ROYAL INSTITUTE
OF TECHNOLOGY

Till Regeringen, Miljödepartementet   26 mars, 2021

Beträffande regeringens pågående prövning av kärnbränsleförvaret enligt miljöbalken (M2018/00217/Me) och kärntekniklagen (M2018/00221/Ke)

Undertecknad vill med denna skrivelse uppmärksamma regeringen på förhållanden som kan vara viktiga för den pågående prövningen av den ansökan som Svenska Kärnbränslehantering AB (SKB) lämnat in för att få bygga ett slutförvar för använt kärnbränsle i Forsmark.

Som bakgrund hänvisas till att mark- och miljödomstolen i sitt yttrande till regeringen den 23 januari 2018 i prövningen enligt miljöbalken sa att kärnbränsleförvaret är tillåtligt endast om SKB redovisar underlag som klargör att slutförvaret är långsiktigt säkert även med avseende på kopparkapselns skyddsförmåga. Domstolen bedömde att följande osäkerheter avseende kapseln har störst betydelse vid den riskbedömning som ska göras:
a. korrosion på grund av reaktion i syrgasfritt vatten
b. gropkorrosion på grund av reaktion med sulfid, inklusive saunaeffektens inverkan på gropkorrosion
c. spänningskorrosion på grund av reaktion med sulfid, inklusive saunaeffektens inverkan på spänningskorrosion
d. väteförsprödning
e. radioaktiv strålnings inverkan på gropkorrosion, spänningskorrosion och väteförsprödning.

För att mer ingående belysa några av dessa frågor med ny kunskap har en nära medarbetare till undertecknad vid KTH, professor Jinshan Pan, lett en vetenskaplig undersökning som nyligen publicerades som en vetenskaplig artikel i tidskriften Corrosion Science (Bilaga A). Den visar tydligt att mark- och miljödomstolens farhågor angående punkterna c och d ovan med avseende på kopparkorrosionsprocesser nu har besannats.

Dessa nya rön, baserade på ett unikt angreppssätt utfört vid synkrotronljusanläggningen DESY i Hamburg, visar att alla förutsättningar för de snabba nedbrytningsprocesserna väteförsprödning och spänningskorrosion föreligger i slutförvarsmiljön med kopparkapslar. Det är bara en tidsfråga innan processerna förväntas uppträda. Även om sulfidhalterna är högre i dessa försök än i Forsmarks grundvatten så förväntas halterna öka lokalt pga. mikrobiell aktivitet samt saltindunstning (den s.k. saunaeffekten, se punkt c ovan). Kopparmetallen försvagas av främst väte men även svavel, vilket leder till sprickbildning där kapslarna är utsatta för mekaniska spänningar.

Lägger man till domstolens punkt e ovan vet man genom andra studier att de processer som observeras i den aktuella artikeln påskyndas än mer av strålning, dels genom ett ökat väteintag i kopparmaterialet dels genom en högre grad av lokalisering av korrosionsangreppen.

För att klargöra undertecknads egen roll kan tilläggas att undertecknad inte står som medförfattare i det aktuella arbetet men deltagit i snarlika mätningar vid anläggningen DESY samt bidragit till kontakten mellan författarna och DESY. Med 30 års erfarenhet som professor och korrosionsforskare har undertecknad dessutom stött på mycket komplicerade praktikfall. Med hänsyn till framtagna fakta hör det nu aktuella fallet inte längre till något av de svårare fallen.
Något bör kanske också sägas om SSMs agerande, även om det bara är undertecknads egen bedömning. Undertecknad var med på huvudförhandlingen i mark- och miljödomstolen hösten 2017. Domstolen kunde på ett imponerande sätt ta in de ofta komplicerade synpunkter som

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framfördes i förhandlingen och i den omfattande skriftväxling som hade ägt rum sedan ansökan lämnades in 2011, och kom fram till att det fortfarande fanns osäkerheter rörande kopparkapselns långsiktiga integritet. Detta framfördes också till regeringen. Den 23 januari, 2018, skickade undertecknad tillsammans med andra forskare vid KTH in en analys av domstolens yttrande (Bilaga B). Till forskarna anslöt sig den tidigare myndighetsexperten på korrosion, Jan Linder, som våren 2016 motsatte sig att Strålsäkerhetsmyndigheten (SSM) tog beslutet att meddela domstolen att ansökan kunde godkännas enligt miljöbalken.

I april 2019 kompletterade SKB till regeringen mer information rörande punkterna a-e ovan. Den 13 september 2019 skickade undertecknad tillsammans med andra KTH-forskare och den tidigare SSM-experten in ett yttrande över bolagets komplettering (Bilaga C). Forskarna kompletterade den 22 november 2019 med en rapport från det granskningsuppdrag av SKB:s komplettering som professor Leygraf tillsammans med tekn. dr. Peter Szakálos utfört för SSM:s räkning (Bilaga D). Såvitt undertecknad kan bedöma har SSM i myndighetens yttrande till regeringen i september 2019 över SKB:s komplettering inte tagit i beaktande det som sägs i de inskickade yttrandet eller i den beställda granskningsrapporten.
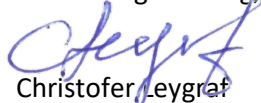
Hösten 2019 tog SKB upp två försökspaket i det s.k. LOT-experimentet ur Äspö-laboratoriet. Bolaget presenterade hösten 2020 en rapport med resultat rörande den kopparkorrosion som ägt rum i försökspaketen. SSM har genomfört en kvalitetsgranskning av kopparkorrosionsresultaten och avrapporterat denna till regeringen. Undertecknad och tekn. dr. Peter Szakálos har den 23 november 2010 och den 26 februari 2021 skickat in två skrivelser med synpunkter rörande LOT-resultaten och SSM:s granskningsarbete (Bilaga E och F). SSM tycks inte heller denna gång tagit synpunkterna i beaktande i rapporteringen till regeringen. <u>Sammantaget har SSM enligt undertecknads syn på händelseutvecklingen inte agerat som den kritiskt granskande oberoende kontrollmyndighet man kunde förvänta sig, utan följt i SKBs fotspår.</u> För att fritt associera till bentonit och koppar: nästan som ler- och långhalm.

<u>Man kan med utgångspunkt från den nya vetenskapliga artikeln summera situationen med att osäkerheterna som påtalades av mark- och miljödomstolen i januari 2018 inte bara kvarstår, utan har ökat till nivåer som måste betraktas som oacceptabla. Tillåtlighet för ett slutförvar enligt KBS-3-modellen kan därför inte rimligtvis tillstyrkas enligt miljöbalken.</u>

Om så önskas ställer undertecknad tillsammans med nära medarbetaren Prof Jinshan Pan, som ledde det aktuella arbetet, gärna upp för mer detaljerad information.

Stockholm, 26 mars, 2021.
Med vänlig hälsning,

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Corrosion-induced microstructure degradation of copper in sulfide-containing simulated anoxic groundwater studied by synchrotron high-energy X-ray diffraction and *ab-initio* density functional theory calculation

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ABSTRACT

Synchrotron high-energy XRD measurements and ab-initio DFT calculations were employed to investigate microstructural degradation of copper upon exposure to sulfide-containing anoxic groundwater simulating nuclear waste repository. After two-month exposure, the high-energy XRD measurements revealed heterogeneous lattice deformation in the microstructure and lattice expansion in near-surface regions. The DFT calculations show that sulfur promotes hydrogen adsorption on copper. Water causes surface reconstruction and promotes hydrogen insertion into the microstructure, occurring via interstitial sites next to vacancies leading to lattice dilation and metal bond weakening. Hydrogen infusion in the presence of sulfur caused lattice degradation, indicating a risk for H-induced cracking.

1. Introduction

A large amount of spent fuel is produced every year from commercial nuclear power plants, 1% of the nuclear waste is highly radioactive and its safe disposal is as important as nuclear safety. Deep geological disposal is the prefered approach for permanent storage of the nuclear waste in several countries. Governmental regulations stipulate safe long-term isolation of nuclear waste for a minimum of 100,000 years, which imposes a great engineering challenge. The nuclear waste disposal concept in Sweden and Finland is based on a multi-barrier system, where the spent fuel is first placed in cast-iron inserts, which are then inserted into canisters as a barrier to seal the cast-iron inserts. The canisters will be placed in bedrock in the depth of 400–1000 meters, surrounded by bentonite clay buffer, to achieve the isolation from the human living environment [1–3]. High-purity copper has been chosen for fabricating the canisters that will be placed under granite environments at anaerobic reduction and anoxic aqueous conditions [4]. The compacted bentonite clay acts as a sealing material providing another barrier

separating groundwater and the canisters, buffering minor movements of the repository system, and retaining eventual release of nuclides upon canister failure [2,3]. The bedrock is considered stable and durable, providing an outer barrier of the multi-barrier structure between nuclear waste and the biosphere.

For the safety assessment, corrosion of copper under oxic and anoxic conditions, and radiation-influenced and microbiologically-influenced corrosion have been intensively investigated over 40 years [5–11]. A recent review gives an overview of the corrosion issues, debated questions, and ongoing research programs [12]. A number of reports assessing corrosion of copper canister under expected repository conditions with conservative assumptions, often using a uniform corrosion rate in the calculation of corrosion allowance, have concluded that there is no considerable risk for canister failure [12]. However, the risks for several complex forms of copper corrosion have been debated in the Land and Environmental Court of Sweden, leading to the statement to the Swedish Government, that supplementary information related to the long-term behaviour of the copper canisters should be presented and

evaluated regarding five issues: i) corrosion due to reaction in oxygen-free water; ii) pitting due to reaction with sulphide; iii) stress corrosion cracking due to reaction with sulphide; iv) hydrogen embrittlement; v) the effect of radioactive radiation on pitting, stress corrosion cracking and hydrogen embrittlement [13]. Clearly, there is a need to gain a deep understanding of the role of sulphur and hydrogen in stress corrosion cracking (SCC) and hydrogen embrittlement of copper in the ground water containing sulphide.

To cover all aspects of safety assessment, it is necessary to evaluate the scenarios when cracks are present in the rock and the bentonite is swelling with groundwater, so copper canisters get into contact with groundwater and even microbes where bentonite sealing could be damaged. Microbial activity on the surface or in the vicinity of the canister was modeled [14], and it was reported to initiate and accelerate general and localized corrosion [15]. Oxygen exists in the initial period of the repository closure and is gradually consumed by oxidation reactions and microorganisms [12]. Oxidation of copper can result in a surface film of Cu_2O or $CuO/Cu(OH)_2$. Once the trapped oxygen is completely consumed, the major threat to the long-term durability of the canister is corrosion by sulfide species (e.g., HS^-) produced in the groundwater by mineral dissolution and/or microbial activity of, e.g., sulfate-reducing bacteria and methanogens in the repository environment [12,16]. Sulfide is known to be a corrosive agent causing SCC of copper in anaerobic chloride containing environments [8,9,17]. Previous studies have shown the role of sulfate-reducing microorganisms [18,19], and biotically-induced formation of Cu_2S layer [20,21], in the corrosion of copper. The sulfide leads to corrosion of copper, forming stable and insoluble sulfides [22–24], e.g.,

$$2Cu + S^{2-} \rightarrow Cu_2S + 2e^- \tag{1}$$

The sulphide-induced corrosion process can be sustained by cathodic reduction of water or HS^-.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

$$2HS^- + 2e^- \rightarrow H_2 + 2S^{2-} \tag{3}$$

Studies on copper corrosion often focused on chemical and electrochemical degradation at the copper/electrolyte interface [25,26]. It was also reported that sulfide-induced corrosion might also have a significant influence on the bulk material of copper. Chemical conversion of a film of Cu_2O to Cu_2S on copper has been shown to proceed to completion and extend deep into the bulk Cu [27]. The conversion was observed to extend into the sub-surface region as deep as 100 nm [28]. Moreover, hydrogen may be produced when copper corrodes in the presence of sulfide. In general, hydrogen has detrimental effects on mechanical properties of copper and can create bubbles and microcracks of copper materials [29–32]. Adsorption and diffusion of hydrogen in copper depend on the surface condition and microstructural defects such as dislocations and inclusions, and grain boundaries are primary trapping sites of hydrogen [33,34]. Hydrogen-induced damage of copper canister has, so far, been considered to be negligible due to the belief that the permeation depth of hydrogen would be too small to influence the mechanical integrity of copper canister [35,36]. However, the previously used method only yielded depth-profiles of hydrogen [33,36], but no information about its role in the SCC and hydrogen embrittlement of copper. In the presence of tensile stress/strain, exposure to ground water containing sulfide can cause SCC of copper [8,9,17]. To achieve an atomistic understanding of the mechanism of the SCC and hydrogen embrittlement, it is necessary to study corrosion-induced lattice degradation of copper, particularly the role of sulfur and hydrogen. To our knowledge, this has not been done before.

Here, we report synchrotron high-energy X-ray diffraction (HEXRD) measurements in transmission mode and *ab-initio* density functional theory (DFT) calculations to investigate the effect of exposure to simulated anoxic groundwater containing sulfide on the lattice degradation

of copper. The interatomic lattice distances (d-spacing) were measured in 20 μm increments through the entire two-mm thick sample to reveal an in-depth gradient of the lattice deformation and thus the extent of the exposure-induced lattice degradation. DFT calculations of Cu-S-H systems (also in water) were carried out to provide an atomistic understanding of the surface adsorption, dissociation, and infusion of hydrogen that lead to degradation of the Cu lattice.

2. Experimental

2.1. Material used

The tested material was hot rolled, oxygen-free, phosphorus-containing copper (> 99.95 wt.% Cu, 0.005 wt.% P), which is the material used for making canisters, and provided by Finnish nuclear waste management company Posiva Oy. The specimens were cut into approximately 10 mm × 10 mm × 2 mm, and the surface was ground and polished down to 1 μm finishing. Prior to exposure, the specimens were cleaned in acetone and ethanol. The copper material had a typical hot-rolled microstructure, with large grains (several tens to hundreds of micrometers in size) and annealing twins, as seen in Fig. 1. As-polished and pre-oxidized samples were investigated. The pre-oxidation was done at 90 °C in ambient air for seven days after the polishing to simulate the effect of exposure to oxic conditions prior to the anoxic stage. It was previously observed that the pre-oxidation increased mass loss of copper specimens during exposure to anoxic conditions [37].

2.2. Corrosion exposure

The specimens were exposed to simulated groundwater in a sealed bottle for 53 days. The chemical components of the water are given in Table 1, which represent the groundwater of the Finnish disposal site and the effects of added bentonite. Sulfide was added in the form of Na_2S with a concentration of 10^{-3} mol/L (32 mg/L). The exposure was done at room temperature (22 °C) in a laboratory-grade borosilicate glass bottle with a volume of 2 L. The experiment environment was anoxic, achieved by purging the water and the vessel with argon before the start of the test and sealing the vessel with butyl rubber stopper.

2.3. High-energy X-ray diffraction experiment

HEXRD measurements were carried out at the Swedish Materials Science beamline P21.2 at PETRA III of the DESY, Hamburg, Germany. The photon energy was 96 keV (corresponding to 0.1291 Å). The distance between the sample and the Varex 4343CT flat panel detector was about 1.6 m. LaB6 was used for geometrical calibration. The sample surface was aligned to be parallel to the X-ray beam. The sample was

Fig. 1. Optical micrograph of an etched copper sample showing typical microstructure (large grains and annealing twins) of canister material.

Table 1
Chemical components of the used simulated groundwater.

	K	Ca	Cl	Na	SO$_4$	Br	HCO$_3$	Mg	Sr	Si	B	F	Mn	PO$_4$	S	lactate
mg/L	54.7	280.0	5274.0	3226.1	595.0	42.3	13.7	100.0	8.8	3.1	1.1	0.8	0.2	0.1	32.0	1.0

positioned 45° towards the beam with respect to its vertical rotational axis and illuminated 1.5 mm away from the edge to reduce the effective sample depth for transmission to about 3 mm. The beam size was 20 μm (vertical) x 55 μm (horizontal). The sample surface was defined as the position where the intensity of the transmitted beam through the specimen had its half intensity when sampling across the sample surface. The sample was moved vertically in steps of 20 μm (z-axis). At each z-position (height), a 2-D diffraction pattern was recorded with a sampling time of 1 s. During each data sampling, the sample was moved by 1 mm along the horizontal axis (parallel to the surface) to improve grain statistics, resulting overall in a serpentine sample movement (transmission was kept less than 3 mm). The measurement at the surface yields diffraction signals from approximately 10 μm beneath the surface and all other measurement points include signals from a volume of 20 μm height. The measurement time for each scanned layer was 3.8–4.0 s, including the summation of sampling time and dead time for stage movement. The sample was scanned from 150 μm above the upper-side surface down to 150 μm below the lower-side surface to capture the entire specimen. The measurement setup is schematically illustrated in Fig. 2. The diffraction patterns were collected and stored as tiff files, which were then integrated azimuthally in a range of ±5° using pyFAI [38]. The diffraction data were also integrated over the entire azimuth full-circle (0–360°). The intensities were normalized using the primary beam intensity, which was collected simultaneously to compensate beam fluctuation. All images were background subtracted. Data analysis was performed using the Peak Analyzer module Fit Peaks (Pro) of OriginPro 2020b V9.7.5.184 software, utilizing a mixture algorithm of Lorentzian and Gaussian peaks for fitting, which gave the best fitting quality. The *d*-spacing was determined from the position of the 111 Bragg peak. The full-ring integration provided average but statistically relevant information about the changes in the lattice size. The d-spacings of the non-exposed specimen was taken as the reference point, and all the relative changes of the lattice parameter were calculated with respect to the non-exposed condition.

3. DFT calculation

DFT calculation was performed to study the surface adsorption and dissociation of S-components (H$_2$S and HS) on Cu(110) surface and the infusion of H into the Cu lattice, to achieve an atomistic understanding of the effect of S and H on the lattice degradation. Cu(110) surface was chosen in the calculation for easy comparison with literature reports, and the results differ only slightly for other surface orientations. Two types of interactions of H$_2$S with Cu were considered, i.e., the adsorption at the Cu(110) surface, and the insertion into defects in the Cu subsurface region. The Cu surface was modelled by a six-layer slab orientated at 110, which contains 36 Cu atoms, which is commonly used in DFT calculations of Cu. A vacuum layer equal to about two times the height of the slab was added to the calculation model. The Dmol3 code was used to theoretically investigate the interaction between environments and Cu [39,40], where the generalized gradient approximation (GGA) with PW91 exchange-correlation function [41] was applied, and a k-point of 3 × 6 × 1 was selected in the calculation. All the core electrons in the system were treated with DFT semi-core pseudopotentials. Optimization was regarded to be complete when the energy, residual force and displacement of each atom of the system converged to 10^{-5} Hartree (Ha), 0.002 Ha/Å, and 0.005 Å, respectively.

4. Results and discussion

4.1. Deformation of Cu lattice

From the HEXRD data, d-spacing of the Cu lattice was determined. Fig. 3 displays polar *d*-spacing plots of a non-exposed sample (reference), a pre-oxidized sample (oxidized), and a pre-oxidized sample after the exposure to the simulated groundwater (exposed or sulfur-exposed). The polar plots show the calculated d-spacing as a function of the azimuthal angle and depth from the surface of the sample. The vertical axis on the left of each polar plot (depth information) indicates the position inside the sample, with units in microns. The depth axis is radial, with 0 μm showing the sample surface. The increasing number of depths indicates the measured d-spacing below the surface. The polar plot shows the measured d-spacing for down to 1000 μm in bulk. The azimuth angle is plotted in the hoop-direction. The color code represents the magnitude of d-spacing, with the lattice size increasing from cold to hot colors. The outer ring of the polar plot shows the d-spacings for the surface along with all azimuth angles.

The non-exposed reference sample (Fig. 3a) shows quite uniform *d*-
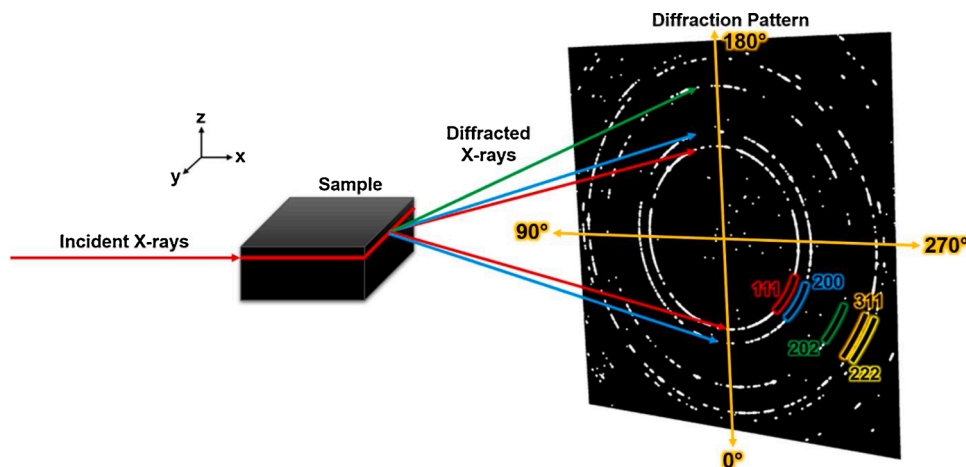
Fig. 2. Schematic illustration of the experimental setup for the HEXRD measurements showing X-rays radiating the copper specimen and the diffracted X-rays with the 2D diffraction pattern collected by a flat-panel detector. The azimuth angles are indicated.
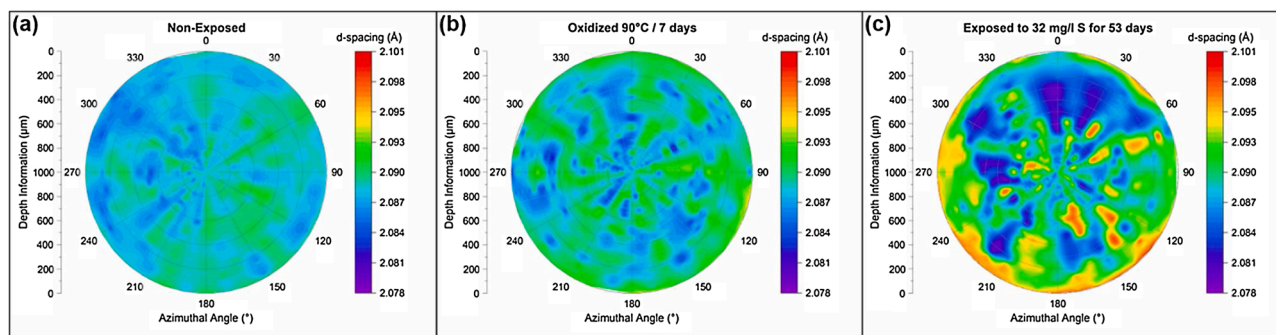
Fig. 3. Polar plots showing the calculated d-spacing of the Bragg peak with (111) orientation as a function of depth from the surface and azimuthal angle for the copper specimens of (a) the non-exposed condition, (b) pre-oxidized at 90 °C for seven days, and (c) pre-oxidized and exposed to 32 mg/l of sulfide-containing groundwater.

spacing values expected for the Cu lattice, with small deviations across the measured depth reflecting the heterogeneities in the microstructure, such as grain boundaries and grains in different sizes as shown in Fig. 1. In contrast, the magnitude and scatter of the *d*-spacings increased for the pre-oxidized sample (Fig. 3b). The sulfur-exposed sample had the largest *d*-spacings, indicating most degradation (Fig. 3c). While the pre-oxidation affected the near-surface region down to a depth of $20-40$ µm (see also Fig. 5), the sulfur-exposure resulted in large lattice expansion down to 400 µm, with some expansion occurred on individual sites in the microstructure between 400 µm and 900 µm in depth. It seems that compensating lattice contraction occurred in the sub-surface microstructure as compared to the non-exposed and pre-oxidized specimens (Fig. 3c). Hence, the exposure to the simulated groundwater caused both heterogeneous lattice expansion and contraction. The size of the large grains of the microstructure was $200-500$ µm and thus much larger than the X-ray beam size (20 µm × 55 µm), which explains the discrete heterogeneities in the d-spacings. Each scan line contained signals form approximately 50–100 grains, which is well-representative for the entire microstructure. Compensating lattice contraction, to a small extent, was also observed for the pre-oxidized specimen (Fig. 3b).

The lattice expansion, measured in the exposed specimen, showed a preferential azimuthal orientation. The lattice expansion was more pronounced along with the azimuthal angles $120-240°$, which means that the lattice expanded orthogonal to the exposed surface. The increase of the interatomic distance of the lattice implies grain elongation due to directional strain formation, which is likely induced by the infusion of H, and possibly also S and/or O atoms, from the environment into the lattice of the Cu (discussed in the sections below).

Furthermore, the change of the *d*-spacing was used to calculate the

relative change of the lattice parameter at different depths, which includes strain development due to H insertion into the lattice. As shown in Fig. 4, the pre-oxidation caused lattice expansion of the surface region, evidenced by positive values of the relative lattice change at most azimuthal angles (Fig. 4a). In contrast, the sulfur-exposure resulted in both lattice expansion and contraction in the surface region (Fig. 4a) and
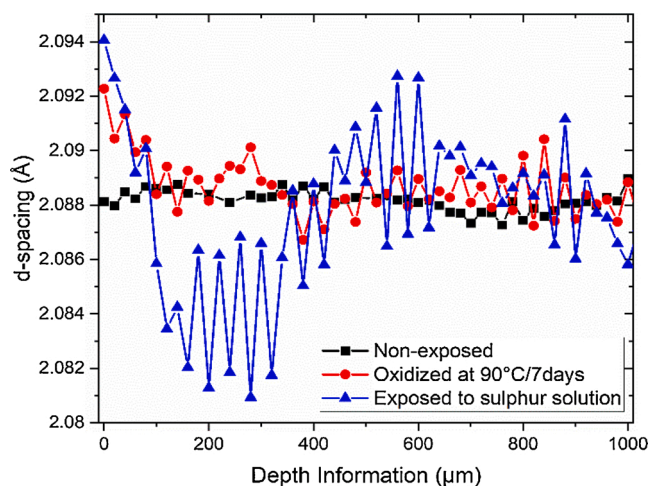
Fig. 5. The measured d-spacings (integrated over the entire (111)-oriented 2D-diffraction ring) plotted against the depth from the surface of the copper specimens.
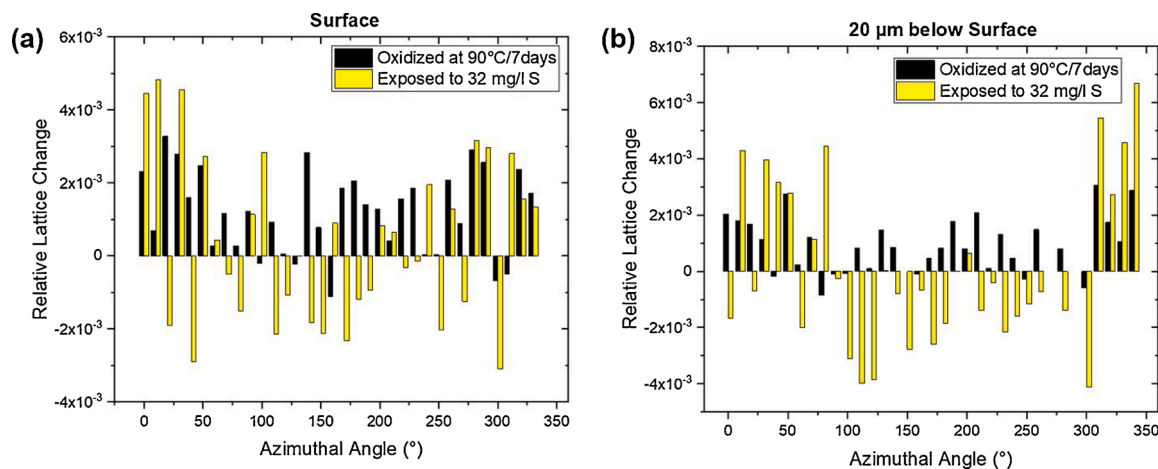
Fig. 4. The calculated relative change of lattice parameter in (a) the near-surface region, and (b) 20 µm below the surface, for the pre-oxidized and the sulfur-exposed sample, respectively.

the sub-surface region at 20 μm (Fig. 4b), varying with azimuthal angle. The non-uniform lattice deformation is due to the large scatter in grain size in the microstructure, as explained above. A histogram figure summarizes the measured d-spacings for all tested specimens can be found in the supplementary material (Fig. S1), which shows the lattice degradation as surface and near-surface lattice expansion and the formation of compensating lattice contraction in the sub-surface, which was more severe for the sulfur-exposed Cu sample than the pre-oxidized one.

4.2. Lattice deformation of the near-surface region

Fig. 5 shows the measured *d*-spacings plotted against the depth, i.e., in-depth gradient, for the samples. The *d*-spacings were calculated from full-ring-integrated data, indicating the lattice expansion in the near-surface region caused by the pre-oxidation and the sulfur-exposure, which is evident by comparison with the non-exposed sample showing nearly constant *d*-spacing across the depth. The pre-oxidation led to lattice expansion of the near-surface region down to ~90 μm. The exposure to the sulfide-containing groundwater resulted in an altered surface layer of ~400 μm. The magnitude of lattice expansion was more pronounced for the sulfur-exposed sample, clearly demonstrating a lattice degradation effect induced by the sulfide-containing groundwater. In addition to lattice expansion of the near-surface region down to ~90 μm, the sulfur-exposure also led to lattice contraction (depth of $100-400$ μm in Fig. 5) beneath the lattice expansion near-surface region. However, the pre-oxidized sample did not show a similar compensation effect; therefore, the mechanism for the sub-surface lattice contraction must be of a different nature. The pronounced lattice contraction in the sulfur-exposed sample might have been generated due to compensation of lattice expansion of the near-surface region.

It is well-known that the pre-oxidation causes the formation of copper oxides, typically CuO/Cu₂O, on the Cu surface. The oxides have higher lattice constants and thus lead to a widening of the Cu lattice underneath the oxides. However, the thickness of the oxide film was reported to be only a few hundreds of nm [42,43]. Our HEXRD results, shown in Fig. 5, suggest that the pre-oxidation causes significant lattice deformation in the near-surface region down to 90 μm in depth. The surface grains became distorted, which led to the evolution of macro-strains. Note that the sulfur-exposed sample was also pre-oxidized; therefore, the measured data represent the effects of the pre-oxidation and sulfidation occurred during the exposure to the simulated groundwater. Therefore, the difference between these two samples shows the effect of interactions of the pre-oxidized sample with the sulfide-containing groundwater. The data of the sulfur-exposed sample show that the relative change of the lattice parameter in the surface region reaches a magnitude of 10^{-3}, indicating a high level of lattice deformation developed in the surface region, which can be explained by considering the H-induced lattice dilation.

The fitting results of the full-ring diffraction data in Fig. 6 revealed that the full-width at half maximum (FWHM) values of all Bragg peaks increased by the pre-oxidation and exposure to the S-containing water, with the latter having the most severe effect. Increase of FWHM typically indicates the formation of micro-deformation, i.e., the deformation within grains, and/or the reduction of the grain size. The deformation of the surface layer due to the formation of corrosion products result in heterogeneous grain deformation, which is reduced with increasing depth in bulk. However, the exposure to the S-containing water resulted in larger surface deformation (lattice expansion) and also sub-surface deformation (lattice contraction). The oxidation on the surface was rather homogeneous and caused a widening of the lattice, but the degradation caused by the exposure to the S-containing water exhibited a more heterogeneous nature. During the exposure to the simulated groundwater, Cu sulfides can form as a result of the corrosion of Cu. Moreover, pre-formed Cu₂O film can also be converted to the Cu₂S film, which was reported to extend into the bulk of Cu for about 100 nm from
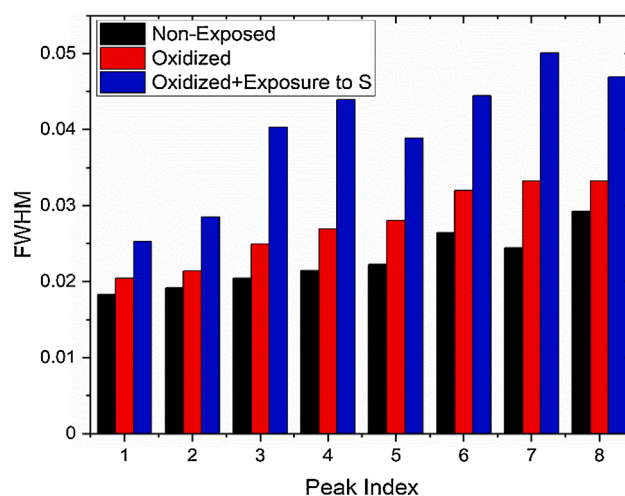

Fig. 6. Full-width at half maximum (FWHM) values from all measured diffraction peaks for the analyzed copper specimens, averaged over the entire sample thickness.

the surface [28]. However, the formation of corrosion products alone cannot explain the large lattice deformation, in particular, not the sub-surface lattice contraction observed in the sulfur-exposed sample. There are, apparently, other effects that resulted in the sub-surface lattice degradation. H and S can absorb and enter into Cu lattice, and their ingress is most favored at grain boundaries. Most likely, the H and S ingress caused the lattice degradation observed in the sulfur-exposed sample.

4.3. Adsorption of H₂S, HS, S, H on Cu(110) surface

In the assessment of corrosion risk of the Cu canister during long-term geological disposal, a key question is the corrosion of material integrity caused by S and H because of their presence in the groundwater in bedrock. DFT calculation of adsorption energies of H₂S, HS, S, H on Cu (110) surface was performed. Fig. 7 shows the calculated adsorption energies (binding strength) and corresponding models for the adsorbate species on Cu(110) surface. As seen in Fig. 7a, individual S atom adsorbs on the Cu(110) surface with adsorption energy (E_{ad}) of -1.5 eV, indicating a strong interaction between S and Cu surface. Compared to one S atom, H₂S molecule shows a low affinity towards Cu surface, the adsorption energy of which agrees well with the calculated value reported in the literature [44,45], while the adsorption energy of HS group is -0.7 eV, slightly lower than that of H₂S [45]. For a single H atom on Cu, a weak binding strength is found, with an adsorption energy of -0.2 eV, agreeing well with the literature [44]. By contrast, H₂S in its full dissociation form, i.e., H_S_H, significantly enhances the adsorption strength, and so is the dissociated HS (H_S), indicating a synergistic effect of H and S on the adsorption onto the Cu surface. Moreover, dissociation of H₂S into H_S_H and HS into H_S most likely proceeds spontaneously on the Cu surface, indicated by the large energy differences.

4.4. Insertion of H into Cu(110) lattice

Vacancies and interstitial atoms are two types of point defects in metals, which render the infusion of atoms from the environment into metal lattice. Interstitial H in metal is utilized for hydrogen storage, in which H dissolves in the metal lattice as solute and thus form hydride [46]. In general, atomic infusion can induce a large strain within metals, which may eventually lead to material rupture [47,48]. Here, we performed DFT calculation to investigate H insertion into Cu(110) lattice via the two types of defects, i.e., Cu vacancy or interstitial site,
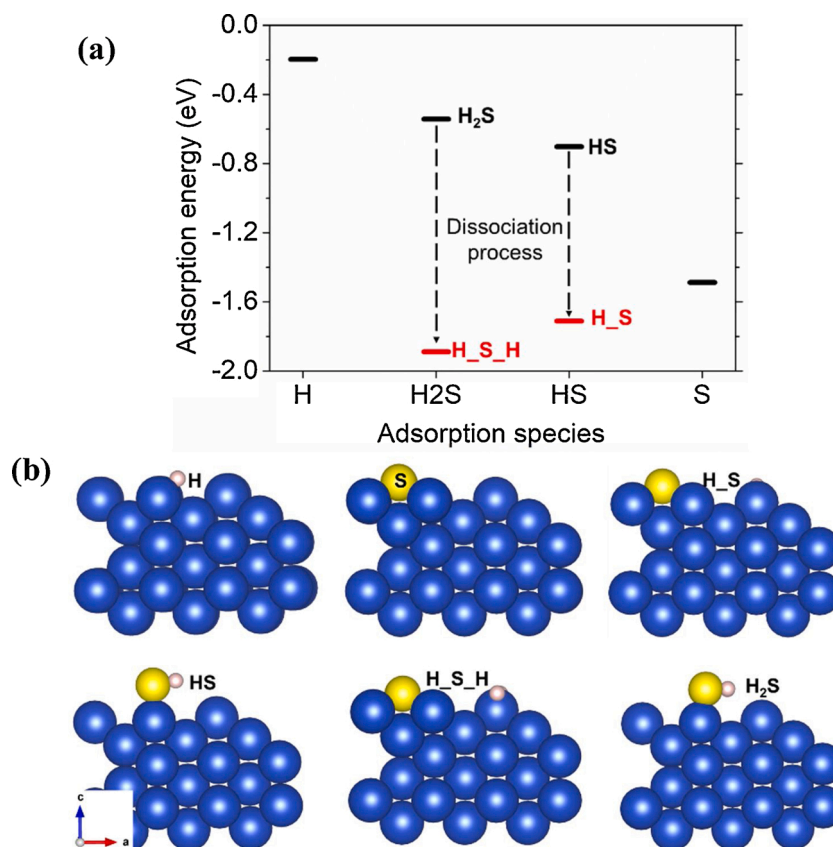
Fig. 7. (a) Calculated adsorption energies (E_{ad}) of H_2S and HS in their molecular form (H_2S, or HS), and full dissociation form (H_S_H, or H_S), and of individual S and individual H. (b) The adsorption configurations of molecular/dissociated H_2S/HS after optimization are depicted in side view, with yellow, light pink, and blue balls representing S, H, and Cu atoms.

respectively. First, individual H atom was introduced into Cu(110) via a Cu vacancy located at different depths, i.e., 1st, 2nd and 3rd atomic layer, denoted as the case "vac" in the modeling. Structure models with one H atom located at an interstitial site at 1st, 2nd and 3rd atomic layers are showing in Fig. 8a. While H stayed at nearly the same location in the first and third layer, the calculated insertion energies indicate that such insertion via vacancy is energetically unfavorable, as shown in Fig. 8b. In the case when H is inserted into a vacancy at the second atomic layer, after optimization the H atom moved up and stayed above

the surface, suggesting a transition from "insertion" mode to "adsorption" mode, which resulted in a more stable configuration (binding energy of H on Cu surface is -0.36 eV) compared to the other two cases. This indicates that Cu vacancy promotes H adsorption, as compared to H adsorption on perfect Cu(110) surface (binding energy is -0.2 eV, see Fig. 8b). Furthermore, by introducing one vacancy next to the H atom, the insertion energy is slightly reduced and even to a native value (favorable) when the vacancy is at the same atomic layer as the H atom (Fig. 8b). The models as well as insertion energy corresponding to an
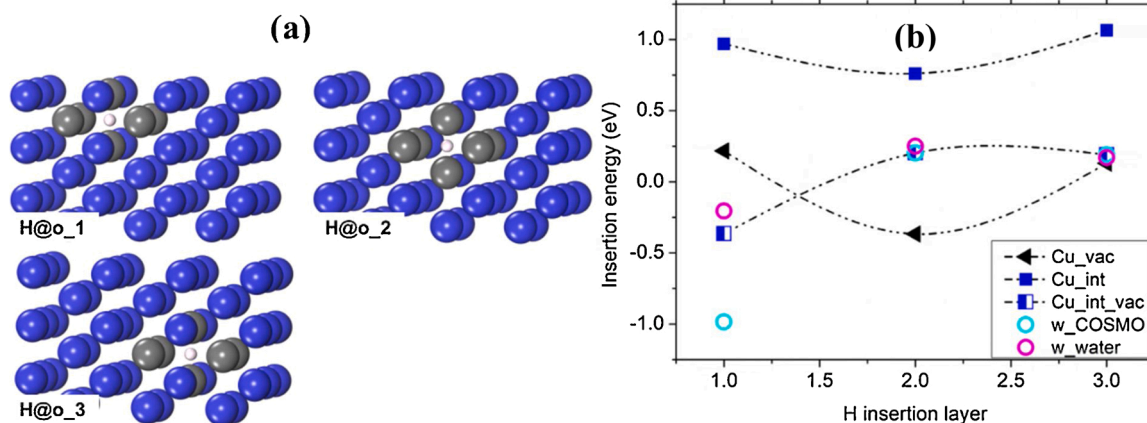
Fig. 8. (a) Models of Cu(110) surface with one H at 1st, 2nd and 3rd atomic layers denoted as H@o_1, H@o_2, H@o_3, respectively. The six Cu atoms comprising the octahedron around H atom (in light pink) are highlighted in grey, whereas other Cu atoms are in blue. (b) Insertion energy of H at a vacancy (case "vac"), an interstitial site (case "int"), and at an interstitial site accompanied by a vacancy (case "vac_int") in Cu(110) at 1st, 2nd and 3rd atomic layers. The effect of both implicit and explicit solvation is considered within the scheme of the "vac_int" case.

extra vacancy at different atomic layers can be found in the supplementary material (Fig. S2).

On the other hand, it is more likely that small atoms insert into metal lattice by occupying interstitial sites. For face-centered cubic metals like copper, its octahedral interstitial sites are usually more accessible for accommodation of small solute atoms. Here we only consider the octahedral interstitial site, the most favorable occupation site of H atom, as an example to show the energetical as well as structural characters of H insertion. The local structure comprised by the H atom and six surrounding Cu atoms are shown in Fig. 9a, and calculated lattice relaxation (expansion or contraction) along different directions are shown in Fig. 9b–d. For the interstitial H atom alone (case "int") without vacancy, the calculated insertion energy is higher (less favorable) compared to the vacancy case discussed above, see Fig. 8b. This could be attributed to large local relaxations within Cu lattice caused by H insertion. Further modeling was done by introducing an extra vacancy besides the H atom (case "vac_int"). Three situations with different relative locations between the H atom and the vacancy were considered, i.e., the vacancy is located at the upper layer, lower layer, or the same layer as the H atom. The results show that only when the vacancy is at the same layer as the H atom, it could significantly stabilize the H insertion (negative insertion energy, Fig. 8b). This can be understood by considering the almost vanished relaxations (especially in the z-direction) when a neighboring Cu vacancy is present, shown as "With vacancy" in Fig. 9b–d. A complete depiction of insertion energy data for different vacancy positions at different atomic layers can be found in the supplementary material (Fig. S3).

In the ideal case, the smallest and biggest distance between two Cu atoms within the local octahedron (Fig. 9a) are 2.578 Å and 3.646 Å, respectively. With one H atom staying at the center of this octahedron after optimization, positive relaxation in the z-direction (i.e., normal to Cu surface) is 17~22 % of the original atomic distance (Cu_0-Cu_5), significantly larger than that in x- or y-direction (Fig. 9b–d). Such large positive relaxations imply that the whole structure in z-direction must bear a large lattice dilation. On the other hand, H-induced relaxation in x-direction decreases as the H atom moves into inner layers, probably due to that the surface allows larger deformation. In contrast,

relaxations in the y-direction are negligibly small (Fig. 9b–d). These calculations suggest that H insertion in octahedral interstitial sites generates strains in an anisotropic way, providing certain evidence for our experimental observations. Moreover, the enlarged Cu—Cu bond length and the lattice relaxation in x, y, and z1/z2 directions induced by H insertion, shown in Fig. 9, indicate a decrease of the metal bond strength, although the local relaxation/bond decrease may not be reflected in the averaged Cu bond strength.

Additionally, both implicit and explicit water environments were included in the modeling to investigate their influence on H insertion into Cu lattice. In the implicit water model, water molecules are treated as a continuum medium (COSMO) model [49,50], whereas in the explicit water model, two monolayers of water molecules (equal to twelve water molecules on the Cu slab) were considered in the calculation. For thick water layers, explicit water models become too difficult for the calculation, while the implicit water model is a good approximation of aqueous environments since water molecules are treated as a continuous aqueous layer. It turns out that the water solvation barely influences the insertion energy, except in the case when H lies at the first octahedral interstitial site under implicit water environment, where the insertion energy decreases largely to a negative value around −1 eV (Fig. 8b). In this case, the water environment causes a considerable reconstruction of the Cu surface, with a surface Cu atom occupying the subsurface Cu vacancy, as illustrated in Fig. 10, which is not observed in the non-solvation case. Such reconstruction could be responsible for the large decrease of the insertion energy. When the H atom moves deeper into the Cu lattice, the effect of solvation on the insertion energy quickly weakens (Fig. 8b).

4.5. Diffusion of H in Cu

The diffusion of H, S, and O in Cu, and self-diffusion of Cu have been reviewed concerning the safety assessment of the copper canister [51]. The transport mechanism and kinetics of these elements depend on the service condition, such as temperature and time [52]. Cu and S are substitutional elements and their diffusion takes place through the movement of point defects in the crystalline lattice. Lattice diffusion via
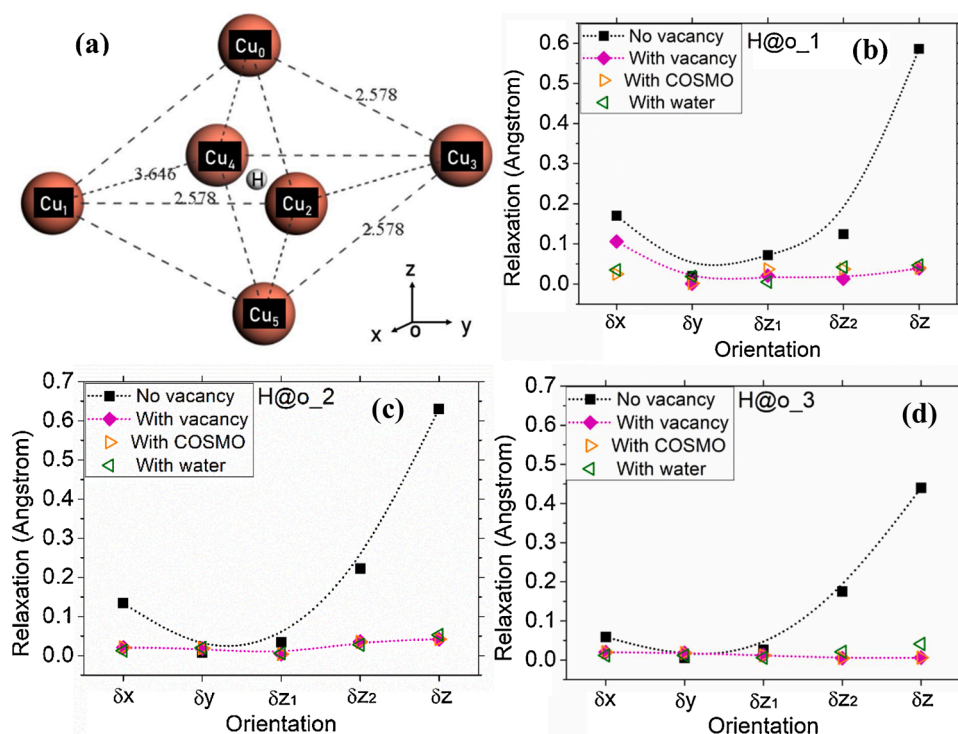
Fig. 9. (a) Configuration (before optimization) with one H atom located at the center of the octahedron comprised by six Cu atoms, which gives initial atomic distances between two Cu atoms: $Cu_{1-4} = Cu_{2-3} = 3.646$ Å (x direction), $Cu_{1-2} = Cu_{3-4} = 2.578$ Å (y direction), while Cu_0 and Cu_5 are both 2.578 Å away from the other four Cu atoms (denoted as z_2, z_1 direction, respectively); $Cu_{0-5} = 2.578$ Å is denoted as z direction. (b)~(d) Comparison between the relaxations induced by H insertion within o_1, o_2, o_3 under differed situations.
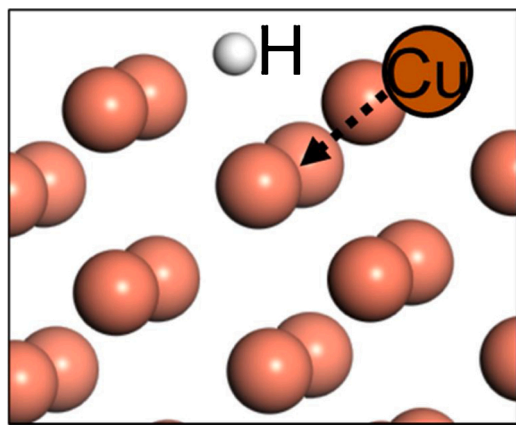
Fig. 10. A snapshot shows a surface Cu atom moves to and finally occupies a subsurface Cu vacancy when H atom is located at the first octahedral interstitial site.

vacancy is the dominating mechanism for diffusion of such large substitutional elements in metals at high temperatures. At temperatures below 100 °C, however, diffusion of Cu and S occurs almost entirely along grain boundaries, and the diffusivity of S is higher than the self-diffusion of Cu. S has very low solubility in Cu due to the formation of sulfides, which is a pinning effect. Estimated by using the diffusion data at room temperature, it takes 100,000 years for S and more than a million years for Cu to diffuse 5 cm distance (the thickness of the canister) along the grain boundaries in Cu [51].

O and H are the interstitial elements that can permeate the whole material via the interstitial sites. The interstitial diffusion occurs typically much faster than substitutional diffusion. However, similar to S, the solubility of O in Cu is very low at ambient temperature due to the formation of oxides. There are experimental data of self-diffusion of Cu at grain boundaries down to 250 °C [53], whereas no experimental data of S and O diffusion in Cu below 500 °C can be found because that is not detectable [51]. Thus, diffusion of S, O, and Cu is negligible at ambient temperature [51,52]. In contrast, H produced from the sulfide-induced corrosion of Cu can diffuse into the Cu [54], along the grain boundaries and also through the grains of Cu lattice. H has high mobility and permeability down to room temperature [55], and hydrogen depth profiles in hydrogen-charged copper specimens could be measured [35, 36]. H diffusion in Cu lattice is much faster than S and O. By using the diffusion data in [51], it is estimated that H diffusion in Cu can reach 5 cm diffusion distance within 1000 years at room temperature. Based on the literature reports about H, S and O diffusion in Cu reviewed recently [56], only H diffusion in Cu lattice is considerable in our system.

4.6. H-induced lattice deformation and its implications

During long-term storage in the repository of the Cu canister, H may be produced on the Cu surface in contact with the groundwater by multiple processes. Microbiological activity in the vicinity, near-field and far-field [12,14,16,57], or on the surface of the canister if the bentonite barrier is damaged [15,19–21], produce sulfide species (mainly HS⁻ ions), and dissociation of the sulfide species on the Cu surface releases atomic S and H, which is a spontaneous process according to the DFT calculation [45, and this work]. Moreover, sulfide-induced corrosion reaction of Cu can generate H on the surface [24,25]. Furthermore, atomic H can also be produced at water/Cu interface through radiolysis of water, and it has been reported that gamma radiation from spent nuclear fuel greatly increases the H infusion into Cu, up to several orders of magnitudes depending on the dose of the radiation [10,11]. The DFT calculations suggest that H adsorption on Cu is energetically favorable, and co-existence with S promotes the H adsorption. H diffusion into Cu via interstitial sites is enhanced in the

presence of vacancies in the Cu lattice. Moreover, water environment leads to a reconstruction of Cu surface, which facilitates the H insertion into Cu lattice. Thus, there is a risk for H-induced damage of the copper material associated with H infusion.

H absorption and diffusion in Cu are affected by the microstructure, and H can be trapped in defects such as grain boundaries and dislocations. H atoms entering the Cu material may lead to formation of voids and bubbles [30,34], and also enhance the creep rate and formation of microcracks showing an intergranular dimpled fracture [58,59]. At atomic level, H insertion into Cu lattice via interstitial sites leads to local lattice dilation, which also indicates a weakening of the Cu—Cu bond strength, implying a tendency for embrittlement. In the Cu material, the grains have different sizes and orientations, and the H-induced lattice deformation may vary and distribute heterogeneously in the microstructure. The lattice dilation due to H insertion is not directly related to macroscopic stress; however, if there is a depth gradient, then stresses may arise, which changes the lattice spacing. So changes of lattice spacings have two superimposed reasons: lattice dilation from H insertion and stresses caused by heterogeneous hydrogen distribution. Therefore, as a result of these two effects, H infusion can lead to the formation of a macroscopic lattice expansion, especially when accumulated in the surface region leading to a depth gradient.

The HEXRD measurements in this work show that deformation of Cu lattice induced by the 2-month exposure to the simulated groundwater occurred from the surface and extended deep into the bulk. The most lattice widening and lattice expansion occurred in the near-surface region down to 90 µm into the bulk. Based on the solubility and diffusion data, only H infusion could explain the measured Cu lattice deformation of this length scale, and the DFT calculation provides support for H-induced expansion of the Cu lattice. In this case, the hydrogen originated only from the corrosion reactions occurring during the exposure. The water environment facilitated the surface degradation, and S diffusion via grain boundaries may have contributed to the lattice deformation in the near-surface region. The measurement results provide clear evidence for highly heterogeneous lattice deformation, which is due to the microstructural heterogeneities in the Cu material. The tensile strain/ stress curves were measured for the Cu material in sulfide-containing synthetic seawater, which show initial yielding starting at about 70 MPa and the maximum stress after about 40 % deformation is about 170 MPa [17]. Taking Young's modulus as 120 GPa, the respective elastic strains are 6×10^{-4} and 1.4×10^{-3}. These numbers should be considered as macroscopic averages over many grains. It was concluded that the Cu material is susceptible to intergranular attack (selective grain boundary dissolution) at low sulfide concentration (<0.005 M) and SCC at higher sulfide concentration (0.01 M). Recent experimental studies have confirmed the susceptibility of the Cu material to intergranular attack and SCC at high sulfide concentration [8,9]. In our work, without hydrogen charging and without applied strain, the two months exposure in the sulfide-containing groundwater already led to highly heterogeneous lattice deformation in the microstructure, and the measured lattice expansion in the surface region (within a depth of 90 µm) reached a magnitude of 10^{-3}, which shows the risk for a transition from elastic to plastic deformation and thus initiation of cracks at individual local sites.

Hydrogen-induced strain localization was observed in the Cu material in the initial stage of plastic deformation [60], and friction stir welding to seal the canister was found to increase hydrogen uptake in the weld zone and lead to strain localization near the weld zone [61]. Most likely, hydrogen infusion and associated local strain development play an important role in the reported susceptibility of Cu to SCC in the ground water containing sulfide [8,9,17]. During long-term storage in the repository of the Cu canister in the ground water containing sulfides, the sulfide-induced corrosion and hydrogen infusion may occur and lead to local strain development to a significant level and extend to a considerable depth. At grain boundaries in the surface region (interface between Cu and corrosion product), the H infusion and associated local tensile strain may lead to the initiation of microcracks, as reported in the

literature [30,34,58,59]. In a review report focusing on SCC of copper canisters, a conclusion of low risk for SCC was made based on considerations of classical SCC mechanisms caused by SCC agents (ammonia, acetate, nitrite, etc.), but the role of hydrogen in the sulfide-induced corrosion was ignored [62]. In the safety assessment reports, the corrosion allowance calculation mainly considers the rates of uniform corrosion in different forms [5,12,13]. For the sulfide-induced corrosion, the consequence was calculated as uniform corrosion thickness based on the amount of sulfur-species that reacts with copper and forms copper sulfide (Cu$_2$S) on the surface [54], without considering the effect of hydrogen that can enter the copper material. However, our HEXRD measurements clearly demonstrate the risk for H-induced SCC of the Cu material exposed to sulfide-containing groundwater. The DFT calculations provide a fundamental understanding of the role of S and H in the lattice degradation (embrittlement), which can result in highly heterogeneous microstructure degradation in the near-surface region leading to SCC of the canister. Considering the new findings from this work and recent studies of S- and H-induced corrosion and SCC [8,9,19–21,45,60, 61], in the safety assessment of Cu canister, the risk for such complex forms of corrosion, i.e., SCC and hydrogen embrittlement, must be considered based on the state-of-the-art of the knowledge. Since the level of sulfide is a crucial issue, further studies are needed to improve our understanding at the atomic level in order to fully assess the risk for SCC and hydrogen embrittlement of Cu canister induced by sulfide-species in the groundwater, and by the radiation of spent fuel, alone and combined. It is necessary to consider not only the general corrosion as measured by the formation of corrosion products on the surface, but also the consequence of SCC and hydrogen embrittlement induced by H infusion into the Cu lattice and the influence of the microstructure.

5. Conclusion

Synchrotron HEXRD measurement and *ab initio* DFT calculation were combined to investigate the effects of pre-oxidation and exposure to simulated anoxic groundwater containing sulfide on the degradation of the lattice of the Cu material. The HEXRD measurement yielded 3-dimensional *d*-spacing data of the Cu samples, showing heterogeneous lattice deformation. The DFT calculation provided energetics of adsorption of H and S on Cu surface, as well as lattice relaxation induced by H insertion via interstitial sites in Cu lattice. The following conclusions can be drawn:

- The pre-oxidation of the Cu sample caused a lattice expansion mainly in the near-surface region ca. 90 μm deep.
- The exposure to the sulfide-containing simulated anoxic groundwater for two months caused a significant lattice deformation extending several hundreds of μm into the bulk, with an in-depth gradient of lattice expansion in the near-surface region ca. 90 μm deep and lattice contraction beneath the expansion region.
- Dissociation of H$_2$S and HS are exothermic processes, indicating spontaneous adsorption of H, H_S and H_S_H on Cu surface. The presence of S promotes the adsorption of H on the Cu surface.
- Water environment causes a considerable surface reconstruction of Cu lattice, leading to a large decrease in the insertion energy of H in the surface layer facilitating H ingress.
- H insertion via interstitial sites in Cu lattice occurs preferably in the presence of vacancies, and causes lattice expansion, mainly in the vertical direction to the surface. H insertion leads to a weakening of Cu-Cu bond strength.
- Only H infusion can explain the measured lattice dilation in the surface region after the exposure to the S-containing simulated anoxic groundwater, which indicates a risk for H-induced initiation of microcracks.

- As an overall implication the results clearly demonstrate the risk for H-induced SCC of Cu as canister material during long-term storage of nuclear fuel when exposed to sulfide-containing ground water.

Author statement

F.Z. performed the first literature survey, conducted the synchrotron experiments, and wrote the manuscript. C.Ö. conducted the synchrotron experiments, performed data analysis, and wrote the manuscript. M.L. performed DFT calculations, joined the synchrotron experiment, and wrote the manuscript. T.M. and U.L. supported and conducted the synchrotron experiments, and contributed to the manuscript writting. V. R.-H., L.C. and E.I. prepared the samples, performed corrosion exposure experiment, and contributed to the manuscript writing. J.P. acquired the funding, coordinated the project, planned and conducted experiments, and wrote the manuscript.

Data availability statement

The raw/processed data required to reproduce these findings will be shared by the corresponding author upon reasonable request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.corsci.2021.109390.

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Analys av kärnbränsleförvarsfrågan efter mark-och miljödomstolens yttrande till regeringen

I NACKA TINGSRÄTT, Mark- och miljödomstolens sammanfattning av sitt yttrande av den 2018-01-23, Mål nr M 1333-11 anges att

Verksamheten är tillåtlig om följande korrosionsfrågor utreds (med gynnsamt utfall):

Svensk Kärnbränslehantering AB redovisar underlag som visar att slutförvarsanläggningen på lång sikt uppfyller miljöbalkens krav trots de osäkerheter som kvarstår om hur kapselns skyddsförmåga påverkas av
a. korrosion på grund av reaktion i syrgasfritt vatten
b. gropkorrosion på grund av reaktion med sulfid, inklusive sauna effektens inverkan på gropkorrosion
c. spänningskorrosion på grund av reaktion med sulfid, inklusive saunaeffektens inverkan på spänningskorrosion
d. väteförsprödning
e. radioaktiv strålnings inverkan på gropkorrosion, spänningskorrosion och väteförsprödning.

Mark- och Miljödomstolen (MMD) har under ledning av domaren Anders Lilienau gjort, enligt vår mening, en mycket noggrann och korrekt analys av bristerna och osäkerheterna med den föreslagna metoden KBS-3 för slutförvar av högaktivt kärnkraftsavfall utvecklad av SKB AB, se ovan.

SKB har studerat kopparkorrosion i 40 år i såväl laboratoriemiljö om under förväntade slutförvarsförhållandena vid Äspö-bergslaboratoriet Oskarshamn. Sammanfattningsvis har SKB vid dessa försök inte en enda gång uppmätt korrosionshastigheter för koppar i grundvattenmiljö som är i närheten av det som anges i säkerhetsanalysen. Vår bedömning är att resultaten från SKB:s försök i grundvattenmiljö och från andra undersökningar är samstämmiga och visar att den allmänna korrosionshastigheten av koppar i grundvatten är 1-20 mikrometer per år, där variationen beror främst på olika vattentemperaturer. Detta kan relateras till SKB:s säkerhetsanalys som anger att kopparkapseln korroderar med ca 2 nanometer per år. En nanometer är en tusendels mikrometer vilket innebär att det i säkerhetsanalysen finns ett fundamentalt fel med en faktor i intervallet 500 till 10 000 gånger.

Kopparns korrosionshastighet i slutförvaret ökar vidare på grund av saltanrikning i deponeringshålen (Sauna-effekten), radioaktiv strålning, läckströmmar (från Fenno-Scankabeln) samt gropfrätning. Kopparkapslarnas mekaniska integritet (resistens mot sprickbildning) kommer vidare att degraderas på grund av spänningskorrosion, väteförsprödning, krypning och försprödning förorsakad av strålning.

Det allvarligaste felet med KBS-3 modellen är inte den grava missbedömningen av den allmänna kopparkorrosionshastigheten i grundvatten utan att SKB anser att alla s.k. lokala korrosionsprocesser samt försprödningsfenomen som beskrivits ovan inte äger rum. Såväl

SSM:s granskning, påpekanden från KTH och som fastställs i MMD:s yttrande visar att betydande osäkerheter rörande dessa snabba nedbrytningsprocesser föreligger. Det är vår mening att är både ovetenskapligt och helt oansvarigt att hävda att dessa nedbrytningsprocesser inte kan ske och kan bortses från i säkerhetsanalysen.

En förklaring till att SKB har vägrat att införa dessa snabba nedbrytningsprocesser i säkerhetsanalysen är att KBS-3 modellen då skulle ha minimala chanser att godkännas. Vetenskapligt underlag saknas idag för att exakt kunna bedöma hur snabbt kopparhöljet kan brytas ned av dessa processer och utan denna kunskap måste man anta att kopparhöljets skyddande kapacitet är mycket begränsad så fort som dessa nedbrytningsprocesser startar. När det väl sker innebär det utläckage av det radioaktiva avfallet inom i sammanhanget korta tidsrymder. I praktiken betyder det att om spänningskorrosion samt övriga snabba processer inkluderas i säkerhetsanalysen så måste man konservativt anta att kapselhaverier initieras redan inom 100 år och att en majoritet av kopparkapslarna är förstörda inom 1000 år. Detta innebär att KBS-3 metoden inte har några vetenskapliga förutsättningar att fungera och är dessutom långt ifrån "bästa tillgängliga teknologi" (BAT). Ren olegerad koppar har helt enkelt inga marginaler överhuvudtaget mot ett flertal korrosions- och försprödningsfenomen i den aggressiva slutförvarsmiljön på 500 meters djup. Att tillstyrka tillståndsansökan med nuvarande skrivning för att i senare steg i tillståndprocessen ta ställning till de betydande osäkerheter i nedbrytningsprocesser som förekommer anser vi därför vara ett helt felaktigt sätt att hantera denna viktiga fråga. Beslut måste baseras på en säkerhetsanalys där samtliga nedbrytningsprocesser och osäkerheter är inkluderade. Därefter kan fortsatt forskning eventuellt reducera de radiologiska riskerna i kommande steg inom i tillståndsprocessen. Detta medför att det enda sättet att på ett robust sätt hantera den uppkomna situationen är att SKB före regeringens beslut gör om säkerhetsanalysen med en referensutveckling där samtliga nedbrytningsprocesser som beskrivs ovan anses som aktiva.

Nyligen (efter MMD:s yttrande) har även forskare på amerikanska myndigheter, Center for Nuclear Waste Regulatory Analyses samt U.S. Nuclear Regulatory Commission, bekräftat att grundkorrosionen av koppar i syrgasfritt vatten sker med en hastighet inom området mikrometer per år [1]. Denna vetenskapliga publikation är intressant då den visar på det paradigmskifte som just nu sker inom kopparkorrosionsforskningen. Bortförklaringen som SKB-kopplade forskare använt genom åren att "syre måste ha läckt in" i alla de försök som påvisat kopparkorrosion i syrgasfritt vatten accepteras inte längre av vetenskapssamhället.

Angående korrosion i rent syrgasfritt vatten så råder det en grav missuppfattning av dess konsekvenser hos både bolaget SKB samt kontrollmyndigheten SSM. Båda organisationerna hävdar att även om koppar korroderar litegrann i rent syrgasfritt vatten så spelar det ingen roll för slutförvaret vilket är fundamentalt felaktigt. Vetskapen om att koppar reagerar direkt med vattenmolekyler, om än långsamt, förklarar varför kopparkorrosionen i slutförvarssammanhang blir så katastrofal. Det öppnar nämligen upp för ett otal olika kopparkorrosionsreaktioner med vattenmolekyler och olika joner samt lösta gaser i den komplexa grundvattenkemin. Dessutom hjälper denna nyvunna kunskap till att vetenskapligt förstå varför det uppstår både spänningskorrosion och väteförsprödning i kopparmetall exponerat för grundvatten.

Från öppna vetenskapliga publikationer rörande kopparkorrosion kan man redan i dag dra slutsatsen att KBS-3 modellen inte fungerar som det var tänkt från början där förutsättningen var att koppar är termodynamiskt immunt i rent syrgasfritt vatten, vilket då skulle innebär att koppar inte korroderar i vatten över huvudtaget. Det har nu även visats att nedbrytnings-

processerna är många fler än vad SKB tar höjd för i sin säkerhetsanalys. Kompletterande korrosionsstudier kan inte ändra på detta faktum, endast minska osäkerheterna om hur stora felaktigheter SKB:s säkerhetsanalys innehåller. Vi och även internationella slutförvarsexperter bedömer det som helt uteslutet att de radiologiska konsekvenserna kan accepteras om kapslarna börjar haverera inom hundra eller några hundra år. Således bör ytterligare forskning fokuseras på korrosionsresistenta metaller såsom legerad koppar, titan och nickelbaslegeringar. Dessa försök kan med fördel baseras på MMD:s utpekade fem områden som kräver komplettering men där ren (SKB-) koppar då endast utgör ett referensmaterial till de övriga mer korrosionsresistenta materialen. Dessutom bör även parallellt forskning initieras på andra slutförvarskoncept (exempelvis slutförvaring i djupa borrhål eller i dränerade "torra" bergrum eller nyttjande av avfallet som bränsle i Gen IV reaktorer).

Om det fortfarande anses relevant att utföra de föreslagna omfattande kompletteringarna vad avser ren koppar (flera års forskning) trots att tillräcklig vetenskaplig kunskap redan finns idag för att underkänna KBS-3 modellen, så är det av yttersta vikt att oberoende forskare anlitas som ej får bakbindas av detaljerade krav i kontrakt med SKB på så sätt som gjorts med bl.a. Uppsalaforskarna, se sidan 5 i Aktbilaga 645 [2].

Enda säkra sättet att systematiskt studera alla korrosionsfenomenen med <u>samtliga</u> tänkbara samverkanseffekter är att genomföra försök där mindre mängder utbränt kärnbränsle omsluts av minikopparkapslar och bentonitlera varefter de installeras i Äspö bergslaboratorium under verkliga förhållanden. Det torde vara fullt möjligt att genomföra denna typ av "skarpa" försök med full säkerhet genom att allokera och försegla en tunnel(del) på 500 meters djup. För att spara tid och forskningsmedel bör ett antal provkuponger av de mer korrosionsresistenta metallerna inkluderas i dessa försök. Förslagsvis installeras två minikapslar som kan tas upp efter 5 och 10 år varpå ingående metallografiska undersökningar genomförs av kapselmaterialet samt de inkluderande provkupongerna av de korrosionsresistenta kandidatmaterialen.

Generell analys av kärnbränsleförvarsfrågan

Orsaken till att slutförvarsforskningen i Sverige har misslyckats beror till stor del på följande punkter:

1) Villkorslagen. I slutet på 70-talet införde regeringen Fälldin villkorslagen som krävde att kärnkraftsindustrin måste visa att en säker slutförvarslösning finns framtagen för att få tillstånd att starta nya kärnkraftverk. Detta ledde till att industrin i all hast tog fram kopparkapselkonceptet (1978) och hävdade att det var den säkraste och bästa lösningen. SKB har vidhållit kopparkapselns förträfflighet under dessa 40 år trots att ett stort antal forskningsrapporter, särskilt under senare år, visat på motsatsen och trots att villkorslagen är avskaffad sedan länge.

2) FUD programmet. SKB har även på uppdrag av reaktorinnehavarna enligt kärntekniklagens 12 § upprättat ett program för att beskriva den allsidiga forsknings- och utvecklingsverksamhet och de övriga åtgärder som behövs för säker hantering av kärnavfall och använt kärnbränsle samt säker avveckling rivning av kärntekniska anläggningar (FUD). Detta program har av SSM och de dåvarande (SKI och SSI) granskats vart tredje år. Myndigheternas granskning av FUD programmet har inte heller

den påtalat de uppenbara bristerna i SKB:s hantering av olika nedbrytningsprocesser på ett tillräckligt tydligt sätt. Vad värre är att det råder en uppfattning på SSM att då dessa brister inte påtalats i tidigare granskningar kan myndigheten inte avstyrka den nu aktuella tillståndsansökan för ett slutförvar enligt KBS-3 metoden.

3) SKB har ett ekonomiskt och ansvarsmässigt incitament att deponera avfallet fortast möjligt. När väl kärnavfallet är deponerat i ett slutförvar så övergår ansvaret till staten, d.v.s. oss skattebetalare.

4) Avsaknad av fri och oberoende forskning. SKB kontrollerar forskningsmedlen på slutförvarsområdet via kärnavfallsfonden och citat "anlitar egna forskare som SKB kan lita på". Detta omöjliggör i praktiken att "dåliga" resultat kommer fram på ett öppet och vetenskapligt korrekt sätt.

5) Ej fungerande kontrollmyndighet på slutförvarsområdet. Vi forskare har försökt slå larm genom åren till dåvarande SKI och nuvarande SSM men med mycket svalt mottagande. Under miljödomstolsförhandlingarna framstod det för oss forskare samt för övriga utomstående som att kontrollmyndigheten SSM i det närmaste stöttade SKB och KBS-3 metoden i stället för att agera som en kritiskt granskande kontrollmyndighet. Detta har bidragit till att det har varit och fortfarande är närmast omöjligt för utomstående experter och forskare att komma med konstruktiv kritik och förslag till förbättringar rörande slutförvaret. Därtill har kontrollmyndigheten SSM:s egna korrosionsexperter inte fått möjligheten att framföra sin allvarliga kritik utan har upplevt att de har blivit starkt styrda av ledningen, vilket är synnerligen allvarligt [3,4].

Undertecknade kommer gärna och gör en muntlig presentation för att förtydliga våra synpunkter och svara på eventuella frågor om så önskas, Stockholm, 26 april 2018.

Tekn. Dr. Peter Szakálos,
Prof. em. Christofer Leygraf
Prof. em. Anders Rosengren
Prof. em. Seshadri Seetharaman
Docent Olle Grinder
Tekn. Dr. Jan Linder (f.d. materialexpert på Strålsäkerhetsmyndigheten)

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Regeringskansliet

Miljödepartementet

2019-09-13

Remissyttrande

Yttrande över Svensk kärnbränslehantering AB:s kompletterande yttrande i ärende om

1. **tillåtlighetsprövning enligt 17 kap. miljöbalken av anläggningar i ett sammanhängande system för slutförvaring av använt kärnbränsle och kärnavfall (M2018/00217/Me)**

2. **tillståndsprövning enligt lagen (1984:3) om kärnteknisk verksamhet av anläggningar i ett sammanhängande system för slutförvaring av använt kärnbränsle och kärnavfall (M2018/00221/Ke)**

Den övergripande slutsatsen som presenteras i detta yttrande är att SKB:s säkerhetsanalys, SR-site från 2011, är föråldrad då de senaste årens korrosionsforskning tyvärr har bekräftat närvaron av lokala (snabba) korrosions- och försprödningsprocesser på olegerad koppar i slutförvarsmiljön. Det betyder att SR-site inte längre kan anses utgöra ett underlag för den Svenska regeringen i slutförvarsfrågan.

Ett fundamentalt problem med ett slutförvar i Forsmark är att det tar några tusen år innan grundvattnet fyllt tunnlarna och samtliga deponeringshål. Dessutom har det nu visats att bentonitlerans svällande förmåga påverkas av mikrobiell aktivitet, saltindunstning samt mineraliseringsprocesser.

Detta gör att den andra barriären, bentonitleran, inte kan fungera som det var tänkt från början. I praktiken har detta visat sig vara ödesdigert för huvudbarriären, den enda barriären som vid deponering av kärnbränslet är helt tät, kopparkapseln. Bentonitleran kommer att bli utsatt för sprickbildning, kanalbildning samt mineralisering/försprödning och kan då inte skydda kopparkapslarna från flera aggressiva korrosionsprocesser. Det kalla och salta grundvatten på ca 12° C som sipprar in i ett deponeringshål kommer att hettas upp av strålningsvärme från kärnavfallet via kopparkapseln, vilket genererar upp till 1700W och en temperatur vid kopparkapseln på ca 90 °C. Detta leder oundvikligen till att fukt och ånga kommer att lämna deponeringshålen, samtidigt som svavel- och klorsalterna stannar kvar och då orsakar oacceptabelt snabb korrosion på den upphettade kopparkapseln. Detta fenomen har kommit att kallas Saunaeffekten. De senaste årens forskning har bekräftat att kopparkorrosion i slutförvarsmiljön inte bara ger synliga skador på kopparytan i form av gropfrätning. Metallen förstörs dessutom genom s.k. väteförsprödning och andra korrosionsrelaterade processer inne i kopparmaterialet. När olegerad koppar korroderar i en syrgasfri miljö bildas fria väteatomer som spontant går in i kopparmetallen och reagerar med kopparoxidpartiklar i svetsfogarna vilket resulterar i små vattenblåsor. Övriga koppargodset drabbas av väteblåsor. Dessa väte-

och vattenblåsor blir fler och fler, inre spänningar uppstår och till slut spricker metallen. Hastigheten på dessa väteförsprödningsprocesser beror på rådande kopparkorrosionshastighet samt temperatur. Baserat på mätningar i riktig slutförvarsmiljö kan man dra slutsatsen att en stor andel av kopparkapslarna, ca 40%, kommer att spricka redan inom 100 år, i huvudsak beroende på dessa väteförsprödningsprocesser.

Kopparmetallen påverkas även av hydroxidjoner samt svavelatomer. Den kombinerade effekten av svavel och väte ger upphov till snabbt växande spänningskorrosionssprickor (SCC) i kapselns områden med mekanisk spänning. Spänningskorrosion och väteförsprödning i kapselmaterialet har alltid ansetts vara helt oacceptabel i en slutförvarsmodell, så även för KBS-3. Under de senaste åren har det bekräftats av flera forskargrupper att SCC sannolikt kommer att ske i slutförvaret, särskilt i kombination med Saunaeffekten. Dessutom har tänkbara skador i kopparmaterialet orsakade av den kombinerade effekten av radioaktiv strålning och exponering i grundvatten helt underskattats av SKB. Nya rön visar att såväl kopparkorrosion som väteupptag accelereras av den radioaktiva strålningen, d.v.s. både väteförsprödning och SCC kan väntas förvärras av strålningen från avfallet, vilket SKB inte ens har börjat studera. Forskare vid KTH har därför påbörjat studier kring frågeställningen.

I Schweiz har man nyligen avslutat en gedigen korrosionsstudie som pågått 19 år (FEBEX-DP) i en riktig slutförvarsmiljö. Flera olika metaller studerades, inklusive legerad och olegerad koppar. Slutsatsen var att olegerad koppar (SKB-koppar) drabbades av gropfrätning och var den sämsta metallen av de undersökta. Bentonitleran, kommer inte att ha mycket till barriäregenskaper i Forsmarks slutförvarsmiljö, då sprickor, kanalbildning, svällningsreduktion p.g.a. mikrober samt mineralisering/försprödning kommer att ske. Därför kommer denna s.k. "barriär" som ska fördröja utsläpp av radioaktiva ämnen när kopparkapslarna går sönder inte heller att fungera på det sätt som SKB redovisar i sin säkerhetsanalys, SR-site. Det faktum att bentonitleran inte kommer att ha några egentliga barriäregenskaper, gör att de samverkande korrosionsmekanismerna kommer att förstöra de återstående 60% av kapslarna redan inom 1000 år.

Alla ovan diskuterade korrosions- och degraderingsprocesser med tillhörande vetenskapliga referenser har utförligt beskrivits i en kommande SSM-rapport [1]. Den viktigaste slutsatsen är att SKB:s säkerhetsanalys, SR site från 2011 [2], är föråldrad då de senaste årens korrosionsforskning har bekräftat närvaron av lokala (snabba) korrosions- och försprödningsprocesser på olegerad koppar i slutförvarsmiljön. Det betyder att SR-site inte längre kan anses utgöra ett underlag för den Svenska regeringen i slutförvarsfrågan. SKB:s kompletterande rapport [3] har inte heller tagit hänsyn till de senaste forskningsrönen på ett adekvat sätt.

SSM upphandlade ett granskningsuppdrag rörande SKB:s kompletterande material [1] under maj månad 2019, men innan uppdraget påbörjades valde myndigheten att skriva ett eget manuskript som skickades in till en vetenskaplig tidskrift den 30 maj 2019 [4]. I denna publikation genomför SSM en genomgång av majoriteten av de degraderingsmekanismer som mark och miljödomstolen har pekat ut och som ingår i granskningsuppdraget [1]. I ref. 4 redovisas hur SSM ser på degraderingsprocesser för kopparkapseln som bl.a. korrosion i syrgasfritt vatten, punktkorrosion, spänningskorrosion och krypskador. SSM konstaterar vidare att dessa degraderingsprocesser i dagsläget skall anses som osannolika. SSM presenterar dessutom en konsekvensanalys av hur stor radioaktiv påverkan som kan drabba människor då kapslarna går sönder. Syftet med artikeln anges vara att utvärdera KBS-3 modellen med avseende på den potentiella inverkan dessa degraderingsprocesser har på människor p.g.a. radioaktiv strålning. Från beräkningen framgår att SSM:s krav enligt ref. 5 inte kan uppfyllas om dessa degraderingsprocesser är verksamma. Baserat på detta resultat är det något förvånande att SSM

vid förhandlingen i mark och miljödomstolen ändå ansåg att KBS-3 modellen uppfyllde SSM:s föreskrifter och därmed tillstyrkte att miljödomstolen skulle bifalla ansökan. Det är vidare anmärkningsvärt att SSM använder ett förvisso förenklat angreppssätt för att utvärdera vilka potentiella effekter olika kapseldegraderingsprocesser har på spridningen av radioaktivt material, men låter de andra barriärfunktionerna, bufferten och berget, vara helt intakta. Det har i ref. 1 redovisats att barriäregenskaperna även för lerbufferten måste ifrågasättas. Ska denna typ av angreppssätt användas måste alla osäkerheter i samtliga barriärer tas med i kombination med varandra och den totala osäkerheten i skadeverkningar på människor p.g.a. radioaktiv strålning beräknas. Att SSM lyfter ut osäkerheter i degraderingsprocesser endast för kapselmaterialet i ref 4 är därför anmärkningsvärt. Det är dessutom oklart varför SSM väljer att publicera detta innan SKB:s komplettering behandlats av myndigheten, övriga remissinstanser samt regeringen. Att SSM publicerar ett arbete där 1000-tals kapslar går sönder efter några tusentals år samtidigt som de anser att SKB:s säkerhetsanalys SR-site där det anges att mindre än en kapsel går sönder efter en miljon år ska bifallas av mark och miljödomstolen är uppseendeväckande. Frågan bör därför ställas om SSM kan anses objektiv i denna fråga.

1) P. Szakálos and C. Leygraf. "Review of SKB:s Supplementary Information on copper canister integrity issues". External reviewers: S. Seetharaman and A. Rosengren. 2019-08-14, SSM-diarie no: 2019-1127. In press.

2) 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

3) Hedin A. et al. 2019. Supplementary information on canister integrity issues. SKB TR-19-15, Svensk Kärnbränslehantering AB.

4) Strömberg, B., Sonnerfelt, L., and Öberg, H. Exploratory what-if analysis of some debated canister failure modes in the review of a licence application for the construction and operation of a spent nuclear fuel repository in Sweden, Adv. Geosci., 49, 67–75, https://doi.org/10.5194/adgeo-49-67-2019, 2019.

5) Strålsäkerhetsmyndighetens föreskrifter om skydd av människors hälsa och miljön vid slutligt omhändertagande av använt kärnbränsle och kärnavfall, SSMFS 2008:37

Tekn. Dr. Peter Szakálos,   Prof. em. Christofer Leygraf

Prof. em. Anders Rosengren   Prof. em. Seshadri Seetharaman

Tekn. Dr. Jan Linder (Ansvarade tidigare för kapselfrågor på Strålsäkerhetsmyndigheten)

From:	Peter Kristian Mikael Szakalos <szakalos@kth.se>
Sent:	den 22 november 2019 16:27
To:	Magnus Moreau; Björn Dufva
Cc:	M Registrator
Subject:	Komplettering, remissyttrande från KTH-forskarna samt J. Linder. Diarienummer M2018/00217/Me samt M2018/00221/KE
Attachments:	SSM2019-2484-8_Rev_granskningsrapport_Szakalos_Leygraf_m_forsattsbl_191009.pdf; KTH forskarna samt J Linder REMISSVAR.pdf

| Categories: | M2018/00221/Ke |

Hej Magnus och Björn,

vi bifogar här en komplettering till vårt tidigare yttrande från 13 september 2019, diarienummer M2018/00217/Me samt M2018/00221/KE. I det yttrandet hänvisar vi till en SSM-rapport som då ej ännu var publik. Denna granskningsrapport som är utarbetad av mig och prof. C. Leygraf är bifogad här. I vårt tidigare remissyttrande (även det bifogat) utgör denna rapport referens [1], där vi angivit dåvarande diarienummer SSM 2019-1127. Denna huvudreferens [1] är nu registrerad i SSM:s diarium som SSM 2019-2484-8. För att komplicera saken ytterligare har SSM valt att integrera denna rapport i en otymplig lunta bestående av fyra enskilda konsultrapporter i ett s.k. "Technical Note" i form av rapporten SSM-2019:22.

Bästa Hälsningar Peter

Peter Szakálos
KTH, division of Surface- and Corrosion Science,
Drottning Kristinas Väg 51, SE-11428 Stockholm
and
Szakálos Materials Science AB
Fridhemsgatan 29b, SE-11240 Stockholm
Mobile: +46(0)707537946

From: Magnus Moreau
Sent: 13 September 2019 17:00
To: Peter Kristian Mikael Szakalos
Subject: RE: Remissvar från KTH-forskarna samt J. Linder. Diarienummer M2018/00217/Me
Hej Peter

Tack för informationen. Vår rutin är att stänga brevlådor även vid tjänstledighet, men eftersom yttrandet har skickats även till registrator har det kommit in.

Hälsningar

Magnus

Från: Peter Kristian Mikael Szakalos <szakalos@kth.se>
Datum: fredag 13 sep. 2019 4:03 em
Till: Magnus Moreau <magnus.moreau@regeringskansliet.se>
Ämne: Fw: Remissvar från KTH-forskarna samt J. Linder. Diarienummer M2018/00217/Me

Bäste Magnus,

vi har försökt skicka in vårt remissvar till Lina Österbergs mailbox, men enligt KTH:s mailserver existerar inte hennes mailadress. Registrator har dock mottagit mailet. Jag ringde till departementet som bekräftar att Lina är tjänstledig, dock märkligt att mailen är avstängd?
För din information så bifogas här vårt remissvar.

Hälsningar Peter samt medförfattare

Peter Szakálos
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From: Peter Kristian Mikael Szakalos
Sent: 13 September 2019 15:23
To: m.registrator@regeringskansliet.se
Cc: lina.osterberg@regeringskansliet.se
Subject: Fw: Remissvar från KTH-forskarna samt J. Linder. Diarienummer M2018/00217/Me
Hej Lina,

vi bifogar här vårt Remissvar som en PDF-fil. Vi bifogar även löptexten i Wordformat enligt önskamål.

Bästa Hälsningar // Peter Szakálos samt medförfattare

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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

2

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 corrosions 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 corrosions 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-chrystal, 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 /Korzhavyi 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 Finish 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 175µm 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 trys 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 m^2, 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/m^2) 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 m^3 groundwater (SKB-TR 17-07).
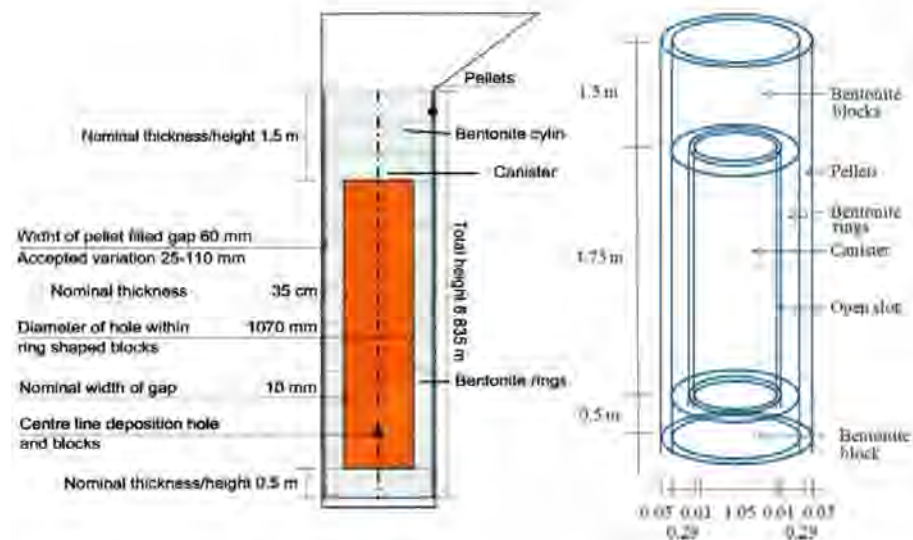
Figure 2.1. Configuration and geometry of the deposition hole with copper canister and bentonite buffer. From SKB-report TR-14-12 (to the left) and from SKB-report TR-17-15, Figure 9-1 (to the right). The drilled hole in the bed rock has a diameter of around 1.8 meter.

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.
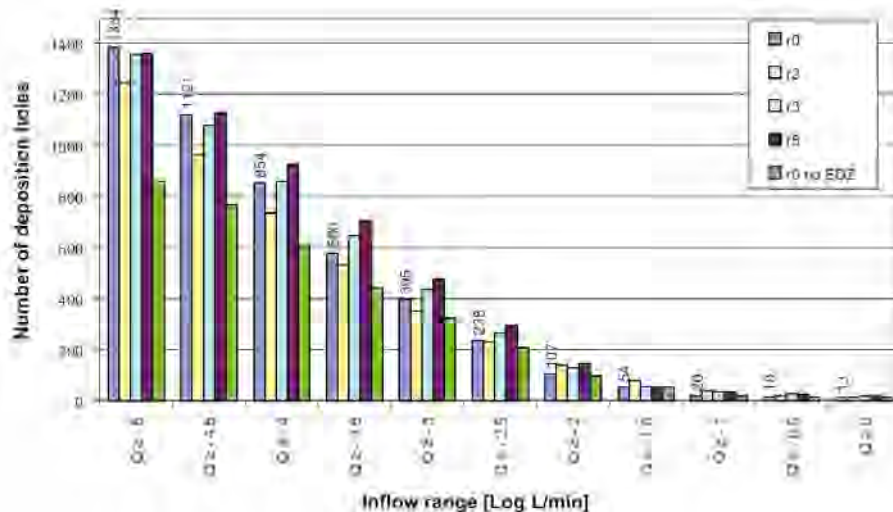
Figure 2.3. From SKB-report R-13-21, Fig. 3-4. Complementary cumulative distributions of the total inflow to each deposition hole for each case. According to case r0 (the five simulations r0-r5, give roughly the same outcome) there are 1384 deposition holes out of 6916 that have at least one crack that 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).
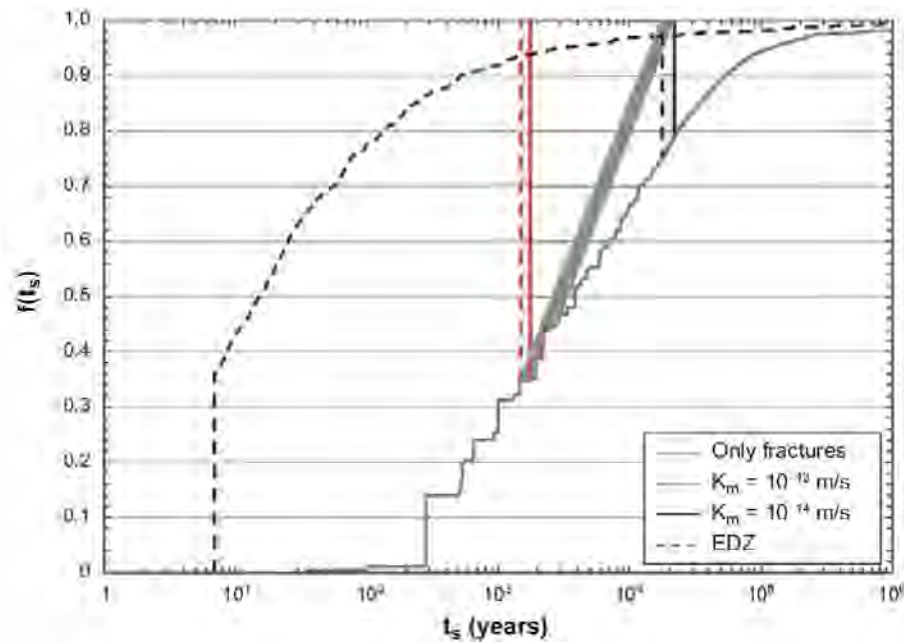
Figure 2.4. Modified graph based on Fig. 7-15 in /Sellin P. et al. 2017/. The solid grey line identifies the cumulative distribution of saturation times, $f(t_S)$, in the Forsmark repository calculated assuming no matrix flow, i.e. only flow via macro cracks. The vertical lines (red and black) identify 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.
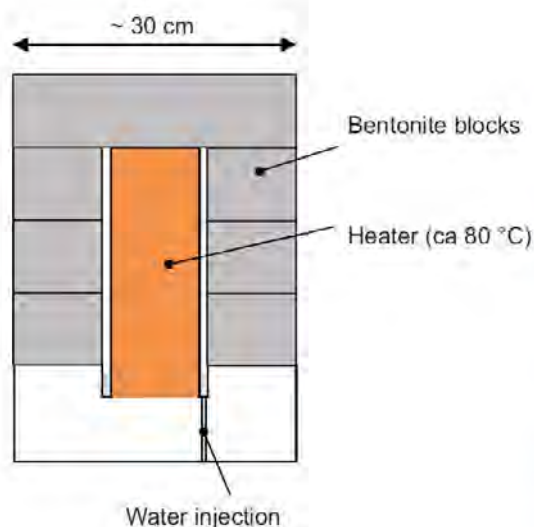
Figure 2.7. From Figure 2-1 in TR 15-09. The test set-up, which to a certain extent is a model of a KBS-3 deposition hole. Mounted on a plastic plate is a copper tube which is heated by circulating water to approximately 80 °C. "Water injection" seen to the left is actually a hole for low pressure water 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 dm^3 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.

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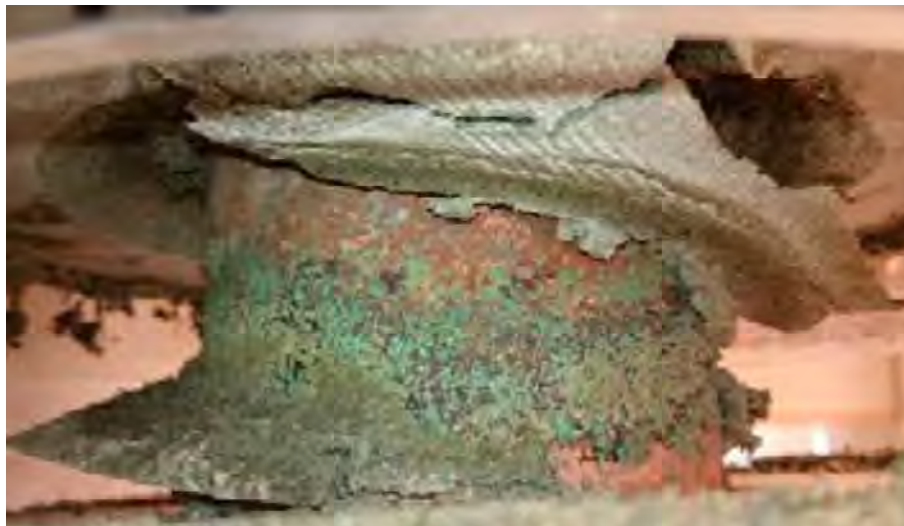
Figure 2.8. Detail from Figure 2-27 in TR 15-09. Severe corrosion of the copper heating tube after only seven days of laboratory exposure that at least reminds of the true Sauna effect, i.e. with only indirect contact with 0.6M chloride solution.

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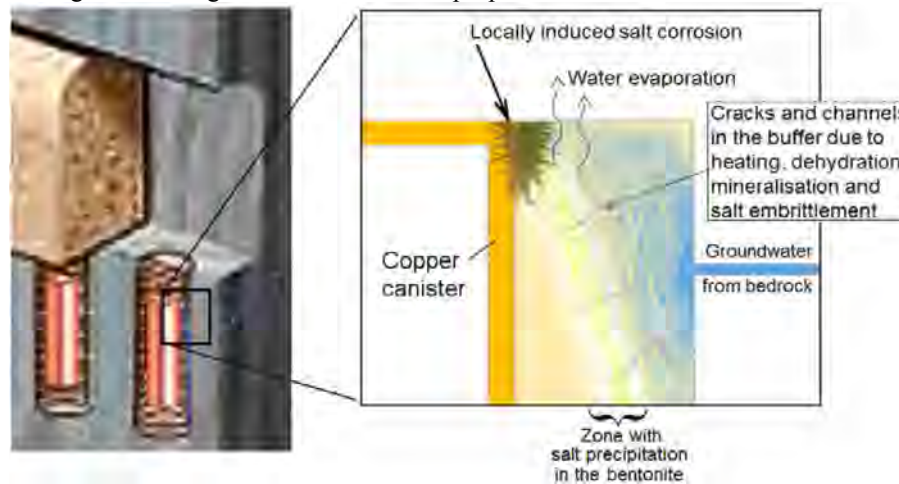
Figure 2.9. The Sauna effect in a repository with water evaporation, salt enrichment and copper corrosion. Furthermore, the precipitated salt will destroy the properties of the bentonite buffer /Szakálos P. and Seetharaman S. 2012/.

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.
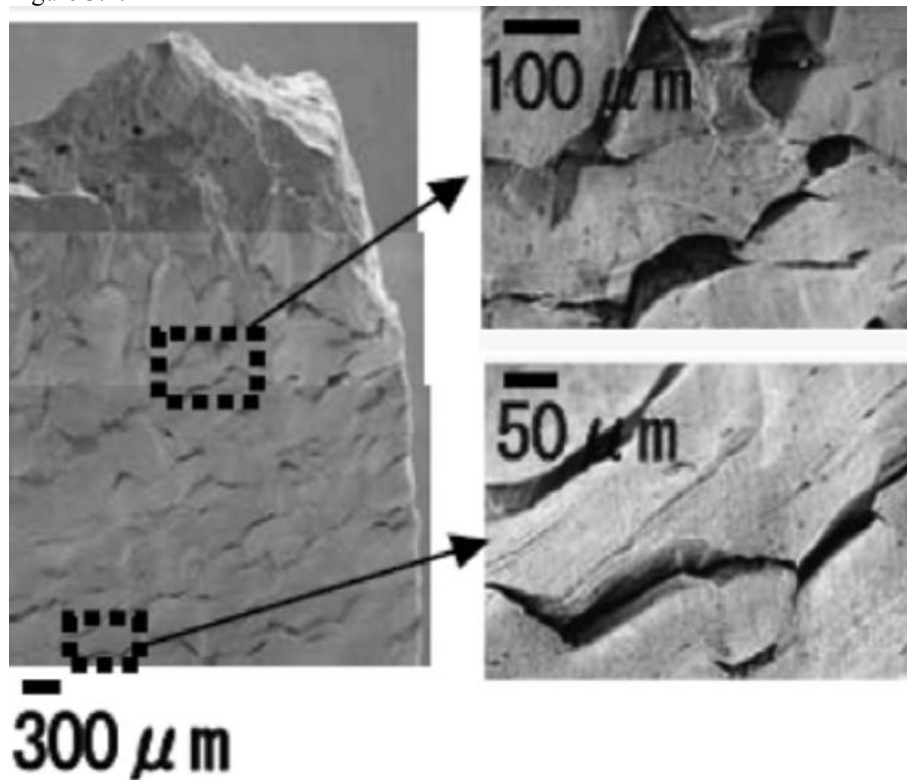
Figure 3.1. Fractured copper sample due to Stress Corrosion Cracking (SCC) in 0.01M sulphide containing seawater at 80°C after 7 days exposure. Initiation of minor cracks was detected at 0.001M sulphide concentration (not shown here). Slow strain rate testing (SSRT) results from Figure 10 in /Taniguchi and Kawasaki 2008/.
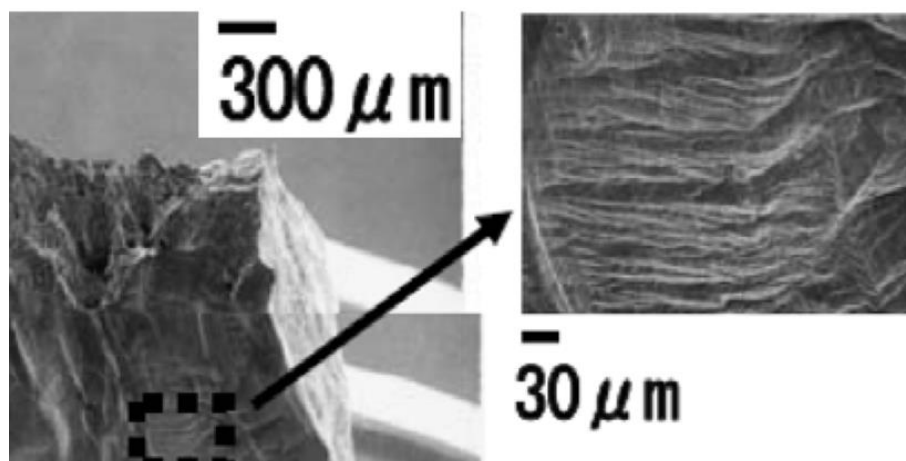
Figure 3.2. Crack-free copper surface when tested during the same conditions as in Figure 3.1 but with a sulphur free (inert) environment. No indication of any crack initiation visible in high magnification, see detailed micrograph to the right. Slow strain rate testing (SSRT) results from Figure 10 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. Öijerholm 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. Öijerholm 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. Öijerholm 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. Öijerholm 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: $7 \cdot \times 10^{-8}$ s^{-1}, maximum strain: 9%. Testing time: 2 weeks.
Exposures 1 and 2 (specimen #3 and #4): 10^{-3} M Na$_2$S
Exposures 3 and 4 (specimen #5 and #6): 10^{-4} M Na$_2$S,
Exposure 5 (specimen #7): 10^{-5} M Na$_2$S

Figure 3.3. Example of SSRT exposed sample, 9 % strain at the thinnest part of the tapered sample (not exposed to final fracture).
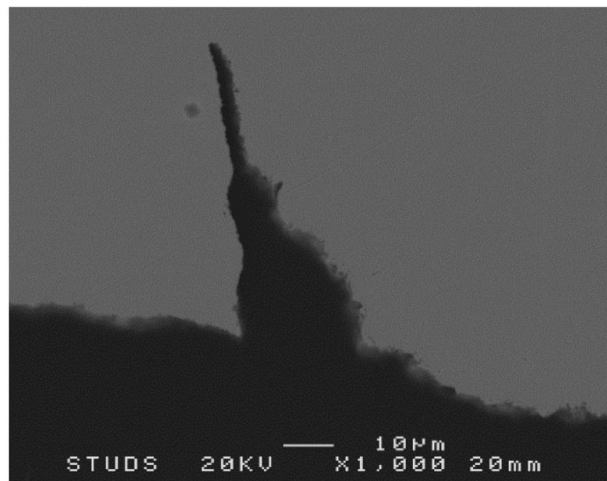
Figure 3.4. From Figure 16 in /R. Becker, J. Öijerholm 2017/: Specimen #3 (10^{-3} M sulphide), SEM image of a crack observed at the narrowest part of tapered gage section.

19
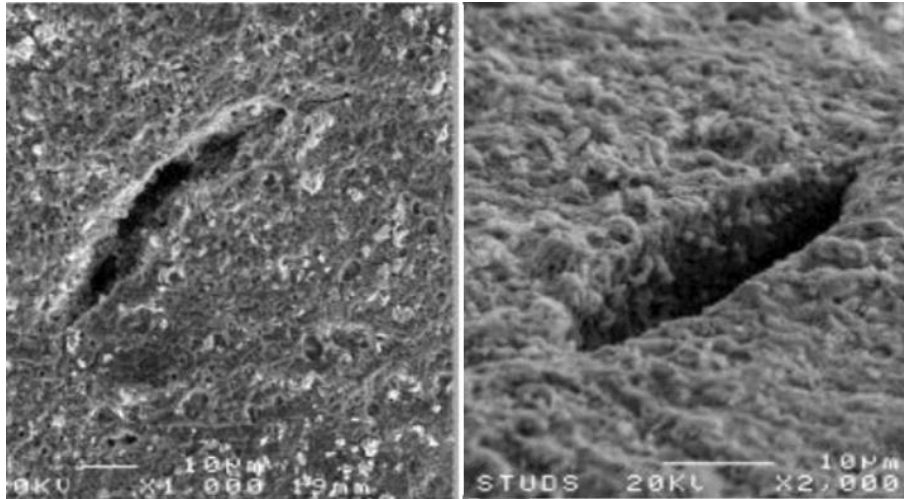
Figure 3.5. From Figure 2 in /Forsström A. et al. 2017/. Surface cracks near the narrowest part of Specimen #3 (10^{-3} M sulphide) after SSRT testing.
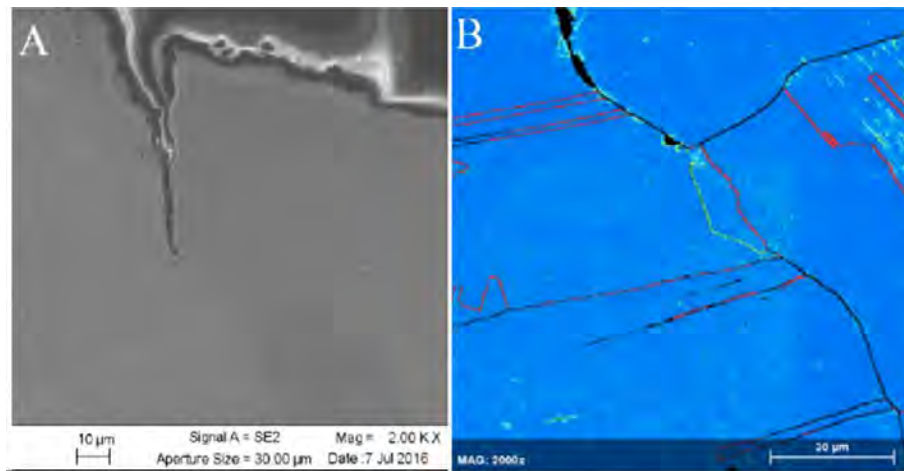
Figure 3.6. From Figure 3 in /Forsström A. et al. 2017/. Cross-section images of a SCC crack in the narrow section of Specimen #3. EBSD image showing crack propagation along a random grain boundary. Twin boundaries are marked in red and local misorientation in shades of green.
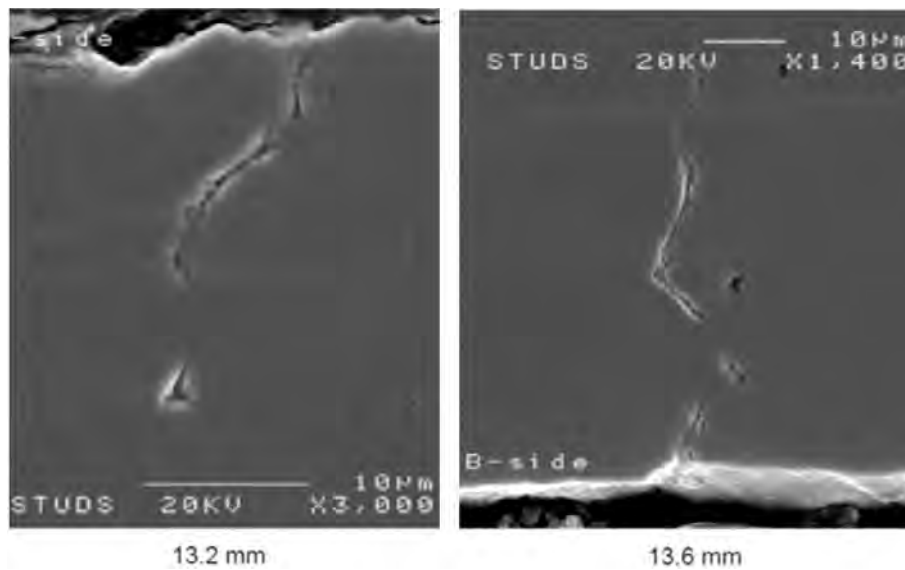
Figure 3.7. Part from Figure 21 in /R. Becker, J. Öijerholm 2017/. Initiation of blisters and cracks could be detected also at lower sulphide concentrations quite far away from the narrowest part (with the highest stress) of the sample, i.e. at a distance of 13.2-13.6 mm. Exposures 3 (specimen #5) exposed to 10^{-4} M sulphide.
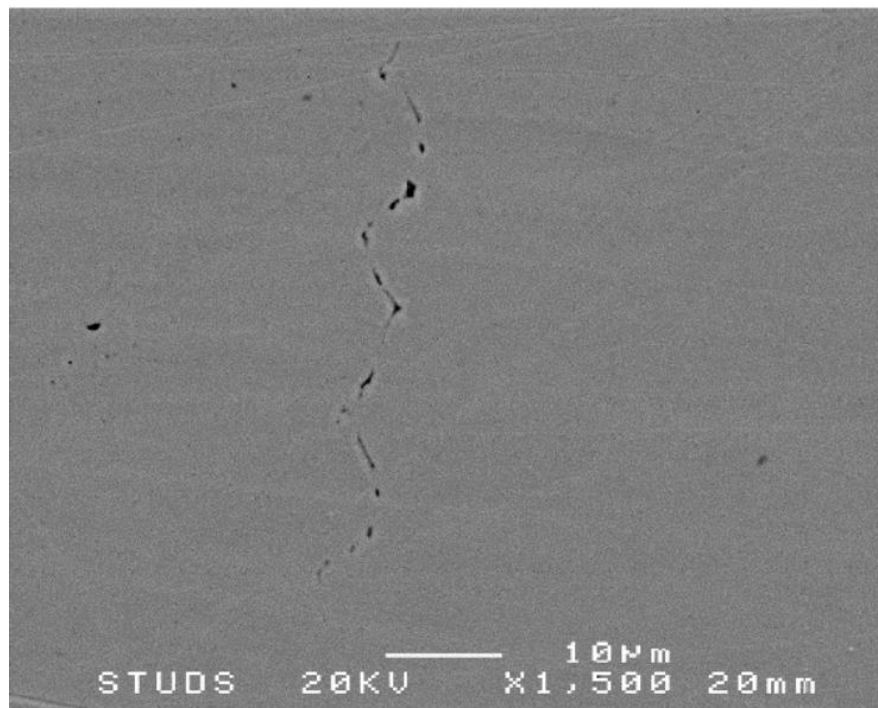
Figure 3.8. From Figure 22 in /R. Becker, J. Öijerholm 2017/, specimen #5, (10^{-5} M sulphide). Defects in shape of blisters in the copper grain boundaries was detected deep inside the SSRT samples. In fact, similar defects were also found in the unloaded head section of the samples, irrespective of 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.*"
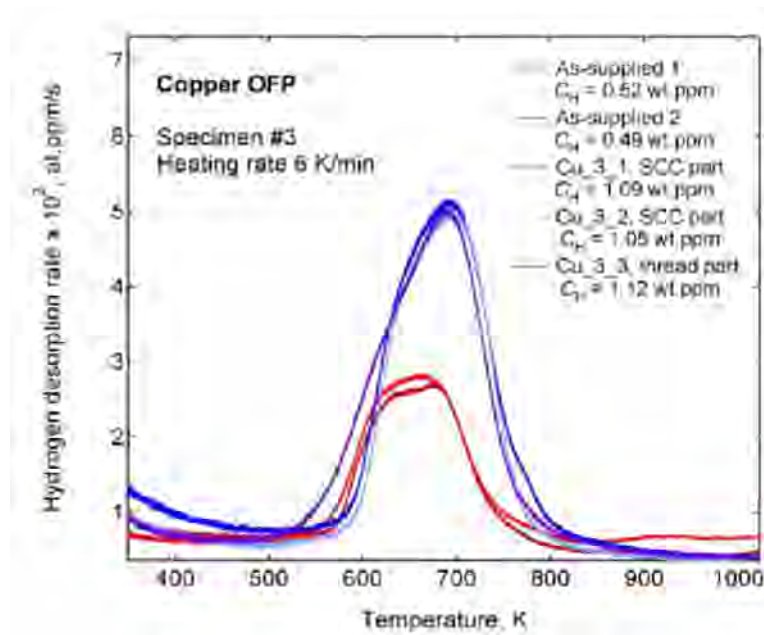
Figure 3.9. Hydrogen desorption curves (TDS) from /Forsström A. et al. 2017/ shows a systematically higher hydrogen content in the SSRT-exposed copper samples (blue and purple curves) compared with the as supplied SKB-copper metal (red curves). The TDS curves looks similar for all tested samples, i.e. #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} m^2/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 × 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.
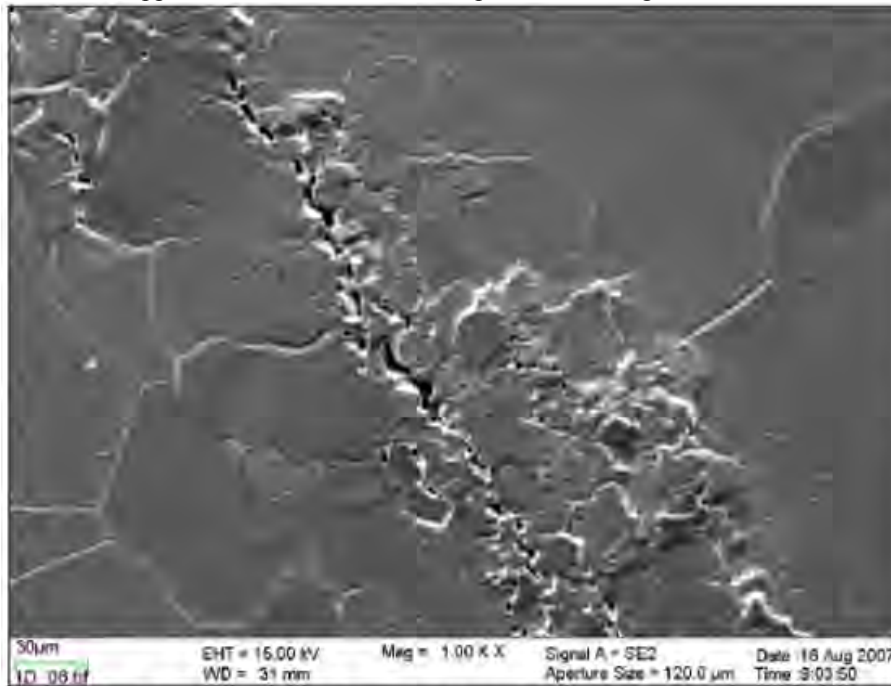
Figure 15. Sample 1DV. Voids and heavy deformation are clearly visible at the region of entrapped oxide particles.

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.

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).
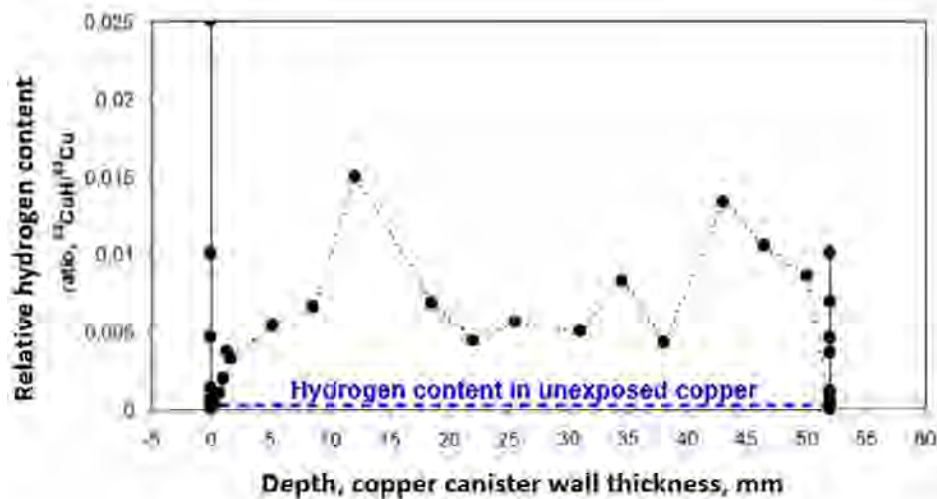
Figure 3.12. Full thickness canister copper exposed to the Swedish groundwater for seven years in the heated prototype repository, 80-90°C, at Äspö hard rock laboratory. The remarkable result shows that the copper canister is hydrogen charged throughout the whole thickness. The outermost surfaces have 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.
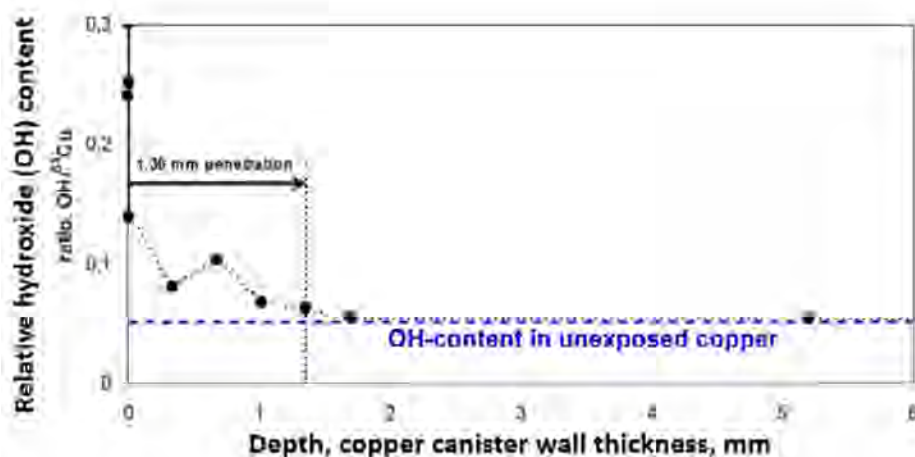
Figure 3.13. The hydroxide content of the first few mm of the full thickness canister copper exposed to the Swedish groundwater for seven years in the prototype repository at Äspö hard rock laboratory. The graph shows that hydroxide penetrates the copper metal, most probably in defects including grain 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 /Korzhavyi 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

/Arilahti 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.
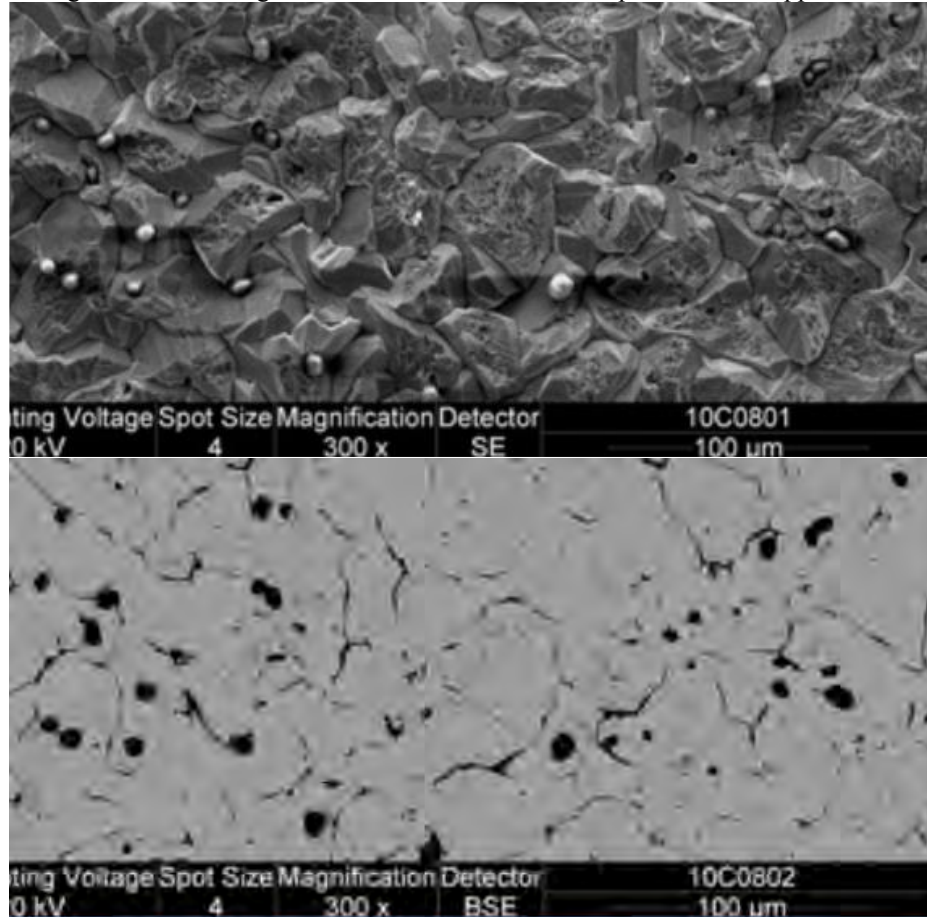
Figure 3.14. Detail from Figure 4 in /Arilahti E. et al 2011/. The SEM-image at the top shows a post exposure fractured area ahead of the true crack tip for which EDS analysis showed average of 22.5 at-% sulphur. The backscatter electron image of the same area (bottom picture) shows darker sulphur-rich 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.
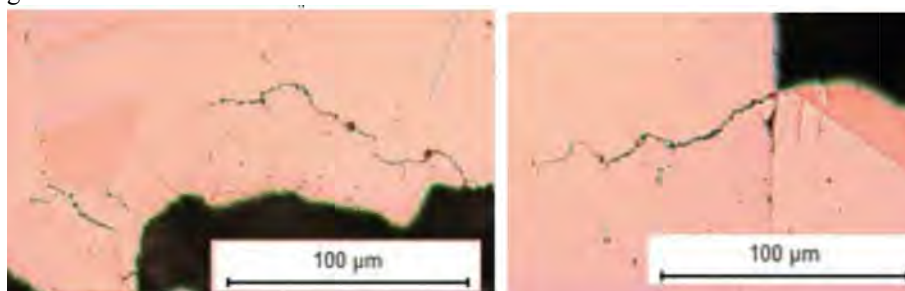
Figure 3.15. Details from Figure 4-7 in /Gordon A. et al. 2017/. Middle part of pre-crack of WOL sample M4 4:1 (MiniCan 4), showing smaller cracks emanating perpendicular to the direction of the main crack.

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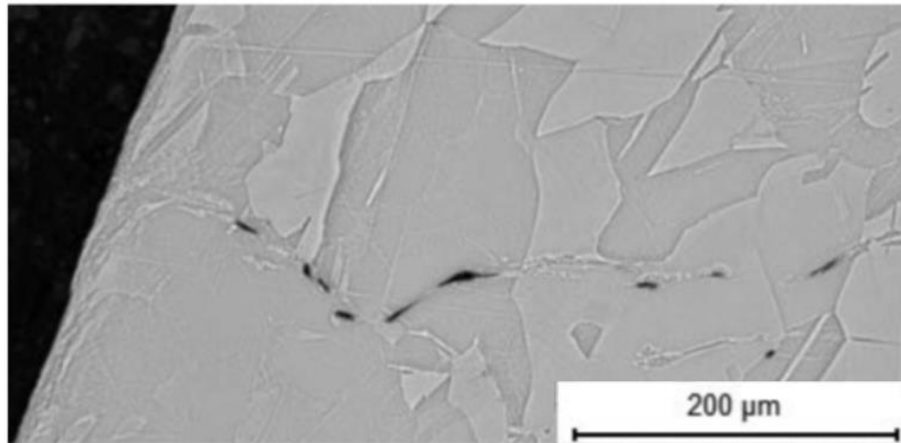
Figure 3.16. Details from Figure 4-5in /Gordon A. et al. 2017/. U-bend sample M4 1.1 had an area of cold deformation near the surface, but also present were pores which appeared to be aligned along the grain boundaries.

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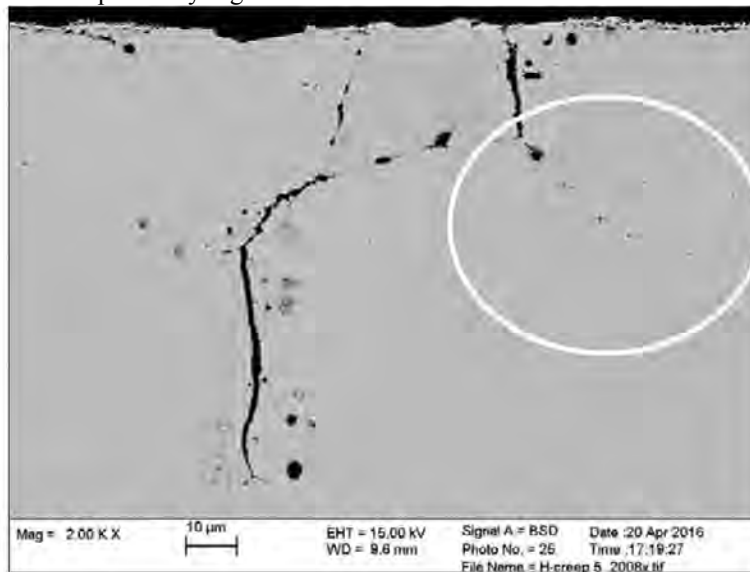
Figure 3-8. Specimen H-creep-05 tested at RT for 1 005.7 hours hydrogen charging time and creep stress of 170 MPa. Larger cracks were discovered. The specimen was tested in soft annealed condition without any pre-strain.

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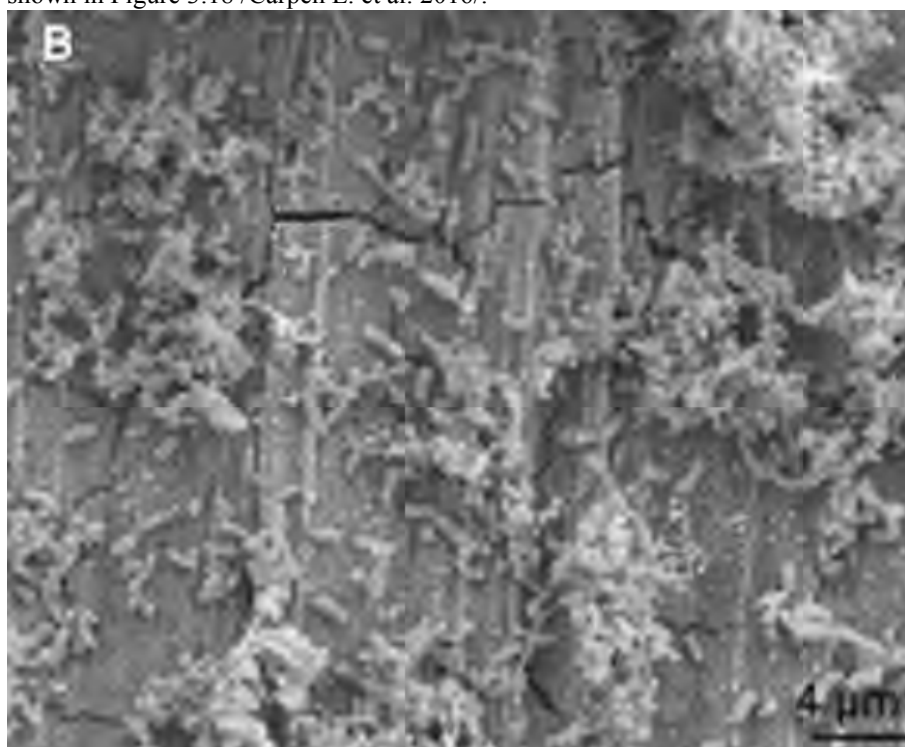
Figure 3.18. Microbial corrosion on the surface of unalloyed copper creates micro cracks due to sulphur enrichment. SRB colonies convert sulphate to sulphide which results in SCC/ Carpén L. et al. 2016/.

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 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 a 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 temperatures10-12°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.
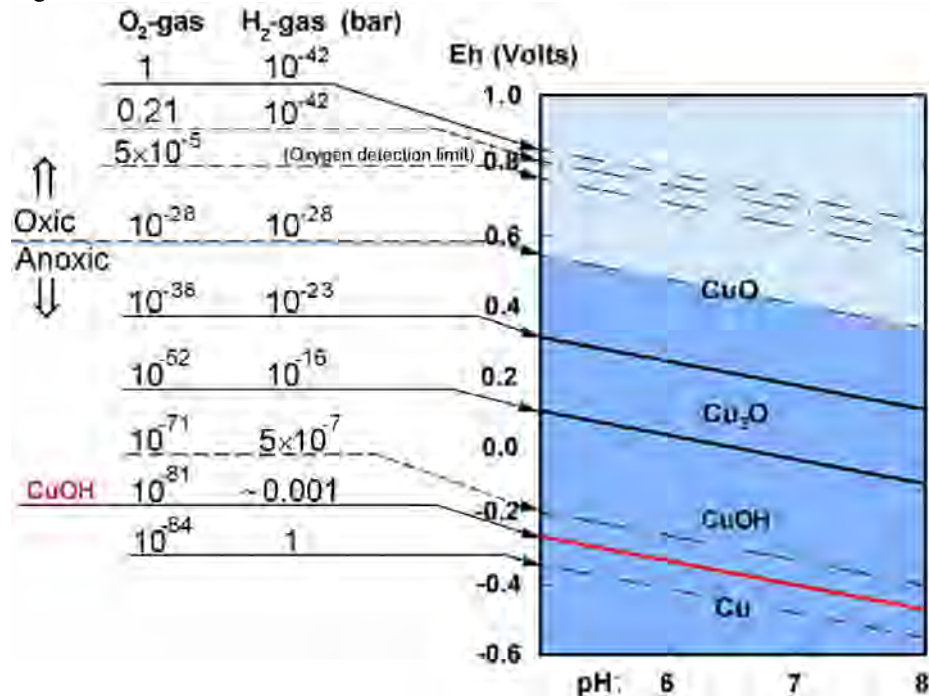
Figure 4.1. Pourbaix diagram based on /Szakálos P et al. 2007/. The light blue area at the top shows the oxic region with predominantly dissolved oxygen gas. The somewhat darker blue area shows the anoxic region with predominately dissolved hydrogen gas. The anoxic corrosion product Cu_2O (cuprite) is 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 (Cu_2O) is visible on the copper surface, but these Cu_2O-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.
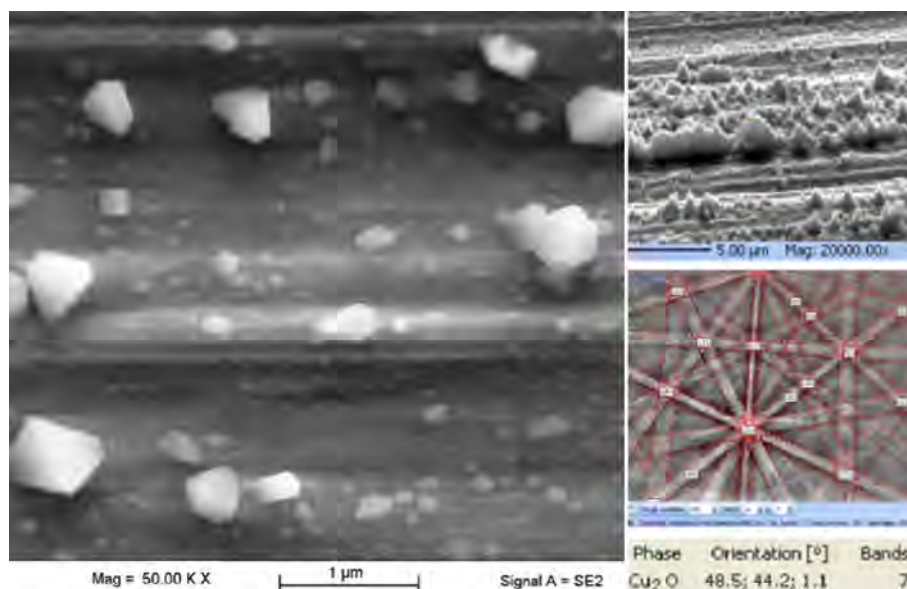
Figure 4.2. Unalloyed copper exposed to pure oxygen free water at 50°C for 12 months. The sample was moved directly from the anoxic water to the SEM/EBSD equipment to avoid any oxic corrosion. The light crystals on the exposed surface have a somewhat distorted Cu_2O-chrystal structure, i.e. cuprite (detected 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 Cu_2O 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 /Korzhavyi 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 (Cu_2O) 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 (Cu_2O) 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, O_2-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.
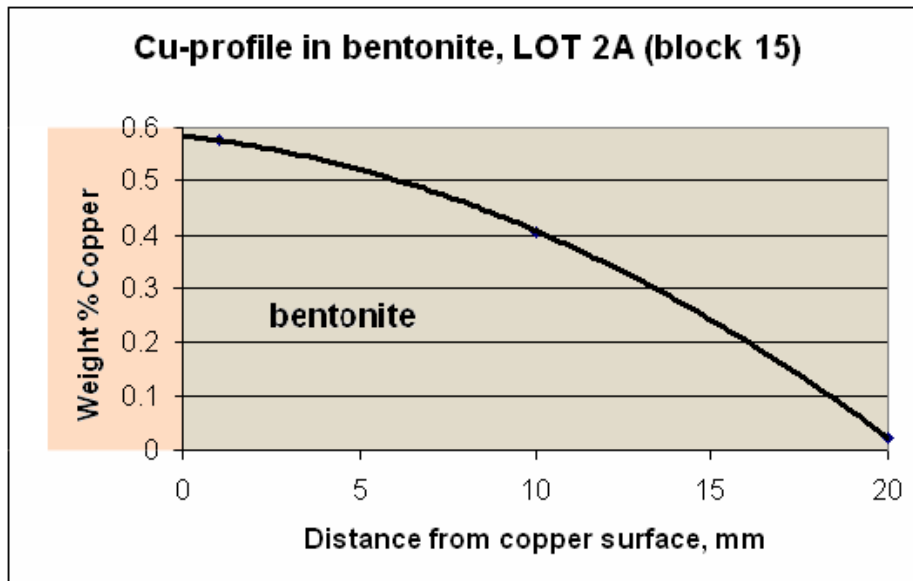
Figure 4.3. The bentonite acts as a Cu-ion sink and both copper and bentonite mutually destroy each other in an accelerated manner. Raw data from /Karnland O. et al. 2009/. LOT A2, Appendix 6; Characterization of the A2 parcel, Bundesanstalt für Geowissenschaften und Rohstoffe.

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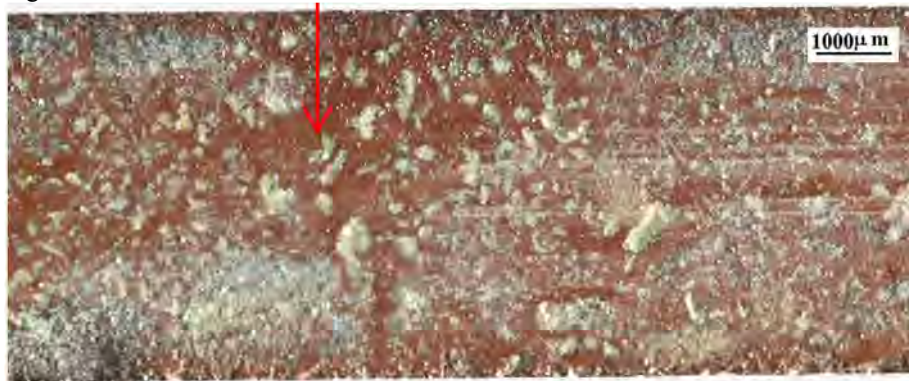
Figure 4.5. A macrograph showing an exposed copper sample severely attacked by pitting corrosion, from Appendix B in the FEBEX-report /Wersin P. and Kober F 2017/.

Figure 4.6. Metallographic cross-sections showing the exposed copper sample with pitting corrosion, up to 100µm 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.*"
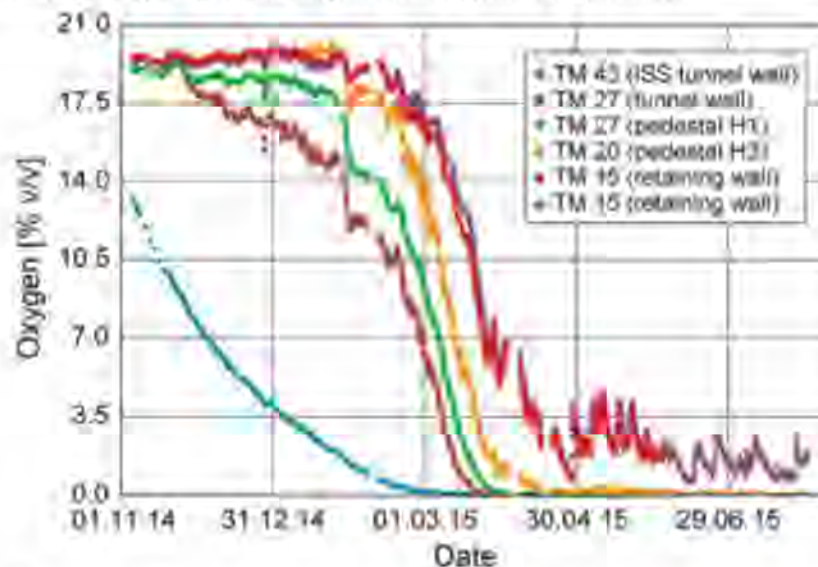
Fig. 11 Oxygen concentrations at different measurement locations along the FE tunnel from November 2014 (shortly after backfilling started) until July 2015

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 ~9 μm. 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.
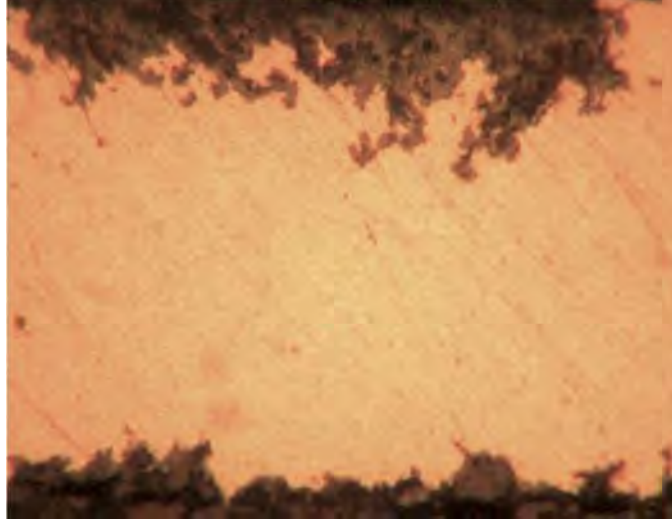
Figure 4.8. Light optical cross-section of the initially 100µm thick copper foil after 15 years exposure in distilled anoxic water at room temperature. Localised corrosion attack is clearly visible. Scale: the height of the micrograph is 90 µm. /Hultquist G. et al. 2008/.

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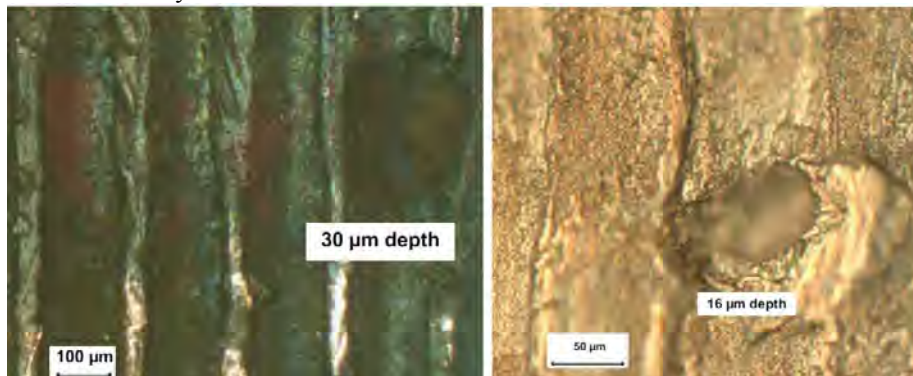
Figure 4.9. Example of pitting corrosion on one acid cleaned sample (to the right) and an un-cleaned sample to the left /Gordon A. et al. 2018b/. Maximum pitting corrosion rate: 6 µm/year.

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.
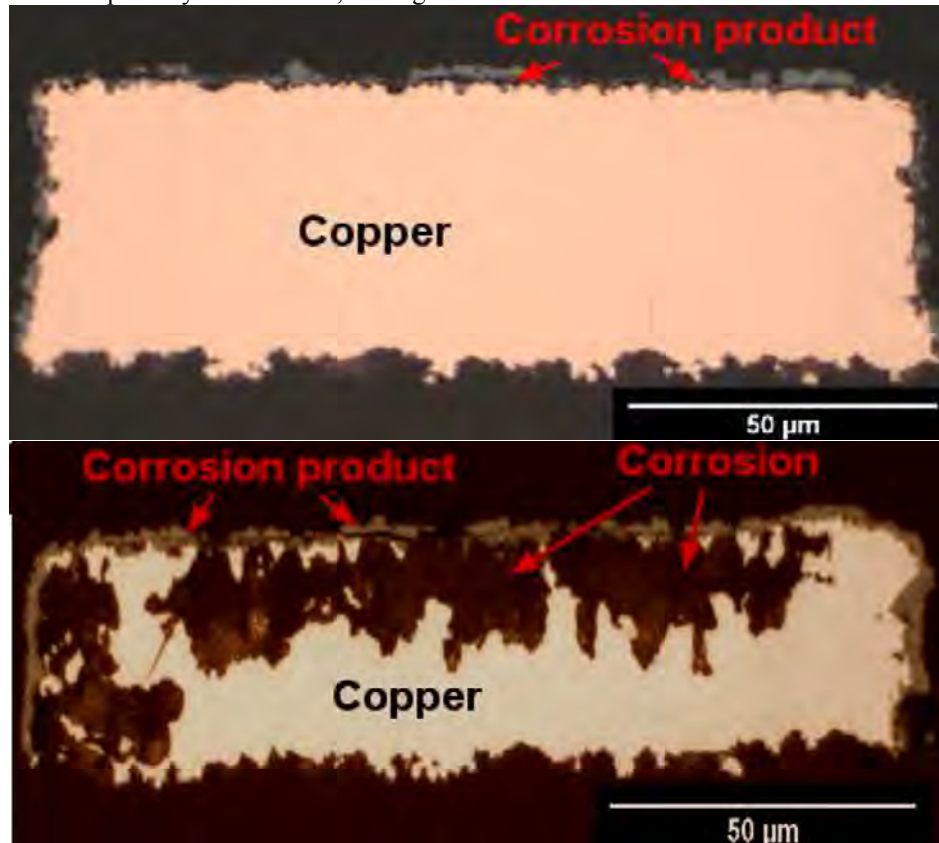
Figure 4.10. Results from Figure 5 in /Marja-aho M. et al. 2018/. Corrosion tests performed in simulated geological nuclear waste repository, at temperatures10–12°C and oxygen level below 1 ppm. Simulated groundwater, with chemical composition of groundwater stabilized with bentonite. The micrograph at the top shows a cross-section, originally $200×35μm^2$, 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 175μm 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. <u>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.</u>

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.

<u>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.</u>

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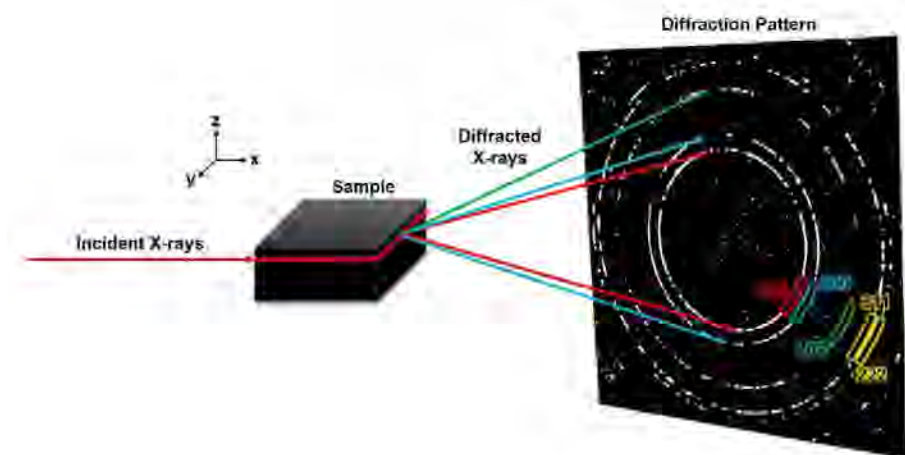
Figure 5.1. Experimental setup of high-energy x-ray diffraction measurements showing x-rays radiating the copper specimen and the diffracted x-rays with the 2D diffraction pattern collected by a detector.

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.
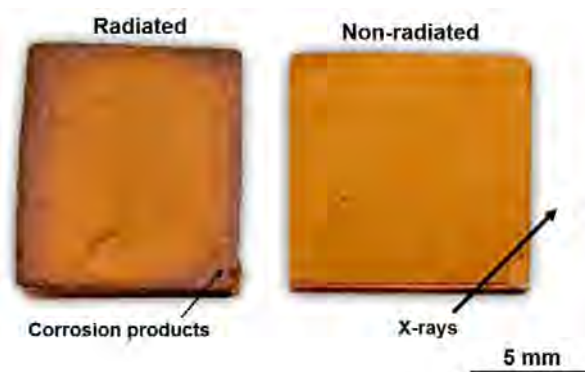
Figure 5.2. Photograph of some of the copper samples to be investigated. The radiated specimen in this case was exposed to oxygen-free water for 64 hours with a simultaneous exposure to 28.6 kGy of gamma radiation. The non-radiated specimen was exposed to oxygen-free water for 64 hours only. The bar 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 +/- 0.0005 Å. 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 /Yagodzinskyy 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 Zacharapoulos 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 within100 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.

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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
[*insert SKB report number and title*]	[*insert reviewed sections*]	[*insert comments, if any*]
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 sulfidesolutions.	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.

The most important comments to the SKB LOT-report TR-20-14

There are two major problems with the SKB report TR-20-14 [1].

i) SKB has excluded scientific facts concerning microbial activity in the ground water and used flawed thermodynamics when they claim that the partially severe copper corrosion in the LOT-project can be explained by oxygen gas from the air.

ii) SKB has omitted to study the most corroded parts of the central copper tubes and the bottom plates.

i. Consumption of dissolved O_2 in anoxic and anaerobic groundwater

All groundwater is anoxic, i.e. without dissolved oxygen gas and it always contains microbial activity that keeps the environment anaerobic. There are detailed studies performed in Äspö hard rock laboratory, for instance the REX-project [2] that shows that added or trapped oxygen is consumed within days by microbial activity or as soon as the studied system or experimental set-up is filled with natural ground water. A full-sized repository tunnel reaches an anoxic state within a few month [3]. Any added oxygen represents fast energy for the microbes in the groundwater, as explained by prof. K. Pedersen.

SKB filled the quite small LOT A3 and S3 test volumes directly with pressurized groundwater via titanium tubes. Therefore, it can be concluded that an anoxic state occurred instantly, especially when considering the 20-year time frame of the LOT-project. It is impossible that the injected natural groundwater via the titanium tubes could have contained dissolved oxygen as SKB implies on page 63. The statement on page 71 has as also no scientific support and is obviously wrong with today's knowledge: *"Estimates of the initially available volume of air in macroscopic gaps and porous materials in the test parcels, were consistent with the interpretation that entrapped O_2 is the main oxidant behind the corrosion."*

SKB uses the identified corrosion products as another evidence for oxic corrosion, from page 9: *"The EDS analysis indicated high levels of chlorine and the XRD showed good agreement with the diffraction pattern of $Cu_2(OH)_3Cl$, an expected corrosion product of copper in the presence of O_2 and chloride (Karnland et al. 2009)."* This is based on flawed thermodynamics since both copper oxides [4] and $Cu_2(OH)_3Cl$, paratacamite [5] are thermodynamically

stable in both anoxic and oxic environments and thus proves nothing in this case. In the potential-pH diagram in part II on page 35 in ref. [4] it is shown that both Cu_2O and CuO are stable in anoxic water. Paratacamite is for instance found naturally in anoxic groundwater/brine bearing sandstone and quarts [6].

To summarize, the detected corrosion in LOT A3 and S3 can only be explained with anoxic copper corrosion by natural groundwater.

ii.   The most important metallographic evaluations are omitted

The hottest part of the central copper tubes, which are expected to corrode the most, corresponds to bentonite blocks 8-15, see Fig. 2-2 in the report. SKB has omitted to present any metallographic cross-section from the hottest part (block 8-15). Only the copper content in the bentonite, which is recalculated to some non-relevant and underestimated corrosion rates are included in the report, see Table 3-19. The highest corrosion rate from Table 3-19, only based on copper content in bentonite, corresponds to 13,8 µm during 20 years for the A3-parcel. However, this must be complemented with several metallographic-cross-sections of the central copper tube in the hot part (block 8-15). The pitting corrosion might be up to 100 µm as observed in a similar repository study with approximately the same exposure time, see the FEBEX-report [7].

The most corroded part of the copper structures are the bottom plates which were exposed directly to the anoxic groundwater. Based on the appearance of the bottom plate from parcel A3, see Figure 3-1 to the left and compare it with the bottom plate from the S3-parcel to the right, it can be estimated that the deepest pits may be in the range of 0.5-1 mm on the A3-parcel which were heated to around 80°C, see Fig. 1-3 to the right. It is of paramount importance to make several metallographic cross-sections of the bottom plates and measure the variation in total thickness. No cleaning of the corrosion products should be done since SKB argues in the report that the removal of the corrosion products might create up to 50-60 µm deep pits, see page 68. This is obviously a wrong statement if a correct cleaning process has been performed.

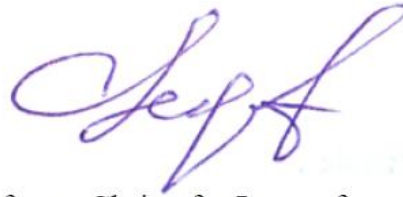Considering the depth of the pits observed it should be remembered that the current LOT-experiments were performed without any radiation. In view of previous experience [8] one can expect that the extent of localized corrosion is accelerated further in the presence of γ-radiation. Hence, it is impossible to predict the actual corrosion effects in the LOT-experiments if γ-radiation would have been present.

Concluding remark

This LOT-study shows, under all circumstances, that the anoxic copper corrosion rate in Swedish groundwater is catastrophic with respect to the KBS-3 model and this conclusion can be made without further considering the radiation induced corrosion (radiolysis), stress corrosion cracking and hydrogen embrittlement.

Tekn. Dr. Peter Szakálos   Prof. em. Christofer Leygraf

References

[1] A. J. Johansson et al.,"Corrosion of copper after 20 years exposure in the bentonite field tests LOT S2 and A3", SKB TR-20-14 (2020).

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Comments to the quality assurance review draft report of the SKB´s LOT experiment (SSM2020-5740-39, SSM reg nr, 2020-3872, ärende nr SSM2020-5740)

The quality assurance (QA) report was performed by T.W. Hicks and T.D. Baldwin at the consultant company Galson Science Ltd and J.R. Scully at the University of Virginia.

The SSM assignment

Unfortunately, it was not included in the assignment from SSM to identify the missing parts in the study that are of scientific importance for the evaluation of the SKB´s LOT-experiment. These topics and tasks should be identified and highlighted as mandatory issues for SKB to perform and implement before the LOT-study could finally be accepted. Only a QA-report is unfortunately not good enough in this case.

Important missing issues in the LOT-report

We have already made comments concerning the missing issues in the LOT-report, which was submitted to SSM 2020-11-23, see Appendix 1. There we highlighted some omitted metallographic studies which could be done with a workload corresponding to one week or so. Additionally, the question of how fast oxygen gets depleted in the LOT-test site should also be evaluated, that could easily be performed retroactively on site within some few weeks. If SSM is interested in guiding and securing that the LOT-project will be of more scientific importance for the KBS-3-model, then these issues must be addressed to SKB.

The QA-report

Concerning the draft QA-report, the main conclusion seems to be that it is not possible to judge whether SKB's implications concerning copper corrosion is right or wrong. That conclusion is based on the information in the LOT-report and by additional information, mainly protocols from SKB-meetings.

If the consultants had considered deeper knowledge in ground water microbiology in general and facultative bacteria in particular, they should have been more critical. Especially concerning SKB´s explanation that remaining oxygen must have been the cause to the severe copper corrosion during the 20-year long exposure in groundwater at 500 meter depth. With today's knowledge about groundwater microbiology, it is clear that the LOT-exposures were exclusively anoxic from a corrosion point of view, as we have already pointed out in Appendix 1. With this knowledge it would have been quite easy to understand that the anoxic copper corrosion had been most problematic with respect to the KBS-3 model, especially since there were not much of sulphides present to explain the partially catastrophic copper corrosion rates.

The hydrogen problem

It should be stressed that the direct reaction between copper metal and water molecules in an anoxic environment enables the fast degradation processes of stress corrosion cracking (SCC) and hydrogen embrittlement. Gunnar Hultquist (KTH) has shown that when copper metal is surrounded by an anoxic environment it will be subjected to hydrogen uptake (hydrogen charging), see Appendix 2. However, there will not be any severe hydrogen charging in the

case with the central copper tube in the LOT-study since the inside of the copper tube contains oxygen (air) which act as an effective sink for the diffusing hydrogen through the tube wall.

Pitting corrosion

From the QA-report summary: "*However, observations of thicker corrosion products in pits and the lack of detailed analysis of surface anomalies versus pitting leaves open the possibility that copper pitting has occurred.*" The authors of the QA-report seem surprised that pitting corrosion has occurred on unalloyed copper exposed to anoxic groundwater. The sulphide content was obviously quite low in the LOT-site, but the chloride content was not low. The groundwater at 500 m depth contains more chlorides than the Baltic sea. In the complex chemistry of groundwater, it is not surprising that unalloyed copper is subjected to pitting corrosion. Especially when accepting the fact that copper does react with water molecules as well, albeit slow in pure water. However, in the aggressive groundwater it is thermodynamically expected that unalloyed copper forms oxides, hydroxides, carbonates, nitrates, sulphides and sulphates and combinations thereof. It is just a question of time before the onset of localized corrosion occurs, and 20 years is obviously more than enough to develop pitting corrosion as was also observed earlier, see Appendix 1.

From the QA-report summary: "*However, any copper corrosion by sulphide attack would far exceed the corrosion depths of penetration that have been estimated could occur by anoxic corrosion in pure water in saturated bentonite. Thus, corrosion by sulphide attack is of greater concern in safety assessments than any postulated corrosion in oxygen-free water.*" This is a wrong statement since groundwater with low sulphide content still contains other corrosive species including a high chloride content (see above) which obviously creates severe copper corrosion, especially when heated, which is unfortunately not included in the safety analysis.

Conclusions

SSM should make requests to SKB concerning minor complementary work (metallography and O_2-depletion measurements) instead of focusing on a QA-report. However, when accepting the scientific knowledge of microbial activity and fast oxygen consumption in the ground water, our earlier statement remains: *The LOT-study shows, under all circumstances, that the anoxic copper corrosion rate in Swedish groundwater is catastrophic with respect to the KBS-3 model and this conclusion can be made without further considering the radiation induced corrosion (radiolysis), stress corrosion cracking and hydrogen embrittlement*.

In more general terms, it is disturbing that SKB has not made any successful studies concerning copper corrosion in the Äspö hard rock laboratory. The copper corrosion has in all studies (LOT, Prototype and MiniCan) been 100-1000 times faster than anticipated by the KBS-3 model. The explanation by SKB has always been the same: oxygen must have been present in the exposures since the copper corrosion was too high. This "explanation" is not valid anymore since it is scientifically proven that the oxygen depletion takes place fast in the groundwater by microbial activity. The question now should be how SSM can approve the KBS-3 model without any relevant and successful copper corrosion studies in the submitted application?

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Opublicerade analyser utförda av Gunnar Hultquist (KTH) på kapselkoppar

Kapselkoppar från prototypförvaret, exponerat 7år i Äspölaboratoriet

(Diagram: Vätehalt, ratio $^{63}CuH/^{63}Cu$ vs Djup i kopparkapselgodset, mm. Oexponerad koppar markerad med streckad blå linje.)

Väteupptag sker i kapselkoppar exponerat i slutförvarsmiljö, dvs i syrgasfritt grundvatten(!)

Både H och OH halter ökar inuti kopparmetallen, detta bekräftas av Ab-Initio beräkningar:

$$Cu + H_2O \Leftrightarrow CuOH + H$$

Reaktionen sker med ett vätejämviktstryck som är ca 1 miljon ggr högre än vad SKB räknar med: 1 mbar i rent vatten.(Bekräftat av Los Alamos National Lab.)

Kapselkoppar från prototypförvaret, exponerat 7år i Äspölaboratoriet

(Diagram: Hydroxidhalt, ratio OH/^{63}Cu vs Djup i kopparkapselgodset, mm. 1.36 mm penetration markerad. Oexponerad koppar markerad med streckad blå linje.)

1.36 mm hydroxid-penetration i koppar-korngränserna under 7 års exponering innebär att hela kapseln (50mm) kommer att genompenetreras på några hundra år.

Både H och OH halter ökar inuti kopparmetallen, detta är en verkan av korrosion som inte nödvändigtvis syns på ytan vilket förklarar varför andra laboratorier ibland inte lyckas "se" någon kopparkorrosion.

Gunnar Hultquist förbjöds att publicera dessa resultat som i praktiken visar att kopparkapseln väteladdades i slutförvarsmiljön, det är således bara en tidsfråga innan kapslarna drabbas av väteförsprödning/vätesjuka, vilket var helt oväntat och oacceptabelt för KBS-3 modellen.

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Gunnar Hultquist (KTH) has shown that the full-size copper canister in SKB´s prototype repository was subjected to severe hydrogen uptake, throughout the whole thickness of 50 mm, during seven years of anoxic exposure in groundwater and bentonite in the Äspö hard rock laboratory (upper curve). The dotted blue line corresponds to the normal hydrogen content in SKB-copper. The relatively low hydrogen contents close to the outer and inner surfaces, around 0 mm and 50 mm, are a consequence of post-exposing the copper to oxygen (air) which act as an effective hydrogen getter. The lower curve shows the uptake of OH in the grain boundaries of the canister copper. This is evidence of internal corrosion which may not be visible on the copper outer surface. By extrapolation based on the OH-profile it can concluded that the whole canister may be penetrated by OH within 250 years. However, hydrogen embrittlement and cracking of the copper canisters is expected much earlier.