



Strålsäkerhetsmyndigheten

Swedish Radiation Safety Authority

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Corrosion of copper canister

SSM perspektiv

Bakgrund

Strålsäkerhetsmyndigheten (SSM) granskar Svensk Kärnbränslehantering AB:s (SKB) ansökningar enligt lagen (1984:3) om kärnteknisk verksamhet om uppförande, innehav och drift av ett slutförvar för använt kärnbränsle och av en inkapslingsanläggning. Som en del i granskningen ger SSM konsulter uppdrag för att inhämta information i avgränsade frågor. I SSM:s Technical note-serie rapporteras resultaten från dessa konsultuppdrag.

Projektets syfte

Syftet med detta granskningsuppdrag inom SSM:s inledande granskning är att beskriva hur SKB behandlat kopparkorrosion inom SR-site med avseende på den förväntade utvecklingen av miljö och då främst syrgasinnehåll i grundvattnet efter deponering av kapslar i slutförvaranläggningen. Baserat på författarnas kunskaper ska bedömning göras om SKB beskrivit de korrosionsmekanismer som kan ske för kopparkapslarna. Det huvudsakliga syftet inom denna inledande granskning av kopparkorrosion är att få en bred belysning av SR-site och underreferenser samt att identifiera eventuella behov av kompletterande information eller förtydliganden som SKB bör tillfoga ansökansunderlaget.

Författarnas sammanfattning

Vatteninflödet i ett slutförvar i Forsmark förväntas vara så långsamt att det kan ta några hundra år till 1000 år innan deponeringshålen är vattensatta och 6000 år innan bentonitbuffereten är fullt trycksatt med grundvatten.

Kopparkapslarna kommer därför att drabbas av två helt olika miljöer:

- en initial period på flera hundra år där koppar ytan kommer att exponeras för korrosion i en gasfasmiljö
- och därefter för korrosion i grundvattenmiljö.

Ur ett korrosionsperspektiv är de första 1000 åren de mest kritiska för kopparkapseln eftersom ren koppar eller fosforlegerad koppar inte är designat att klara korrosion vid förhöjda temperaturer. Den yttre kopparytan kommer att nå ca 100°C efter några tiotalet år efter förslutning av slutförvaret för att sedan långsamt av svalna till ca 50°C efter 1000 år.

I SKB's säkerhetsanalys är gaskorrosionen behandlad som endast beroende av syrgas och därför beräknad med en enkel massbalansberäkning. En sådan enkel modell har inget vetenskapligt stöd då flera spårgaser, bl.a. de som innehåller svavel och kväve korroderar koppar tillsammans med vattenmolekyler (fukt) och korrosionsprodukterna är uppbyggda av oxider samt hydroxider som till stor del härstammar från vattenmolekyler.

Dessa spårgaser har dessutom en accelererande effekt på kopparkorrosionen. En korrosionsmodell som skall beskriva dessa komplexa gaskorrosionsprocesser måste således vara baserad på experimentella data. Fosforlegerad koppar är känslig för spänningskorrosion (SCC) i vatten

innehållande reducerade kväve- eller svavelföreningar eller i en kombination därav, vilket kan förväntas i ett slutförvar. Man kan därför inte bortse från risken för SCC.

Försprödning av koppar orsakat av antingen väte eller svavel kan ej heller uteslutas. SKB har dock uteslutit SCC på vag grund och försprödningsfenomen har man valt att helt bortse ifrån i säkerhetsanalysen. Man vet att jord- och läckströmmar pga högspänningskablarna Fenno-Scan till Finland skapar allvarliga korrosionsproblem i borrhålen i Forsmarks slutförvarsområde. SKB har valt att bortse från detta och hävdar att det inte finns någon risk för läckströmskorrosion baserat på diffusa teoretiska resonemang.

Experimentella data behövs för alla korrosionsproblem som diskuterats här för att kunna nå en vetenskapligt grundad korrosionsutvärdering. Det duger således ej men enkla syre- och sulfidmassbalansberäkningar för att kunna uppskatta kopparkorrosionen i ett slutförvar.

Projektinformation

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SSM perspective

Background

The Swedish Radiation Safety Authority (SSM) reviews the Swedish Nuclear Fuel Company's (SKB) applications under the Act on Nuclear Activities (SFS 1984:3) for the construction and operation of a repository for spent nuclear fuel and for an encapsulation facility. As part of the review, SSM commissions consultants to carry out work in order to obtain information on specific issues. The results from the consultants' tasks are reported in SSM's Technical Note series.

Objectives of the project

In this review assignment, SKB's treatment of copper corrosion processes or mechanisms in SR-Site shall be reviewed both for the anticipated oxic and anoxic repository environments. The reviewer(s) shall consider if corrosion and corrosion mechanisms of the copper canisters in different possible evolutionary repository environments have been properly described. The objectives of this initial review phase in the area of copper corrosion is to achieve a broad coverage of SR-Site and its supporting references and in particular identify the need for complementary information and clarifications to be delivered by SKB.

Summary by the authors

It is expected that the inflow of ground water to the deposition holes and tunnels in the Forsmark repository will be very slow. Thus, it might take some few hundred years up to thousand years before the deposition holes are filled with ground water and it might take 6000 years or more before the bentonite buffer is fully water saturated and pressurized.

The copper canisters will therefore meet to two completely different environments:

- an initial period of several hundreds of years when copper is exposed to gaseous corrosion
- and then to aqueous corrosion

From a corrosion point of view the first 1000 years are the most critical for the copper canister since pure, or phosphorus alloyed copper, is not designed to cope with corrosion at elevated temperatures. The outer copper surface temperature is expected to reach 100°C within some decades after closure of the repository and then slowly cool down to around 50°C after 1000 years.

The gaseous corrosion is treated in SKB's safety assessment as being only dependent on oxygen gas and thus easily estimated by an oxygen mass-balance calculation. This simple model has no scientific support since several corrosive trace gases, such as sulphurous and nitrous compounds, operates together with water molecules (moisture) and the corrosion product consists mostly of oxides and hydroxides derived from water molecules. These trace gases are known to have an accelerating

effect on copper corrosion. Any corrosion model describing the gaseous copper corrosion period must therefore be based on experimental data.

The aqueous copper corrosion phase (without dissolved oxygen) is treated in SKB's safety assessment as being only dependent on sulphide ions and thus easily estimated by a sulphide mass-balance calculation. This is again a too simple model since copper reacts with water, especially when activated by chlorides in the ground water. A copper corrosion model must again be based on experimental data.

Phosphorus copper is sensitive to stress corrosion cracking (SCC) in nitrous or sulphurous containing waters or in a combined environment, as will be the case in a repository, and cannot be ruled out as a potential problem. Embrittlement phenomena in copper caused by either hydrogen or sulphur cannot be ruled out as well. However SKB has disregarded SCC on vague basis in the safety assessment and copper embrittlement phenomena are not considered at all.

Earth/stray current from the high voltage direct current Fenno-Scan cables to Finland are known to cause severe corrosion problem in bore holes in the Forsmark repository area. SKB has stated that there is no risk for earth current corrosion based on vague theoretical discussions.

Experimental data are thus needed regarding all corrosion problems discussed here in order to reach a scientific basis for the copper corrosion assessment. It is not enough with simple oxygen- and sulphide mass-balance calculations for estimation the copper corrosion in a deep repository.

Project information

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This report was commissioned by the Swedish Radiation Safety Authority (SSM). The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of SSM.

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1. Introduction

It is expected that the inflow of ground water to the deposition holes and tunnels in the Forsmark repository will be limited. Thus, it might take some few hundred years up to thousand years before the deposition holes are water saturated and it might take 6000 years or more before the bentonite is fully pressurized. The copper canisters will therefore encounter two completely different environments;

- an initial period of several hundreds of years when copper is exposed to gaseous corrosion
- and then to aqueous corrosion

From a corrosion point of view the first 1000 years are the most critical for the copper canister since pure, or phosphorus alloyed copper, is not designed to cope with corrosion at elevated temperatures. The outer copper surface temperature is expected to reach 100°C within some decades after closure of the repository and then slowly cool down to around 50°C after 1000 years. With the slow ground water ingress in the proposed repository in Forsmark, the copper canisters are likely to be exposed to gaseous corrosion, hygroscopic salt enrichment and radiolysis effects. This technical note will therefore be somewhat more focused on these initial processes since most of the question marks regarding KBS-3 model is coupled to the initial hot period. When the canister eventually reaches ambient ground water temperature, the overall corrosion rate is reduced.

2. Gas phase corrosion

The ground water inflow in Forsmark is very slow and it might take 6000 years for the bentonite buffer to reach its ideal state, i.e. to be fully water saturated and pressurized. However, the deposition holes might be water saturated after some hundred or maybe 1000 years.

The copper canister is therefore expected to be exposed to different atmospheric or gas phase corrosion processes resulting from the transport of corrosive trace gases dissolved in the surrounding ground water to the enclosed gas volume in a deposition tunnel. Such a mass transport could prolong for up to 1000 years which seems to be neglected in the KBS-3 proposal. It is stated in TR-11-01, section 10.3.8:

“The safety functions for the buffer and backfill assumes a fully water saturated state. This should mean that the buffer and backfill need to be saturated to perform properly. However, no performance is needed from the buffer as long as the deposition hole is unsaturated, since no mass-transfer between the canister and the groundwater in the rock can take place in the unsaturated stage.”

Initially, the gas phase contains oxygen, at the most during the first 300 years but probably shorter, and thus the next period, the anoxic gas phase period may prolong 2-3 times longer. Eventually, after 1000 years or so the environment is expected to be mainly aqueous and after at least 6000 years, the whole repository may have reached its ideal state, i.e. the fully saturated and pressurized state. The system is very complex and the copper canisters may experience long periods with both gaseous and aqueous corrosion.

Several gas phase corrosion processes are not included or not satisfactory treated in the safety analysis and those processes will be discussed in detail here.

2.1. Atmospheric copper corrosion- oxic conditions

Environment: Heated canister surface, 100-60°C, in contact with a gas phase containing oxygen, nitrogen and water vapor and some trace gases.

Due to radiolysis, some quantities of HNO₃ and radicals will form, see section 2.1.3. The tunnel and deposition holes with cracks in the bedrock in direct contact with the surrounding groundwater will act as sinks for dissolved trace gases, such as CH₄, H₂ and H₂S.

Additionally, deposition holes with the highest water inflow will experience water redistribution and hygroscopic salt enrichment, not only in the bentonite buffer but also at the canister surface, see section 3.

Time scale: It could take up to 300 years to consume all oxygen in the gas phase, according to TR-10-46 page 106.

2.1.1. Oxygen depletion

It is assumed in /TR 11-01/ page 314 and TR-10-67 on page 57 that no oxygen enters the deposition tunnels after their closure. It is assumed in TR-10-67 on page 57 that no oxygen enters the deposition tunnels after their closure. This requires that deposition tunnels are hermetically sealed by concrete plugs and that no cracks in the blasted bed rock around the tunnels communicate with the main tunnel until the repository is closed.

SKB has considered estimation of gas phase corrosion during this initial period. However, this estimate is based on the assumption that oxygen is the only oxidant /TR-10-66/ section 5.5.2 and /TR-10-67/ section 4.3, which is not correct. It is shown by isotope studies that most of the copper oxidation takes place with oxygen from water molecules, i.e. from moisture in the air /Hultquist et al. 1994/.

The oxygen depletion process is expected to be fast in groundwater mainly due to microbial activity and no oxygen will remain in the deposition holes and tunnels after some weeks. However, the bentonite will be biologically inactive in a gas phase and the oxygen depletion process will be much slower. Additionally, oxygen from the free air in the main tunnel during repository operation is expected to continuously enter the deposition tunnels, through the air-filled cracks in the bedrock.

From a corrosion point of view, this oxic gaseous corrosion phase with heated copper is problematic. The main copper corrosion reaction will be with water molecules (moisture) and with oxygen and other trace gases as “accelerators” of the corrosion process. Additionally, some chlorides, sulfides and other salts from the groundwater will probably reach the canister already during this oxic period.

Suggested recommendation of complementary information/studies: Could a blasted deposition tunnel with fractured rock be expected to be gas tight up to 100 years?

In a mixed gas environment, it should be expected that not only oxygen gas but even moisture acts as an oxidant. This does not seem to be included in the safety analysis. In the safety assessment, it is stated that “corrosion is modeled based on mass balance and transport capacity considerations whereas reaction rates are disregarded.” It is not possible to estimate the corrosion with mass balance models

since water (moisture) is included in the corrosion process; this is a general problem not only for this initial period.

2.1.2. Corrosive trace gases

The groundwater in the bedrock contains trace gases such as methane, hydrogen and hydrogen sulphide. The gas volumes present in the deposition holes and tunnels will act as sinks for the gases dissolved in the groundwater. Trace gas corrosion is expected during the oxic as well as during the anoxic period, i.e. during up to 1000 years.

The measured amount of dissolved gases and sulfide in the Forsmark groundwater /TR-10-39/ page 46 and /TR-10-58/ pages 99-103 and /TR-11-01/ page 361 are: $H_2 = 10^{-3}$ to 10^{-2} mM, $CH_4 = 5 \times 10^{-3}$ to 0.2 mM, total sulphide = 10^{-3} (average) to 0.12 mM, The concentration in a gas phase in equilibrium with respective compound at a total pressure of one bar are according to Henry's law, 0.3 to 3 mbar H_2 , 1 to 50 mbar CH_4 and 10^{-2} to 1 mbar H_2S (10 - 1000 ppm H_2S). However, maybe 10% of the total sulfide in the groundwater is expected to be dissolved H_2S -gas at pH=8 /Hägg G. 1984/, i.e. **around 1 ppm** H_2S as an average and 100 ppm H_2S as a max value in a gas phase in equilibrium with the ground water in Forsmark. If pH is lowered to 7, the amount of H_2S -gas is expected to increase by a factor of five /Hägg G. 1984/. SKB seems only to have measured the total sulfide content in Forsmark and not the amount of dissolved H_2S , see /TR-11-01/ page 361.

If a tenth of the average sulfide concentration in the groundwater is dissolved as hydrogen sulfide, it corresponds to 1 ppm H_2S . The ground water in close vicinity to the deposition tunnel would be depleted in all dissolved trace gases.

In TR-10-67 on page 53 it is quoted:

“ The maximum levels of pollutants detrimental to copper are estimated to be (Leygraf and Graedel 2000, Shreir et al. 1994):

SO_2 100 $mg \cdot m^{-3}$

NO_2 75 $mg \cdot m^{-3}$

NH_3 < 20 $mg \cdot m^{-3}$

H_2S < 3 $mg \cdot m^{-3}$ ”

These values above, expressed as part per million, are 2.5 ppm for H_2S and 30-40 ppm for the other listed gases. However, these maximum or threshold levels might be considered as too high for sensitive applications or for applications with long design life time.

The electronic industry has developed a standard with a “Copper Reactivity Level” and it is stated that more than 3 ppb H_2S is considered as “moderately ” corrosive in dry atmosphere at room temperature /ANSI/ISA S71.04-1985/. More than 50 ppb H_2S is classified as “Severe” since it gives a copper corrosion rate larger than 0.2 μm /month at room temperature in a dry atmosphere. A temperature increase or any humidity increase over 50% RH increases the corrosion rapidly. An increase from 50% RH to 60% RH doubles the corrosion rate.

Among the trace gases, hydrogen sulphide is considered as especially problematic since corrosion continues also at low humidity and that H_2S induced gaseous corrosion accelerates greatly in combination with other trace gases. It is stated in the standard /ANSI/ISA S71.04-1985/:

“Active sulfur compounds (H_2S). This group includes hydrogen sulfide (H_2S), elemental sulfur (S), and organic sulfur compounds such as the mercaptans (RSH). When present at low parts per billion levels, they rapidly attack copper, silver,

aluminum, and iron alloys. The presence of moisture and small amounts of inorganic chlorine compounds and/or nitrogen oxides greatly accelerate sulfide corrosion. Note, however, that attack still occurs in low relative humidity environments.”

The average hydrogen sulphide concentration in Forsmark would most likely be classified as level GX (“Severe” >50 ppb H₂S) according to the standard /ANSI/ISA S71.04-1985/. The levels of nitrous compounds might also exceed their threshold levels due to radiolysis and natural occurrence in the repository environment, see section 2.1.3. The H₂S-content can vary considerably in the groundwater and can locally be as high as 3 to 30 mM /POSIVA 2007-04/, i.e. 25 - 250 times higher than the highest concentration measured in the Forsmark repository area.

Copper corrosion by H₂S could be a serious problem in a deep geological repository. The problem with the Forsmark site (with its limited flow of groundwater) is that a H₂S-induced gaseous corrosion is expected to continue during both the oxic and anoxic period, see section 2.2, and could thus prolong for 1000 years.

Theoretically, it is expected that equilibrium will be reached between the gas phase and dissolved gases in the groundwater. However, some of these trace gases, such as H₂S, will effectively be scavenged/consumed by a corrosion reaction with copper which thus is likely to act as a local sink for H₂S. This should promote the microbial activity further around the deposition holes by SRB (sulphate reducing bacteria) via easily accessed sulfate in the groundwater. This will potentially result in an increased production rate of sulfide.

/Demirkan K. et al 2010/ have studied gas phase corrosion of copper in an atmosphere consisting of air polluted with 1.7 ppm H₂S and sub ppm levels of some other trace gases, SO₂, NO₂ and Cl₂. It was found that copper corrodes more than 100 µm per year, already at 40°C and 69% RH. The corrosion product consisted of a non-adherent scale with Cu₂O closest to the metal and Cu₂S (or Cu_xS) on the top. An important fact is that the atmospheric copper corrosion rate is found to be linear when exposed to atmospheres with corrosive trace gases at high relative humidity, i.e. no protective “passive” film is developed.

SKB has evaluated gas phase corrosion of the copper canisters in Forsmark repository and the result is summarized in /TR 11-01/ page 315 /TR-10-46/ page 105 and in TR-10-67 section 4.3 “Corrosion in unsaturated bentonite after emplacement” by F. King. This evaluation is based on the assumption that only oxygen from entrapped air will react with the canisters and the total amount of gaseous corrosion of copper is based on a simple mass-balance calculation. The result indicates a total gas phase copper corrosion of around 0.8 mm. This estimation is not considering the effect of the combined corrosion by moisture, hydrogen sulfide, nitrous compounds (from radiolysis) and initially also with oxygen and obviously a mass-balance calculation is not valid.

The estimation performed by /Mattsson E. 1997/ which is supported by later experimental data /Demirkan K. 2010/ indicate gaseous copper corrosion rates of 100-300 µm per year at 90°C. The estimation by Mattsson was done with normal level of atmospheric pollutants and not with the presence of radiolysis products and corrosive trace gases such as H₂S.

Suggested recommendation of complementary information/studies: The expected H₂S concentrations in a Forsmark repository would most likely be classified as level GX (“Severe” >50 ppb H₂S) according to the standard /ANSI/ISA S71.04-1985/. However, SKB should measure the dissolved H₂S concentrations and not only the total sulfide. Copper corrosion by trace gases is not included in the safety analysis.

The sulfide gas corrosion processes in the proposed repository in Forsmark will not be limited by slow diffusion processes through saturated bentonite. Corrosion kinetics in gas corrosion exposures with trace gases in enclosed volumes with heated copper and relevant moisture content, i.e. high RH, are most essential. With such data, it is possible to estimate the gaseous corrosion rate which is not possible with a mass-balance calculation.

2.1.3. HNO₃-formation due to radiolysis

All references used by SKB regarding estimation of HNO₃-formation are based on a work by /Jones 1959/. In /TR-10-66/ page 27 and in/TR-10-46/ on page 109 it is stated that “Of the papers reviewed, the study by /Jones 1959/ of the nitrogen-oxygen-water homogeneous systems appear to be directly applicable to repository conditions.” This is questionable since the work by Jones differs in many respects from the expected repository conditions.

The experimental work by Jones was performed in a gold-plated cell with NaCl-windows for IR-analysis and β-radiation was used instead of γ-radiation. The atmosphere was relatively dry and no condensation could be attained due to the use of NaCl-windows. In reality, a metal like copper would act as an effective sink for any formed HNO₃ and thus increase the formation kinetics. In the introduction, it was discussed that “However, if water vapor and a metal which could react with nitric acid were present, fixation of nitrogen continued”. The most important information that should discard the study of Jones as a base for HNO₃-formation calculations in a repository environment was the fact that the gold surface it selves “greatly decreased the yield of nitric acid”, /Jones 1959/ page 660. Thus it could be expected that much more HNO₃ should be formed than the calculation based on /Jones 1959/indicates inTR-10-46 at page 109.

Atmospheric copper corrosion accelerates drastically in atmospheres containing trace levels of HNO₃. The atmospheric copper corrosion rate increases with a factor of 10 when 150 ppb HNO₃ is added to an atmosphere with 65% RH /Samie F. 2006/. In the same study it is found that the corrosion rate increases linear with increased HNO₃-concentration.

The corrosion rate is more than 10 times higher at a relative humidity of 60% RH or more compared to a drier atmosphere, both containing HNO₃. The same RH-dependence is shown for copper corrosion in irradiated gas atmospheres, which is not surprising since HNO₃ is the main corrosive agent formed under irradiation and the corrosion products are the same, viz. basic copper nitrate (gerhardtite) and copper oxide. The corrosion product at higher relative humidity and at higher reaction temperatures /Reed D. and Konynenburg R. 1991/ contains higher amount of Cu₂O thus indicating that HNO₃ is not only forming a basic copper nitrate but also accelerates a complex oxidation reaction with water vapor at elevated temperatures. On the outside of the canister, the initial gas environment is beneficial for HNO₃-formation with abundant access to oxygen, water vapor and nitrogen. Another important fact is that a copper surface represents an effective sink for HNO₃ by a high sticking probability and fast reaction with copper, thus increasing the driving force and kinetics for radiolysis induced formation.

The electronic industry has developed a standard with a “Copper Reactivity Level” and it is stated that more than 1.25 ppm NO_x is classified as “Severe” since it gives a copper corrosion rate larger than 0.2 μm/month at room temperature in a dry atmosphere /ANSI/ISA S71.04-1985/. NO_x is produced by radiolysis and is a precursor to HNO₃ in moist atmospheres.

The radiolysis effect is of course weaker on the outside of the copper. Copper corrosion is especially sensitive to HNO₃ already at a ppm level, see above, makes the conclusion by SKB that it is of no importance, questionable.

Additionally, it is pointed by /Reed D. and Konynenburg R. 1991/ that pure copper are the most sensitive metal to radiolysis among the tested metals and that pitting corrosion occurs in moist atmospheres.

Suggested recommendation of complementary information/studies: Radiolysis studies with copper corrosion under relevant gas environment are needed. The environments in the references used by SKB are not relevant. The true production rate of HNO₃, for example measured as N₂ consumption in a closed system with relevant temperatures and radiolysis conditions and with the presence of copper surfaces which represents an effective sink or scavenger for HNO₃ should be studied.

2.2. Atmospheric copper corrosion- anoxic conditions

Environment: Heated canister surface, 90-50°C, in contact with a gas phase containing N₂ and H₂O with traces from ground water such as CH₄, H₂, H₂S and nitrous compounds (from radiolysis) as discussed previously.

Time scale: This period could last for several hundreds of years, locally up to thousand years. The whole gas phase corrosion problem with different gases which could operate for up to 1000 years on the copper canisters in Forsmark, is summarized In TR-10-46 section 4.3 “Corrosion in unsaturated bentonite after emplacement” by Frasier King as simple oxygen mass-balance calculation. This is as mentioned before not a correct assumption. There are not many studies performed with pure copper in anoxic gaseous environments. However in a handbook /Bruce D. 1995/ it is stated that alloyed copper corrodes 50-75 µm/year in moist hydrogen sulfide gas at elevated temperatures (without oxygen gas) and it was found in the same study that pure copper was especially sensitive and corrodes up to 1625 µm/year in the same environment. Obviously, gaseous copper corrosion with moisture at high relative humidity in presence of corrosive trace gases such as H₂S and ammonia might be as fast as with oxygen present but the actual corrosion rate in a repository should be limited by the microbial production rate of sulfide. Japanese researchers /JNC 2000/ have estimated the total sulfide induced copper corrosion during 1000 years in a repository to be up to 2.6 cm (26 µm per year) if sulfate is continuously converted to sulfide, but in this report the sulfide flux was restricted by diffusion in water.

Recommendations of complementary information/studies: It is plausible that the sulfide gas corrosion processes in the proposed repository in Forsmark is not limited by slow diffusion processes through water-saturated bentonite. It is essential that gas corrosion studies are carried out with heated copper in environments with moisture, and corrosive trace gases but without oxygen. In more general terms, the different atmospheric corrosion processes during the first 1000 years will, to a large extent, be governed by moisture and trace gases. The trace compounds have a tendency to recirculate and react with moisture and create much more corrosion than the sum of available sulfide, nitrous compounds and oxygen would indicate. These complicated processes should be studied by isotope labeled gases in order to develop corrosion

models with reasonably good predictions, since mass-balance calculations will not be valid when moisture is included in the corrosion process.

3. Hygroscopic salt induced copper corrosion

It was found already in 1988 that salt deposition in the Yucca mountain repository could cause serious corrosion problems, at least for one of the candidate metals, namely copper. It is stated in Part 2, Copper-Based Candidate Materials /Gdowski G. E. and Bullen D. B. 1988/, "In the repository, two additional factors might influence the corrosion rate. The first is that salt deposits might form on the container surface by the evaporation of dripping water from the hot container or by dissolution in a smaller amount of water of salts previously left behind in the rock by distillation. When resolved, concentrated chloride salts will enhance the electrochemical action of the water."

The initial situation in the Forsmark site is similar to that in Yucca Mountain, perhaps more salt and moisture is expected to accumulate in a deposition hole in Forsmark, as will be discussed here. The water inflow is less than 0.01 l/min in 99.9% of the deposition holes in Forsmark, see SKB TR-06-102. Assume that some deposition holes will experience half that inflow rate, 0.005 l/min. This corresponds to an inflow of saline ground water of 2.6 m³/year in such a deposition hole. Each canister evolves 1700 W as heat. The temperature on the outer surface of the copper canister will reach 100°C and the rock surface of the deposition hole will reach 60°C. The temperature in the deposition tunnels above is around 12°C. It can be assumed that the groundwater flowing into the deposition holes will evaporate and at least partly condense in the colder deposition tunnels. Different salts, i.e. chlorides, sulfates and sulfides will then be enriched in the deposition holes. The groundwater contains 0.95 wt-% salts which gives 25 kg per year or 2.6 ton salts in 100 years if the entire amount of water evaporates and condensates in the tunnel. The bentonite buffer might suppress this scenario to some extent. Naturally, the bentonite buffer is also expected to be heated and dehydrated which makes it possible for moisture/steam to flow freely in the slots between canister/bentonite and bentonite/rock. A sufficiently slow water inflow could result in a continuous transport of moisture to the depositions tunnel instead of creating an ideal water saturated bentonite buffer. An argument against this salt enrichment process has been that a counter pressure from the tunnel should develop and stop the process. This could only happen if the repository would be saturated sufficiently fast, which actually was the original idea. However, it is expected to take about 6000 years to saturate and pressurize the repository in Forsmark.

This calculation might be a theoretical extreme point; nevertheless all deposition holes will experience some degree of evaporation/salt precipitation due to the 1700W "sauna effect", see Figure 1. Dehydration and salt precipitation in the bentonite is detrimental and it is expected to induce cracks and thus create a "short circuit" of the bentonite barrier. From a corrosion point of view, a heated metal surface in contact with saline water, which evaporates, is normally considered an extremely corrosive environment. The local salt enrichment and re-wetting is expected to take place on a significant part of the surfaces of the copper canisters already during the oxic period which could enhance the corrosion rates locally. All criteria for SCC might also be fulfilled since high level of all salts can be expected including nitrous compound and sulfides see further section 4.2.

Before the water saturated phase occurs, a lot of salt is expected to have precipitated as discussed above and this could create severe additional copper corrosion in the contact spots. Another troublesome part with salt deposition is that it might destroy the barrier properties of the buffer which will basically accelerate all the corrosion processes to come.

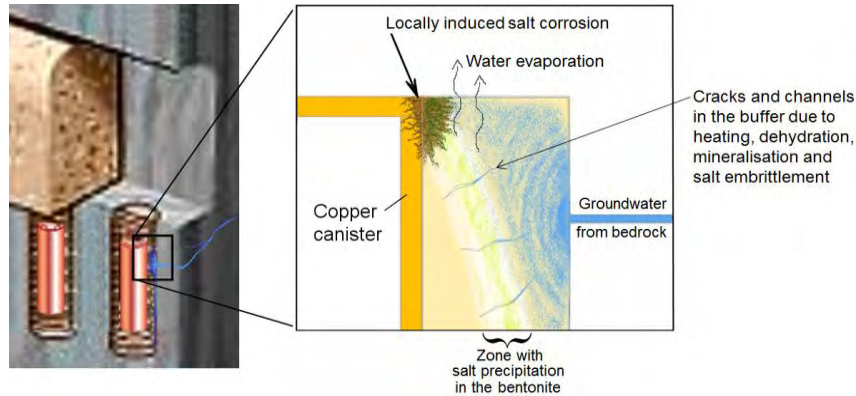


Figure 1: Expected salt enrichment in the buffer and on the canister surface with accelerated copper corrosion if uncontrolled water evaporation/transport from the heated deposition hole towards the cold tunnel takes place, the “sauna effect” /Szakalos P and Seetharaman S. 2012/.

In TR-10-46, section 3.5.7 “Deposition of salts on the canister surface” (page 127), local water transport inside a deposition hole is discussed and modeled based on data from the Long Term Test of Buffer Materials, the LOT project. The studied “deposition holes” in the LOT-project had a diameter of 0.3 m and height of 4 m. The holes were carefully sealed in order to be pressurized and to avoid that a mass transport of moisture or water vapor to the tunnel. The issue of water redistribution between deposition holes and tunnel was not studied in the LOT-project. It seems therefore that only a “near field” model has been developed based on the LOT-data, see /TR-10-59/, section 2.1 and potential water transport between the heated deposition holes and the cold tunnel in a real repository has not been evaluated. Basically all corrosion processes are expected to be accelerated and all environmental prerequisites for localized corrosion such as stress corrosion cracking (SCC) and pitting corrosion will be fulfilled if an uncontrolled enrichment of different salts take place. Also general corrosion could be substantial at local areas due to large chemical gradients.

Lars Werme and Kastriot Spahiu have the following statement on copper corrosion due to enrichment of salts from the ground water in TR-10-46 (page 127) “Also, an increase in the chloride concentration would lower the susceptibility of copper to pitting corrosion, since it would favor general corrosion /King et al. 2001/. A high chloride concentration will, however, not lead to increased general corrosion, since the near field pH is always expected to be slightly alkaline and, consequently, the extent of the corrosion will be determined by the amount of available oxygen. Thus, exposure to temperatures over 100°C is not expected to have an effect on the corrosion behavior of the copper canister .The maximum allowed surface temperature of the canister is, therefore, set more by the requirements for chemical stability of the bentonite buffer than by any possible influence on canister corrosion.” It is in this context important also to consider the enrichment not only of chlorides, but also of other salts in the ground water such as sulfates, nitrates, bromides and sulfides. Lars Werme and Kastriot Spahiu seem to believe that only chlorides will be enriched and no other corrosive salts.

Suggested recommendation of complementary information/studies: The macroscopic water transport from the heated deposition holes to the cold tunnel with subsequent salt enrichment in the holes must be considered and studied in case of a repository with slow water inflow such as in Forsmark.

It is also important to experimentally clarify the risk for corrosion of copper exposed to anoxic saline and highly saline water at high temperatures. There are reports that indicate severe corrosion under these conditions. According to, for example, a study by /King F. and Litke C. D. 1987/ (see page 25) anoxic copper corrosion in 0.97M chloride solution results in a copper corrosion rate of 110 $\mu\text{m}/\text{year}$ at higher temperatures.

4. Copper corrosion in anoxic water

It was known already 90 years ago /Evans U. 1926/ that anoxic copper corrosion should not liberate hydrogen bubbles of one bar, but it was expected and experimentally shown that smaller, detectable amount of hydrogen was released when the copper ion concentration in the solution was kept low, for instance by complex anion formation.

Several papers and reports have been published in modern time, for instance /Hultquist et al.1986/, /Szakalos et al 2007/ and /Becker and Hermansson 2011/, showing that copper is not thermodynamically immune in pure water and that it is possible to measure hydrogen evolution with sensitive equipment. One possible explanation for an equilibrium hydrogen pressure of around one millibar could be the formation of an amorphous CuOH-compound as shown in Figure 2.

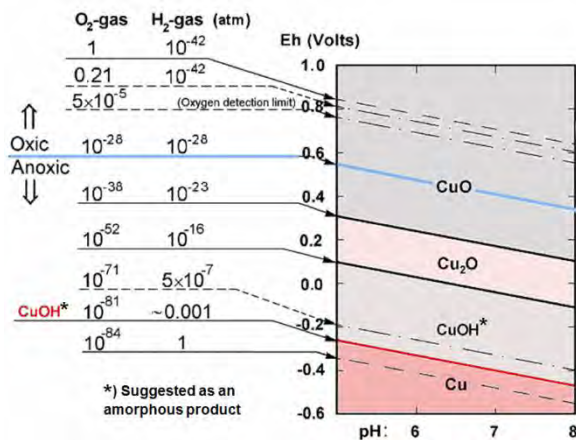


Figure 2. A modified Pourbaix diagram from /Szakalos et al. 2007/ showing the borderline between oxic and anoxic conditions.

The anoxic region covers 2/3 of the water stability area and includes both bivalent and monovalent copper corrosion products. CuOH is proposed /G. Hultquist et al. 2009/ and /Belonoshko A. B. and Rosengren A. 2010/ as an amorphous phase that might be stable during low redox potentials. However it should be noted that copper is not thermodynamically immune in pure anoxic water independently of the possible existence of a stable or metastable phase under the Cu₂O- stability area.

It is interesting to note that short time experimental data by /Protopopoff E. and Marcus P. 2005/ show that CuOH is stable as a surface layer (OH_{ads}), see Figure 3 and that the equilibrium hydrogen pressure is around one millibar.

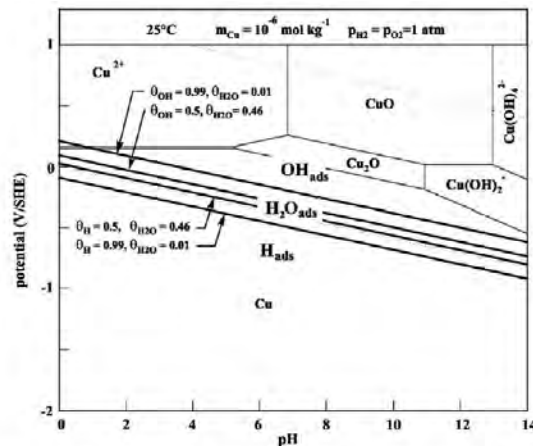


Fig. 1. Calculated equilibrium potential-pH diagrams for adsorbed hydrogen (H_{ads}), hydroxyl (OH_{ads}) and water (H_2O_{ads}) on copper(111) at 25 °C, in an aqueous electrolyte containing no specifically adsorbable anions. The molality of the dissolved copper species is $m_{Cu} = 10^{-6} \text{ mol kg}^{-1}$. The stability domains are limited by the following lines: (...) H_2O system; (—) $Cu-H_2O$ system; (—) $H_{ads}-OH_{ads}-H_2O_{ads}$ system. θ_H , θ_{OH} and θ_{H_2O} are the relative surface coverages of adsorbed hydrogen, hydroxyl and water. The total coverage by the different co-adsorbed species is unity: $\theta_H + \theta_{OH} + \theta_{H_2O} = 1$.

Figure 3. Modified Pourbaix diagram by /Protopopoff E. and Marcus P. 2005/.

Thermodynamic analyses made by prof. D. D. Macdonald et al /SSM-report 2011:09/ and /SSM-report 2012:11/ have confirmed that copper is expected to corrode in pure water with hydrogen evolution and that it is not surprising that it reaches measurable hydrogen pressures. The remaining question mark is whether some intermediate/metastable or amorphous corrosion product is involved in the overall anoxic copper corrosion process. Mechanism of corrosion in pure water is of prime importance since it may explain why copper corrodes more than expected. For instance, in copper cooling systems in accelerators, large generators and ITER /Di Pace L. et al. 2007/, copper corrosion is a real problem. It is not difficult to assemble perfectly air (oxygen) tight metallic couplings but it is impossible to make systems hydrogen-tight since hydrogen diffuses through the copper tubes and reacts with available oxygen on the outer side. This explains why hydrogen, released from corrosion, is normally not accumulated in the copper and as long as hydrogen can escape (or be consumed) copper corrosion is expected, also in pure water.

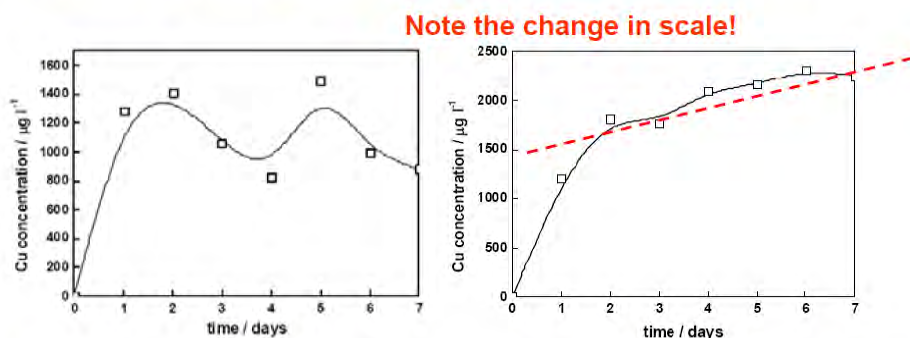
SKB has chosen to treat the anoxic copper corrosion only as an “what if” case /TR-10-46/ page 23, which is questionable, especially since the groundwater contains chlorides. As already pointed out by /Evans U. 1926/, chloride reacts with copper ions under formation of copper complex ions which drive the anoxic corrosion further. This is also discussed in a /U.K. Environment Agency report 2009/ on technical issues associated with deep repositories for radioactive waste in different geological environments and it is stated on page 96:

“Under anoxic conditions, copper corrosion will be accompanied by reduction of water to produce hydrogen gas, the solids produced being Cu-bearing hydroxide phases that will typically contain some chloride within their structures; the concentration of Cl in a solid corrosion product depends upon the concentration of Cl in the aqueous phase.”

In TR-11-01 page 364, it is stated that “Chloride concentrations below 2 M imply that chloride assisted corrosion of the canister can be excluded (safety function indicator R1f).” This is in contradiction to experimental data since chloride addition to pure water contributes to the anoxic copper corrosion. Posiva OY has made experimental observations with copper in anoxic 1M NaCl-solutions (with an oxygen scavenger, oxisorb) that shows high dissolution rates and high solubility at

80°C, see Figure 4. The Figure is taken from the presentation made by G. K. Chuah, who was in the expert panel of the international hearing about copper corrosion in Stockholm, 16 Nov. 2009 /Chuah G.K. 2009/. Data was originally taken from POSIVA Working Report 2003-45.

Solution Analyses for Dissolved Copper



Test Nr. 1 (without Oxisorb)

Test Nr. 2 (with Oxisorb)

Figure 4. Copper dissolution/corrosion in 1M saline (anoxic) water is not negligible and should be studied further as pointed out by G. K. Chuah, see slide 18, /Chuah G.K. 2009/.

The copper corrosion rate due to dissolution at 80°C, i.e. weight loss, was measured to 11.8 µm per year. This should be alarming since the chloride concentration was half of that as considered as negligible chloride levels.

In TR-10-46 page 104 is stated “High chloride concentration in combination with very low pH could cause copper corrosion in oxygen-free water. /Beverkog and Puigdomenech 1998/ calculated Pourbaix diagrams for 0.2 and 1.5 molal chloride concentrations and later for 5 molal chloride concentration in /Beverkog and Pettersson 2002/. At 5 molal chloride, copper corrodes below pH 5 at 25°C to the extent that $[Cu(aq)]_{TOT} > 10^{-6}$ molal. The corresponding pH value for 1.5 molal chloride is approximately 3.2. A simplified calculation may be done with data (ΔG and activity coefficients) from /Puigdomenech and Taxén 2000/ which gives a $CuCl_3^{2-}$ concentration close to 10^{-6} M for the combination of pH=4 and $[Cl^-]=2$ M. It is therefore suggested this combination is used as the safety function indicator criteria in SR-Site.”

This is a questionable conclusion since it is of general praxis that Pourbaix diagram and theoretical assumptions based on a threshold ion-level, i.e. 10^{-6} M, should only be a guideline of what could happen. Especially in the case with complex chloride chemistry in combination with very long desired life times, experimental data should of course be considered as more important for the safety assessment. It is interesting to note that Frasier Kings own experimental data for anoxic copper corrosion in 0.97M chloride solution results in a copper corrosion rate of 110 µm/year albeit with 0.008M sulphate and at higher temperature, see page 25 in /King F. and Litke C. D. 1987/.

In fact, there is already a large discrepancy between thermodynamic data for copper solubility in pure anoxic water compared with experimental data. Within the European ITER-project it is found that /Di Pace L. et al. 2007/:

“The copper concentrations determined by tests are four or five orders of magnitude larger than the copper solubility obtained by thermodynamic data.” This is a strong

indication that copper species exists which is not described thermodynamically in a satisfactory way.

SKB has, in fact, important long-term results regarding copper corrosion in anoxic groundwater performed in the Äspö HRL (hard rock laboratory) at 450 m depth. SKB has disregarded those copper corrosion data as being a result of initial oxygen corrosion. However, it is acknowledged in TR-10-67 that oxygen is expected to be consumed fast, i.e. within weeks, in Äspö HRL due to microbial activity in the groundwater:

“During the construction of the Äspö HRL tunnel, the fate of oxygen during shallow groundwater intrusion was explored on a large scale at 70 m depth (Banwart et al. 1996). It was found that microorganisms reduced the intruding oxygen concomitant with organic carbon oxidation. These results were followed up with a small scale experiment denoted REX at 380 m depth (Puigdomenech et al.2001). Again, it was found that microorganisms played a major role in the reduction of introduced oxygen. Modelling of the REX data suggested that microorganisms will rapidly reduce oxygen in backfill and buffer, within weeks after water saturation (Yang et al. 2007).”

This is an important facts, since it confirms that the high corrosion rates observed in for instance the LOT A2 project have occurred under anoxic conditions, as will be discussed in more detail here.

A copper tube was heated in water saturated bentonite during 5 years in Äspö HRL. The post exposure analyses of the bentonite performed by BGR (Bundesanstalt für Geowissenschaften und Rohstoffe) in Germany are discussed TR-09-29 page 228-234. The copper precipitation observed in the bentonite is shown in Figure 5, data taken from Table A7-2.

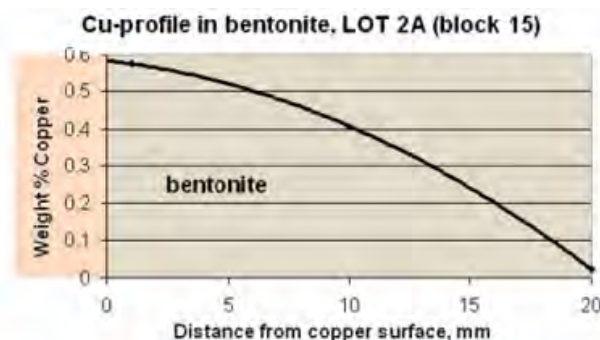


Figure 5. Data from TR-09-29 page 234. Copper dissolution and precipitation in bentonite.

It is stated that surprisingly high amount of copper was detected in the bentonite. Elevated copper levels were detected up to 4 cm from the copper canister surface.

A report from the Canister Retrieval Test, /TR-09-29/, supports the data from LOT A2 and shows that copper is precipitated in the bentonite during anoxic conditions. The copper samples in the Retrieval test were heated to 90°C for only 1.4 years with less amounts of copper corrosion products in the bentonite, as shown in page 23 in the same report.

It was shown in a two year long laboratory study with copper and water-saturated bentonite /King F. et al.1992/ that the copper corrosion was stabilised on a very high rate, around 20 µm per year, see Figure 6. On page 1991, it was concluded that “O₂-

transport was not rate-limiting” and that the corrosion took place with a dissolution–precipitation process; “Precipitation of copper inevitably occurred in all of the tests, with usually more than half of the total copper corroded being in the form of precipitate rather than being sorbed on the clay”.

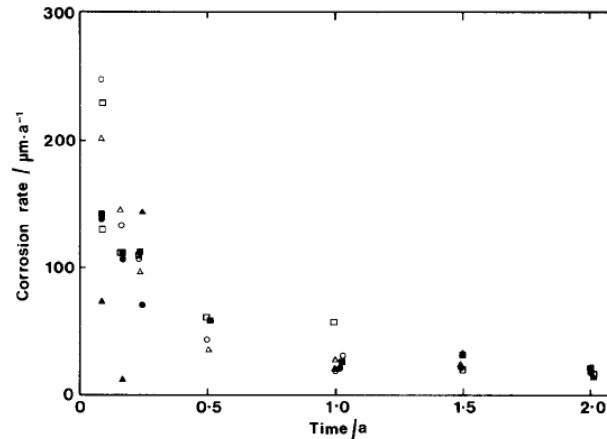


Fig. 8. Copper corrosion rates determined from weight loss of coupon in contact with compacted buffer material in absence of γ -radiation. ● 50°C, 1.45 g cm⁻³ buffer density; ■ 50°C, 1.65 g cm⁻³; ▲ 50°C, 1.79 g cm⁻³; ○ 100°C, 1.45 g cm⁻³; □ 100°C, 1.65 g cm⁻³; △ 100°C, 1.79 g cm⁻³.

Figure 6. The copper corrosion rate was stabilized around 20 µm per year in saturated bentonite after two years exposure /King F. et al.1992/.

This laboratory study confirms the LOT *in-situ* exposure, i.e. the general corrosion rate of heated copper in saturated bentonite is 10-20 µm/y at elevated temperatures.

There is an important connection to the observations in the Äspö HRL and the issue of missing thermodynamic data regarding anoxic copper corrosion in saline water. A crystalline Cu-hydroxide-chloride was identified in the LOT-project as well as in the Canister Retrieval Test. The corrosion product was identified as paratacamite, Cu₂(OH)₃Cl. This phase is not included in the Pourbaix diagram that F. King uses to exclude copper corrosion in anoxic saline water, see page 63 in /TR-11-67/. The thermodynamic data regarding this phase are scarce and it is not indicated in any Pourbaix diagram for systems with copper/various ground waters /SSM-report 2009:28/ or in Europe’s most comprehensive thermodynamic database, /SGTE 2009/. The equilibrium hydrogen pressure for paratacamite formation/reduction is therefore most likely unknown. However, paratacamite is found to be more stable than Cu₂O as shown by electrochemical measurements, i.e. stable at lower redox potentials than Cu₂O /Doménech-Carbó A. et al. 2008/. Both the atacamite phase, orthorhombic Cu₂(OH)₃Cl, and paratacamite (rhombohedral) are detected in various oxic and anoxic environments. Atacamite seems to be the dominating Cu-hydroxychloride at ambient atmospheric conditions /Krätschmer A., et al. 2002/ and paratacamite in aqueous corrosion of copper /Sharkey J.B. et al. 1971/. This means that the identified corrosion products in the 5-year LOT exposure; CuS, (Cu,Fe)S, Cu₂(OH)₃Cl and Cu₂O are all thermodynamically expected in an anoxic environment. In fact the formations of copper sulphide, copper-iron sulphide are strong evidence that the environment was anoxic (copper oxide and paratacamite are expected in both anoxic and oxic environments).

The insight that copper is not immune in pure degassed water and the possible corrosion route with copper hydroxide as a precursor to more stable hydroxychlorides means that copper do corrode by water molecules and chlorides. This is not taken into account in the present safety assessment. In fact, the

precipitation of copper as different phases and partially as unidentified species in the bentonite shows that the copper corrosion in a repository continues with short range diffusion as described in Figure 7.

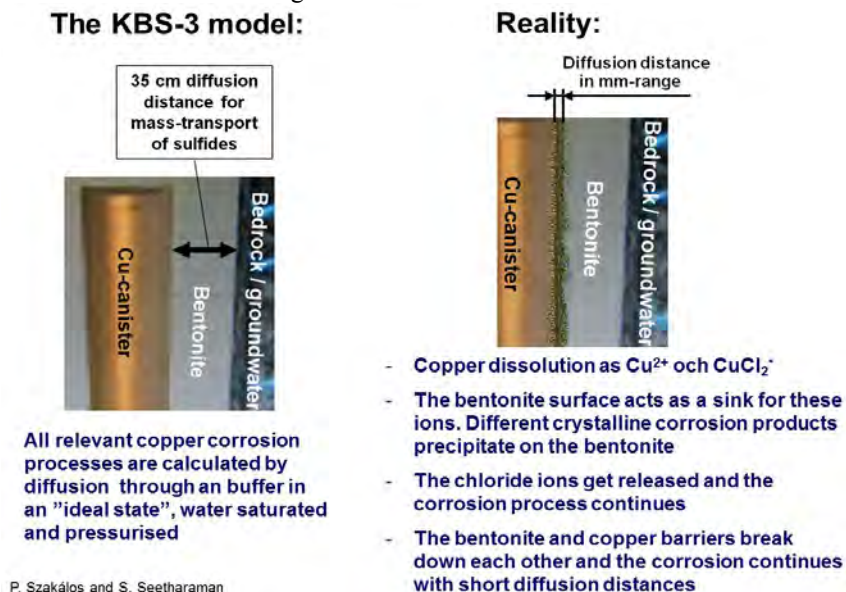


Figure 7. Presented material on the SSM conference in Rånäs, May 2012 /Szakalos P and Seetharaman S. 2012/.

Corrosion processes take place locally at the copper-bentonite interface and it is suggested that the copper chloride ion complexes and hydroxide ions from the ground water takes a vital part in the corrosion process.

It is likely that sulphide ions also take part in such a corrosion process. These processes are of vital importance for the whole safety analysis and as such more detailed corrosion studies must be performed to understand these corrosion mechanisms.

To summarize, the discussions made in this section, Anoxic aqueous copper corrosion, stands in contradiction to SKB's safety analysis which is summarised in R-04-36, section 2.5, by Allan Hedin:

"Copper is a highly stable metal in Swedish granitic groundwaters. The slow corrosion due to the low concentrations of corrodants in the slowly moving groundwater and diffusion controlled transport in the buffer is calculated with simple mass balance considerations in process models. These are directly adopted in the system sub-model as are expressions for corrosion due to impurities initially present in the buffer. The natural variability of the groundwater flow as calculated in geohydrological models of a particular site is readily taken into account in the sub-model. See further Appendix D."

Suggested recommendation of complementary information/studies:

Since copper is not immune in anoxic water and less immune in saline (neutral) anoxic water, there is no threshold limit for chloride concentrations regarding copper dissolution corrosion. The statement in /TR-11-01/ page 364, that "Chloride concentrations below 2 M imply that chloride assisted corrosion of the canister can be excluded (safety function indicator R1f)." is thus not correct. This is in contradiction to experimental data. It is not possible to estimate the extent of corrosion by anoxic saline water with the aid of simple mass-balance calculations

since hydroxide ions and water molecules are taking part in the complex corrosion process.

The corrosion mechanism seems to be influenced by chloride and sulphide ions acting as corrosion activators by reacting with hydroxide ions from water. The bentonite acts as a sink for copper ions and corrosion products. It is of vital importance for the safety analysis to study these phenomena further.

Copper corrosion rates in anoxic neutral saline water with less chlorides than 2M, must be determined as a function of temperature. These kinetics, i.e. corrosion rate based models, should be included in the safety assessment.

The copper-bentonite interactions must be studied in detail. How is copper integrated in the bentonite, in what positions? In different oxidation states? It is known that the bentonite acts as a sink for copper ions and corrosion products. Some part is detected as copper sulphides but are there some other phases? Cross-sections, not only of the bentonite, but also of the copper material in contact with bentonite should be examined. The central copper tube in LOT A2 would be the best copper object to study since the heaters were in operation most of the time and the adjacent bentonite is quite well characterised. Crucial questions such as if localized corrosion has occurred, what type, and to what extent, must be answered.

The fact that the central copper tube was not alloyed with phosphorus is of less importance since phosphorus is not contributing to the corrosion resistance.

It seems that important thermodynamic data is missing or deviates from experimental results for example regarding solubility of copper in water containing chlorides. This limits the accuracy of assessing the corrosion rates of copper under the prevailing conditions.

4.1. Localised corrosion in anoxic groundwater: pitting corrosion

In /TR-10-46/ at page 107 is stated that pitting corrosion in anoxic environment is unlikely and therefore neglected in the safety assessment.

Several different copper pitting environments have been described since 1950's when it was thought that pitting on copper could be described as one single type (Type 1). Today there are at least four different types described in the scientific literature, all in oxic environments and clearly there is no theory describing why pitting should be restricted to these four types other than that copper (as water tubes) is extensively used in those environments. Anoxic pitting corrosion of copper has been studied only to a limited extent. However, at least one research group has shown that anoxic pitting copper corrosion in sulphide containing water exists.

Hermansson H.-P. and Eriksson at Studsvik Nuclear AB /SKI-report 99-52/ have studied copper exposed to synthetic ground water. These authors show shown that pitting/localised corrosion can proceed as whisker growth if sulphide is present: "There are at least two mechanisms available, depending on circumstances. One pure sulphide whisker growth mechanism and another oxide/hydroxide whisker growth mechanism." These results with pitting corrosion in sulphide containing waters was confirmed by a new study in the year 2004 by the same research group /SKI 2004-56/.

Suggested recommendation of complementary information/studies: Anoxic copper corrosion with chloride and sulfide present need to be studied also regarding localized corrosion processes, i.e. both pitting corrosion and crevice corrosion (with bentonite clay). With the possible salt enrichment problem, see section 3, different localized corrosion processes are inevitable and should be included in the safety assessment.

4.2. Localised corrosion in anoxic groundwater: SCC

The safety assessment regarding Stress Corrosion Cracking (SCC) in copper, has been summarized in TR-10-46 page 23: “Stress corrosion cracking in the copper canister is neglected due to the combined effect of very low (if any) concentrations of SCC promoting agents and the insufficient availability of oxidants.”

This should be questioned as shown here.

F. King and R. Newman /TR-10-04/ discuss in detail the current knowledge of stress corrosion cracking (SCC) in copper and copper alloys and evaluate the risk for SCC of the copper canisters in the repository environment /TR-10-46/ on page 117 (section 3.5.5 Stress corrosion cracking of the copper canister). It is pointed out that the chemical species of interest are those that have been shown to support the SCC of copper, namely, nitrite, ammonia, and acetate ions. However, new findings regarding sulfide induced SCC in phosphorus alloyed copper is also discussed but disregarded later. In TR-10-46, page 118 it is stated: “/Taniguchi and Kawasaki 2008/ reported SCC of pure copper (with 45 ppm P) in synthetic seawater solutions containing sulphide. The experiments were carried out at a temperature of 80°C with 0, 0.001, 0.005, and 0.01 M HS⁻, added to solution as Na₂S. Tensile specimens were strained to failure by SSRT (slow strain rate tests) at a strain rate of 8·10⁻⁷ per second. Loss of ductility was reported at a HS⁻ concentration of 0.01 M due to intergranular SCC. Only single experiments were reported. From these data, the authors concluded that pure copper is susceptible to SCC in sulphide solutions above a threshold concentration of between 0.005 M and 0.01 M. This concentration is 2–3 orders of magnitude higher than that expected in a Swedish repository.

A later follow-up study was performed by /Bhaskaran G. 2010/ as a master thesis work with Prof. R. Newman as supervisor. The work was inspired by the newly discovered SCC-problem concerning phosphorus alloyed copper in sulfide containing waters. The Japanese study was discussed in detail on page 31:

“Recently, Taniguchi and Kawasaki [14] reported the intergranular cracking of pure copper in sulfide polluted synthetic seawater at 80°C. The sulfide concentrations ranged from 0.001M to 0.01M and the samples were strained at a constant extension rate of 8.3 x 10⁻⁷ s⁻¹. The electrode potential was fixed at the rest potential value that was measured in N₂ atmosphere under the same conditions before slow strain rate test.”

Later on the same page it was stated: “Similarly, the mechanism behind the intergranular cracking was not discussed too. So we took this paper as our starting point to probe more on this less understood phenomenon.”

It is unclear why G. Bhaskaran and R. Newman decided to chance some crucial parameters such as the strain rate and preload compared with the Japanese study, see page 34: “Tensile samples were strained at a rate of 1x 10⁻⁶ s⁻¹ in air and in synthetic seawater containing different concentrations of sodium sulfide (5 and 10 mM) both at room temperature and at 80°C, using a CORTEST slow strain rate testing system. During all the experiments the samples were preloaded to 70 MPa before addition of sulfide.”

Accordingly, with changed test parameters, the main conclusion of the master thesis was “Under the tested conditions, the high pure copper is not susceptible to stress corrosion cracking”.

F. King and R. Newman speculate regarding the Japanese study in /TR-10-04/ page 17: “*The key is the ability of such cracks to continue growing under static loading after having been initiated by slow straining. Perhaps the Taniguchi cracking is really just an example of “SICC”.*”

In the same report it is stated about SICC on page 16; “There will always be a compression induced by the intergranular sulphidation that will tend to counteract the externally applied stress. Some might argue that instead there will be a wedging effect – this requires that the crack walls continue to sulphidise and press against each other. But in one well-studied case where such a ‘tarnishing’ mechanism of SCC occurs – the so-called SICC or strain-induced corrosion cracking of steel in hot water, the induced compression effect from the iron oxide film strongly hinders cracking, unless there is an applied dynamic tensile strain /Heldt and Siefert 2000/.”

Finnish researchers /Ariilahti E. et al 2010/ have recently confirmed that sulfide diffuses in the copper grain boundaries ahead of a *propagating crack during static loading*, see further section 6.1. This means that the speculations made by F. King and R. Newman /TR-10-04/, page 17, is not correct and that sulfide induced SCC is a real threat, especially during accumulation of sulfide salts in the deposition holes as discussed in section 3. In the conclusions in /TR-10-04/ it is again obvious that the authors F. King and R. Newman has disregarded the risk of accumulation or enrichments of corrosive species in the deposition holes due to the “sauna effect” and radiolysis; “However, there will be insufficient SCC agent (ammonia, acetate, or nitrite) to support cracking during this period. During the anaerobic phase, the supply of sulphide ions to the free surface will be transport limited by diffusion through the highly compacted bentonite.”

In the European Commission 5th Euratom Framework Programme /Kursten B, Werme L et al. 2002/ it is stated on page 166: “The candidate container material copper, and especially those containing phosphorus, has been found, in the past, to be highly susceptible to SCC”

Suggested recommendation of complementary information/studies:

Obviously more SCC-studies and embrittlement studies in sulphide environment is needed and SCC of phosphorus copper should not be excluded from the safety assessment.

5. Corrosion inside the canister due to radiolysis

It is probable that there will be a gas communication between the inner cast iron insert and the inside of the copper canister since any seal might fail in the harsh environment within some decades. The main corrosion problem could occur either on the cast iron or on the copper, depending on how fast gas communication occurs between the water vapor in the fuel rods and the cast iron insert and finally the gas volume in contact with the copper

The main argument to disregard the SCC-risk on the iron insert seems to be the temperature, see TR-10-46 page 100: “Shortly after deposition and closure, the temperature of the insert nearest the fuel is expected to be over 150°C. At this temperature there will be no water in liquid form in the canister, and the relative humidity is too low for a water film to form on the metal surface, even if there was

water in the canister trapped in the fuel rods.” This raises the question what happens to those canisters where the water from the fuel rods releases somewhat later when the coldest spot on the iron insert is around 100°C and condensation takes place?

TR-10-46 on page 22 it is concluded that corrosion of cast iron insert is not relevant issue which seems to be a too hasty conclusion.

It is interesting to note that the corrosion calculations made by /Marsh 1990/ regarding the KBS-3 model assumed around 10 grams of water inside the canister and it was warned that if greater quantities of water is available, SCC due to formation of nitrous compounds would be expected. “Stress corrosion cracking could fully penetrate the inner vessel in a few years at the most and would destroy the structural integrity”. The maximum amount of water in today’s KBS-3 model is expected to be substantially higher i.e. 600 gram /TR 11-01/ page 168. Obviously, the problem with inside SCC of the cast iron insert has to be studied further.

From a copper corrosion point of view, the worst case scenario would be that the seal on the iron insert lid is leaking water vapor to the gas volume between the insert and the copper canister. As mentioned, the enclosed amount of water in the iron insert, i.e. fuel rods, could be up to 600 g or 33 moles and as the temperature is well above 100°C inside the iron insert, a significant amount will be leaking out as water vapor. The cast iron insert is always warmer than the copper canister which means that any water condensation process will take place on the colder copper surface, given the situation that the cast iron insert is not perfectly gas tight. Nitrogen gas is expected to react with water and oxygen due to radiolysis under formation of nitrous/nitric compounds including HNO₃ gas which condenses as nitric acid. If the enclosed gas phase contains hydrogen, released from previous corrosion by water, ammonia is expected to form.

If the internal pressure is one bar, around 30% of the water vapor is expected to condense as liquid water if the coldest spot on the copper is 70°C. The condensate is continuously consumed due to copper corrosion and “refilled” as long as the coldest spot is at the same position. If the internal pressure is higher, the condensation process could of course start earlier at a higher temperature.

The condensate will preferably be accumulated and consumed due to copper corrosion since the coldest spot will always be found somewhere on the copper surface, as mentioned. A worst case scenario would be that the initially small slot between the copper base and the copper tube in contact with the friction stir weld (FSW), as shown in Figure 8, represents the coldest spot. As the condensation and radiolysis prolong, a slurry of non-adherent copper corrosion products mixed in a corrosive liquid containing different radicals based on N, O and H is expected to form. In /TR 10-46/, page 47 it is stated that the maximum amount of nitric acid that might form is 450 gram and it is limited to the nitrogen content that will be enclosed in the gas volume, 90% argon and 10% air, inside the canister. If a condensation process starts to take place somewhere on the copper surface relatively short after closure, severe corrosion damage is expected locally with some kilogram of copper consumption and if stresses exist in the copper at such a cold spot SCC is expected.

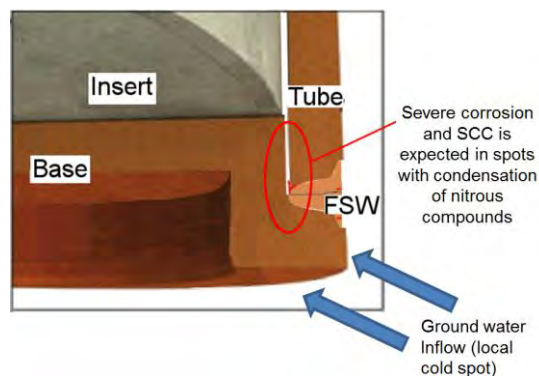


Figure 8. Radiolysis of water and air could create 450 gram of water soluble nitrous compounds which could create severe corrosion locally on the coldest spot.

If 600 gram of water reacts with copper, it could consume up to 4.2 kg Cu based on monovalent corrosion products. Some corrosion will of course take place in the gas phase on the cast iron insert and on the copper tube but it is expected that the corrosion in the liquid condensate will be faster and more severe. As mentioned, /TR-10-46/ page 100, the temperature on the cast iron insert is initially over 150°C and no nitric acid is formed at such hot and dry surfaces. This means that, over time, all nitrous compounds are expected to be condensed at the coldest spot at the copper surface. The corrosion rate in such an acidic or ammonia containing condensate could easily be several mm/y. However, the corrosion rate in this case might not be that important since it is the total amount of oxidants that limits the corrosion. In fact this truly confined, inside canister corrosion, is well defined corrosion case in the repository where it is scientifically sound to use a simple mass-balance calculation. If 50% of the total amount of oxidants is consumed locally at the coldest spot, i.e. around two kilogram of copper is expected to be consumed which could easily correspond to a local thinning of some centimeters.

In /TR-10-46/ section 2.5.2, it is concluded that all corrosion processes inside the canister are considered negligible, based on theoretical assumptions which does not includes the possibility of corrosion in a nitrous and radical containing condensate which will be collected at the coldest spot on the copper inner surface.

In more general terms, as it is shown by /Lillard R.S. et al. 2000/ that copper corrodes most among the tested engineering alloys due to radiolysis and it is recommended that copper and copper alloyed components should be avoided in radiolysis exposed systems. A new study on copper corrosion in pure anoxic water has confirmed that copper is sensitive to radiolysis /Björkbacka Å. et al. 2012/.

Suggested recommendation of complementary information/studies:

The main corrosion problem could occur either on the cast iron or on the copper, depending on how fast that gas communication occurs between the water vapor in the fuel rods and the cast iron insert and finally the gas volume in contact with the copper, the latter is dependent on how long time the cast iron insert is expected to be gas tight. A lot of different case scenarios are thus possible which should be analyzed further.

Radiolysis studies ought to be carried out with copper in confined cells or autoclaves under relevant gas environment at elevated temperatures and at RH up to 100% (with condense). Prof. E. Mattsson pointed out many years ago /Mattsson 1997/ that the formation of nitrite and ammonia due to gamma radiation must be evaluated experimentally and SCC-tests must be done in relevant environment containing such nitrous compounds. It seems that this has not been done yet or at least not reported.

6. Copper embrittlement phenomena

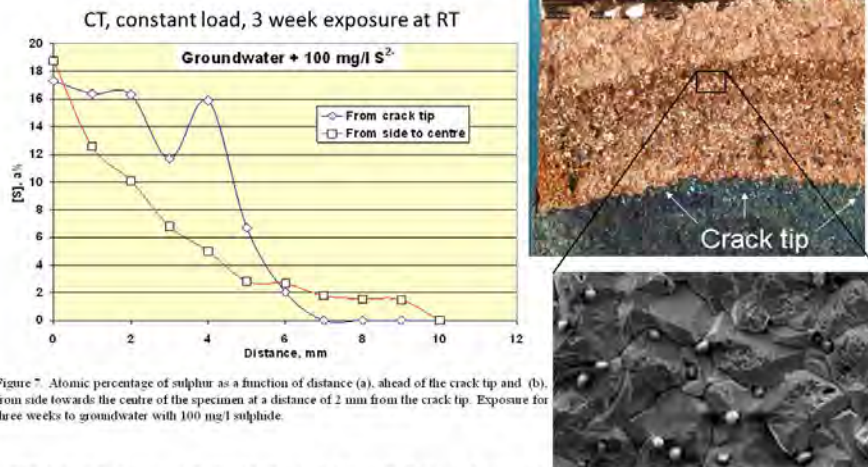
Neither hydrogen embrittlement nor sulfur embrittlement in copper is discussed in the safety assessment TR-10-46. However it is mentioned as a design criteria that the hydrogen content should not exceed 0.6 ppm due to brittleness of copper/TR-11-01/ page 168. None of the phenomena could be excluded on a scientific basis with today's knowledge.

6.1. Sulphur embrittlement of copper

/Ariilahti E. et al 2010/ have shown the existence of a new copper embrittlement phenomena:

"Based on the results, it is clear that sulphur can diffuse into the Cu OFP material when it is exposed at room temperature to saline groundwater with 100 to 200 mg/l sulphide. Indications were found that the in-diffusion preferentially occurs through grain boundaries. Individual grain boundaries were found to contain above 20 at-% sulphur. Based on SEM/EDS studies of the surfaces, the extent of diffusion depth of sulphide into Cu OFP was more than one millimetre per week". An overview of the experimental results is shown in Figure 9.

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



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

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Figure 9. A compilation by /Szakalos P. and Seetharaman S. 2012/ of the results from /Ariilahti E. et al 2010/ showing the discovery of a new copper embrittlement mechanism.

The SEM picture, down to the right, shows the post exposure fractured surface, i.e. a copper surface that should be unaffected since it is taken some mm ahead of the actual crack tip and most unexpected, a lot of sulphides is visible in the copper grain boundaries.

Suggested recommendation of complementary information/studies:

This mechanism is important since it explains the newly observed SCC in copper by sulfide, as discussed in section 4.2 and must therefore be studied further.

6.2. Hydrogen embrittlement and hydrogen sickness in copper

Hydrogen is expected to be accumulated in a metal that is exposed to an anoxic environment on all sides. The copper canister in a repository will eventually be exposed to a strictly anoxic environment and hydrogen charging due to anoxic corrosion will start. Copper is not specially sensitive to hydrogen embrittlement but the problem exists /Nakahara S et al. 1985/ and /Nakahara S. and Okinaka Y. 1988/ and the mechanical properties are affected negatively before any serious embrittlement occurs /Panagopoulos C.N. et al. 1994/. A more acute hydrogen charging process than by anoxic corrosion is by earth or stray currents which could be expected in the Forsmark repository, see section 7.

Another hydrogen embrittlement phenomenon, hydrogen sickness occurs in copper containing small oxide inclusions when exposed to hydrogen charging conditions. 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 potential problem, see Figure 10.

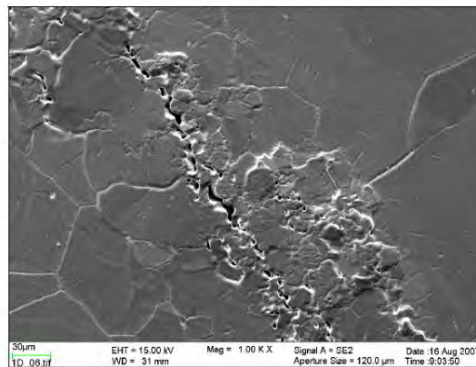


Figure 15. Sample 1DV. Voids and heavy deformation are clearly visible at the region of entrapped oxide particles.

Figure 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.

From the report it is stated. “An interesting microstructural feature is the pinning effect of the entrapped oxide particles. After annealing the samples for 30 min at 850 °C, the general grain size was considerably larger, but the grains near the entrapped oxide particles remained small. Grain growth is suppressed by pinning of the grain boundaries caused by the entrapped oxide particles. Hydrogen annealed samples 1DV and 2DV contained voids and signs of deformation visible at the region of entrapped oxide particles (Figures 15 and 16). It seems that hydrogen sickness has occurred in the samples.”

Suggested recommendation of complementary information/studies:

Hydrogen charging and embrittlement in anoxic salt water due to stray currents should be studied since weak hydrogen charging is expected already due to anoxic corrosion and any stray current is expected to accelerate the hydrogen charging. This does not seem to be discussed at all in the safety assessment /TR-10-46/.

Hydrogen sickness in FSW is a dangerous problem that might affect all canisters and more studies is needed. For instance, how long time does it take for hydrogen sickness to evolve in a FSW at 100°C during hydrogen charging conditions? The problem with hydrogen sickness does not seem to be discussed at all in the safety assessment /TR-10-46/.

7. Corrosion by stray currents

Fenno-Scan 1 is a 400 kV high voltage direct current transmission between Dannebo in Sweden, close to Forsmark, and Rauma in Finland. The Fenno-Scan was first installed as a monopolar system with a maximum transmission rate of 550 MW. Fenno-Scan 2 was installed 2011 with increased energy transport capacity to 800 MW. Depending on the imbalance between the two cables the stray or earth current and corresponding corrosion could be either higher or lower than that observed with the monopolar Fenno-Scan 1.

Severe crevice and pitting corrosion due to stray/earth current was observed on stainless steel equipment already after 10 days operation at 360 m depth at the Forsmark site, see /P-05-265/. Corresponding corrosion problem was also observed at the Laxemar site, in a 970 m borehole in this case the stray current originated from the HVDC-cable to Gotland. A circumstance regarding the Forsmark site is that the stray current corrosion problem was equally fast on equipment which was galvanically isolated by using aramid braiding instead of steel wire /P-05-265/. This indicates that the stray current corrosion problem in the Forsmark site is unusually problematic. In /P-05-265/, Appendix 3, it is recommended that corrosion studies should be performed to elucidate the potentially severe copper corrosion due to stray current. SKB has not published any such studies yet, instead they have a theoretical discussion in /TR-10-46/, pages 121-126, with the conclusion that the copper canisters in a repository should not suffer from stray current corrosion. It is claimed in /TR-10-46/ page 126, that “The effect of earth currents on canister corrosion can thus be neglected in the long-term perspective”. SKB’s theoretical discussions of stray current corrosion is obviously not complete since it is described in SKB report /P-05-265/ page 43, regarding observed crevice corrosion on the stainless equipment used in borehole KLX03A: “This type of corrosion was unexpected in the oxygen-free environment at 970 m.”

The thermodynamically favored corrosion reaction for copper exposed to saline water is copper dissolution, i.e. formation of copper ions and copper-chloride ion complex. The bentonite particles act as a sink for these ions. This reaction occurs spontaneously under a weak hydrogen evolution, as discussed in section 4 and is expected to be accelerated by any external stray/earth current.

The electron flow is expected to be transported through the copper canister in the potential field and exits the canister in a cathodic spot where several reactions are possible and one is hydrogen charging of the copper by reduction of hydrogen ions. The cathodic process is potentially even more dangerous than the corrosion reaction since it means accelerated hydrogen charging of the copper. A worst case scenario would be that a Friction Stir Weld (FSW) happens to be situated in a cathodic area which would result in hydrogen sickness. This creates porosity and cracks in the copper metal, see further details in section 6.2.

Stray current corrosion in the Forsmark repository could potentially turn out to be very severe. The surrounding rock will be drained during the excavation process and the heated canisters will dry out the bentonite rings further. This ensures a low electrical conductivity in the repository. There is a certain time point when saline

ground water eventually enters the bottom of some deposition holes and the tunnel starts to be at least partially saturated with saline groundwater. This represents the worst case scenario where most of the stray/earth current passing around the repository will suddenly pass through those canisters. It is known from failure cases that the corrosion rates due to stray/earth currents could, under adverse conditions, reach millimeters per week.

SKB has described the earth current problem with thermodynamically less favored anodic reactions and not the expected reaction, copper dissolution in saline water. Furthermore, only anodic problems are discussed but not the potentially more dangerous cathodic hydrogen charging problem of the copper.

Suggested recommendation of complementary information/studies:

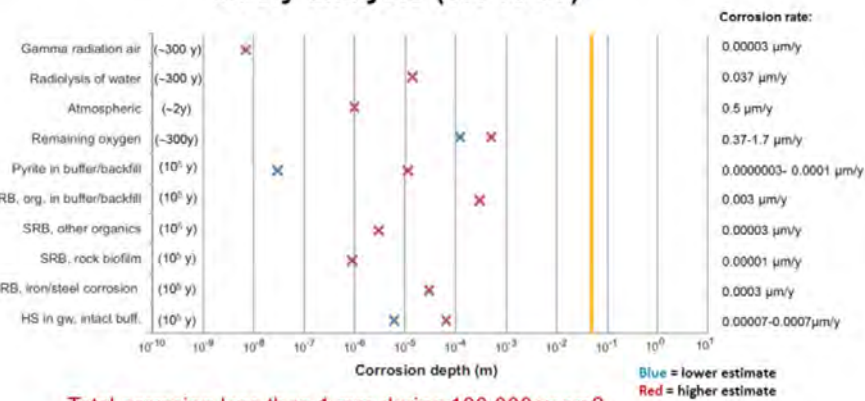
The potential seriousness of stray current corrosion should mean that theoretical discussions on vague basis is not enough, i.e. copper corrosion exposures should be done in boreholes in Forsmark at different depths.

8. Copper corrosion rates

In this technical note it is shown that is not possible to estimate the copper corrosion rates by oxygen and sulfur mass balance calculation since other species takes part in the copper corrosion process as well. Water molecules as moisture or in aqueous corrosion as hydroxide ions are probably the most frequent species that will react and form copper corrosion products in such a complex environment as expected in a repository with different trace gases and salts.

SKB has tried to estimate the copper corrosion by mass-balance calculations and based on those data /TR-11-01/ section 10.3.13 and /TR-10-67/, a compilation for corrosion during 100.000 years was presented on the SSM conference in Rånäs, May 2012, see Figure 11.

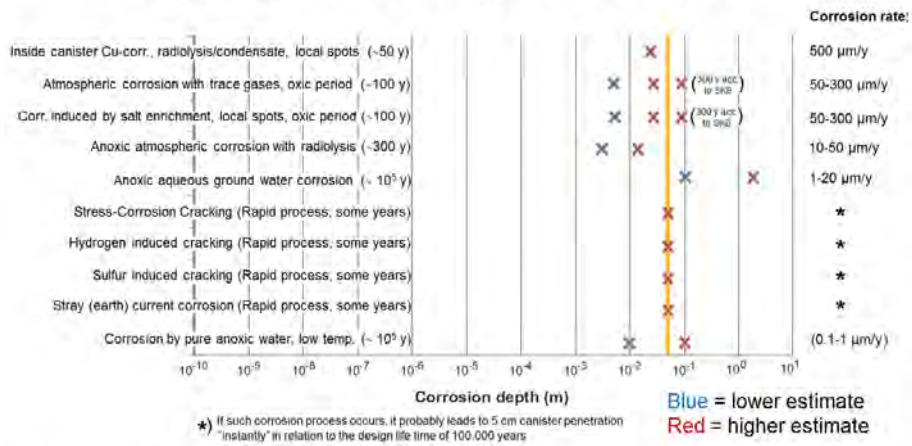
Corrosion during 10⁵ years based on data from SKB's safety analysis (TR-10-67)



Total corrosion less than 1 mm during 100.000 years?
Figure 11. The total copper corrosion based on mass-balance calculations. Corresponding corrosion rates are shown to the right /Szakalos P. and Seetharaman S. 2012/.

These corrosion estimations cannot be correct when knowing that copper reacts with more species than oxygen and sulfide. An estimation of corrosion based on copper corrosion kinetics was also presented on the same conference, see Figure 12.

Corrosion in a proposed Forsmark repository during 10⁵ years according to our estimations



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Figure 12. Copper corrosion estimations based on copper corrosion rate data /Szakalos P. and Seetharaman S. 2012./

There is a huge discrepancy between the two different models as seen by comparing the Figures 11 and 12. In conclusion, copper corrosion kinetic data, i.e. experimental data, must be used in a corrosion model that should describe corrosion in such a complex environment as in a deep geological repository.

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Coverage of SKB reports

We believe that we have a full coverage of what SKB have considered regarding copper corrosion and probably an almost full coverage of what SKB have not considered regarding copper corrosion in a deep geological repository in the proposed Forsmark site.

Table 1: The main reports and sections reviewed.

Reviewed report	Reviewed sections	Comments
SKB TR-11-01 SR-Site main report	5.4, 10.2.5, 10.3.7, 10.3.8, 10.3.13, 10.4.7, 10.4.9	
SKB TR-10-46 Fuel and canister process report for the safety assessment	3.5	
SKB TR-10-52 Data report for the safety assessment	4	
SKB TR-10-45	appendix 5	
SKB TR-10-67 An update on the corrosion of copper under expected conditions in a deep geologic repository	3, 4, 5, 6, 7	
SKB TR-10-04. Stress corrosion cracking of copper canisters	all	
SKB TR-10-66: Corrosion calculations report for the safety assessment	all	

Suggested needs for complementary information from SKB

1. Oxygen transport between deposition tunnels and main tunnel. It is assumed in /TR 11-01/ page 314 and /TR-10-67/ on page 57 that no oxygen enters the deposition tunnels after their closure. This requires that deposition tunnels are hermetically sealed by concrete plugs and that no cracks in the blasted bed rock around the tunnels communicate with the main tunnel until the repository is closed. This should be proven.
2. Gas phase corrosion up to 1000 years, both oxic and anoxic. SKB has estimated the total gas phase corrosion of the copper canisters in a Forsmark repository and the result is summarized in /TR 11-01/ page 315 and in TR-10-66/ section 5.2.2 and in TR-10-46 page 105 and in TR-10-67 section 4.3 "Corrosion in unsaturated bentonite after emplacement" This evaluation is based on the assumption that only oxygen from entrapped air will react with the canisters and the amount of corrosion of copper is based on a simple mass-balance calculation. The result indicates a total gas phase copper corrosion of around 0.8 mm. This estimation is not considering the effect of the combined corrosion by moisture, hydrogen sulfide, nitrous compounds (from radiolysis) and initially also with oxygen and obviously a mass-balance calculation is not valid. According to the industry standard /ANSI/ISA S71.04-1985/ it can be concluded that the gaseous environment in a Forsmark repository can be classified as "Severe" regarding copper corrosion and that is already at room temperature in a dry atmosphere with trace gases like H₂S (>50 ppb H₂S) and NO_x (>1.25 ppm). SKB seems only to have measured the total sulfide content in Forsmark and not the amount of dissolved H₂S, see /TR-11-01/ page 361. Gaseous corrosion by trace gases at high RH and at elevated temperatures with and without oxygen must be studied and used as a basis for a kinetic corrosion model. Furthermore, it is important to study the combined corrosion effects of different trace gases since for instance NO_x greatly accelerate H₂S corrosion /ANSI/ISA S71.04-1985/. It is stated in TR-11-01, section 10.3.8: "The safety functions for the buffer and backfill assumes a fully water saturated state. This should mean that the buffer and backfill need to be saturated to perform properly. However, no performance is needed from the buffer as long as the deposition hole is unsaturated, since no mass-transfer between the canister and the groundwater in the rock can take place in the unsaturated stage." This statement is obviously wrong.
1. Radiolysis in the gas phase. All references used by SKB regarding estimation of HNO₃-formation are based on a work by /Jones 1959/. In /TR-10-66/ page 27 and in TR-10-46 on page 109 it is stated that "Of the papers reviewed, the study by /Jones 1959/ of the nitrogen-oxygen-water homogeneous systems appear to be directly applicable to repository conditions." This is questionable since the work by Jones differs in many respects from the expected repository conditions. Radiolysis studies with copper corrosion under relevant gas environment are needed. The

environments in the references used by SKB are not relevant. The true production rate of HNO_3 , for example measured as N_2 consumption in a closed system with relevant temperatures and radiolysis conditions and with the presence of copper surfaces which represents an effective sink or scavenger for HNO_3 should be studied.

2. Salt enrichment, the "sauna effect". The macroscopic water transport from the heated deposition holes to the cold tunnel with subsequent salt enrichment in the holes must be considered and studied in case of a repository with slow water inflow such as in Forsmark. In TR-10-46, section 3.5.7 "Deposition of salts on the canister surface" (page 127), local water transport inside a deposition hole is discussed and modeled based on data from the Long Term Test of Buffer Materials, the LOT project. The LOT-holes were carefully sealed in order to be pressurized and to avoid that a mass transport of moisture or water vapor to the tunnel. The issue of water redistribution between deposition holes and tunnel was not studied in the LOT-project. It seems therefore that only a "near field" model has been developed, see /TR-10-59/, section 2.1 and potential water transport between the heated deposition holes and the cold tunnel in a real repository has not been evaluated.
3. Corrosion due to the "sauna effect". Lars Werme and Kastriot Spahiu have the following statement on copper corrosion due to enrichment of salts from the ground water in TR-10-46 (page 127) "Also, an increase in the chloride concentration would lower the susceptibility of copper to pitting corrosion, since it would favor general corrosion /King et al. 2001/. A high chloride concentration will, however, not lead to increased general corrosion, since the near field pH is always expected to be slightly alkaline and, consequently, the extent of the corrosion will be determined by the amount of available oxygen. Thus, exposure to temperatures over 100°C is not expected to have an effect on the corrosion behavior of the copper canister. The maximum allowed surface temperature of the canister is, therefore, set more by the requirements for chemical stability of the bentonite buffer than by any possible influence on canister corrosion." It is in this context important also to consider the enrichment not only of chlorides, but also of other salts in the ground water such as sulfates, nitrates, bromides and sulfides. Lars Werme and Kastriot Spahiu seems to believe that only chlorides will be enriched and no other corrosive salts. It is important to experimentally clarify the risk for corrosion of copper exposed to anoxic saline and highly saline water at high temperatures. There are reports that indicate severe corrosion under these conditions. According to a study by /King F. and Litke C. D. 1987/anoxic copper corrosion in 0.97M chloride solution results in a copper corrosion rate of $110 \mu\text{m}/\text{year}$ at higher temperature.
4. Copper corrosion in anoxic water. Since copper is not immune in anoxic water and less immune in saline (neutral) anoxic water, there is no threshold limit for chloride concentrations regarding copper dissolution corrosion. The statement in TR-11-01 page 364, (A discussion with the same conclusion is seen in TR-10-46 page 104) that "Chloride concentrations below 2 M imply that chloride assisted corrosion of the canister can be excluded (safety function indicator R1f)." is thus not correct. This is in contradiction to experimental data and corrosion by anoxic saline water is not possible to estimate with simple mass-balance calculations since hydroxide ions and water molecules are taking part in the complex corrosion process. The corrosion mechanism seems to be influenced by chloride and sulphide ions acting as corrosion activators by reacting with hydroxide ions from water. The bentonite acts as a sink for copper ions and corrosion products. It is of vital importance for the safety analysis to study these phenomena further. Copper corrosion rates in

anoxic neutral saline water with less chloride than 2M, must be determined as a function of temperature. These kinetics, i.e. corrosion rate based models, should be included in the safety assessment. The copper-bentonite interactions must be studied in detail. How is copper integrated in the bentonite, in what positions? In different oxidation states? It is known that the bentonite acts as a sink for copper ions and corrosion products. Some part is detected as copper sulphides but are there some other phases? Cross-sections, not only of the bentonite, but also of the copper material in contact with bentonite should be examined. The central copper tube in LOT A2 would be the best copper object to study since the heaters were in operation most of the time and the adjacent bentonite is quite well characterised. Crucial questions such as if localized corrosion has occurred, what type, and to what extent, must be answered. The fact that the central copper tube was not alloyed with phosphorus is of less importance since phosphorus is not contributing to the corrosion resistance. It seems that important thermodynamic data is missing or deviates from experimental results for example regarding solubility of copper in water containing chlorides and the formation of solid products such as paratacamite. This limits the accuracy of assessing the corrosion rates of copper under the prevailing conditions.

5. Pitting corrosion in anoxic environment. In TR-10-46 at page 107 is stated that pitting corrosion in anoxic environment is unlikely and therefore neglected in the safety assessment.
Anoxic copper corrosion with chloride and sulfide present need to be studied also regarding localized corrosion processes, i.e. both pitting corrosion and crevice corrosion (with bentonite clay). With the possible salt enrichment problem, see the "sauna effect", different localized corrosion processes is inevitable and should be included in the safety assessment.
6. Stress Corrosion Cracking. The safety assessment regarding Stress Corrosion Cracking (SCC) in copper, has been summarized in TR-10-46 page 23: "Stress corrosion cracking in the copper canister is neglected due to the combined effect of very low (if any) concentrations of SCC promoting agents and the insufficient availability of oxidants." This statement has been proven to be wrong by /Taniguchi and Kawasaki 2008/. F. King and R. Newman speculate regarding the Japanese study in /TR-10-04/ page 17: "The key is the ability of such cracks to continue growing under static loading after having been initiated by slow straining. Finnish researchers /Ari-Lahti E. et al 2010/ have recently confirmed that sulfide diffuses in the copper grain boundaries ahead of a propagating crack during static loading. This means that the speculations made by F. King and R. Newman /TR-10-04/, page 17, is not correct and that sulfide induced SCC is a real threat, especially during accumulation of sulfide (and nitrite) salts in the deposition holes as discussed in section 3. In the conclusions in /TR-10-04/ it is again obvious that the authors F. King and R. Newman has disregarded the risk of accumulation or enrichments of corrosive species in the deposition holes due to the "sauna effect" and radiolysis; "However, there will be insufficient SCC agent (ammonia, acetate, or nitrite) to support cracking during this period. During the anaerobic phase, the supply of sulphide ions to the free surface will be transport limited by diffusion through the highly compacted bentonite."
7. Inside canister corrosion due to radiolysis It is probable that there will be a gas communication between the inner cast iron insert and the inside of the copper canister since any seal might fail in the harsh environment within some decades. The main corrosion problem could occur either on the cast iron or on the copper, depending on how fast gas communication occurs between the water vapor in the fuel rods and the cast iron insert and

finally the gas volume in contact with the copper. TR-10-46 on page 22 it is concluded that corrosion of cast iron insert is not relevant issue which seems to be a too hasty conclusion. It is interesting to note that the corrosion calculations made by /Marsh 1990/ regarding the KBS-3 model assumed around 10 grams of water inside the canister and it was warned that if greater quantities of water is available, SCC due to formation of nitrous compounds would be expected. "Stress corrosion cracking could fully penetrate the inner vessel in a few years at the most and would destroy the structural integrity". The maximum amount of water in today's KBS-3 model is expected to be substantially higher i.e. 600 gram. Obviously, the problem with inside SCC of the cast iron insert has to be studied further. The cast iron insert is always warmer than the copper canister which means that any water condensation process will take place on the colder copper surface, given the situation that the cast iron insert is not perfectly gas tight. Nitrogen gas is expected to react with water and oxygen due to radiolysis under formation of nitrous compounds including HNO_3 gas which condensates as nitric acid. If the enclosed gas phase contains hydrogen, released from previous corrosion by water, ammonia is expected to form. In TR 10-46, page 47 it is stated that the maximum amount of nitric acid that might form is 450 gram. If a condensation process starts to take place somewhere on the copper surface relatively short after closure, severe corrosion damage is expected locally with some kilogram of copper consumption and if stresses exist in the copper at such a cold spot SCC is expected. A lot of different case scenarios are thus possible which should be analyzed further. Radiolysis studies ought to be carried out with copper in confined cells or autoclaves under relevant gas environment at elevated temperatures and at RH up to 100% (with condense). Prof. E. Mattsson pointed out many years ago /Mattsson 1997/ that the formation of nitrite and ammonia due to gamma radiation must be evaluated experimentally and SCC-tests must be done in relevant environment containing such nitrous compounds. It seems that this has not been done yet or at least not reported.

8. Copper Embrittlement. Neither hydrogen embrittlement nor sulfur embrittlement in copper is discussed in the safety assesment TR-10-46. None of the phenomena could be excluded on a scientific basis with today's knowledge. /Ariolahti E. et al 2010/ have shown the existence of a new sulphur copper embrittlement phenomena. This mechanism is important since it explains the newly observed SCC in copper by sulfide, as discussed in section 4.2 and must therefore be studied further.

Hydrogen charging and embrittlement in anoxic salt water due to stray currents should be studied since weak hydrogen charging is expected already due to anoxic corrosion and any stray current is expected to accelerate the hydrogen charging. This seems not to be discussed at all in the safety assessment /TR-10-46/.

Hydrogen sickness in FSW is a dangerous problem that might affect all canisters and more studies is needed. For instance, how long time does it take for hydrogen sickness to evolve in a FSW at 100°C during hydrogen charging conditions? The problem with hydrogen sickness seems not to be discussed at all in the safety assessment /TR-10-46/.

9. Earth or stray current corrosion. The potential seriousness of stray current corrosion should mean that theoretical discussions on vague basis is not enough, i.e. copper corrosion exposures should be done in boreholes in Forsmark at different depths.

SKB has not published any such studies yet, instead they have a theoretical discussion in /TR-10-46/, pages 121-126, with the conclusion that the copper canisters in a repository should not suffer from stray current corrosion. For example, it is claimed in /TR-10-46/ page 126, that stray

current corrosion should not be possible in anoxic environments. This should be compared with what is described in the SKB report /P-05-265/ page 43, where crevice corrosion was observed on the stainless equipment used in borehole KLX03A: "This type of corrosion was unexpected in the oxygen-free environment at 970 m."

10. Copper corrosion rates. *In this technical note it is shown that it is not possible to estimate the copper corrosion rates by oxygen and sulfur mass balance calculation since other species takes part in the copper corrosion process as well. Water molecules as moisture or in aqueous corrosion as hydroxide ions are probably the most frequent species that will react and form copper corrosion products in such a complex environment as expected in a repository with different trace gases and salts.*

SKB has tried to estimate the different copper corrosion mechanisms by mass-balance calculations, see the compilations in /TR-11-01/ section 10.3.13 and /TR-10-67/. These corrosion estimations cannot be correct when knowing that copper reacts with more species than oxygen and sulfide. There is a huge discrepancy between the mass-balance models and estimations made on experimental data, i.e. observed copper corrosion rates. In conclusion, copper corrosion kinetic data, i.e. experimental data, must be used in a corrosion model that should describe corrosion in such a complex environment as in a deep geological repository.

Suggested review topics for SSM

1. *Gaseous copper corrosion at elevated temperatures and high RH with/without oxygen and with/without radiolysis.*
2. *Aqueous corrosion at elevated temperatures in anoxic saline water*



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