Ministry of Environment is consequently not complete. The Swedish Land and Environment Court statement published in early 2018, in which SKB’s plans were judged to be acceptable only if this additional information is provided, is therefore not fulfilled. To conclude, the basis for compliance to the environmental code is missing.

2. Salt enrichment in the deposition holes, the Sauna effect

2.1. Short summary

There are several SKB-reports concerning the Sauna -effect and the results are disappointing in several ways. Firstly, it is clear that it is impossible to inject water in the deposition holes without destroying the bentonite rings with cracking and piping. Secondly, water, as steam and moisture, will escape through the cracks and slots from the heated deposition holes and condensate in the colder tunnel above, thus accumulating sulphur and chloride salts in the holes. Thirdly, the salt enrichment which induces several severe corrosion processes on the unalloyed copper canister will continue until saturation/swelling is reached in the whole repository tunnel (fully flooded and pressurized). This insight is indicated in TR-17-15 /Sellin P. et al. 2017/, page 117, quote: *“The displacements (with cracks and channels) that take place are to a large part expected to be reversed by the late swelling of the other parts of the buffer”*. Finally, in a Forsmark repository, this saturation/swelling process of the tunnels that will create a proper counter pressure to neutralize the Sauna effect will unfortunately take several thousand years which is devastating for the life time of the copper canisters. In fact, the bentonite rings in the deposition holes will be destroyed as well by mineralization and cementation in a Forsmark repository. It can be concluded that SKB has not submitted any new information or studies concerning the sauna effect on pitting corrosion and stress corrosion cracking which was requested by the environmental court.

2.2. The Sauna effect- introduction

The major problem with a deep repository in the Forsmark site is the unusual slow ground water ingress which will jeopardise the barrier function of both the bentonite buffer and the copper canister. Each canister evolves 1700 W as heat which will generate temperatures on the outer surface close to 100°C and the bedrock surface in the deposition hole will reach 60°C. The temperature in the tunnel above the deposition holes will be stable around 12°C. Thus the groundwater that flows directly into a deposition hole will evaporate and condense in the colder tunnels. Different salts, i.e. chlorides, sulphates and sulphides will then be enriched in those deposition holes.

An argument against the seriousness of this Sauna effect or salt enrichment process has been that a counter pressure from the tunnel should stop the process. This could only happen if the tunnels would be water saturated sufficiently fast, which actually was the original idea with the KBS-3 model. However, it is expected to take a few to several thousand years to saturate and pressurize the repository in Forsmark /Sellin P. et al. 2017/, i.e. the bentonite buffer will not work properly for a long time, if ever. Thus, the “sauna” effect will result in severe salt enrichment and copper corrosion and a significant amount of premature canister failures in a Forsmark repository, these problems will be discussed in detail here.

2.3. Background data and information taken from different SKB-reports

Background data concerning the deposition holes, canisters and tunnels and general physical and chemical data connected to the Forsmark repository will be listed up below in bullet point's denoted a-j without any mutual ranking.

a) The drilled deposition holes in the bed rock have a diameter of around 1.8 meter and thus an area of 2.54 m², see Figure 2.1.

b) The groundwater is highly pressurized at 500 meter depth, i.e. 50 bar which is around 15 times higher pressure than in normal tap water. An example of seeping groundwater in a drilled hole in Äspö hard rock laboratory at normal repository depth is shown in Figure 2.2.

c) The saturation pressure of 50 bar corresponds to 5 million Pa (N/m²) or 500 ton per square meter. The force on the bentonite top blocks in a deposition hole with seeping groundwater would thus reach more than 1200 tons if they would be hermetically tight. The only possibility to stop the water/moisture transport and bentonite ring cracking and push out from a heated deposition hole would be to create an equally high counter pressure from above, i.e. a fully water and pressure saturation of all bentonite in the whole deposition tunnel.

d) A fully flooded and saturated deposition hole with bentonite rings and a copper canister will contain 6.45 m³ groundwater (SKB-TR 17-07).

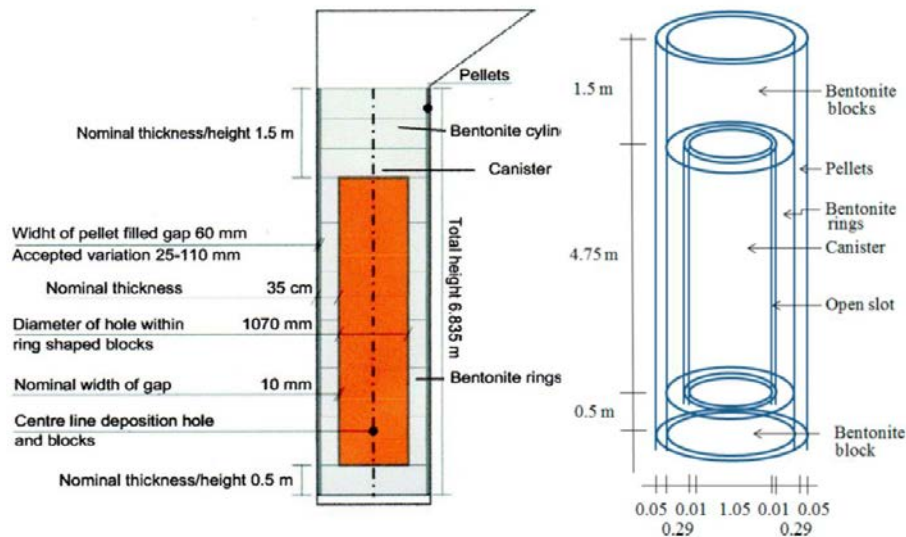


Figure 2.1. Configuration and geometry of the deposition hole with copper canister and bentonite buffer. From SKB-report TR-14-12 (to the left) and from SKB-report TR-17-15, Figure 9-1 (to the right). The drilled hole in the bed rock has a diameter of around 1.8 meter.



Figure 2.2. From Figure 3 in SKB-report R-05-44. Typical inflow pattern in Äspö hard rock laboratory showing high pressurized groundwater seeping out of a drilled rock surface. This photo is taken from a depth of only 220 m, i.e. the water pressure is around 22 bar, only half of that prevailing in a real repository. The cracks in the deposition holes in Forsmark are believed to be smaller but the pressure of the ground water is still 50 bar.

e) The groundwater at the Forsmark site contains around 0.95 wt-% mixed salts containing chlorides, carbonates, sulphates and sulphides, see Table 1.1. Unalloyed copper reacts with all of these species also under strictly anoxic (oxygen free) repository conditions since water molecules (moisture or liquid water) are present, see further Chapter 4.

Predicted groundwater composition for a repository at Forsmark (contents in mg/dm³)

	At emplacement	After saturation (<100 years after emplacement)	10000 years into the future
pH	6-8	7.0-7.9	7-9
E_{redox}^*	0 to -400	-200/-250	-200 to -300
Na ⁺	300-2000	1700	100-1000
K ⁺	2-13	13	2-10
Ca ²⁺	150-1650	1650	20-1000
Mg ²⁺	17-110	110	4-100
HCO ₃ ⁻	50-300	47	20-40
Cl ⁻	500-5000	5500	200-5000
SO ₄ ²⁻	40-400	370	1-400
HS ⁻	0-10	<0.01	0-1

* mV SHE.

Table 1.1. Groundwater composition in the Forsmark repository. The higher range of sulphate and sulphide concentrations are around 4×10^{-3} M and 3×10^{-4} respectively /Rosborg B. and Werme L. 2008/.

f) The copper canister bentonite interface temperature peaks around 95°C after 20 years and is still around 40°C after 1000 years.

g) Approximately 20% of the deposition holes in Forsmark have at least one water seeping crack of significance (SKB TR-17-15), i.e. around 1384 copper canisters will

more or less directly experience the Sauna effect, see Figure 2.3. 854 deposition holes have an inflow of more than 10^{-5} L/min (≥ 53 litre/year) and 395 deposition holes has an inflow of more than 10^{-4} L/min (≥ 530 litre/year).

h) At least 10%, i.e. around 700 additional deposition holes (without seeping cracks), are situated close (some few meters) from a major water seeping crack in a deposition tunnel (SKB TR-17-15).

i) According to the authors in the original report SKB P-07-162 it can be concluded that the representative hydraulic conductivity (K_m) of in situ conditions (pressurized bed rock) in Forsmark at 500 meter depth varies between 10^{-13} to 10^{-14} m/s (experimental measurements: 1.6×10^{-13} to 6.4×10^{-15} m/s). Matrix ground water flow in the bed rock means transport through microscopic porosity and cracks. These measurements show that the ground water transport through the bed rock matrix in Forsmark at 500 meter depth is particularly slow.

j) Given the low hydraulic conductivity in Forsmark, see point (i) above, there will be a distribution between 1500 to 15.000 years to flood and saturate all bentonite in the deposition holes and tunnels with water, see Figure 2.4. No deposition hole can be fully saturated before the whole tunnel is fully water saturated and pressurized. Around 50% of the deposition holes will be saturated after 3000 years and it will take up to 15.000 years to fully saturate the Forsmark repository and it will do so by water transport through the bed rock matrix (microscopic cracks) as well as by bed rock macroscopic cracks.

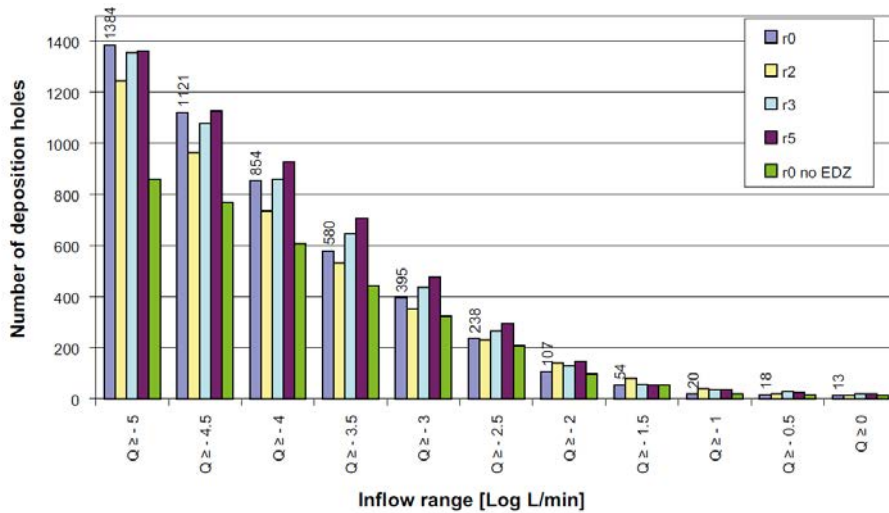


Figure 2.3. From SKB-report R-13-21, Fig. 3-4. Complementary cumulative distributions of the total inflow to each deposition hole for each case. According to case r0 (the five simulations r0-r5, give roughly the same outcome) there are 1384 deposition holes out of 6916 that have at least one crack that gives an inflow of ground water more than 10^{-5} L/min (≥ 5.3 litre/year). 854 deposition holes have an inflow of more than 10^{-4} L/min (≥ 53 litre/year) and 395 deposition holes has an inflow of more than 10^{-3} L/min (≥ 530 litre/year).

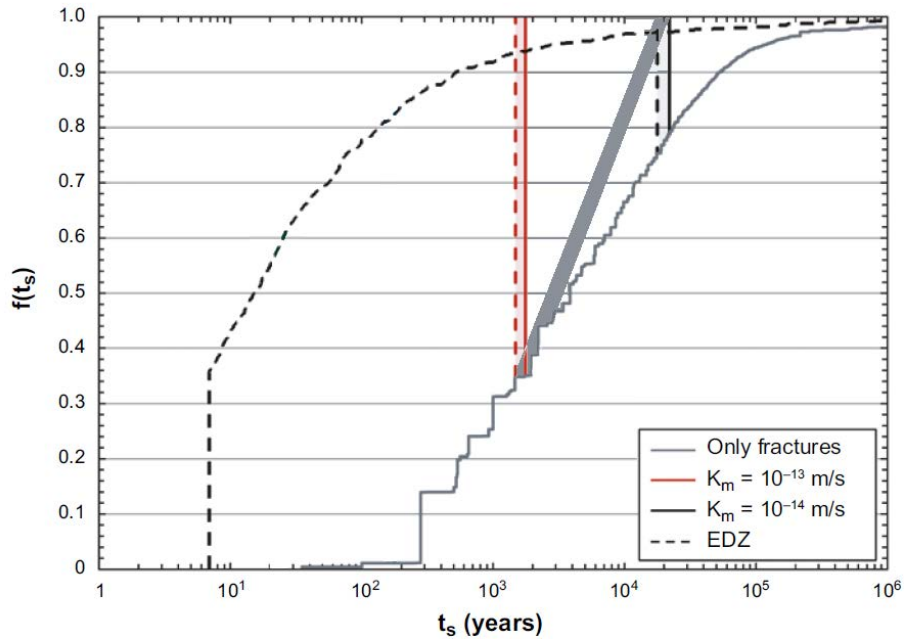


Figure 2.4. Modified graph based on Fig. 7-15 in /Sellin P. et al. 2017/. The solid grey line identifies the cumulative distribution of saturation times, $f(t_s)$, in the Forsmark repository calculated assuming no matrix flow, i.e. only flow via macro cracks. The vertical lines (red and black) identify the time interval within which all deposition holes will reach full saturation if the matrix hydraulic conductivity has the value $K_m = 10^{-13}$ m/s and $K_m = 10^{-14}$ m/s respectively, see point (i) above. The fat grey line represents a linear distribution (realistic simplification), taking into account the variations in measured K_m values in Forsmark. It is thus indicated that the last tunnel and deposition holes with the lowest hydraulic conductivity will be water saturated only after ≥ 15.000 years by matrix inflow and that it takes around 3000 years to saturate 50% of the deposition holes, mainly by cracks in the deposition holes and tunnels. The dashed black line identifies the distribution of saturation times if no flow resistance was present in the tunnels (only of theoretical interest).

2.4. SKB reports concerning the Sauna effect

Basically all SKB-reports concerning the Sauna effect /Birgersson M, Goudarzi R, 2013, 2016, 2017 and 2018/ have actually confirmed that unpressurized bentonite will experience displacements, cracking and piping in contact with liquid ground water, as shown in Figures 2.5 and 2.6. However, these cracking and piping processes should not be so dangerous according to SKB; “*The displacements (with cracks and channels) that take place are to a large part expected to be reversed by the late swelling of the other parts of the buffer*”, see page 117 in TR-17-15 /Sellin P. et al. 2017/. Obviously these displacements and cracks will occur in the bentonite blocks in the tunnels as well as in the deposition holes when in contact with ground water. The “late swelling” is most troublesome, since it might take several thousand, up to around 15.000 years (see point j) in a Forsmark repository, if at all, to “reverse” the cracks and water channels in the bentonite buffer. The important bentonite buffer barrier will thus not work during the most critical hot period and the unalloyed copper corrosion rate will not be reduced by any diffusion barrier.



Figure 2.5. From SKB-report TR-17-15, Fig 2.9. SKB has shown in several reports that it is impossible to add water to bentonite blocks without severe cracking under normal pressure.



Figure 2.6. From Figure 2-8 in SKB TR-15-09. Left: Test 3 at termination. Right: Bottom side of the bentonite ring showing a condensation “nucleus” and cracks. Severe cracking of the bentonite rings occurred already within 7 days, which was the experiment duration time.

SKB claims in the supplementary information, TR-19-15, section 3.2.1, page 34 /Hedin A. et al. 2019/ that virtually no water will escape to the tunnel through the top bentonite blocks. When reading the reports that SKB used as a basis for that conclusion, it is obvious that it has no scientific support, as will be discussed in detail in next section, 2.4.1.

2.4.1. Detailed comments on TR-15-09 and TR-17-07, concerning tests 1-9 of the Sauna effect

These reports constitute the main studies financed by SKB regarding the Sauna effect, i.e. the water evaporation and salt enrichment process in the deposition holes.

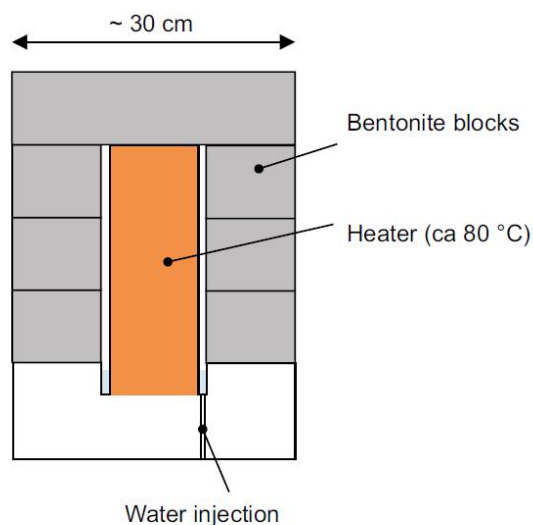


Figure 2.7. From Figure 2-1 in TR 15-09. The test set-up, which to a certain extent is a model of a KBS-3 deposition hole. Mounted on a plastic plate is a copper tube which is heated by circulating water to approximately 80 °C. “Water injection” seen to the left is actually a hole for low pressure water vapour to enter the slot between the Cu-heater and the bentonite rings. The outside of the set-up was covered by a plexiglass tube (not visible here).

Fundamentally, the set-up for Sauna tests 1-9, TR-15-09 and TR-17-07, has a known major flaw concerning the water supply system compared to the real repository situation. In reality the major supply of water will be by liquid water seeping out from bed rock cracks as shown in Figure 2.2 and not as moist air as in the set-up, see Figure 2.7. The authors Birgersson and Goudarzi, as well as SKB, are fully aware of that it has been proven impossible to inject liquid water without destroying the bentonite buffer totally with cracks and piping, as shown in Figure 2.5 and 2.6. The only way to solve this fundamental problem for the whole concept of KBS-3 is to apply a proper water counter pressure of 50 bar, i.e. reach saturation in the tunnels, so the cracks and piping would eventually heal, but unfortunately that will occur far too late in a Forsmark repository. The proper counter pressure in the tunnels will only be reached after around 2000-15.000 years, see Figure 2.4, thus the “sauna”-effect will be impossible to stop for several thousands of years in Forsmark. The main four arguments, already listed up in the Abstract in TR-17-07 that are claimed to indicate that “severe amount of salt in a KBS-3 deposition hole during the saturation process is highly unlikely and can be disregarded” are based on experiments that are not relevant due to several reasons:

1) Flawed water supply system in the used set-up, unpressurized moist air instead of seeping pressurized liquid water as it would be in a real repository, see description above. This point is fundamental and makes it impossible from this set-up to make any conclusions regarding the Sauna effect in a Forsmark repository.

2) Too short exposure times and thus too little water was added in the used set-up. The experiments which SKB refer to as relevant for calculating the seriousness of the Sauna effect are test 5 and 6. The volume of the bentonite rings used in the set-up can be estimated to be around 40 dm³ and the water added was far too little to give any true indications of the Sauna effect:

-Test 5: In total 1.4 litre tap water without salt was added as ambient moist air during 21 days exposure.

-Test 6: In total 0.7 litre tap water without salt was added as ambient moist air during 90 days.

At least the same volume of water as the simulated deposition hole, i.e. 40 litre of water should have been injected during a sufficient long period to avoid flooding of the equipment. Furthermore, liquid water should have been injected directly to the bentonite and the water should be saline, not tap water, in order to have any implication on the seriousness of the Sauna effect.

3) The temperature gradient is not relevant in the test set-up. All bentonite in a given cross-section will be heated up significantly including the surrounding bed rock in a real deposition hole which means that a major part of the formed water vapour will condensate in the cold tunnel of around 12°C above the deposition hole, thus a vertical water transport out from the deposition hole is promoted. The outer part of the bentonite rings in the described set-up is effectively cooled by air convection in the room and the top part is not colder than the ambient temperature thus a vertical water transport is not promoted in a realistic way.

4) The only test that used salt water was Test 7 and that exposure did experience real Sauna effect with massive copper corrosion during only seven days of salt exposure, see Figure 2.8. However SKB omitted to discuss this at least more relevant test in their supplementary report TR-19-15.

Interestingly it is noted in the conclusions in TR-15-09 that “Vapour was shown to be able to be transported rather far in this types of slots without substantially being absorbed by the bentonite; a substantial amount of water was lost to the environment in tests where the slot was directly opened to the environment (test 2 and 3)”. This is relevant since the “open slots” can be compared with the cracks and piping in a real deposition hole in connection with the surrounding environment, i.e. the cold tunnel above. Thus test 2 and 3 imply a devastating Sauna effect with fast water transport and thus severe salt accumulation that will last for thousands of years until saturation of the tunnels is reached in Forsmark.



Figure 2.8. Detail from Figure 2-27 in TR 15-09. Severe corrosion of the copper heating tube after only seven days of laboratory exposure that at least reminds of the true Sauna effect, i.e. with only indirect contact with 0.6M chloride solution.

2.5. Detailed analysis and consequences of salt enrichment in a Forsmark repository (Sauna effect)

The deposition holes will basically be flooded/saturated in three different ways:

- i) by internal ground water bearing cracks in the deposition hole, around 1400 out of around 6916 deposition holes, see Figure 2.3.
- ii) by larger water bearing cracks in the tunnel. The seeping groundwater creates displacements and cracks in the bentonite blocks and eventually water paths and channels, preferably at the bentonite/bedrock interface at the tunnel floor due to gravity. The water channels will eventually reach the deposition holes and continue to create displacements and cracks in the bentonite rings around the heated copper canister thus starting the evaporation and salt enrichment process in those deposition holes. Around 40% of the deposition holes are expected to be flooded via larger cracks in the deposition holes or in the tunnels, i.e. around 2800 deposition holes, see Figure 2.4. Apparently, half of those, 1400 deposition holes (2400-1400), will be flooded via larger cracks in the tunnel.
- iii) the remaining 60%, around 4100 deposition holes, will be flooded by micro crack and porosity in the bed rock, i.e. matrix ground water flow and it will take around 3.000-15.000 years to reach saturation, see Figure 2.4.

The Sauna effect will have a severe impact on the copper corrosion during the first 1000 years since the temperature difference is large between the deposition hole (95°C to 40°C) and the cold tunnel above the deposition hole (around 12°C). However, salt enrichment in the deposition holes with increased copper corrosion will continue until the accumulated salt is dissolved which will take around 3000 years for half of the deposition holes when saturation is reached. For tunnels with restricted inflow from macroscopic cracks and with a bed rock hydraulic conductivity in the lower region, around 10^{-14} m/s, it will take at least 15.000 years to dissolve the salt and stop the Sauna effect, see point (j), at page 6.

The most disturbing fact with the Forsmark repository is that the copper corrosion will be accelerated by salt accumulation and basically without any corrosion reduction by the bentonite buffer during the first thousands of years since no saturation is obtained. The first thousand years is critical to unalloyed copper since the corrosion rate roughly doubles with every 10 degrees of temperature increase /E. Mattsson 1997/. When unalloyed copper is heated to 80-90°C in moist environment with high concentration of mixed salts (chlorides, sulphates, sulphides and carbonates etc.) a corrosion rate of 300 micrometers per year (0.3 mm/year) should be expected. Most importantly, there are additional rapid degradation processes such as stress corrosion cracking (SCC), hydrogen embrittlement (HE), hydrogen sickness and radiolysis operating on the copper canisters, see further Chapter 3 and 5. When only considering the salt accumulation induced copper corrosion, i.e. a mix between atmospheric corrosion, general corrosion and pitting corrosion, following conclusions can be drawn (based on case r0, see Figure 2.3):

- 395 deposition holes/canisters will have an inflow larger than 530 liter per year corresponding to more than 5.3 kg mixed salts per year, see point (g) at page 6. Since unsaturated bentonite cannot hinder any transport (k) severe corrosion will occur. With this massive inflow of salt and freely evaporating water already when the canisters reaches its peak temperature around 90°C it can be concluded that all of them will collapse within 300 years already by general corrosion and pitting corrosion.
- 459 deposition holes/canisters (854-395) will have an inflow larger than 53 litre per year corresponding to more than 0.53 kg mixed salts per year (g). These canisters will experience almost the same corrosion rate as the previous 395 canisters since the local salt concentration will still be high enough within some tenth of years albeit the canister maximum temperature might appear before the local corrosion environment

has reached its peak in terms of corrosiveness. All canisters in this category are expected to collapse within 500 years and perhaps half of them within 300 years due to salt accelerated copper corrosion.

- 530 deposition holes/canisters (1384-854) will have an inflow larger than 5.3 litre per year corresponding to more than 0.5 kg mixed salts per year (g). Which still corresponds to more than 500 kg salt during the first one thousand “hot” years, i.e. with both heat and radiolysis. The fact that the all salt is inhomogeneously distributed or even accumulated locally in the respective deposition hole makes it most likely that all 530 canisters will collapse within 1000 years.
- The remaining 5532 canisters (80%), will slowly be saturated via cracks in the tunnels in combination with ground water matrix transport or solely by matrix transport which will take 3000 to 15000 years depending on the hydraulic conductivity in each tunnel. A slow salt accumulation will thus take place in all these deposition holes under a very long time period until saturation and salt dissolution initiates. Unalloyed copper will be seriously weakened due to salt induced corrosion and when the full pressure of 50 bar is applied on the canisters is most likely that the canisters will collapse. Thus one possible assessment would be that the failure distribution follows the saturation distribution according to the thick grey line in Figure 2.4. Important notice, this failure distribution is certainly not conservative since, as mentioned, SCC, HE, hydrogen sickness and radiolysis will shorten the canister life time in the whole population further, as will be discussed further in Chapter 3.

The Sauna effect will also destroy the bentonite buffer, as shown in Figure 2.9. When the salt crystals precipitate in the bentonite it will convert the clay to a brittle and cracked mineral “cake” for several thousand years and most likely it will never regain its original swelling and diffusion barrier properties.

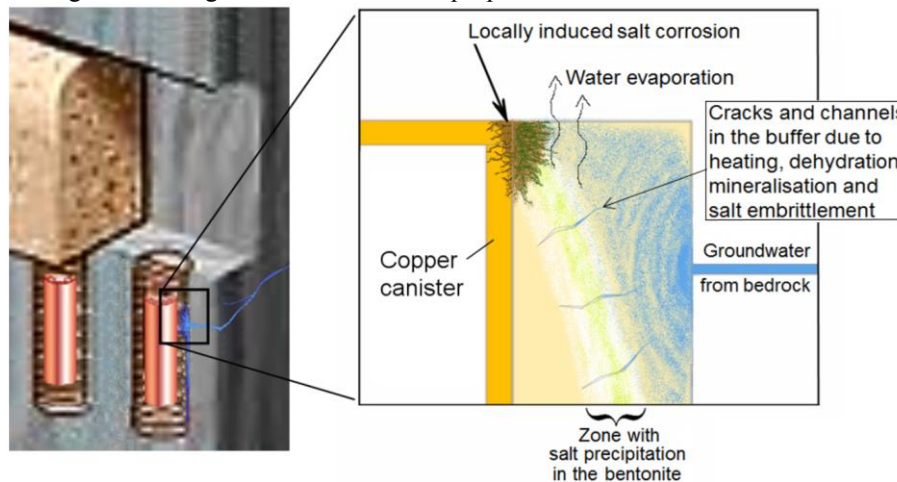


Figure 2.9. The Sauna effect in a repository with water evaporation, salt enrichment and copper corrosion. Furthermore, the precipitated salt will destroy the properties of the bentonite buffer /Szakálos P. and Seetharaman S. 2012/.

Professor Roland Pusch /Pusch R. 2019/ explains that "locally induced salt corrosion" occurs along the canister's entire mantle surface because the temperature is substantially higher at the canister's half height than at the ends, leading to dehydration and an open gap along the entire mantle surface. "Water evaporation" from the buffer clay up through the backfill in the tunnel therefore occurs in the gap along the entire mantle surface and the mechanical ("effective") swelling pressure there will be low for a very long time in a Forsmark repository. Up to a distance of 10-20 cm from the canister surface of the canister, mineral conversion from “expandable smectite” to “non-expandable illite” (hydrous mica) will occur, thereby releasing silicon which

precipitates as a cementing substance. Since horizontal and vertical drying cracks are formed before the silicon has been released and diffused into the buffer, these cracks will be filled with silicon aggregates and create precipitates that have much higher water permeability than the buffer clay in un-cemented condition. When the temperature in the buffer clay begins to drop after 50 years and groundwater eventually penetrates, the silicon fillings will not provide self-healing but will remain as permeable layers in the clay. In other words, a devastating short-cut concerning the diffusional transport barrier properties of the bentonite. The scientific references supporting these conclusions are /Pusch, R. et al 2019/, /Pusch, R. 2015/, /Pusch R. et al. 2015/ and /Kasbohm, J. N. et al. 2019/

3. Stress corrosion cracking and hydrogen embrittlement in unalloyed copper (CuOFP)

3.1. Short summary

There is compelling scientific evidence that stress corrosion cracking (SCC), hydrogen embrittlement (HE) and hydrogen sickness (HS) will affect the copper canisters in a repository environment. SKB seems to believe that the surface cracks and hydrogen blisters observed in the copper grain boundaries in several studies are only “manufacturing defects”. In SKB R-18-03, /Huotilainen C. et al. 2018/, page 25, it is concluded: *“The findings of Taniguchi and Kawasaki (2008), and Becker and Öijerholm (2017) of claimed small (of the maximum depth of a few tens of microns) SCC cracks on the surface of copper after SSRT experiments in sulphide containing environments can be alternatively explained as follows. The pre-existing manufacturing defects (which Becker and Öijerholm showed to exist also in the unexposed material, that had never been in contact with the sulphide containing environment) extending to the specimen surface, open up due to the effect of surface active sulphide species on the cohesive forces of the opposing surfaces of a defect.”*. This explanation has no scientific support, on the contrary, it is scientifically erroneous to claim that the cracks shown in for instance Figure 3.1 should be initiated by pre-existing manufacturing defects in as-delivered copper. Virtually all grain boundaries in Figures 3.1 and 3.4-3.7 have initiated a crack close to the main fracture and for obvious reasons this cannot be due to pre-existing manufacturing defects, instead it is a scientific proof of sulphur induced SCC in copper. It was shown in a study connected to SKB’s prototype repository /Szakálos P. and Hultquist G. 2013/ that the whole canister thickness was hydrogen charged during only 7 years exposure at elevated temperature and that the canister was subjected to internal corrosion by hydroxide. A conservative safety analysis would estimate that 40% of the canisters collapse already within 100 years after repository closure and the remaining 60% within 1000 years after closure due to SCC, HE and HS (in the welds). SKB has chosen to not include these fast degradation processes in the safety analysis, despite the even more compelling evidence of today compared with the situation during the court process in 2017.

3.2. Introduction SCC and HE

Stress corrosion cracking (SCC) and hydrogen embrittlement (HE) are two degradation mechanisms that are related to each other and operate closely together in many cases, such as in a deep repository environment in combination with unalloyed copper. This will be discussed in detail in this chapter in relation to the KBS-3 model and whether SKB has considered and included these most important degradation mechanisms in their complementary information and safety analysis in an adequate way or not.

The most relevant scientific publications that have a direct impact on the KBS-3 model will be summarized and discussed here.

3.3. Slow strain rate testing of copper performed at Japan Atomic Energy Agency (JAEA)

/Taniguchi and Kawasaki 2008/ showed that unalloyed copper (CuOFP copper) is indeed sensitive to stress corrosion cracking (SCC) in sulphide containing sea water. Multiple cracks due to SCC, preferably in the copper grain boundaries are seen in Figure 3.1.

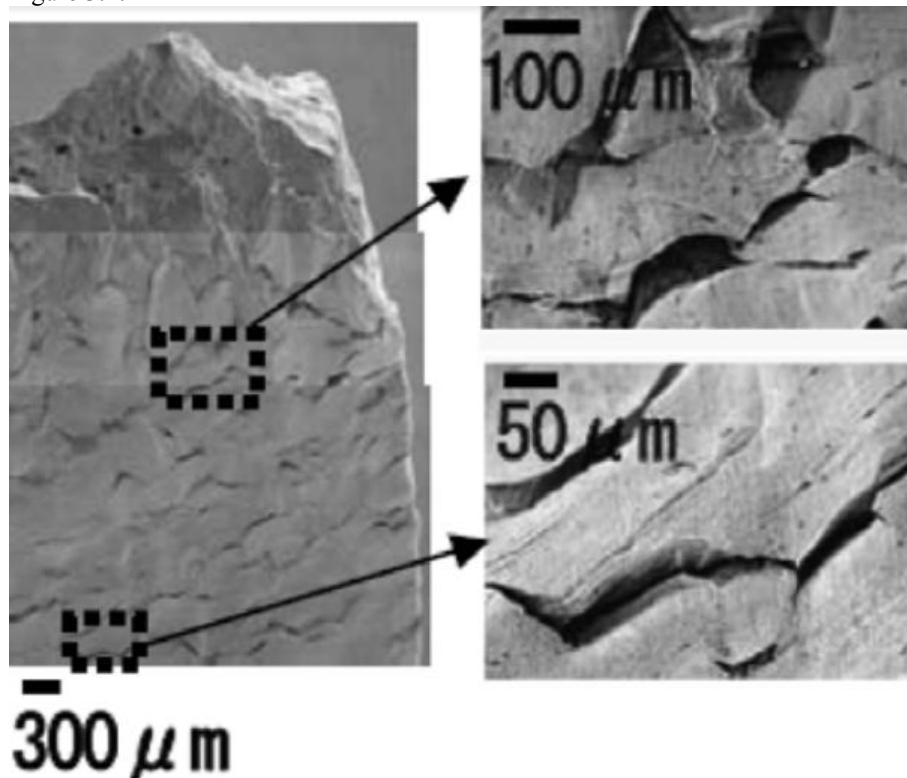


Figure 3.1. Fractured copper sample due to Stress Corrosion Cracking (SCC) in 0.01M sulphide containing seawater at 80°C after 7 days exposure. Initiation of minor cracks was detected at 0.001M sulphide concentration (not shown here). Slow strain rate testing (SSRT) results from Figure 10 in /Taniguchi and Kawasaki 2008/.

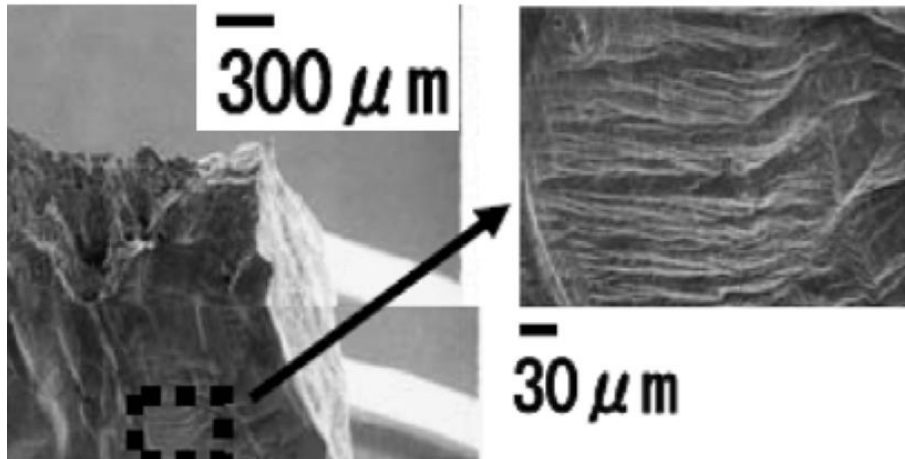


Figure 3.2. Crack-free copper surface when tested during the same conditions as in Figure 3.1 but with a sulphur free (inert) environment. No indication of any crack initiation visible in high magnification, see detailed micrograph to the right. Slow strain rate testing (SSRT) results from Figure 10 in /Taniguchi and Kawasaki 2008/.

Coupons were strained to fracture at a constant and ordinary extension rate of 8.3×10^{-7} /s. The test solutions in the cell were renewed every second or third day during the SSRTs in order to avoid decreased sulphide concentration.

The authors conclude regarding the use of copper canister in a repository: *“rather early penetration due to SCC could be possible under high sulfide concentrations.”* and *“High sulfide concentrations could be achieved by a special process such as sulfate reduction due to microbial action. Although sulfate reduction by microbial action in buffer material is not likely to occur because sulfate reducing bacteria (SRB) can hardly proliferate in compacted bentonite”*

However, there are two reasons why sulphide will be accumulated to dangerous concentrations in the Forsmark repository;

- 1) Sulphide and sulphate accumulation in the deposition holes due to water evaporation, i.e. the Sauna effect as described in previous chapter.
- 2) Sulphate reducing bacteria (SRB) convert sulphate to corrosive sulphide as will be discussed in sections 3.10, 4.5 and 4.6.3. SRB can survive and thrive in a Forsmark repository for several thousands of years since full pressure/compacted bentonite will only be achieved after such long time scales as described in previous chapter.

3.4. Slow strain rate testing of copper at Studsvik AB

Another important SSRT-study was performed by Studsvik AB and published in two scientific reports, /R. Becker, J. Öjjerholm 2017/ and /Forsström A. et al. 2017/.

Slow Strain Rate Testing (SSRT) has been frequently used within the nuclear industry for screening tests concerning SCC. However, the design life of a reactor is around 50–60 years, which is two orders of magnitudes shorter compared to the duration under which the copper material is suspected to be exposed for conditions which might initiate SCC in the final repository /R. Becker, J. Öjjerholm 2017/. SSRT can be seen as a very slow tensile test with a duration of typically one to four weeks.

The specimens in this case were elongated to a certain strain, i.e. 9% at the thinnest part of the tapered samples after which any crack initiation is accounted for. With the experience from the nuclear industry it can be concluded that if cracking readily appears in SSRT under otherwise relevant exposure conditions, it is likely only a matter of time before cracking appears in the real application /R. Becker, J. Öjjerholm 2017/. The other extreme is if no cracks appear at all even if the specimen is exposed

to stress equivalent to the tensile stress during prolonged SSRT. An example in this case is the nickel base material Alloy 690 TT in the non-cold worked state, which does not develop SCC under SSRT in simulated reactor environments. Indeed, the material has performed excellent in reactor applications for around 30 years, where to the best knowledge no case of SCC has been reported /R. Becker, J. Öjjerholm 2017/. Thus if a material does not develop cracking during prolonged SSRT, it means that the material is very resilient towards initiation of SCC, however one can't draw the conclusion that the material is completely immune.

Testing parameters used at Studsvik AB in their experiments on SSRT: Temperature 90°C, NaCl 0.1 M, strain rate: $7 \cdot 10^{-8} \text{ s}^{-1}$, maximum strain: 9%. Testing time: 2 weeks.
Exposures 1 and 2 (specimen #3 and #4): $10^{-3} \text{ M Na}_2\text{S}$
Exposures 3 and 4 (specimen #5 and #6): $10^{-4} \text{ M Na}_2\text{S}$,
Exposure 5 (specimen #7): $10^{-5} \text{ M Na}_2\text{S}$



Figure 3.3. Example of SSRT exposed sample, 9 % strain at the thinnest part of the tapered sample (not exposed to final fracture).

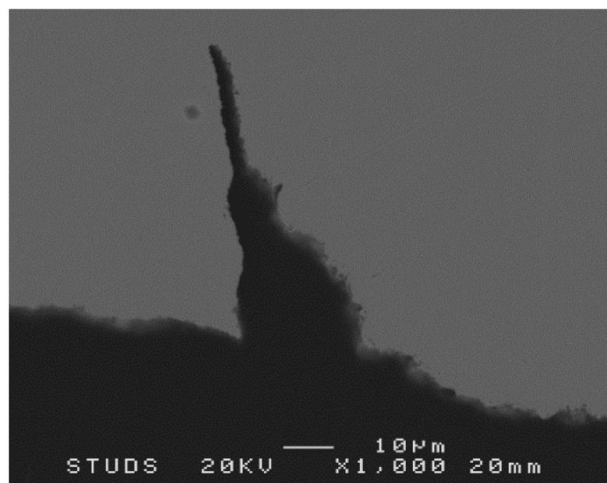


Figure 3.4. From Figure 16 in /R. Becker, J. Öjjerholm 2017/: Specimen #3 (10^{-3} M sulphide), SEM image of a crack observed at the narrowest part of tapered gage section.

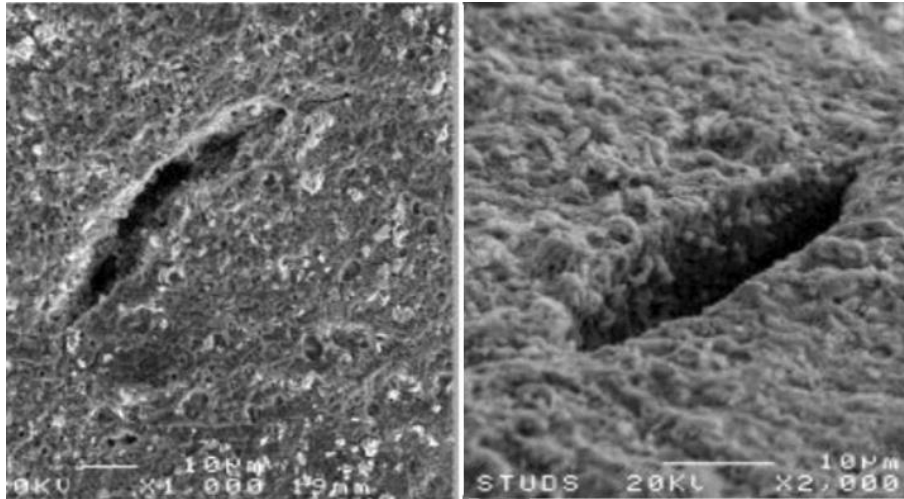


Figure 3.5. From Figure 2 in /Forsström A. et al. 2017/. Surface cracks near the narrowest part of Specimen #3 (10^{-3} M sulphide) after SSRT testing.

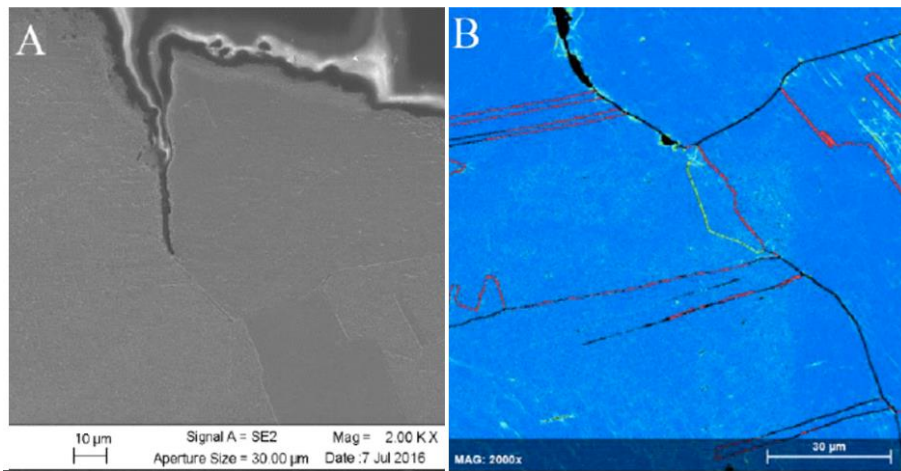


Figure 3.6. From Figure 3 in /Forsström A. et al. 2017/. Cross-section images of a SCC crack in the narrow section of Specimen #3. EBSD image showing crack propagation along a random grain boundary. Twin boundaries are marked in red and local misorientation in shades of green.

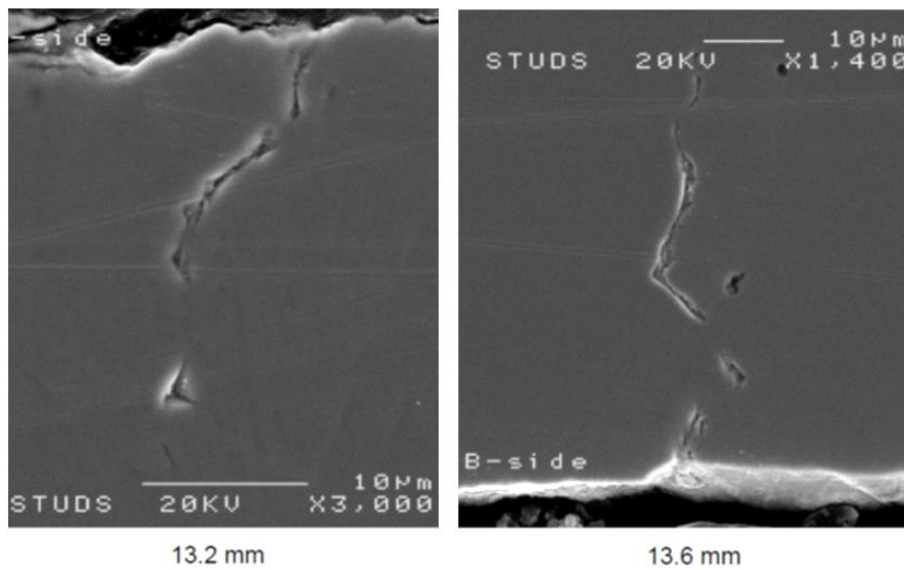


Figure 3.7. Part from Figure 21 in /R. Becker, J. Öjjerholm 2017/. Initiation of blisters and cracks could be detected also at lower sulphide concentrations quite far away from the narrowest part (with the highest stress) of the sample, i.e. at a distance of 13.2-13.6 mm. Exposures 3 (specimen #5) exposed to 10^{-4} M sulphide.

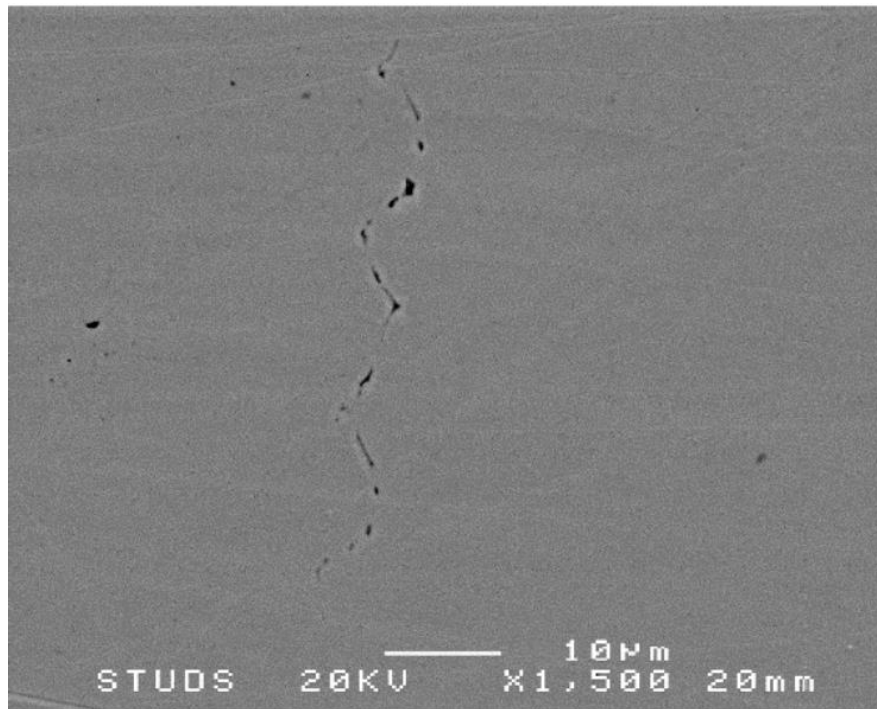


Figure 3.8. From Figure 22 in /R. Becker, J. Öjjerholm 2017/, specimen #5, (10^{-5} M sulphide). Defects in shape of blisters in the copper grain boundaries was detected deep inside the SSRT samples. In fact, similar defects were also found in the unloaded head section of the samples, irrespective of the sulphide content during the various exposures. These grain boundary blisters cannot be initiated by sulphur since they are formed deep inside the metal, they are instead initiated by fast moving hydrogen.

The defects 10^{-4} M sulphide with only 9 % strain at the thinnest part of the tapered sample clearly shows the effect of sulphur and/or hydrogen on the initiation of SCC.

All these defects have indeed been initiated by the corrosive environment, compare with a copper sample SSRT-exposed in an inert environment, without any cracks and blisters, as shown in Figure 3.2.

3.4.1. Hydrogen measurement on SSRT-exposed samples

It is known that hydrogen can be transported fast in copper grain boundaries especially if they are decorated with hydrogen blisters /Forsström et al 2017/. The hydrogen content in the SSRT-exposed copper was measured by thermal desorption (TDS) and the most important conclusion, quote: “*The main finding of the TDS (hydrogen) measurements is remarkable; about two times increase of hydrogen content in the copper specimens subjected to SSRT in deoxygenated sulphide environment, when compared to hydrogen content in the as-supplied state of copper.*”

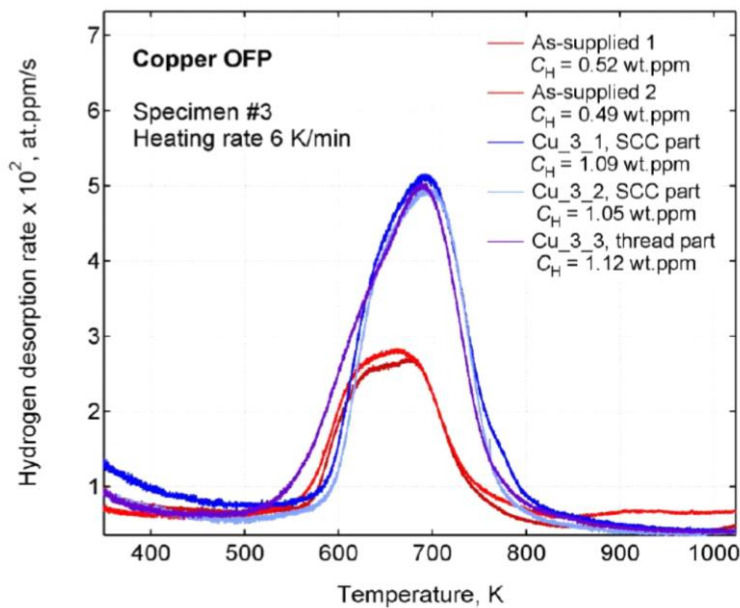


Figure 3.9. Hydrogen desorption curves (TDS) from /Forsström A. et al. 2017/ shows a systematically higher hydrogen content in the SSRT-exposed copper samples (blue and purple curves) compared with the as supplied SKB-copper metal (red curves). The TDS curves look similar for all tested samples, i.e. #3, #5 and #7. The systematic increase in hydrogen content in combination with the detected blisters in the inner sections of the copper samples (crack like defects, see Fig. 3.8) shows that copper exposed in an anoxic corrosive environment will suffer not only from SCC (surface cracking) but also from hydrogen induced grain boundary blisters and eventually cracking inside the bulk metal. This represents, in other words, the evidence for hydrogen embrittlement in oxygen free copper.

SKB argue that it is impossible for hydrogen to diffuse deep into the bulk metal in the thicker part of the SSRT-samples within the short time of two weeks, see page 93 in TR-19-15 /Hedin A. et al. 2019/: *At 90 °C, the diffusivity of H in Cu is around 10^{-12} m²/s. With an approximate diffusion distance of 1 cm between the exposed part of the specimen and the unexposed sample, the diffusion time is of the order of $0.012/(4 \times 10^{-12})$ s or almost 300 days, whereas the duration of the exposure was only about 14 days.*

This simple estimation based on bulk diffusion is wrong since the hydrogen has only to diffuse some few hundred micrometres, preferably in the grain boundaries, before hydrogen blisters (and cracks) appear in the copper grain boundaries, as seen in

several studies, see Figures 3.7, 3.8, 3.16 and 3.17. The effective grain boundary diffusion of hydrogen in copper with such blisters will be several decades faster than the estimation done by SKB, since hydrogen diffusion in a gas blister is instantaneous.

3.5. Hydrogen charging of bulk metal and welds due to copper corrosion

The only prerequisite for hydrogen embrittlement (“hydrogen sickness”) in oxygen containing copper is the presence of an anoxic environment with hydrogen on at least one side of the exposed copper metal. No load or stress in the copper metal is needed since the moving hydrogen atoms will simply react with the small oxide particles inside the copper metal under formation of water/steam blisters and eventually crack formation. In fact, this is exactly what will happen in the copper canister welds. The friction stir welds (FSW) will inevitably contain some oxygen particles. In TR-11-01 p. 173 it is stated that some oxide particles will always form in a FSW, also when using a shielding gas, especially at the inner lid/tube interface, i.e. at the root of the weld zone. /Savolainen K. et al 2008/ has studied the problem with hydrogen sickness in FSW in copper and shown that it is a real problem, see Figure 3.10.

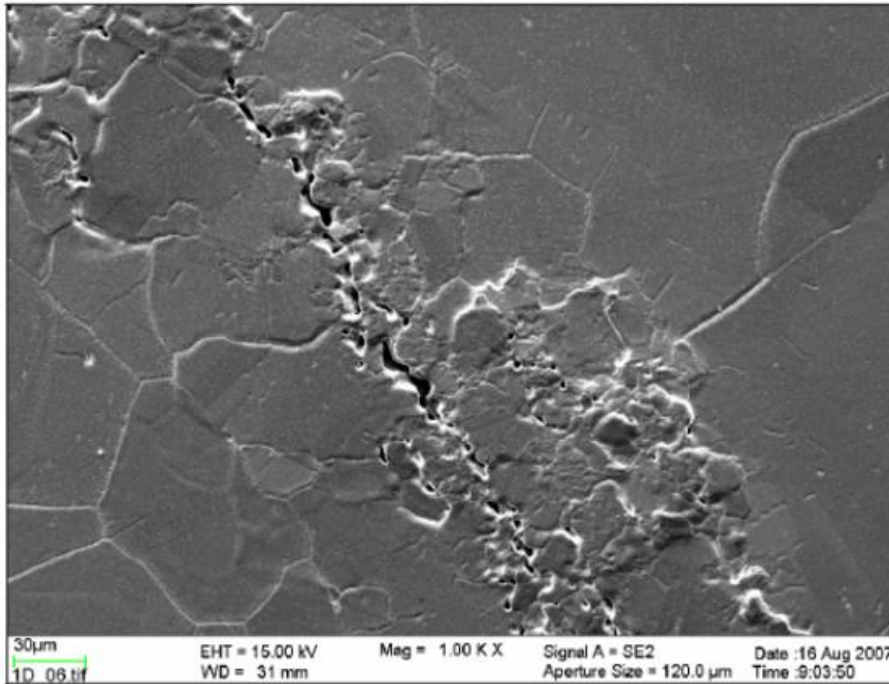


Figure 15. Sample 1DV. Voids and heavy deformation are clearly visible at the region of entrapped oxide particles.

Figure 3.10. Hydrogen sickness. SEM cross-section of a FSW in copper exposed to hydrogen at high temperature for 30 minutes, a stretch of voids, formerly as an oxide particle stretch, in the center of the FSW is visible /Savolainen K. et al 2008/.

SKB still claims in their complementary information /Hedin A. et al. 2019/, quote: *In conclusion, oxides can be detected with standard metallographic tests, and welds essentially oxide free can be produced using a properly designed gas shield.*

“Essentially oxide free welds” is not good enough since any tiny oxide particle will accelerate the hydrogen embrittlement/hydrogen sickness especially in unalloyed copper. The hydrogen charging process is driven by copper corrosion and it takes only

7-9 years in a repository environment to reach dangerous levels of hydrogen, see sections 3.6 and 3.8.

Most importantly, it is impossible to detect small oxygen particles and thin streaks of oxygen by any non-destructive testing /Björck M. et al. 2019/ and thus FSW is certainly not a safe weld method to use, at least not when welding unalloyed copper.

The weakest point of the copper canister, the friction stir weld

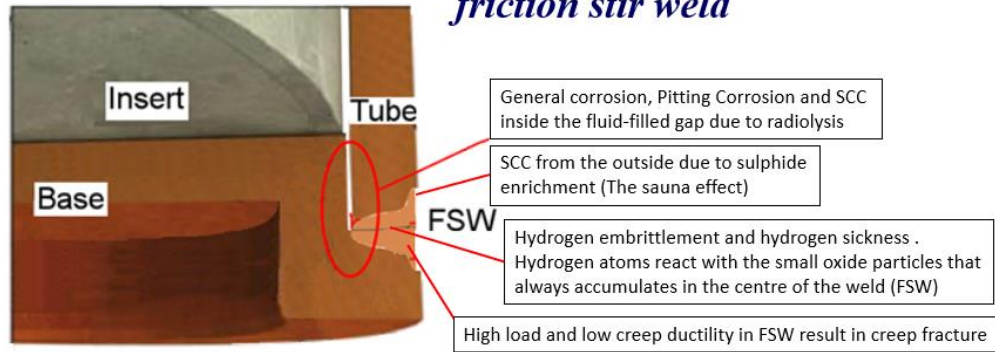


Figure 3.11. Detail from /Szakálos P. et al. 2017/. The weakest point of the canister is the Friction Stir Weld (FSW) and the fastest degradation mechanism is “hydrogen sickness” in the welds.

The copper canister is welded together by FSW as shown in Figure 3.11. A more detailed discussion concerning the “hydrogen sickness” in the canister welds can be found in SSM report 2012-17 /Szakálos P. and Seetharaman S./

When oxygen free copper (OFP-Cu) is considered, it seems that the copper metal must be surrounded by an anoxic environment which will induce a hydrogen charging process of the copper metal by corrosion. The copper will eventually suffer from internal hydrogen blisters in the grain boundaries and cracks, i.e. hydrogen embrittlement. It is known that a slow hydrogen charging takes place in copper metal already when exposed to pure water under strictly anoxic conditions, i.e. a slow charging process takes place by a copper corrosion reaction with water /G. Hultquist et al. 2008/ and /G. Hultquist et al. 2011/. The hydrogen content, measured by thermal desorption, increased from around 1 wt-ppm to 6-40 wt-ppm when exposed to pure anoxic water for several years. In fact, it was demonstrated that the exposed Cu-foils were embrittled by hydrogen since they failed a simple bending test after the long-term exposure in pure anoxic water /G. Hultquist et al. 2008/. Obviously, the hydrogen charging process is much faster (only 2 weeks) in corrosive groundwater containing sulphide /Forsström A. et al. 2017/ compared to slow corrosion and charging in pure water.

Normally, if an oxygen free copper tube is exposed to hydrogen on the inside but to oxygen/air on the outside it will not suffer from hydrogen embrittlement since the hydrogen gradient goes to zero at the oxidizing side, i.e. the hydrogen atoms moves only through the copper tube wall and react with oxygen molecules on the air side without causing any harm. The problematic fact of “hydrogen sickness” in oxygen containing copper and hydrogen embrittlement in oxygen free copper is that no load or stress is needed in the metal, grain boundary blisters and cracks form spontaneously by the influx of hydrogen. This is also confirmed in the SSRT-samples, see Fig. 3.8 where hydrogen blisters have been detected in the un-loaded parts of the samples.

From Discussions in /Forsström A. et al. 2017/, quotes: “*The specimens were studied for hydrogen uptake during testing and the hydrogen content of copper increased from 0.5 wt.ppm to 1.2 wt.ppm during the short time SSRT testing of two weeks. This can be compared to the maximum allowed hydrogen content of copper in the KBS-3 concept, which is 0.6 wt.ppm. The current study suggests that the SCC cracking mechanism of copper in reducing anoxic sulphide environment is possibly related to*

hydrogen uptake in copper and hydrogen-enhanced opening of grain boundaries.” and from Conclusions in /Forsström A. et al. 2017/, quotes: “*The increased hydrogen content indicates that corrosion reactions in sulphide and chloride containing anoxic conditions result in hydrogen absorption in copper even with a sulphide concentration of 0.00001 M. Similar hydrogen content in all the specimens, regardless of the environment, suggests rapid diffusion and saturation of copper with hydrogen.*”

Obviously, the hydrogen charging process in these tests had reached its maximum rate already at the lowest sulphide content.

Considering the situation with the KBS-3 model when the whole copper sample, i.e. copper canister, is surrounded by an anoxic corrosive environment, it is obviously just a question of time until the whole canister is hydrogen charged and thus subjected to hydrogen blisters and cracks. This conclusion is supported by real exposures in the prototype repository, as will be discussed in next section.

3.6. Hydrogen and hydroxide uptake of canister copper exposed 7 years in SKB prototype repository in the Äspö Hard rock laboratory.

Measurements were performed by Gunnar Hultquist (KTH) and Mike Graham and his colleagues (NRC, Ottawa) the results were presented at a conference /Szakálos P. and Hultquist G. 2013/ and at the Land and Environmental Court in Nacka, Sweden, case no. M 1333-11, closing argument, KTH (Addendum 821).

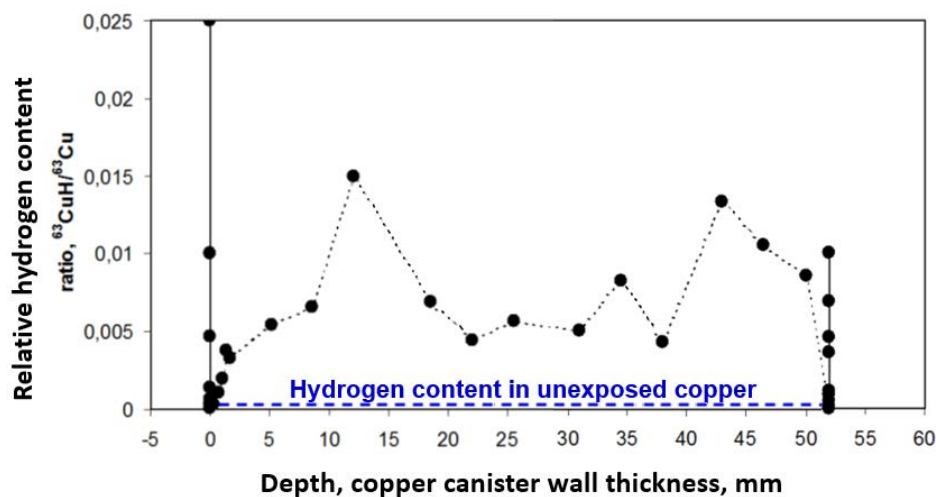


Figure 3.12. Full thickness canister copper exposed to the Swedish groundwater for seven years in the heated prototype repository, 80-90°C, at Äspö hard rock laboratory. The remarkable result shows that the copper canister is hydrogen charged throughout the whole thickness. The outermost surfaces have a very high H-content due to formation of corrosion products containing hydrogen and hydroxide. The hydrogen content in the first 10 mm of the inner/outer thickness has been subjected to spontaneous de-gassing when exposed to air since the hydrogen activity in the copper metal in contact with air is close to zero. The accepted hydrogen content in canister copper is 0.6 weight-ppm which coincide with the blue dotted line (unexposed copper). The hydrogen is detected by SIMS measurements and based on the H/Cu-ratio it can be estimated that the average hydrogen content in the copper is significantly higher than 1 wt-ppm.

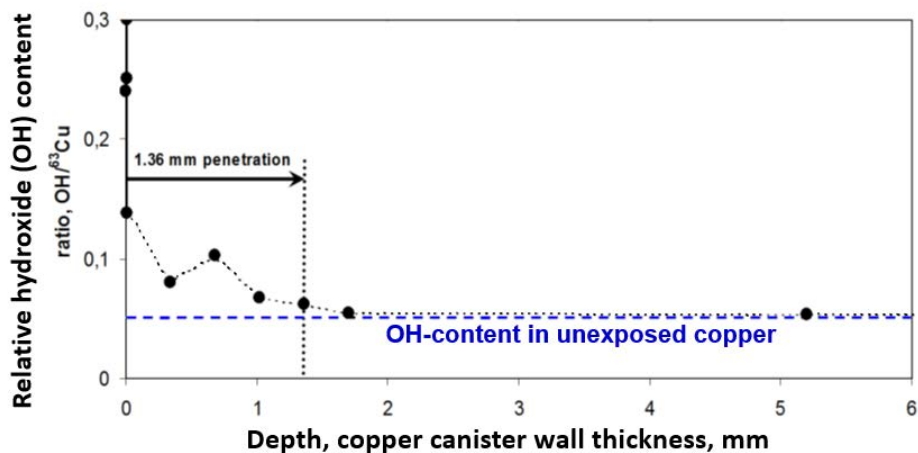


Figure 3.13. The hydroxide content of the first few mm of the full thickness canister copper exposed to the Swedish groundwater for seven years in the prototype repository at Äspö hard rock laboratory. The graph shows that hydroxide penetrates the copper metal, most probably in defects including grain boundaries. Once OH has entered the metal it is accumulated there, i.e. it is thermodynamically stable, i.e. evidence for internal anoxic corrosion. The hydroxide is detected by SIMS measurements.

Hydrogen atoms penetrate the whole canister thickness in shorter time than 7 years, at least when heated, as shown in Figure 3.12. The hydrogen originates mostly from the water molecules that have been actively involved in the various corrosion reactions on the copper surface that can take place in the complex chemistry of anoxic groundwater. If the concentration of hydrogen sulphide is high it is expected that most of the hydrogen in the H-charged copper metal originates from corrosion reaction with sulphide, which has surprisingly fast kinetics, as shown in /Forsström A. et al. 2017/. With an average value of only some few weight ppm of hydrogen in the copper metal it is obviously enough to initiate hydrogen blisters in the grain boundaries, as seen in Figure 3.8 /Forsström A. et al. 2017/. The penetration of hydroxide in the copper metal is much slower, i.e. 1.36 mm during the seven-year exposure, see Figure 3.13. However, it still indicates that the whole canister (50 mm) will be penetrated by hydroxides in the grain boundaries within some few hundred years. Both H and OH will increase in the copper metal when it is totally surrounded by a corrosive and anoxic environment. In fact, this is supported by Ab-initio calculations that show that both hydrogen and OH are thermodynamically stable already in a single point defect in the copper metal /Korzavyi P. and Sandström R. 2014/. One single point defect can harbour up to 6 hydrogen atoms or, even more thermodynamically favourable, one OH species.

This means that anoxic copper corrosion takes place not only at the water/copper metal interface but also inside the copper metal, i.e. internal corrosion in the grain boundaries and other defects.

With the summarized knowledge of today it can be concluded that when the copper canister is exposed to an anoxic environment in a deep repository, it will be subjected to internal corrosion, SCC and most alarming, hydrogen blister formation in the grain boundaries, i.e. hydrogen embrittlement (HE). Based on the work by G. Hultquist regarding the SKB prototype repository it can be anticipated that 5 cm of unalloyed copper will be penetrated by corrosion products (hydroxides) within some few hundred years and hydrogen blisters/hydrogen embrittlement may occur within some decades after the appearance of a strictly anoxic and corrosive environment. The copper canisters that will be exposed to accumulated sulphur containing salts (the Sauna effect) will be destroyed faster by SCC and HE.

3.7. Precracked CT-specimens under constant load exposed in sulphide containing groundwater at room temperature

/Ariilahti E. et al. 2011/ found convincing evidence for internal diffusion of sulphide from groundwater into grain boundaries ahead of crack tip in Cu OFP copper.

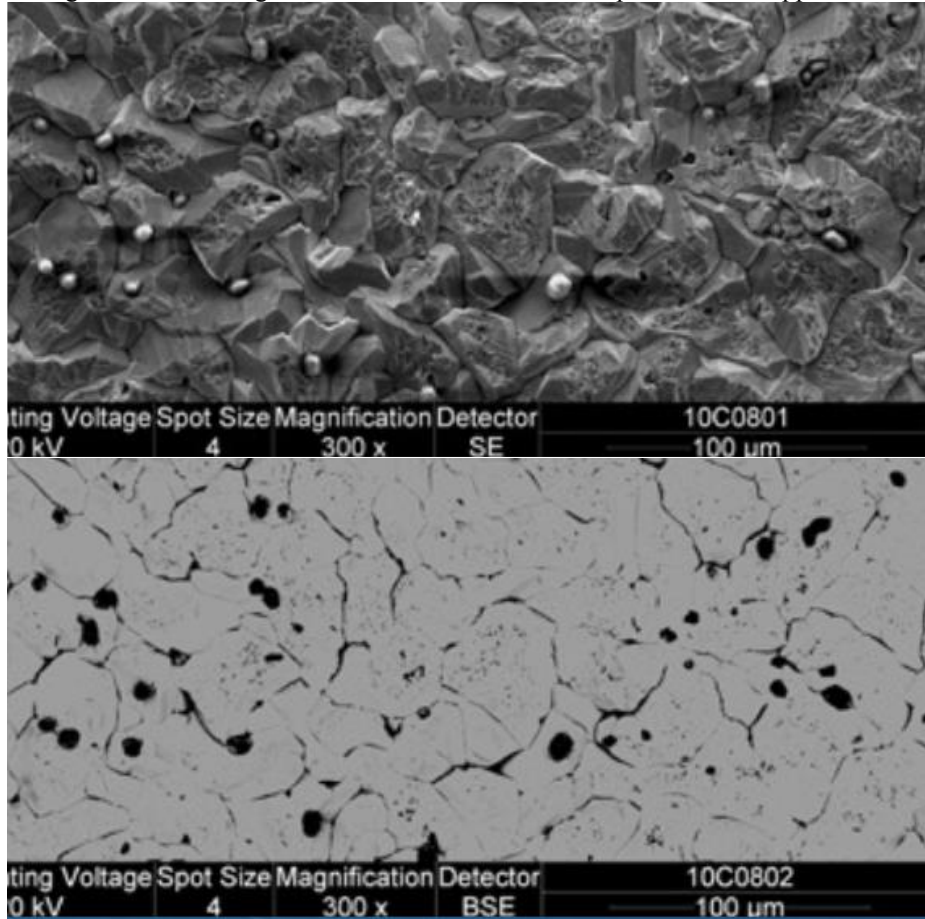


Figure 3.14. Detail from Figure 4 in /Ariilahti E. et al 2011/. The SEM-image at the top shows a post exposure fractured area ahead of the true crack tip for which EDS analysis showed average of 22.5 at-% sulphur. The backscatter electron image of the same area (bottom picture) shows darker sulphur-rich precipitates mostly at the grain boundaries.

It was concluded regarding the SEM-images in the paper (Fig. 3.14), quote: “*Figure 4 shows a comparison of normal and backscattered SEM images of a representative area ahead of the crack tip, revealing that there are some particles which seem like precipitates, and that also most grain boundaries that are perpendicular to the fracture surface contain a lighter phase, presumably a Cu-S precipitate.*” And from conclusions: “*These results suggest that the main driving force for the sulphur ingress into Cu OFP is the stress-strain field ahead of the crack tip.*”

It is obvious that the sulphur rich particles seen in the SEM-micrographs in Figure 3.14 are real precipitates that are incorporated in the metallographic structure, not any artefacts (dirt) produced by possibly erroneous sample preparation, as suggested in a later publication /Sipilä K, et al. 2014/ and /Huotilainen C. et al. 2018/

3.8. Retrieval and post-test examination of packages 4 and 5 of the MiniCan field experiment.

MiniCan is an *in situ* or field test of certain aspects of corrosion in the KBS-3 concept for deep geological disposal of spent nuclear fuel in bentonite embedded copper-cast iron canisters. The experiment is being performed by the Swedish Nuclear Fuel and Waste Management Company (SKB) at a depth of about 450 m in the Äspö HRL. The exposure time of the studied samples were 9 years. In package 4 (MiniCan 4) the canister was embedded in high density clay made from prefabricated blocks in direct contact with the copper surface, thus restricting water flow to the surface of the canister and associated samples. In package 5, there was no clay present in the experiment, meaning that the canister and samples were directly exposed to the ground water in the bore hole.

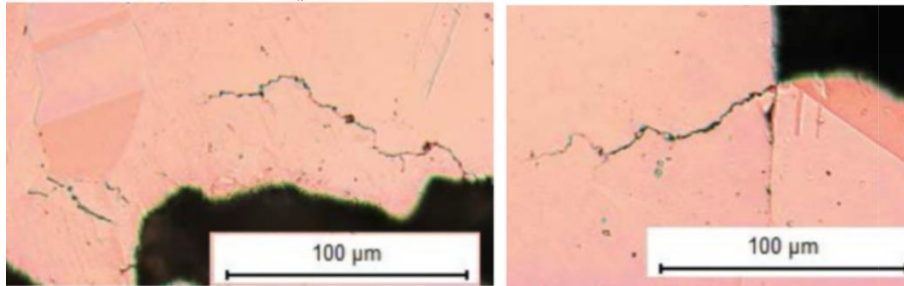


Figure 3.15. Details from Figure 4-7 in /Gordon A. et al. 2017/. Middle part of pre-crack of WOL sample M4 4:1 (MiniCan 4), showing smaller cracks emanating perpendicular to the direction of the main crack.

Both types of SCC samples, U-bend samples and pre-cracked samples (WOL), experienced unexpected damages and cracks as shown in Figures 3.15 and 3.16. From the report, quote:

“These smaller cracks were notable as some of them were seen to be travelling perpendicular to the direction of the pre-crack (i.e. parallel to the load applied when fatiguing the specimens) and had more branches. These features are consistent with SCC but it is not possible to say if these smaller cracks are due to SCC in this instance or if they occurred during the original fatiguing of the samples.”

Furthermore, post exposure hydrogen measurements showed that the copper metal was subjected to hydrogen charging and the highest value measured were around 1.8 wt-ppm (page 45) which actually is a higher hydrogen content than was measured in /Forsström A. et al. 2017/. With the knowledge of the recent publication by /Forsström A et al. 2017/ and the work by G. Hultquist, see section 3.6, it is obvious that the copper canisters are subjected to hydrogen charging and SCC in a repository environment and that it is only a question of time before hydrogen blisters and cracks occurs. The damages seen in Figure 3.16 are most likely hydrogen blisters, compare with Figure 3.8 and the feature of the thin cracks seen in Figure 3.15 are typical for SCC.

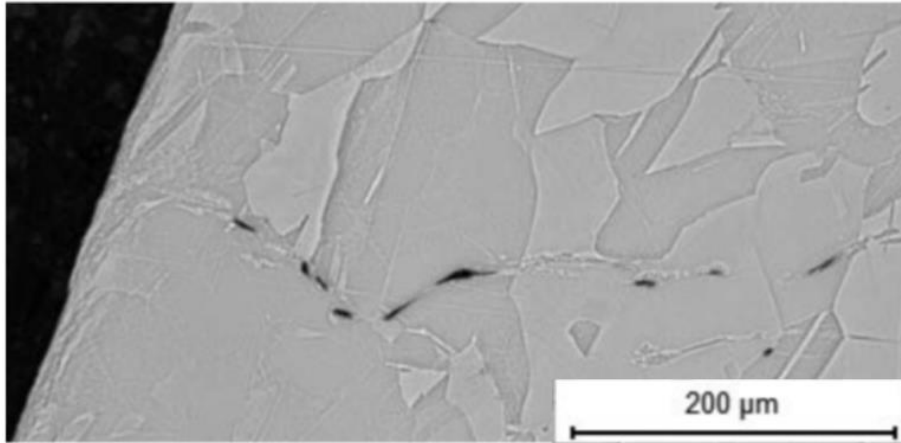


Figure 3.16. Details from Figure 4-5in /Gordon A. et al. 2017/. U-bend sample M4 1.1 had an area of cold deformation near the surface, but also present were pores which appeared to be aligned along the grain boundaries.

3.9. A study of hydrogen effects on creep ductility

Another problematic issue connected to hydrogen charging is the low creep ductility, here exemplified by Figure 3.17.

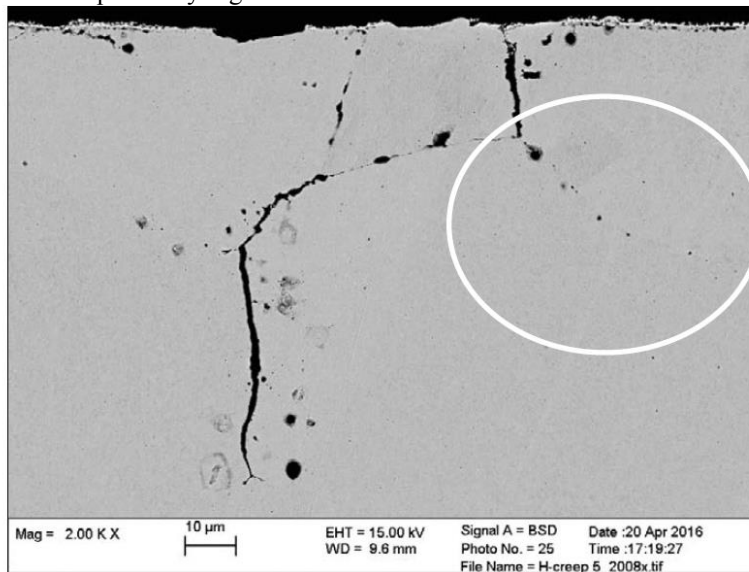


Figure 3-8. Specimen H-creep-05 tested at RT for 1 005.7 hours hydrogen charging time and creep stress of 170 MPa. Larger cracks were discovered. The specimen was tested in soft annealed condition without any pre-strain.

Figure 3.17. From /Leijon G. et al. 2017/. Hydrogen charging resulted in severe cracking, more than 100 μm deep cracks was formed already at room temperature. Hydrogen blisters was also detected in not yet cracked grain boundaries, see the encircled area.

However, SKB have made an overhasty assessment of the seriousness of hydrogen assisted creep, quote from /Hedin A. et al. 2019/ regarding the results in /Leijon G. et al. 2017: “In their tests in which the creep rate was measured, the rate was either above or below results from standard creep tests in air indicating that the influence of hydrogen was limited and presumably smaller than the variation between samples.” More studies of hydrogen assisted creep are obviously needed before such conclusions could be made.

3.10. Microbial influence on corrosion of copper in the repository environment, Aalto University.

Microorganisms can accelerate canister corrosion in the nearfield in two ways, by hydrogen scavenging and by sulphide and/or acetate production. Microbial induced corrosion (MIC) by sulphate reduced bacteria (SRB) will indeed increase the SCC-failure distribution since the main effects of SRB are sulphur accumulation and conversion of sulphate to sulphide which results in SCC in unalloyed copper, as shown in Figure 3.18 /Carpén L. et al. 2016/.

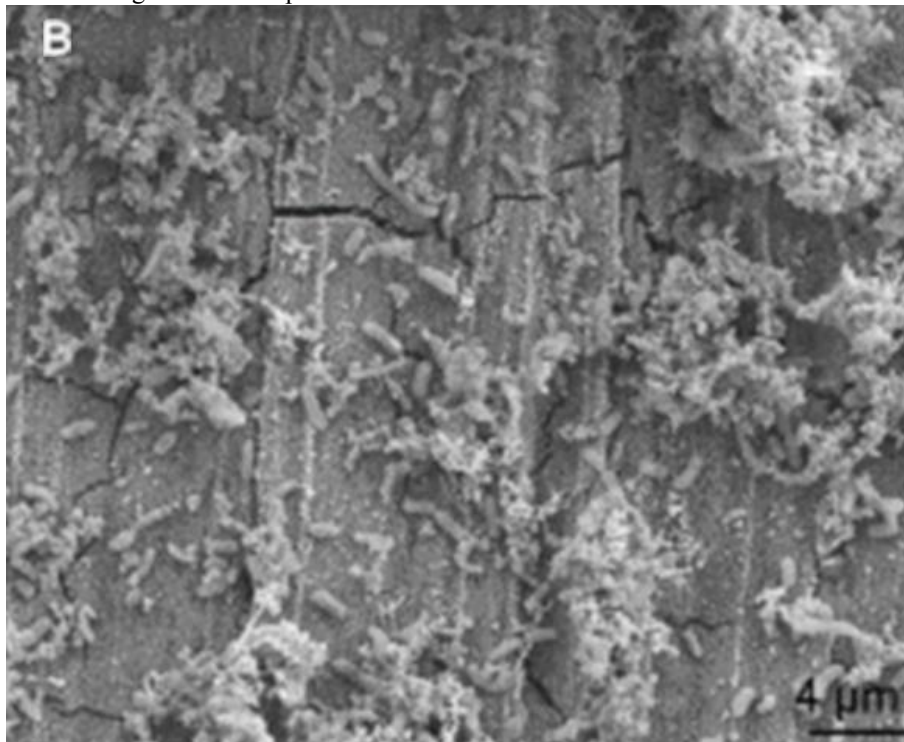


Figure 3.18. Microbial corrosion on the surface of unalloyed copper creates micro cracks due to sulphur enrichment. SRB colonies convert sulphate to sulphide which results in SCC/ Carpén L. et al. 2016/.

3.11. Discussion and conclusions regarding SCC and hydrogen embrittlement (HE) and hydrogen sickness (HS) of unalloyed copper (CuOFP) in a deep repository environment

All prerequisites for SCC and hydrogen embrittlement are fulfilled in a KBS-3 deep geological repository in Forsmark as described in the previous sections. These circumstances, i.e. the obvious risk for SCC, HE and HS are unfortunately not adequately discussed in SKB supplementary information on canister integrity issues and disregarded in the safety analysis. In SKB R-18-03 /Huotilainen C. et al. 2018/ it is concluded: *“The findings of Taniguchi and Kawasaki (2008), and Becker and Öijerholm (2017) of claimed small (of the maximum depth of a few tens of microns) SCC cracks on the surface of copper after SSRT experiments in sulphide containing environments can be alternatively explained as follows. The pre-existing manufacturing defects (which Becker and Öijerholm showed to exist also in the unexposed material, that had never been in contact with the sulphide containing*

environment) extending to the specimen surface, open up due to the effect of surface active sulphide species on the cohesive forces of the opposing surfaces of a defect.” and in TR-19-15 at page 84 it is commented: *“The involvement of absorbed H in the reported SCC of Taniguchi and Kawasaki (2008) and Becker and Öijerholm (2017) has not been proven and it is important to note that Bhaskaran et al. (2013) did not observe cracking when they cathodically polarised specimens.*

These comments are not supported by any scientific publication, on the contrary, it is scientifically erroneous to claim that the cracks shown in for instance Figure 3.1 should be initiated by *pre-existing manufacturing defects* in as-delivered copper. Virtually all grain boundaries in Figure 3.1 have initiated a crack close to the main fracture and for obvious reasons this cannot be due to *pre-existing manufacturing defects*, instead it is a scientific proof of sulphur induced SCC in copper. In fact, all surface cracks shown in Figure 3.1 and Figures 3.4-3.7 have clear evidence of being environmentally induced grain boundary cracks and have nothing to do with manufacturing defects since those would not be connected to the copper grain boundaries.

Furthermore, SKB seems to believe that the hydrogen induced blisters and cracks deeper inside the copper metal, as seen in Figure 3.8 are manufacturing defects as well, which is obviously wrong when understanding the mechanism of hydrogen charging of copper exposed to an anoxic environment. The maximum allowed hydrogen content of copper in the KBS-3 concept is 0.6 wt-ppm in order to avoid hydrogen embrittlement. The hydrogen content rises quickly in copper exposed to an anoxic and corrosive environment containing different concentrations of sulphide. The corrosion induced hydrogen charging of copper for only 2 weeks results in dangerous levels (1.2 wt-ppm) of hydrogen as shown in Figure 3.9 with formation of hydrogen blisters in the grain boundaries as shown in Figure 3.8. Furthermore, in a real repository exposure in the MiniCan-project, see section 3.8, even higher hydrogen content was detected in the copper metal (1.8 wt-ppm) and subsequent HE-blisters and SCC.

The comment that /Bhaskaran et al. 2013/ did not observe cracking when they cathodically polarised specimens is irrelevant since all slow strain rate tests at elevated temperature were performed too fast for SCC or HE to occur, i.e. with a strain rate of 10^{-6} in combination with a preload of 70 MPa or 98MPa. The most relevant publications concerning SCC of copper, /Taniguchi and Kawasaki 2008/ and /Becker and Öijerholm 2017/ have used slower strain rates and no preload which explains why /Bhaskaran et al. 2013/ did not observe any cracking. Concerning hydrogen charging effects, /Bhaskaran et al. 2013/ did not perform any hydrogen measurements either before or after their slow strain rate tests.

From conclusions in the hydrogen embrittlement chapter in TR-19-15: *“The longest charging times that have been used are 6 weeks. Modelling results suggest that the surface layer with bubbles and cracks will not grow much even if very long times are considered. The reason is that bubbles and cracks create easy paths for the outflow of hydrogen and a steady state is eventually reached between inflow and outflow. For the copper canisters, only a very thin layer would be affected even if hydrogen charging comparable to the rate in the experiments were to occur. However, under repository conditions, the generation rate of hydrogen on the canister surface would be many orders of magnitude lower than in the experiments.”*

SKB seems not to understand that anoxic copper corrosion always includes an electrochemical hydrogen charging process and there is no thermodynamic reason why the hydrogen should just penetrate the surface layer, on the contrary it is already shown by Gunnar Hultquist at the Royal Institute of Technology, that the copper canister exposed in the prototype repository in fact was subjected to hydrogen charging throughout the whole thickness of 50 mm already after 7 years exposure, as shown in Figure 3.12. The copper metal will unfortunately be decorated with hydrogen

blisters and cracks, see Figures 3.8 and 3.16, long before a possibly steady state is eventually reached between inflow and outflow of hydrogen.

Regarding the reports of /Taxén et al. 2018, 2019/ they indeed detected surface cracks when following the procedure of /Taniguchi and Kawasaki (2008)/, however, they denoted the cracks as “intergranular attack”.

In TR-19-15 at pages 85-86 it is commented: “*The environmental conditions for which cracks have been reported are generally harsh compared with those to which the canisters will be exposed. // Not only is the minimum sulphide concentration at which cracking has been observed (10^{-3} mol/L, Becker and Öijerholm 2017) a factor of 10 to 100 times higher than that measured in the groundwater at Forsmark, but more importantly the flux of sulphide to the copper surface is orders of magnitude lower than the experimental fluxes, as long as the buffer is in place.*” and on page 86: “*It is thus concluded that the possibility of SCC in copper, even at high sulphide fluxes has questionable scientific support. Even if copper is susceptible to SCC in the presence of sulphide, the sulphide fluxes in the repository environment are far too low to induce the phenomena observed and sometimes interpreted as SCC.*”

In fact, cracks were already initiated at 10 times lower sulphide content, see Figure 3.7, i.e. 10^{-4} mol/L, /Becker and Öijerholm 2017/. This is a highly relevant and probable sulphide concentration in a deep repository, especially at Forsmark with the sauna effect (sulphur salt enrichment) and non-saturated and non-functional bentonite buffer for several thousands of years as discussed in chapter 2. Furthermore, sulphate reducing bacteria (SRB) will thrive in a Forsmark repository with severe sulphide enrichment, as discussed in sections 3.10, 4.5 and 4.6.3. Based on the latest years new insights in H, OH and S penetration and internal corrosion of unalloyed copper under anoxic conditions it is just a question of time before SCC occurs in the canisters. Since hydrogen blisters in the copper grain boundaries could form already after two weeks of laboratory exposure in an anoxic and corrosive repository environment /Forsström A. et al. 2017/ and that the whole canister thickness is found to be hydrogen charged within 7-9 years of real exposure in the prototype repository /Szakálos P. and Hultquist G. 2013/ and in the MiniCan exposure, it should be obvious that HE and HS in the welds (see Figures 3.10 and 3.11) must be included in the safety analysis, especially since no external load or internal stresses are needed to initiate HE and HS in copper.

To conclude, SKB has not added any significantly new information or knowledge regarding SCC, HE and HS in their complementary information and reports, TR-19-15, TR-19-13 and TR-17-16, since the Land and Environmental Court in Nacka made their assessment 23 January 2018. With today's knowledge and collected findings, these fast degradation processes should all be included in the safety analysis SR-site as already described above. At least 40%, i.e. 2800 canisters, will be dependent on local inflow in the deposition holes and thus be subjected to the Sauna effect (salt enrichment) until being flooded after around 2000 years, see Figure 2.4 in previous chapter. Knowing that both SCC, HE and HS in the welds, operate with almost instant kinetics with respect to repository time scales it is important to make a conservative safety analysis. It is realistic to assume that 2800 canisters (40 %) collapse within 100 to 200 years after repository closure and that all remaining canisters collapse within 1000 years. A conservative safety analysis should therefore calculate with that 40% of the canisters collapse already within 100 years after repository closure and the remaining 60% within 1000 years after closure. More specifically, failures due to HE and HS will dominate in a Forsmark repository since these degradation processes operate without any applied load, in contrast to SCC.

This shows that the SR-site /Hedin A. et al. 2011/ (SKB safety analysis from 2011) is not valid anymore and that it cannot be used as basis for a decision concerning the final storage of high-level waste by the Swedish government.

4. General corrosion and pitting corrosion

4.1. Short summary

General corrosion in pure anoxic (free from dissolved oxygen) water is found to be more corrosive and detrimental to unalloyed copper than SKB has anticipated. There are several possible corrosion reactions in pure anoxic water, including internal corrosion and hydrogen charging of the bulk metal which are supported by theoretical calculations. A important long term study, FEBEX /Wersin P. and Kober F, 2017/ performed by SKB's Swiss equivalent NAGRA, has shown that unalloyed copper is susceptible to pitting corrosion in an oxygen free repository environment. In another study by /Marja-aho, M. et al.2018/, it was found that severe pitting corrosion was induced by sulphate reducing bacteria (SRB) in simulated geological nuclear waste repository at temperatures 10-12°C. It was concluded in the report that the copper sample in the biotic environment with SRB for 4 months had experienced the most severe corrosion, with the maximum corrosion rate reaching 175 µm/year. According to /Hedin A. et al. 2019/, SKB believes that a compact copper sulphide layer is needed on the copper surface in order to get pitting corrosion and that “neither biofilm formation nor localised corrosion in the presence of SRB have been observed under repository conditions”. Both statements are incorrect, no compact copper sulphide film is needed on the copper surface in order to get pitting corrosion during anoxic conditions, as shown in Figures 4.5, 4.6 and 4.8. Localised corrosion on copper has definitely been connected to SRB under repository conditions, see Figure 3.18 and Figure 4.10.

4.2. General- and pitting corrosion- introduction

General corrosion will most likely not be a cause of canister failure since there are much faster degradation mechanisms that will destroy the copper canisters in a Forsmark repository as discussed in detail in Chapter 3. However, general corrosion of copper is still detrimental since the corrosion rate will be accelerated by temperature, MIC and radiolysis. Unalloyed copper is very sensitive to a temperature increase and the corrosion rate is expected to double for every 10 degrees increased temperature /Mattsson E. 1997/. Anoxic (oxygen free) copper corrosion produces hydrogen, which gives energy to the microbes in the repository, see section 4.5. This means that the microbes act as a hydrogen sink and will thus accelerate the copper canister corrosion, furthermore copper ions and copper corrosion products as such are known to destroy the bentonite buffer, see section 4.4.

4.3. General copper corrosion in pure oxygen gas free water

An updated potential–pH diagram (Pourbaix) for copper metal in water is seen in Figure 4.1.

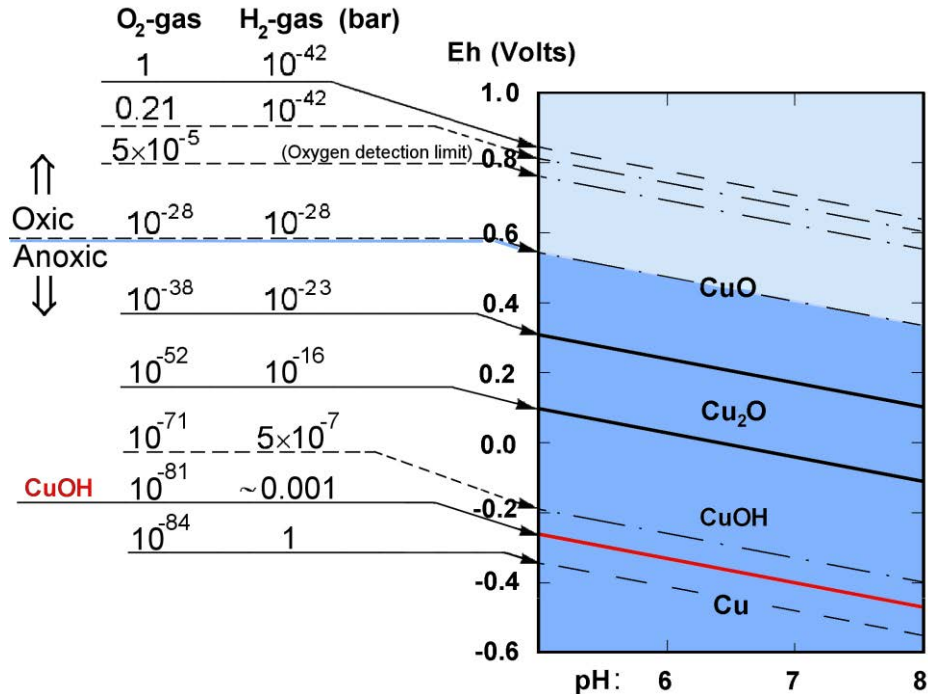


Figure 4.1. Pourbaix diagram based on /Szakálos P et al. 2007/. The light blue area at the top shows the oxic region with predominantly dissolved oxygen gas. The somewhat darker blue area shows the anoxic region with predominately dissolved hydrogen gas. The anoxic corrosion product Cu₂O (cuprite) is only formed at very low oxygen and hydrogen partial pressures represented by the black solid lines. The solid red line marks the lower stability region for the monovalent hydroxide CuOH, which is stable up to around 1 mbar hydrogen gas pressure.

Cupric oxide (CuO) is formed predominantly in oxic environment and the absence of CuO when copper is exposed to water is a clear evidence for that an anoxic environment has prevailed. Copper exposed to strictly anoxic and pure water is visible in Figure 4.2. Only crystals of cuprite (Cu₂O) is visible on the copper surface, but these Cu₂O-crystals contain high amount of hydrogen which may explain why they are stable at a quite high hydrogen pressure of around 0.5 mbar at 50°C.

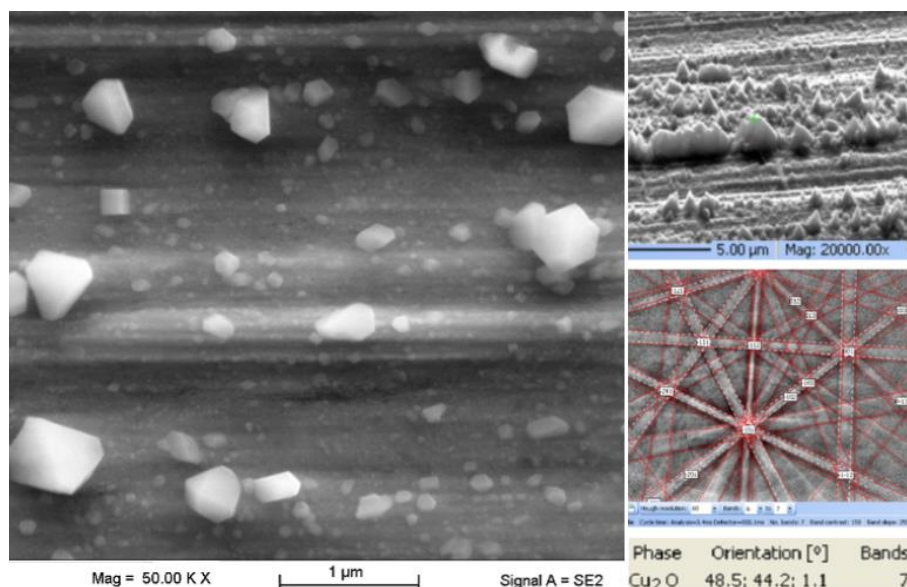


Figure 4.2. Unalloyed copper exposed to pure oxygen free water at 50°C for 12 months. The sample was moved directly from the anoxic water to the SEM/EBSD equipment to avoid any oxidic corrosion. The light crystals on the exposed surface have a somewhat distorted Cu₂O-crystal structure, i.e. cuprite (detected by EBSD), but contain high amount of hydrogen (SIMS) /Szakálos P. and Hultquist G. 2013/ and Land and Environmental Court in Nacka, Sweden, case no. M 1333-11, Addendum 690.

These results with formation of a solid corrosion product consisting of hydrogenated Cu₂O and hydroxide with an equilibrium hydrogen pressure roughly around 1 mbar in a strictly anoxic and pure water have been confirmed in several exposures in a project financed by the Swedish Radiation Safety Authority, see /Hultquist et al. 2013/, SSM-report 2013-07.

The non-crystalline corrosion product CuOH has experimentally been found to be stable up to a hydrogen pressure of around 1 mbar /Szakálos et al. 2007/, /Hultquist G. et al. 2009/, /Hultquist G. et al.2011/. Ab-initio calculations /Belonoshko A.B. and Rosengren A. 2010/, /Belonoshko A.B. and Rosengren A. 2012/ and /Johansson, A. J. et al. 2011/ have confirmed the stability of a CuOH-layer on copper. In fact, it is confirmed by Ab-initio calculations /Belonoshko A.B. and Rosengren A. 2012/ that the theoretical equilibrium hydrogen pressure for CuOH is around 1 mbar, as indicated in the Pourbaix diagram in Figure 4.1. Furthermore, it has been shown again both experimentally, see Figure 3.13 and theoretically that the monovalent hydroxide is stable, not only on the copper surface but also inside the copper metal in defects /Korzavyi P. and Sandström R. 2014/. These combined findings explain why copper do corrode continuously in pure anoxic water.

According to old thermodynamic databases there exists only one anoxic copper corrosion product in pure water and that is a “dry” hydrogen free cuprite (Cu₂O) that has a hydrogen equilibrium pressure of 10⁻¹⁶ bar, as can be seen in Figure 4.1. However, there exists at least two more anoxic copper corrosion products, CuOH as shown in Figure 4.1 (red line) and a hydrogen “saturated” cuprite (Cu₂O) as shown in Figure 4.2. Both these corrosion products have an equilibrium hydrogen pressure in the region of 0.1-1 mbar which means that copper corrodes much more in pure anoxic water than predicted by SKB and by old thermodynamic databases. In fact, several research groups around the world have confirmed Gunnar Hultquists original copper corrosion results /Hultquist G. 1986/ during the latest years /Becker R and Hermansson, H.-P. 2011/, /Bengtsson, A. et al. 2013/, /Cleveland C. et al. 2014/, /Kaufhold S. et al. 2017/, /He, X. et al. 2018/. However there is one research group at

Uppsala University led by Mats Boman and financed by SKB, that has not been able to detect any significant anoxic copper corrosion, but the research group has had problems concerning copper surface pre-treatment, hydrogen control, gas leakage and poor steel quality in the equipment during the years, problems which have been thoroughly described in /Szakálos P. et al. 2018/. In their rebuttal /Ottosson M. et al 2018/ it is confirmed that they still have no control over the hydrogen release from the equipment. Despite all warnings from Assoc. prof. G. Hultquist (KTH) during the years, they still use Mo-free stainless steel, AISI 304L, which does corrode in heated pure anoxic water/steam, albeit with slow hydrogen release, but still enough to hinder the weak copper corrosion reaction. Furthermore, we understand that Ottosson et al. still believe that their special copper sample pre-treatment with electrochemical polishing in phosphoric acid and high temperature furnace heat treatments will not affect the initiation of copper corrosion in pure anoxic water. We still strongly disagree with that assumption.

SKB refers also to a recent anoxic copper corrosion study by /Senior N A. et al. 2019/, which in fact detects substantial amount of hydrogen which was evacuated from the equipment 1-2 times per month. The experimental set-up with a large copper surface area (2600 thin copper wires in a small jar with water) is suitable for studying sensitive equilibrium reaction but not corrosion rates and certainly not a “conservative upper bound on copper corrosion rates” as SKB claims in /Hedin A. et al. 2019/, at page 51. According to SKB /Hedin A. et al. 2019/, page 47 in the supplementary information, quote: *“No stable Cu-O-H compound that could act as the thermodynamic driving force of a continuing corrosion reaction in pure, O₂-free water was found. Furthermore, surface reactions between water and the copper or copper oxide surface may lead to the oxidation of about one half of a monolayer of copper at most, potentially releasing a corresponding amount of hydrogen. This is far too little to explain the results observed by Hultquist et al. (2011, 2015)”*

Obviously, SKB has not made any thorough literature survey in the field of copper corrosion and did not take in any new information in the Land and Environmental Court in Nacka, Sweden, case no. M 1333-11, since there is convincing scientific evidence that at least two more anoxic corrosion products exist in the Cu-O-H system. With both experimental (Figure 3.13 and Figure 4.2) and Ab-initio calculations showing that the monovalent hydroxide does not only form on the copper surface but also in defects in the bulk metal (internal corrosion), the measured hydrogen pressures and increased copper corrosion observed in /Hultquist et al. 2011, 2015/ are certainly expected with the scientific knowledge of today.

The latest year’s research has shown that the seriousness of anoxic copper corrosion, by water molecules alone, is detrimental since both OH and H penetrates and accumulates in the copper metal by time. This inevitably results in internal corrosion and severe degradation of the mechanical properties, as discussed in Chapter 3.

4.4. Increased general copper corrosion in contact with bentonite

The copper canister will be in close contact with bentonite clay in a deep repository which is not only positive. It has been shown that copper corrosion may increase since the clay acts as a sink for copper ions and that in turn destroys the bentonite. Results from SKB’s LOT-project are shown in Figure 4.3.

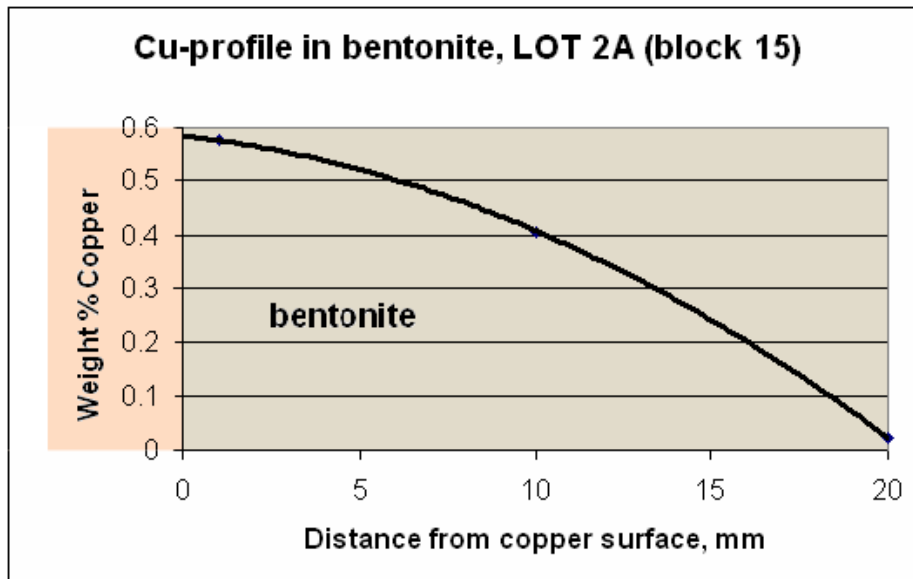


Figure 4.3. The bentonite acts as a Cu-ion sink and both copper and bentonite mutually destroy each other in an accelerated manner. Raw data from /Karlund O. et al. 2009/. LOT A2, Appendix 6; Characterization of the A2 parcel, Bundesanstalt für Geowissenschaften und Rohstoffe.

Heated copper surrounded by bentonite and groundwater was exposed for 5 years in the Äspö hard rock laboratory. A significant part of the copper in bentonite is precipitated as Cu- and Cu(Fe)-sulphides, representing ca 4 $\mu\text{m}/\text{y}$ in corrosion rate. Considering the total amount of copper corrosion products, especially the thick layer on the copper surface, which is not included in Figure 4.3, it is most likely that the copper corrosion rate is around 10 $\mu\text{m}/\text{y}$ (pitting corrosion not taken into account).

4.5. Microbial induced “corrosion” degradation of the bentonite buffer

New research has shown that not only the copper canister will be attacked by the prevailing microbes in a deep repository but also the bentonite buffer, see Figure 4.4. Microorganisms such as SRB can accelerate degradation of bentonite-based buffers and influence the long-term behaviour of plug systems and seals /Taborowski T. et al, 2019/ and /Pedersen K. et al. 2017/. The sulphide producing bacteria can, as shown in Figure 4.4, destroy the bentonite buffer by consuming iron from the clay mineral and precipitate quite large numbers of iron sulphide mineralizations. It was concluded in /Taborowski T. et al, 2019/, that the important swelling properties are jeopardised, quote:

“In MX-80 the lowest sulphide concentration produced the highest swelling pressure and the highest sulphide concentration the lowest swelling pressure. This indicates that the oxidation of sulphide to sulphur and concomitant with the reduction of a range of different ferric iron minerals to ferrous iron negatively affected the swelling pressure in MX-80.”

Anoxic (oxygen free) copper corrosion produces hydrogen, which gives energy to the microbes in the repository /Taborowski T. et al, 2019/. This means that the microbes act as a hydrogen sink and will thus accelerate the copper canister corrosion, furthermore copper ions and copper corrosion products as such are known to destroy the bentonite buffer see section 4.4. Furthermore, the fast degradation of the bentonite by microbes, within months, with significant reduction of the bentonite swelling

pressure will, in combination with cementation, cracking, piping and erosion of the buffer, as discussed in section 2.5, deprive the barrier properties of the bentonite clay in a Forsmark repository.



Black colonies of iron sulphide produced by sulphide producing bacteria in Asha bentonite at 1750 kg/m³ wet density and with addition of lactate and sulphide producing bacteria



Black colonies of iron sulphide produced by sulphide producing bacteria observed during sampling of test cell with GMZ bentonite.

Figure 4.4. Details from page 79 in /Taborowski T. et al, 2019/. Sulphate reducing bacteria (SRB) are found to be capable of destroying fully pressurized bentonite by precipitation of iron sulphide mineralizations.

4.6. Pitting corrosion in the repository environment

4.6.1. FEBEX, 18-year long term study in a repository environment.

An 18-year long term study, FEBEX (Full-scale Engineered Barrier EXperiment in Crystalline Host Rock), performed by SKB's Swiss equivalent NAGRA (National Cooperative for the Disposal of Radioactive Waste), has shown that unalloyed copper is susceptible to pitting corrosion in an oxygen free repository environment, see Figures 4.5 and 4.6.

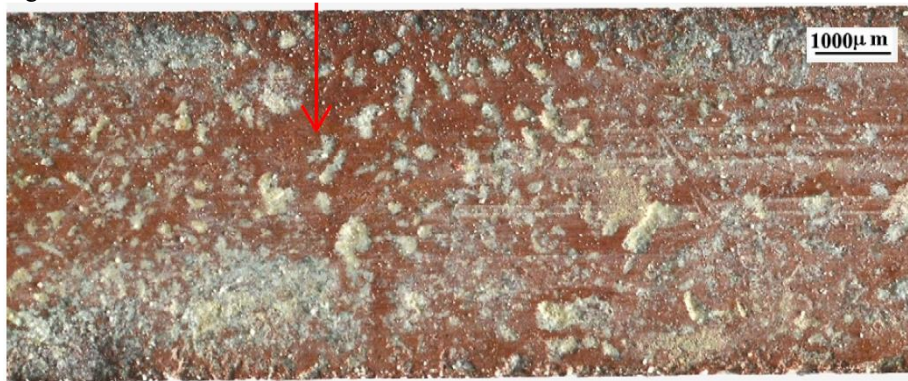


Figure 4.5. A macrograph showing an exposed copper sample severely attacked by pitting corrosion, from Appendix B in the FEBEX-report /Wersin P. and Kober F 2017/.

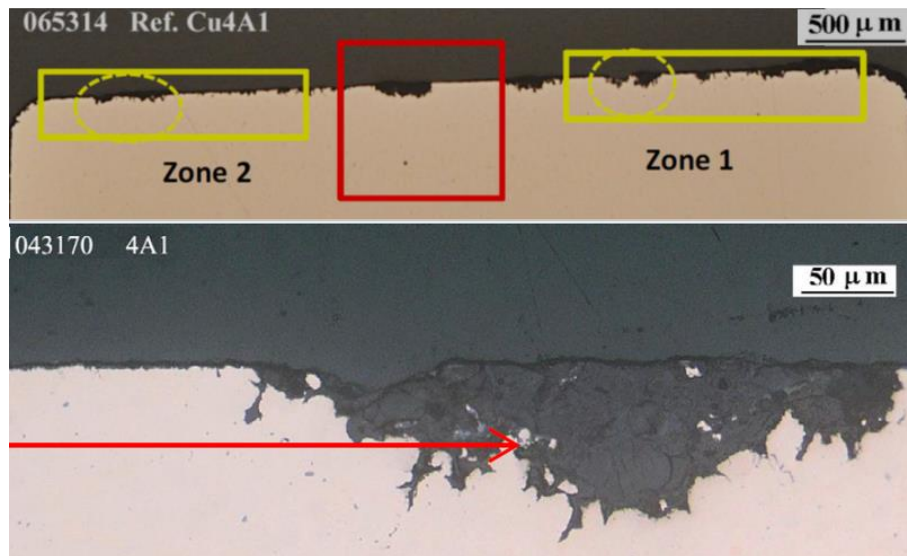


Figure 4.6. Metallographic cross-sections showing the exposed copper sample with pitting corrosion, up to 100 μm in depth. From Appendix B in the FEBEX-report /Wersin P. and Kober F 2017/.

It is commented in the report, concerning the corroded copper samples, that “No effects of anaerobic corrosion could be observed on these surfaces.” This is a strange comment since the corrosion products and the corrosion features are consistent with anoxic copper corrosion. The only copper oxide detected is Cu_2O (no CuO) and as seen in Figure 4.1 that indicates that the exposure was indeed anoxic. Furthermore, quote from page 28 concerning copper corrosion: “These pits were filled with clay material and little or no Cu-corrosion products.” This feature, with no corrosion

product in the pits is a clear evidence of anoxic dissolution corrosion. The pits would have been covered with copper oxides if dissolved oxygen would have been present. Minerals and water with Fe^{2+} -ions is further evidence for that normal anoxic groundwater has prevailed in the long-term exposure.

It has recently been proven in a parallel study by the same organisation, NAGRA, that all oxygen that remains after the closure of a deep repository tunnel is consumed fast by the prevailing bio-/chemistry in the bentonite pore water, as shown in Figure 4.7. It is stated in the report /Müller H. 2017/: “The surrounding minerals confirm that the environment was indeed oxygen free and it is expected that any remaining oxygen was consumed during the first month after closure of the test repository.”

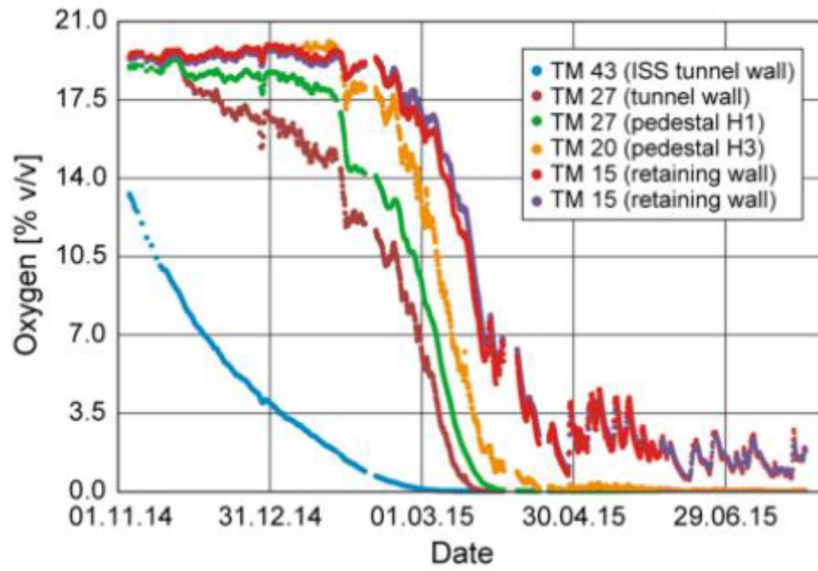


Fig. 11 Oxygen concentrations at different measurement locations along the FE tunnel from November 2014 (shortly after backfilling started) until July 2015

Figure 4.7. Monitoring of the oxygen content in a deep repository. All oxygen was consumed already during the first months after closure of the test repository /Müller H. et al. 2017/.

The FEBEX-report /Wersin P. and Kober F 2017/ confirms that an alloyed copper (Cu-Ni), is much more corrosion resistant than unalloyed copper in a deep geological repository:

“Analysis of copper and Cu-Ni alloy coupons placed close to the heater revealed moderate corrosion effects with general corrosion as the main corrosion mode. The total corrosion depth estimated from one sample was $\sim 9 \mu\text{m}$. For the Cu coupons, in some spots localised corrosion with maximum penetration lengths of 20-100 μm was observed. Cu-Ni alloys showed less corrosion than the unalloyed Cu samples.” Additionally, it was shown that stainless steels were attacked by different localised corrosion processes, but titanium metal (with and without welds) was virtually unaffected during the 18-year exposure.

4.6.2. A 15-year exposure in pure anoxic water and observed pitting corrosion in the SKB-project Alternative Buffer Material (ABM)

Another evidence for that unalloyed copper is sensitive to pitting corrosion also in pure anoxic water is seen in Figure 4.8.

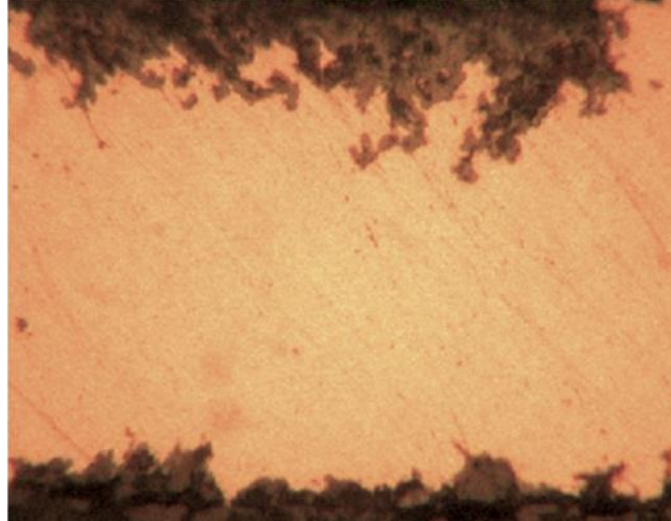


Figure 4.8. Light optical cross-section of the initially 100µm thick copper foil after 15 years exposure in distilled anoxic water at room temperature. Localised corrosion attack is clearly visible. Scale: the height of the micrograph is 90 µm. /Hultquist G. et al. 2008/.

The long-term exposure was performed in a set-up with an air-tight palladium membrane in the lid that allowed hydrogen to escape from the equipment, thus allowing the anoxic copper corrosion process to continue.

In the SKB-project Alternative Buffer Material (ABM) /Gordon A. et al. 2018b/ it is clear that pitting corrosion has occurred, see Figure 4.9. The copper samples were exposed to heated (80°C) groundwater and bentonite during 5 years in Äspö Hard Rock Laboratory.

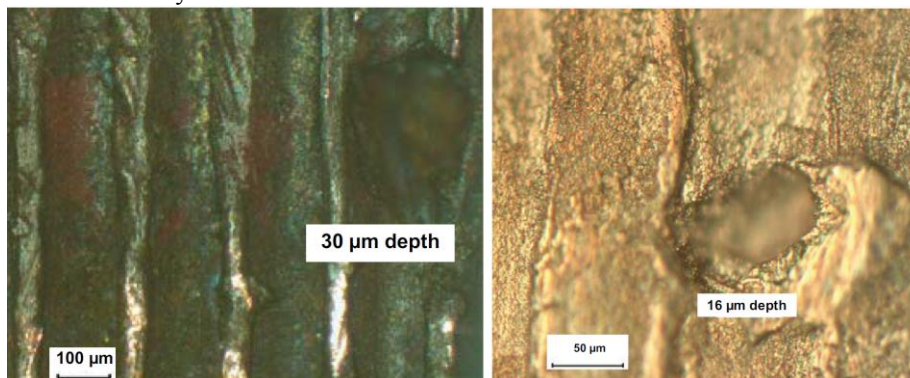


Figure 4.9. Example of pitting corrosion on one acid cleaned sample (to the right) and an un-cleaned sample to the left /Gordon A. et al. 2018b/. Maximum pitting corrosion rate: 6 µm/year.

4.6.3. Pitting corrosion of copper in anoxic groundwater environment in the presence and absence of sulphate reducing bacteria (SRB)

SRB have been proven to induce severe pitting corrosion on unalloyed copper in an anoxic repository environment, see Figure 4.10.

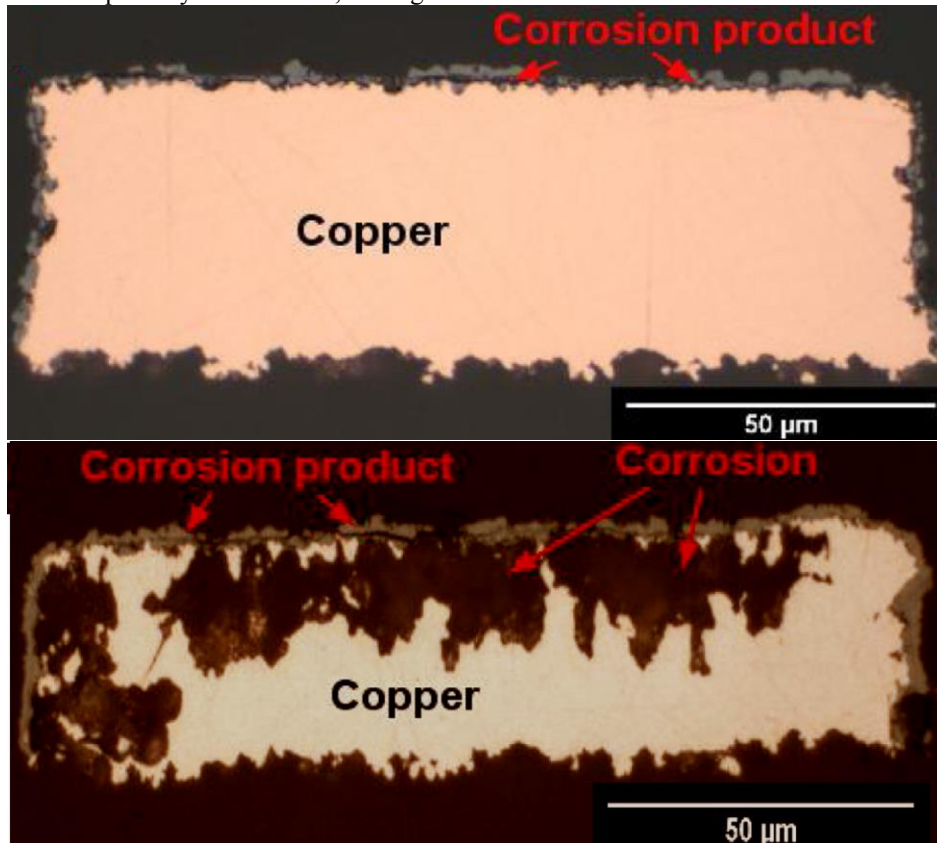


Figure 4.10. Results from Figure 5 in /Marja-aho M. et al. 2018/. Corrosion tests performed in simulated geological nuclear waste repository, at temperatures 10–12°C and oxygen level below 1 ppm. Simulated groundwater, with chemical composition of groundwater stabilized with bentonite. The micrograph at the top shows a cross-section, originally 200×35µm², of a sample exposed for 4 months without SRB (abiotic environment) and micrograph at the bottom shows a sample exposed 4 months with naturally occurring SRB in groundwater (biotic environment).

It was concluded in the report that the copper sample in the biotic environment with SRB for 4 months had experienced the most severe corrosion, with the maximum instantaneous corrosion rate reaching 175 µm/year.

SKB have financed much shorter studies, 10-32 days, with copper exposed to SRB, see report TR-18-14 /Gordon A et al. 2018/, where pitting corrosion was detected despite short exposure times. The deepest pitting corrosion detected was 10-20 µm/month which indeed indicate severe SRB-induced pitting corrosion in the long term, as shown in /Marja-aho M. et al. 2018/, however that was not discussed at all in the conclusions in /Gordon A et al. 2018/.

4.7. Discussion regarding pitting corrosion in a repository environment

According to SKB /Hedin A. et al. 2019/, page 74 in the supplementary information, SKB believes that a compact copper sulphide layer is needed on the copper surface in order to get pitting corrosion, quote:

“...The sulphide fluxes are below the threshold fluxes for formation of a compact film (a prerequisite for a passive film to give pitting). • Localised corrosion of copper due to the presence of a metabolically active biofilm of SRB on the canister surface exposed directly to the ground water seems unlikely, since neither biofilm formation nor localised corrosion in the presence of SRB have been observed under repository conditions.”

Both statements are obviously incorrect, no compact copper sulphide film is needed on the copper surface in order to get pitting corrosion during anoxic conditions, as shown in Figures 4.5, 4.6 and 4.8. Localised corrosion on copper has definitely been connected to SRB under repository conditions, see Figure 3.18 and Figure 4.10.

If we consider the most unlikely situation where SCC, HE and HS do not occur in a Forsmark repository then the canisters would fail by pitting corrosion and general corrosion accelerated by temperature, radiation, MIC and salt enrichment/the Sauna effect. The corrosion rate can vary considerably and in a case with no influence from MIC and radiation an average corrosion rate of 5-10 μm per year is realistic, see sections 4.4 and 4.6 (LOT, FEBEX, ABM projects). More severe pitting corrosion can occur with MIC as seen in Figure 4.10, with measured corrosion rates up to 175 μm at 10-12°C in a repository environment. Assuming the canisters may collapse when 50% of the wall thickness has been consumed by corrosion, i.e. 25 mm, and that the persistent corrosion rate during the first thousand years could be up to 10 μm per year, it would indicate, that the canisters would collapse within 2500 years. This shows again that the SR-site /Hedin A. et al. 2011/ (SKB safety analysis from 2011) is not valid anymore and that it cannot be used as basis for a decision concerning the final storage of high-level waste by the Swedish government.

5. The effect of radioactive radiation.

5.1. Summary.

In the SKB-report /Hedin A. et al. 2019/ regarding this issue is concluded *“...that irradiation will cause insignificant levels of radiation damage in the canister materials. This is concluded on the basis of revised calculations of radiation damage and to some degree also demonstrated by new experiments”*.

This overall conclusion is based on experimental /Padovani C. et al. 2019/ and theoretical /Yang Q. et al 2019/ investigations in which copper is exposed to gamma radiation alone, without any simultaneous exposure to any aqueous environment. However, the situation turns out to be completely different if copper is exposed not only to radiation but simultaneously also to an aqueous environment. In our Concluding Speech at Nacka Land and Environmental Court on Oct 26, 2017, it was exactly this condition, the combined effect of gamma radiation and water exposure, that was stressed by us to possibly impose an obvious threat on copper's mechanical integrity.

To our surprise this combined effect has not at all been dealt with in /Hedin A. et al. 2019/. All conclusions in the experimental study /Padovani C. et al. 2019/ have been based on the exposure of copper to gamma radiation under an inert atmosphere, not

to gamma radiation in water and some aqueous environment. Our conclusion is therefore that SKB in the main report /Hedin A. et al. 2019/ and the supporting reports /Padovani C. et al. 2019/ and /Yang Q. et al 2019/ by no means have met the arguments presented by us in the Court and formulated by the Court as an unresolved issue.

To fill some gaps in our lack of fundamental understanding of the combined effect of gamma radiation and oxygen-free water in SKB-copper we will use a unique technique based on high-resolution X-ray diffraction performed at the synchrotron radiation facility DESY in Hamburg, Germany. Below follow more details concerning the arguments put forward by SKB, and also more details on the new measurements to be performed at DESY. The intent is that these measurements will shed more light on the possible changes in microstructure of SKB-copper during simultaneous exposure to gamma radiation and oxygen-free water.

To conclude: The combined effect on the microstructure of SKB-Cu of radiation and water exposure is still an unresolved issue and has not been met by SKB in their Supplementary Study /Hedin A. et al. 2019/. This fact and also the circumstance that there is a new high-precision tool available for these investigations forms strong argument that one needs to wait before a final decision can be made regarding copper as canister material for long-term storage of nuclear waste.

5.2. More detailed report.

5.2.1. The difference between separate and combined effects of radiation and water exposure

In their Concluding Speech at Nacka Land and Environmental Court against SKBs application for final disposal of nuclear waste on Oct 26, 2017, the authors argued that the combined effect of gamma radiation and water exposure could result in additional phenomena which were not yet explored and understood. These include the formation of defects in the bulk of copper when the metal undergoes gamma-radiation annealing and structural alterations of the surface and sub-surface layers of copper, also the enhanced diffusion of hydrogen atoms into the bulk. Important spin-off effects of gamma radiation are the additional hydrogen sources produced during exposure in aqueous environments, and their further implications. Radiation effects outside the copper canister can result in further increase in hydrogen production at the copper/water interface. In addition, radiation inside the copper canister can result in increased hydrogen transport in the metal, also in hydrogen induced vacancy formation during early plastic deformation with increased risk of creep deformation, hydrogen embrittlement and stress corrosion cracking.

These arguments were taken by the Court and formulated as one of the five unresolved corrosion-related issues in their statement to the Government, Jan 23, 2018.

An obvious consequence of the KBS-3 concept is that copper will be simultaneously exposed to ionizing radiation and aqueous environments representative for long-term repository conditions. In view of this, the Swedish Nuclear Fuel and Waste Management Co. (SKB) has initiated several investigations in order to explore the effect of gamma radiation on the microstructure and integrity of copper. Guinan analysed gamma-spectra supplied by SKB for the spent fuel canisters and concluded that no practical effect of radiation could be discerned of any physical property changes of copper, such as yield stress, creep rate, segregation, dimensional change or brittleness /Guinan M. 2001/. As a result of the Court statement, the calculations by Guinan were recently repeated using more updated computational techniques for exploring possible radiation damages in copper /Yang Q. et al 2019/. In agreement with Guinan, it was concluded that no significant radiation-induced damage of copper

could be seen. A complementary experimental research programme was initiated in parallel to examine possible effects induced by gamma radiation on the microstructure of copper by using several highly sensitive characterization techniques /Padovani C. et al. 2019/. When comparing copper samples irradiated up to the full repository dose of 100 kGy with unirradiated control samples it was concluded that no radiation effect could be discerned with respect to copper microstructure and some material properties. Hence, the overall conclusion from these theoretical and experimental investigations is that gamma radiation alone, under conditions given by the KBS-3 concept, seems to impose no constraints on copper used as canister material for spent nuclear fuel.

The situation turns out to be different if copper is exposed not only to radiation but simultaneously also to an aqueous environment. When copper has been exposed to similar gamma radiation rates and doses in an aqueous environment, significant effects could be observed both with respect to localized corrosion of copper /Björkbacka Å. et al. 2012/ and /Björkbacka Å. et al. 2013/ and with respect to increased uptakes of hydrogen in the bulk of copper /Lousada C. M. et al 2016/. Both effects turned out to increase with the total dose of gamma radiation. The results were discussed in terms of production of H-atoms at the water-copper interface induced by gamma radiation, enhanced transport of H-atoms into copper and the formation of defects in the bulk of copper induced by the combined effect of hydrogen and radiation /Lousada C. M. et al 2016/.

Despite the Court statement and to our great surprise, SKB has not initiated any studies of SKB-copper exposed to simultaneous gamma radiation and an aqueous environment. In order to provide more information on the possible combined influence of gamma radiation and water on copper, studies will be undertaken within the next months based on a largely unexplored technique related to this issue, high-energy synchrotron x-ray diffraction (HEXRD, 8). The technique takes advantage of the high-flux of high-energy photons generated by a synchrotron source and has found many new opportunities for in situ probing of, e.g., structural phase transformations or small lattice parameter changes of individual grains in a polycrystalline metal matrix. In what follows, we explain the technique in some detail, also some reports from the scientific literature with relevance for the possible new insight generated.

5.2.2. High-energy synchrotron x-ray diffraction (HEXRD)

The study to be undertaken is a collaboration between scientists at KTH Royal Institute of Technology, Stockholm, Sweden, and Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany. Copper specimens from SKB copper will be prepared in the same way as in previous work /Björkbacka Å. et al. 2012/, i.e. polished copper placed in 10 mL deaerated Millipore Milli-Q water in glass beakers and exposed to gamma radiation using a Cs-137 gamma source at KTH Royal Institute of Technology with a dose of radiation up to around 100 kGy, representing a total dose of a copper canister during 100,000 years of final disposal in the Swedish bedrock /Björkbacka Å. et al. 2012/.

HEXRD measurements in transmission mode (Debye-Scherrer method) will be performed at the German Synchrotron radiation facility (DESY) PETRA III beamline P21.2. Here, the samples will be mounted onto a high-precision motorized multiaxial positioning and rotary stage with their radiation-exposed surfaces being parallel to the incident x-rays, see Figure 5.1.

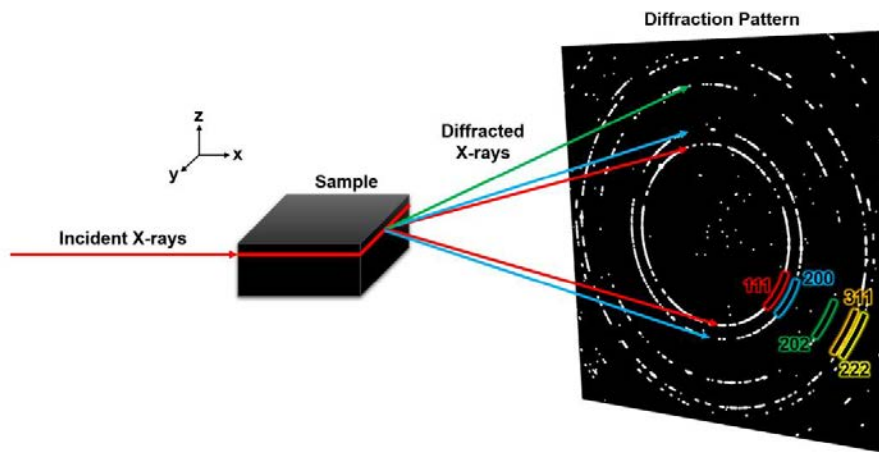


Figure 5.1. Experimental setup of high-energy x-ray diffraction measurements showing x-rays radiating the copper specimen and the diffracted x-rays with the 2D diffraction pattern collected by a detector.

The samples will be irradiated with the x-rays through the width of the specimen by angle of 45° and scanned from top to bottom in 20 μm steps (z-direction). The position of the scan direction through the specimen is shown in Figure 4.2.

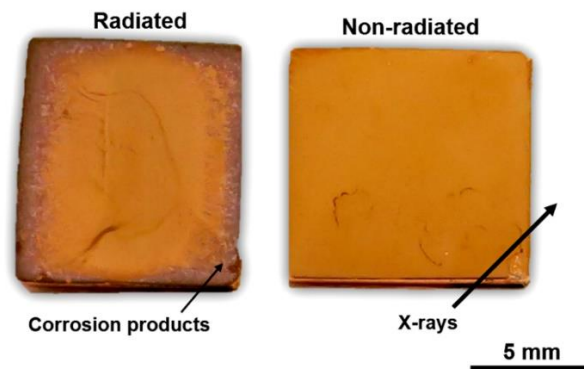


Figure 5.2. Photograph of some of the copper samples to be investigated. The radiated specimen in this case was exposed to oxygen-free water for 64 hours with a simultaneous exposure to 28.6 kGy of gamma radiation. The non-radiated specimen was exposed to oxygen-free water for 64 hours only. The bar shows the scan direction of x-rays through the specimen.

The x-rays have an energy of 72 keV with a beam size of 18 μm perpendicular to the sample surface and 55 μm to its horizontal. With a sample-to-detector distance of 1.6 m the first five full diffraction rings (Figure 5.1) with the highest intensities will be collected. During each scan, the sample is moved parallel to its surface (in the y-direction) by 2 mm to collect more diffraction signals from each z-position and thereby improving statistics. The samples will be scanned from 200 μm above the upper surface down to 200 μm below the lower surface, capturing the entire specimen thickness. The surface is defined as that position where the first analysable diffraction patterns with intensities strong enough can be seen. Using Match! XRD analysis software to read the d-spacing of each diffraction peak, the lattice constant, a , can be calculated using the classical relationship between d-spacing and each reflector:

$$a = d_{hkl} \cdot \sqrt{(h^2 + k^2 + l^2)}$$

The average of all five values will be considered as the lattice constant. The standard deviation obtained in introductory studies of SKB-copper at DESY shows that the

accuracy in determining the lattice constant is $\pm 0.0005 \text{ \AA}$. This is an accuracy by far higher than can be achieved with any conventional x-ray diffraction technique.

5.2.3. Discussion

Figure 5.2 is a photograph of the copper samples investigated from our introductory studies, showing the surface of the irradiated and non-irradiated specimens. The irradiated specimen in this case was exposed for 64 hours in oxygen-free water corresponding to a total gamma dose of 28.6 kGy. The surface appearance is similar to what has been previously observed /Guinan M. 2001/, /Björkbacka Å. et al. 2013/ and is caused by a thin layer of mainly cuprite (Cu_2O), which is unevenly distributed along the copper surface. The radiation-induced corrosion of copper has been the subject of extensive investigations /Björkbacka Å. 2015/ measured both as the concentration of dissolved copper in the water solution and as the formation of cuprite. Earlier analysis has shown that the corrosion effects increase with radiation dose /Björkbacka Å. et al. 2013/. For comparison, on the sample exposed to oxygen-free water without radiation for 64 hours no visible layers of corrosion products were seen. An earlier observed consequence of the simultaneous exposure of copper to gamma radiation and oxygen-free water is an accelerated ingress of hydrogen into copper, which increases with gamma radiation dose in the interval from around 35 to 70 kGy /Lousada C. M. et al 2016/. Hydrogen in steels has been the subject of extensive experimental and computational investigations because of the well-known risk of loss in metal ductility and hydrogen induced brittle failures at stresses below the yield stress of the susceptible steel /Barrera O. et al 2018/. The modes of failure mechanisms include hydrogen-induced decohesion of adjacent metal atoms, hydrogen-enhanced local plasticity, hydrogen-induced phase transformations and hydrogen-enhanced strain-induced vacancy formation /Barrera O. et al 2018/. For copper, much less information is available on hydrogen-related microstructural effects than for steel. It has been concluded through computational studies that H-atoms accumulate in vacancy-type defects and change their properties /Ganchenkova M. G. et al. 2014/. The results may be a marked change in dislocation slips and in early plastic straining of copper /Yagodzinsky Y. et al. 2018/. Earlier studies have also shown that hydrogen in copper can cause changes in the physical properties of copper, such as tensile yield stress /Butt M. Z. 1983/ and hardness /Kim J. J. and Byrne J. G. 1983/. The mechanisms for these observations have been described in terms of hydrogen interaction with dislocations and hydrogen pinning effects of point defects. Cathodically charged hydrogen into copper has furthermore resulted in a decrease in ultimate tensile strength and in the failure strain of copper /Panagopoulos C. N. and Zacharopoulos N. 1994/

In order to shed more light onto the possible combined effect of gamma radiation and exposure in oxygen-free water the introductory studies based on HEXRD are planned to determine possible lattice-spacing changes with higher precision than ever. It is expected that the combined effect of radiation and water exposure results in local changes of microstructure, which is probably stronger near the surface region of the exposed SKB-Cu material closest to the water. Hence, the studies at DESY should focus on the precise positioning of the sample with radiation dosages up to 100 kGy.

6. Summary

There are several SKB-reports concerning the Sauna-effect and the results are disappointing in several ways. Firstly, it is clear that it is impossible to inject water in the deposition holes without destroying the bentonite rings with cracking and piping. Secondly, water, as steam and moisture, will escape through the cracks and slots from the heated deposition holes and condensate in the colder tunnel above, thus accumulating sulphur and chloride salts in the holes. Thirdly, the salt enrichment which induces several severe corrosion processes on the unalloyed copper canister will continue until saturation/swelling is reached in the whole repository tunnel (fully flooded and pressurized). Finally, in a Forsmark repository, the saturation/swelling process in the tunnels that will create a proper counter pressure to neutralize the Sauna effect will unfortunately take several thousand years which is devastating for the lifetime of the copper canisters. It can be concluded that SKB has not submitted any new information or studies concerning salt enrichment (the Sauna effect) on pitting corrosion and stress corrosion cracking, which was requested by the Environmental Court (E.C.), items (b) and (c).

There is compelling scientific evidence that fast degradation by stress corrosion cracking (SCC), hydrogen embrittlement (HE) and hydrogen sickness (HS) will penetrate the copper canisters in a repository environment. SKB seems to believe that the surface cracks and hydrogen blisters observed in the copper grain boundaries in several studies are only “manufacturing defects”. This explanation has no scientific support at all, and we can conclude that SKB has not seriously considered the uncertainties connected to (c), (d) and (e), as was requested by the E.C. The new evidence for these fast degradation mechanisms in copper shows that the safety analysis SR-site /Hedin A. et al. 2011/ is obsolete.

In their Supplementary Study /Hedin A. et al. 2019/ SKB has given more evidence that radiation effects alone cause no significant effects on the microstructure of copper. However, the situation turns out to be completely different if copper is exposed not only to radiation but simultaneously also to an aqueous environment. This was exactly the condition that was stressed by the authors to impose an obvious threat on copper’s mechanical integrity. To our surprise this condition has not at all been dealt with in the Supplementary Study /Hedin A. et al. 2019/ and in the supporting reports Padovani C. et al. 2019/ and /Yang Q. et al 2019/. To conclude, the combined effect of radiation and exposure in an aqueous environment on the microstructure of SKB-Cu is still an unresolved issue, i.e. request (e) by the E.C.

An issue not commented by the E.C. is the fast degradation of the bentonite buffer by microbes which has shown to significantly reduce the bentonite swelling pressure /Taborowski T. et al, 2019. Furthermore, the added degradation processes with copper ion infiltration in the clay minerals (due to copper corrosion), cementation, cracking, piping and erosion of the buffer, as discussed in sections 2.5, 4.4 and 4.5, deprive the barrier properties of the bentonite clay in a Forsmark repository. The combined effect of failures of both the engineered barriers at the same time, i.e. bentonite and copper, must be included in the safety analysis as a main scenario according to SSMFS 2008:21, especially considering the Forsmark specific problems.

In a study connected to SKB’s prototype repository /Szakálos P. and Hultquist G. 2013/ it was shown that the whole canister thickness was penetrated by hydrogen during only seven years exposure at elevated temperature and that the canister was subjected to internal corrosion by hydroxide. At least 40%, i.e. 2800 canisters, will be dependent on local inflow (Figure 2.3) in the deposition holes and thus be subjected to the Sauna effect (salt enrichment) until being flooded after around 2000 years (Figure 2.4). A conservative safety analysis would estimate that 40% of the canisters collapse already within 100 years after repository closure due to SCC, HE and HS (in the welds) and the remaining 60% within 1000 years after closure due to SCC, HE

and internal corrosion. More specifically, failures due to HE a HS will dominate in a Forsmark repository since these degradation processes operate without any applied load, in contrast to SCC, see section 3.11.

If we consider the most unlikely situation where SCC, HE and HS do not occur in a Forsmark repository then the canisters would fail by pitting corrosion and general corrosion accelerated by temperature, radiation, microbial induced corrosion (MIC) and salt enrichment (the Sauna effect). The corrosion can vary considerably and copper corrosion rates in the range from 5 μm to 175 μm per year are documented, see sections 4.4 and 4.6. Again, it can be concluded that SKB has not considered corrosion by pure anoxic anoxic water (a) and pitting corrosion (b) in a proper way. A realistic estimation based on only general- and pitting corrosion indicates that the canisters would collapse within 2500 years. In fact, in an 18-year long experiment in a real repository environment, FEBEX /Wersin P. and Kober F 2017/, it was shown that unalloyed copper was the least corrosion resistant metallic material tested.

The overall conclusion is that the SR-site safety analysis /Hedin A. et al. 2011/ is not valid anymore and that it cannot be used as basis for a decision concerning the final storage of high-level waste by the Swedish government.

7. References

- Ari-Lahti E, Lehtikuusi T, Olin M, Saario T, Varis P, 2011.** Evidence for internal diffusion of sulphide from groundwater into grain boundaries ahead of crack tip in Cu OFP copper. *Corrosion Engineering, Science and Technology* 46, 134 – 137.
- Barrera O. et al 2018.** Understanding and mitigating hydrogen embrittlement of steels: a review of experimental, modelling and design progress from atomistic to continuum, *Journal of Material Science*, 53 (2018) 6251-6290
- Becker R and Hermansson, H.-P. 2011.** Evolution of Hydrogen by Copper in Ultrapure Water Without Dissolved Oxygen, Swedish Radiation Safety Authority SSM Report 2011:34 (2011), ISSN: 2000-0456.
- Becker R. and Öijerholm J. 2017.** Slow strain rate testing of copper in sulfide rich chloride containing deoxygenated water at 90 °C., SSM Report number 2017:02.
- Belonoshko A.B. and Rosengren A. 2010.** Ab Initio Study of Water Interaction with a Cu Surface. *Langmuir* 26, 16267–16270. (2010)
- Belonoshko A.B. and Rosengren A. 2012.** A possible mechanism of copper corrosion in anoxic water. *Phil. Mag.* 92, 4618-4627 (2012)
- Bengtsson A., Chukharkina A., Eriksson L., Hallbeck B., Hallbeck L., Johansson J., Johansson L., Pedersen K. 2013.** Development of a method for the study of H₂ gas emission in sealed compartments containing canister copper immersed in O₂ free water, (2013) SKB Rapport TR-13-13.
- Bhaskaran G, Carcea A, Ulaganathan J, Wang S, Huang Y, Newman R C, 2013.** Fundamental aspects of stress corrosion cracking of copper relevant to the Swedish deep geologic repository concept. SKB TR-12-06, Svensk Kärnbränslehantering AB.
- Birgersson M, Goudarzi R, 2013.** Studies of vapor transport from buffer to tunnel backfill (“sauna” effects). SKB R-13-42, Svensk Kärnbränslehantering AB.
- Birgersson M, Goudarzi R, 2016.** Vapor transport and sealing capacity of buffer slots (“sauna” effects). SKB TR-15-09, Svensk Kärnbränslehantering AB.
- Birgersson M, Goudarzi R, 2017.** Summary report on “sauna” effects. SKB TR-17-07, Svensk Kärnbränslehantering AB.
- Birgersson M, Goudarzi R, 2018.** Investigations of gas evolution in an unsaturated KBS-3 repository. SKB TR-18-11, Svensk Kärnbränslehantering AB.
- Björck M, Taxén C, Vuoristo T, Elger R, Zavalis T, Wikström L, Sparr M, 2019.** Embedded oxide particles in FSW. Posiva SKB Report 10, Posiva Oy, Svensk Kärnbränslehantering AB
- Björkbacka Å, Hosseinpour S, Leygraf C, Jonsson M, 2012.** Radiation induced corrosion of copper in anoxic aqueous solution, *Electrochemical and Solid-State letters*, 15 C5-C7.
- Björkbacka Å, Hosseinpour S, Johnson M, Leygraf M, Jonsson M, 2013.** Radiation induced corrosion of copper for spent nuclear fuel storage, *Radiation Physics and Chemistry*, 92, 80-86.
- Björkbacka Å. 2015.** Radiation induced corrosion of copper, Doctoral Thesis, KTH Royal Institute of Technology, Stockholm, Sweden, ISBN 978-91-7595-710-4
- Butt M. Z. 1983.** Effect of hydrogen attack on the strength of high purity copper, *J. Material Sci. Lett.*, 2 (1983) 1-2
- Carpén L., Rajala P., and Bomberg M. 2016.** Microbial influence on corrosion of copper in the repository environment. Copper corrosion seminar, 15.12.2016 Aalto University, Otaniemi.
- Chen J, Qin Z, Martino T, Shoesmith D W, 2017.** Non-uniform film growth and micro/macrogalvanic corrosion of copper in aqueous sulphide solutions containing chloride. *Corrosion Science*, 114, 72 – 78.
- Chen J, Qin Z, Martino T, Guo M, Shoesmith D W, 2018.** Copper transport and sulphide sequestration during copper corrosion in anaerobic aqueous sulphide solutions. *Corrosion Science*, 131, 245 – 251.

- Cleveland C., Moghaddam, S., Orazem, M.E. 2014.** Nanometer-scale corrosion of copper in de-aerated deionized water, *J. Electrochem. Soc.* 161 (2014) C107–C114.
- Forsström A, Becker R, Öijerholm J, Yagodzinskyy Y, Hänninen H, Linder J, 2017.** Hydrogen absorption in copper as a result of corrosion reactions in sulphide and chloride containing deoxygenated water at 90 °C in simulated spent nuclear fuel repository conditions. In *Proceedings of EUROCORR 2017 – The Annual Congress of the European Federation of Corrosion, 20th International Corrosion Congress and Process Safety Congress, Prague, Czechia, 3 – 7 September 2017.*
- Ganchenkova M G, Yagodzinskyy Y N, Borodin V A, Hänninen H, 2014.** Effects of hydrogen and impurities on void nucleation in copper: Simulation point of view. *Philosophical Magazine* 94, 3522 – 3548.
- Gordon A., Sjögren L., Taxén C., Johansson A. J. 2017.** Retrieval and post-test examination of packages 4 and 5 of the MiniCan field experiment, (2017) SKB rapport TR-16-12.
- Gordon A, Johansson J, Pahverk H, Börjesson E, Sjögren L, 2018.** Corrosion morphology of copper in anoxic sulphide environments. SKB TR-18-14, Svensk Kärnbränslehantering AB.
- Gordon A., Pahverk H., Börjesson E., Johansson A. J. 2018b.** Examination of copper corrosion specimens from ABM 45, package 5. SKB technical report TR-18-17.
- Guinan M W, 2001.** Radiation effects in spent nuclear fuel canisters, SKB Technical Report TR-01-32
- He, X., Ahn T. and Gwo J.-P. 2018.** Corrosion of Copper as a Nuclear Waste Container Material in Simulated Anoxic Granitic Groundwater. *Corrosion*, Feb 2018, Vol.74(2), pp.158-168
- Hedin A. et al. 2011.** Long-term safety for the final repository for spent nuclear fuel at Forsmark. Main report of the SR-Site project SR-Site main report, SKB TR-11-01
- Hedin A. et al. 2019.** Supplementary information on canister integrity issues. SKB TR-19-15, Svensk Kärnbränslehantering AB.
- Hultquist G. 1986.** Hydrogen evolution in corrosion of copper. *Corros. Sci.*, 26, 173-176 (1986)
- Hultquist G. Szakálos P., Graham M.J., Sproule G.I., Wikmark G. 2008.** “Detection of hydrogen in corrosion of copper in pure water”, *Proceedings of the 2008 International Corrosion Congress (2008) 1–9, Paper 3884.*
- Hultquist G. Szakálos P., Graham M.J., Belonoshko A.B., Sproule G.I., Gråsjö, Dorogokupets P., Danilow B., Aastrup T., Wikmark G., Chuah G.K., Eriksson J.C., Rosengren A., 2009.** ”Water corrodes copper”, *Catal. Lett.* 132 311–316.
- Hultquist G. Graham M.J., Szakálos P., Sproule G.I., Rosengren A., Gråsjö L., 2011.** Hydrogen gas production during corrosion of copper by water. *Corros. Sci.* 53 310–319.
- Hultquist G., Graham M.J., Kodra O., Moisa S., Liu R., Bexell U., Smialek J.L. 2013.** Corrosion of copper in distilled water without molecular oxygen and the detection of produced hydrogen, SSM-report 2013-07.
- Hultquist G., Graham M.J., Kodra O., Moisa S., Liu R., Bexell U., Smialek J., 2015.** Corrosion of copper in distilled water without oxygen and the detection of hydrogen. *Corros. Sci.* 95 162–167. (2015)
- Huotilainen C., Saario T., Toivonen A. 2018.** Review of the Aaltonen-mechanism. SKB-report R-18-03.
- Johansson, A. J. Lilja, C. Brinck, T. 2011.** On the formation of hydrogen gas on copper in anoxic water. *The Journal of Chemical Physics*, 28, Vol.135(8)
- Karnland O. et al. 2009.** Long term test of buffer material at the Äspö Hard Rock Laboratory, LOT project. Final report on the A2 test parcel. SKB-report TR-09-29.

- Kasbohm, J., Nguyen-Thanh, L., Hoang-Minh, T., Pusch, R., Knutsson, S. Pham, T. N. 2019.** Mechanisms of Mineralogical Alteration of Dioctahedral Smectites in Contact with Water – A Review. In: Earth Sciences and Geotechnical Engineering.
- Kaufhold S., Dohrmann R., Gröger-Trampe J. 2017.** Reaction of native copper in contact with pyrite and bentonite in anaerobic water at elevated temperatures, *Corr. Eng., Sci. and Tech.*, 52 (2017) 349-358.
- King F. and Newman R. 2010.** SKB Report number TR-10-04.
- Korzhavyi P. and Sandström R. 2014.** Monovacancy in copper: Trapping efficiency for hydrogen and oxygen. *Computational Materials Science* 84 (2014) 122–128
- Leijon G. et al. 2017.** In situ hydrogen charging of OFP copper during creep. SKB report R-17-17.
- Lousada C M, Soroka I L, Yagodzinskyy Y, Tarakina N V, Todoshchenko O, Hänninen H, Korzhavyi P A, Jonsson M, 2016.** Gamma radiation induces hydrogen absorption by copper in water. *Nature Scientific Reports* 6, 24234. doi:10.1038/srep24234
- Marja-aho, M., Rajala, P., Huttunen-Saarivirta, E., Legat, A., Kranjc, A., Kosec, T., Carpén, L. 2018.** “Copper corrosion monitoring by electrical resistance probes in anoxic groundwater environment in the presence and absence of sulfate reducing bacteria” *Sensors and Actuators A* 274 (2018) 252–261.
- Mattsson E. 1997.** Projekt Inkapsling, PM 97-3420-22.
- Müller H. et al. 2017.** Implementation of the full-scale emplacement (FE) experiment at the Mont Terri rock laboratory. *Swiss J. Geosci.* (2017) 110:287–306.
- Ottosson, M., Boman, M., Berastegui, P., Andersson, Y., Hahlin, M., Korvela, M., Berger, R. 2018.** Response to the comments by P. Szakálos, T. Åkermark and C. Leygraf on the paper “Copper in ultrapure water, a scientific issue under debate”. *Corrosion Science*, Sep 2018, Vol.142, p.308
- Padovani C., Pletser D., Jurkschat K., Armstrong D., Dugdale S., Brunt D., Faulkner R., Was G., Johansson. A. J. 2019.** Assessment of microstructural changes in copper due to gamma radiation damage, SKB Technical Report TR-19-12.
- Panagopoulos C. N. and Zacharopoulos N. 1994.** Cathodic hydrogen charging and mechanical properties of copper, *J. Materials Sci.*, 29 (1994) 3843-3846
- Pedersen K., Bengtsson, A., Blom, A., Johansson, L., Taborowski, T. 2017.** Mobility and reactivity of sulphide in bentonite clays – Implications for engineered bentonite barriers in geological repositories for radioactive wastes. *Applied Clay Science* Volume 146, 15 September 2017, Pages 495-502.
- Pusch R. 2019.** Personal Communication 2019 09-12.
- Pusch, R., Yong, R.N., Nakano, M., 2019.** *Geologic Disposal of High-Level Radioactive Waste.* CRC Press, New York (Taylor & Francis Group).
- Pusch, R., 2015.** *Bentonite Clay, Environmental Properties and Applications.* CRC Press, New York (Taylor & Francis Group).
- Pusch R., Kasbohm J., Knutsson S., Yang T., Nguyen-Thanh L. 2015.** The Role of Smectite Clay Barriers for Isolating High-Level Radioactive Waste (HLW) In Shallow and Deep Repositories. *Procedia Earth and Planetary Science* 15, p. 680 – 687.
- Raja V.S. and Shoji T. 2011.** *Stress Corrosion Cracking Theory and Practice,* Woodhead Publishing Book Series in Metals and Surface Engineering, ISBN 978-1-84569-673-3.
- Rosborg B. and Werme L 2008.** *J. Nuclear Materials* 379 (2008) pp. 142-153
- Savolainen K., Saukkonen T., Mononen J., and Hänninen H. 2008.** Entrapped Oxide Particles in Friction Stir Welds of Copper. 7th Int. Symposium on Friction Stir Welding. Awaji Island, Japan 20-22 May, 2008.
- Sellin P. et al. 2017.** Long re-saturation phase of a final repository Additional supplementary information. SKB TR-17-15

- Senior N A., Newman R C, Artymowicz D, Binns W J, Keech P G, Hall D S. 2019.** Communication– A method to measure extremely low corrosion rates of copper metal in anoxic aqueous media. *Journal of The Electrochemical Society* 166, C3015–C3017.
- Sipilä K., Arilahti, E., Lehtikuusi, T., Saario, T. 2014.** Effect of sulphide exposure on mechanical properties of CuOFP. *Corrosion Engineering, Science and Technology* 49, 410 – 414.
- Szakálos P., Hultquist G., Wikmark G. 2007.** Corrosion of Copper by Water. *Electrochem Solid State Lett.* 10:C63 (2007)
- Szakálos P. and Hultquist G. 2013.** Scientific symposium arranged by the Swedish National Council for Nuclear Waste: New insights into the repository’s engineered barriers, Stockholm, 20 –21 November 2013
- Szakálos P. and Seetharaman S. 2012.** Corrosion of copper canister, SSM-report 2012-17.
<http://www.stralsakerhetsmyndigheten.se/Global/Publikationer/Rapport/Technical%20Note/2012/SSM-Rapport-2012-17.pdf>
- Szakálos P., Rosengren A., Leygraf C., Seetharaman S. 2017.** Land and Environmental Court in Nacka, Sweden, case no. M 1333-11, closing argument, KTH (Addendum 821).
- Szakálos P., Åkermark, T., Leygraf, C. 2018.** Comments on the paper “Copper in ultrapure water, a scientific issue under debate” by M. Ottosson, M. Boman, P. Berastegui, Y. Andersson, M. Hahlin, M. Korvela, and R. Berger. *Corrosion Science*, 09/2018, Vol.142, C, pp.305-307
- Taborowski T. et al, 2019.** Microbiology In Nuclear waste Disposal, MIND, Horizon 2020 project, grant agreement no. 661880. Deliverable D2.4, v2.
- Taniguchi N and Kawasaki M, 2008.** Influence of sulfide concentration on the corrosion behavior of pure copper in synthetic seawater. *J. of Nuclear Materials*, 379, pp 154–161.
- Taxén C., Flyg J., Bergqvist H. 2018.** Stress corrosion testing of copper in sulfide solutions. SKB-report TR-17-16.
- Taxén C., Flyg J., Bergqvist H 2019.** Stress corrosion testing of copper in near neutral sulfidesolutions. SKB -report TR-19-13.
- Wersin P. and Kober F, 2017.** FEBEX-DP, Metal Corrosion and Iron-Bentonite Interaction Studies. Arbeitsbericht NAB 16-16.
- Yagodzinsky Y., Malitckii, E., Tuomisto, F., Hänninen, H. 2018.** Hydrogen-induced strain localisation in oxygen-free copper in the initial stage of plastic deformation, *Philosophical Magazine* 98 (2018) 727-740
- Yang Q. Toijer E., Olsson P. 2019.** Analysis of radiation damage in the KBS-3 canister materials, SKB Technical Report TR-19-14

Coverage of SKB reports

Following reports have been covered in the review.

Table 1: SKB-Reports covered in the review.

Reviewed report	Reviewed sections	Comments
<i>[insert SKB report number and title]</i>	<i>[insert reviewed sections]</i>	<i>[insert comments, if any]</i>
SKB TR-19-15. Supplementary information on canister integrity issues	All	
SKB TR-18-11. Investigations of gas evolution in an unsaturated KBS-3 repository.	All	
TR-18-14. Corrosion morphology of copper in anoxic sulphide environments.	All	
TR-17-16. Stress corrosion testing of copper in sulfide solutions.	All	
TR-19-13. Stress corrosion testing of copper in near neutral sulfide solutions.	All	
R-18-03. Review of the Aaltonen-mechanism	All	
R-17-17. In situ hydrogen charging of OFP copper during creep	All	
Posiva SKB Report 10. Embedded oxide particles in FSW.	Chapters/Sections: 1., 3.1, 3.2.1, 4.1, 4.5 and 5	
TR-19-14. Analysis of radiation damage in the KBS-3 canister materials,	All	

TR-19-12. Assessment of microstructural changes in copper due to gamma radiation damage.	All
--	-----

TR-18-17. Examination of copper corrosion specimens from ABM 45, package 5.	All
--	-----

Following additional SKB-reports has been covered partially or fully:
TR-13-13, R-13-42, TR-15-09, TR-17-07, TR-16-12, TR-01-32, TR-11-01, TR-09-
29, TR-10-04, TR-17-15, SKB TR-12-06 and the preliminary SKB-report ID:
1602591.