

Miljöorganisationernas kärnavfallsgranskning, MKG
Swedish NGO Office for Nuclear Waste Review, MKG

Translation and slight amendment of Appendix 2 to the consultation document submitted by the Swedish Society for Nature Conservation, SSNC, and MKG on June 1, 2012 to the Swedish Radiation Safety Authority and the Swedish Environmental Court (<http://www.mkg.se/stora-brister-i-slutforvarsansokan-naturskyddsforeningen-och-mkg-kraver-omfattande-kompletteringar>).

Analysis of the need for additional work concerning problem with the barrier system

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Comments on SKB's application for final disposal of nuclear waste and the associated safety assessment SR-Site.

1. INTRODUCTION

The Swedish Nuclear Fuel and Waste Management Co. (SKB) have in its permit application for the final disposal of spent nuclear waste proposed, that this shall be deposited in the bedrock at a depth of 500 m at Forsmark, Sweden. The deposition in the repository shall be done according to the KBS-3 concept. It is worth noting that the various safety aspects relating to this repository have previously been experimentally studied almost only at the Äspö laboratory in Oskarshamn and that the conditions at the proposed repository at Forsmark are in many aspects substantially different from those at the Äspö laboratory. This means that there are for the deposit at Forsmark great uncertainties and lack of data of fundamental importance for the safety analysis e.g. regarding the inflow of groundwater to the deposition holes for the canisters containing the nuclear waste and the time it takes for the bentonite surrounding the canisters to reach water saturation.

2. SKB'S METHODOLOGY

2.1 Mathematical Models

SKB have chosen a methodology for the evaluation of the various aspects of the repository safety, which to a great extent is based on mathematical models and simulation of different conditions that are important for the safety. Mathematical models have been developed to describe for example to describe:

- Water saturation of the bentonite in the deposition holes
- Erosion of the bentonite
- Different corrosion mechanisms of copper

These mathematical models are based on different assumptions regarding the estimated mechanisms for mass transport of the chemical compounds and ions present in the bentonite and the groundwater. Specific values are thereafter assigned for the different equilibrium reactions and diffusion rates. SKB have in this way theoretically calculated various conditions of vital importance for the safety of the future repository, such as copper corrosion rates for due to some mechanisms and erosion of the bentonite.

It is normal practice, when mathematical models are used, that the data assigned in the models, the theoretical assumptions and the results obtained are verified by experiments under relevant conditions. If then the experimentally determined values or data are found to deviate from the theoretical ones (estimated and assigned), it is according to good scientific practice to use the measured values in the forthcoming calculations in the model. SKB have in some cases chosen to do the reverse i.e. that when there is a discrepancy between theoretically calculated and experimentally measured corrosion rates for copper, SKB have chosen to reject the experimental

results. SKB have for these cases concluded that the experiments could not have been carried out correctly, as higher corrosion rates are measured experimentally relative to the theoretical calculated ones.

SKB have also chosen in the project Minican to exclude complete test runs for the same reason - the experimentally measured corrosion rate of copper was significantly higher than the theoretically calculated, (Baldwin et al, SSM 2010:17) and (Smart et al, SKB TR-09- 20).

Exclusion of these test runs were made without any comments in the report SKB TR-09-20, which is definitely not consistent with good scientific practice.

SKB have not yet in May 2012 reported the results of corrosion studies from the so-called Retrieval Trial project in which a copper canister of full size was placed in water saturated bentonite and heated from inside. The test lasted for 5 years and the canister and surrounding bentonite was taken up for examination in May 2006 (SKB TR-07-10). It is stated in the report SKB TR-11-10 on page 5 that the canister and surrounding bentonite buffer had been studied in 2008-2009 and that the analysis were almost finished.

It is essential that theoretical calculations are built on mathematical models that are verified experimentally as the results of these calculations are directly dependent on

- the approaches and the assumption made in the development of models
- the data that have subsequently been used in the calculations

There is therefore always a risk that the assumptions and data assessed in the theoretical models are selected subjectively. This shall be corrected by carrying out relevant experiments and evaluate these in an objective way.

2.2 Good scientific practice

It has been reported in section 2.1. above that SKB, when preparing the safety analysis, have deviated from good scientific practice, which of course reduces the confidence in this analysis.

It is very valuable when the results of mathematical modeling by one part can be compared with similar works by an independent, qualified organization. JNC, Japan Nuclear Cycle Development Institute (JNC TN1410 Ref. 2000-03) have made theoretical calculations, based on mathematical modeling, of the corrosion rate of the copper canisters, according to the KBS-3 concept. The calculations were carried out for two cases with respect to the sulfide concentration in the groundwater.

	Corrosion attack after 1 000 years	
	General corrosion	General corrosion + pitting
Very high sulphide content	9 – 13 mm	18 – 26 mm
Normal sulphide content	-	14 mm

Table 1. Theoretical calculations of copper corrosion in water saturated bentonite after 1 000 years according to the Japan Nuclear Cycle Development Institute, JNC.

The corresponding analysis carried out by SKB gave a general corrosion + pitting attack amounting to 3 mm after 1 million years.

SKB have referred to these Japanese theoretical calculations, but only to the extreme case with the very high sulphide content (King et al, SKB TR-01-23, pp. 135). SKB stated that these results were irrelevant due to the unrealistically high sulphide content and could be neglected. SKB have not mentioned in the report SKB TR-01-23, the very high copper corrosion rates found in the JNC analysis for the case with normal sulphide content in the ground water. This work has further not been referred to or discussed in the SR-Site. This behavior can clearly be considered to deviate from good scientific practice as the corrosion attacks in the normal case, which must be considered to be the most interesting.

In the Japanese work, the copper corrosion rate caused by sulphide corrosion was calculated to be 14 microns / yr (including pitting corrosion) with normal sulphide contents. The corrosion rate is thus 5000 times higher than the corresponding rate calculated by the SKB.

This clearly illustrates the uncertainty of theoretical calculations based on mathematical models and how important it is to verify such models with relevant experiments.

It is shown in paragraph 3.6 and 3.7 below that the Japanese calculated corrosion rates are in good agreement with SKB's own experimental results from the LOT -and Minican trials, and also from other studies (King, F. et al, 1992).

SKB's methodology to selectively present important information on such an important issue as copper corrosion is definitely not in tune with the concept of good scientific practice.

SKB have published experimental results from their own laboratory, pilot and full scale experiments regarding copper corrosion. These reports are often incomplete, sometimes inaccurate, and in many cases there is a lack of vital information. SKB make further sometimes conclusions regarding rates of corrosion and corrosion mechanisms that are not supported by the reported experimental results, see below under section 3.6 Corrosion tests of copper placed in water-saturated bentonite.

2.3 Implementation and evaluation of experimental trials

The copper canisters have in the KBS-3 concept a crucial function as a barrier to prevent leakage of the radioactive nuclear waste. The canisters are exposed to corrosive attack during the entire storage period and are expected to be sufficiently intact after 100 000 years of exposure that they are not penetrated by the surrounding groundwater.

The copper canisters will be exposed during these 100 000 years to a very complex corrosion environment, including a plurality of different corrosion mechanisms and mechanical loading. There is a complex interaction of various corrosion mechanisms as well as between mechanical stress and corrosion, potentially in the latter case resulting in stress corrosion cracking. The copper will also be subjected to various embrittlement mechanisms such as hydrogen and sulphur embrittlement, which probably also interacts.

It is crucial from a safety point of view that studies of the corrosion resistance and strength of the copper canisters are conducted under conditions relevant to the final repository. The canisters shall therefore be of full size, embedded in water saturated bentonite and exposed to both relevant corrosive environments as well as mechanical loading. The value of such tests increases with increasing test duration, leading to improved understanding of;

- Current corrosion mechanisms
- Interaction between the copper canister and surrounding water-saturated bentonite
- Formation of corrosion products on the copper surfaces
- Precipitation of copper compounds in the bentonite
- Precipitation of salts in the bentonite and on the copper surfaces
- Corrosion rates
- Mass transport and transport mechanisms in the bentonite

This information is essential for assessing the relevance of current SKB mathematical models for the preparation of the safety analysis.

SKB have worked with the KBS-3 concept for over 30 years and should therefore be able to present experimental tests carried out under relevant full-scale conditions with test duration of at least 25 years.

SKB have carried corrosion experiments on copper samples for maximum 6 years (the LOT-experiments). The conditions were somewhat relevant to those of the suggested repository at Forsmark. However, in these experiments were only studied small copper plates embedded in water-saturated bentonite. It seems that SKB have not conducted any copper corrosion tests during the first 15-20 years of the existence of the company, alternatively, SKB has chosen not to report such attempts.

It is remarkable is that no full-scale copper canister has been corrosion tested by SKB at the Äspö laboratory. It is also important to emphasize that the corrosion environment, exposure times and corrosion mechanisms differ considerably between the Äspö Laboratory and the planned repository in Forsmark.

It is common practice at corrosion testing of metals to determine the occurrence of corrosion attacks and corrosion products by means of metallographic examinations. Figure 1 shows the different corrosion attacks on a copper sheet, which was exposed to distilled and oxygen-free water for 15 years (Hultquist, 2009). The copper sheet was cut, ground, polished and then subsequently studied in metal microscope. It appears from the photograph that the copper was subjected to general corrosion, pitting and grain boundary corrosion. It is also common to examine corroded surfaces in light optical microscope and SEM (scanning electron microscope).

Cross-section of 0.1 mm copper foil

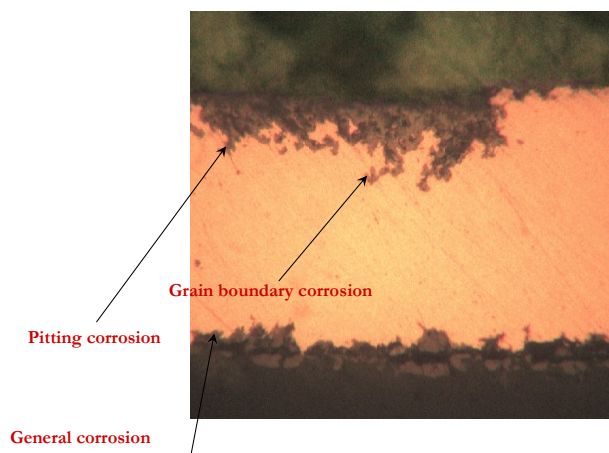


Figure 1. G. Hultquist, (2009).

Important information is obtained from microscopic investigations e.g. regarding corrosion products, corrosion rates and mechanisms, the occurrence of cracking and pitting of the corroded metal. SKB have consistently chosen not to carry out metallographic studies of cross-sections of corrosion-tested copper. SKB have further in a few reports shown photographs taken in light optical microscope or by scanning electron microscope.

Karnland et al (SKB TR-09-29) have chosen when presenting the results from the LOT project (Sample A2) both in the report and the enclosures (see e.g. Rosborg in Appendix 3) not to present any metallographic photograph showing corrosion attack in a cross-section of the copper sample.

This is very surprising, differs definitely from good scientific practice and prevents readers of the report to judge if there is any corrosion, pitting or cracking of the tested copper samples. The SKB have chosen instead to verbally describe the corrosion attacks (Hedin SKB TR-10-46 page 107 and 108) "There is no pitting (pitting) of the copper, however, depressions on the surface." This conclusion should also readers of the reports have the opportunity to make.

2.4 Interaction between different corrosion mechanisms and embrittlement of copper canisters

SKB have in the safety analysis consistently assumed that different corrosion mechanisms can not interact and thus strengthen the overall corrosion attack. According to the SKB's analysis, can the total corrosion attack of the copper canisters be calculated by adding the effect from the individual mechanisms?

This reasoning is highly questionable and must be verified experimentally by long-term trials. SKB make the same assumption regarding various embrittlement mechanisms, which may occur in copper canisters. This assumption is also in this case very doubtful, and must be verified.

3. NEED FOR ADDITIONAL INFORMATION AND STUDIES

3.1 How long is the period until the bentonite is saturated with water?

It will take a very long time, perhaps some thousand years, to water saturated the bentonite placed in the deposition holes and overlying tunnels in the repository. How long time is it expected to take before the bentonite in most of the deposition holes and tunnels is saturated? How large is the groundwater flow to the deposition holes? There are large differences in water flow between the projected repositories in Laxemar and Forsmark. The extensive cracking of the rock in Laxemar provides high flow rates of groundwater, causing the deposition holes to be filled with water in some year's time. This results in water saturation of the bentonite surrounding the canisters and of the bentonite in the transportation tunnels.

SKB state that the inflow of water is very limited in Forsmark: "An Additional analysis of inflow into individual deposition holes [...] using the same model as described above indicates that 99.9% of all deposition holes in the Forsmark repository have an inflow smaller than 0.01 l/min, when no grouting is applied "(SKB TR-06-09, page 212).

The bentonite surrounding the copper canisters will be heated by heat transfer from the canisters for a very long time, in the order of a thousand years, before the deposition holes are filled with water. Will the material and functional properties of the bentonite be affected by this heat flow? The quantity of water flowing into the deposition holes is a very important parameter in several of the key safety aspects of the repository such as:

- Corrosion conditions, the corrosion mechanisms that are prevailing and the corrosion rates of the respective mechanism. It is believed that copper corrodes in the projected repositories in Forsmark (but not in Laxemar) by atmospheric corrosion, gas/water interface corrosion and corrosion caused by precipitates of salt on the copper surfaces
- The precipitation of salts from the ground water in the bentonite buffer and on the copper surfaces
- The temperature distribution in the deposition hole, the heat transfer from the fuel rods to the copper canisters, from these to the bentonite and finally to the rock walls. The occurrence of air gaps between the copper canister and the bentonite and also between the bentonite and the bedrock wall
- Erosion and formation of cracks and channels in the bentonite

These issues are of central importance in the safety analysis of the Forsmark repository. It must be impossible to theoretically calculate the expected corrosion rate for copper if one does not know the corrosion mechanisms involved. It is therefore crucial that SKB account for the expected water flow in liter / minute to the deposition holes and how this flow will vary over time. It is also important determine how the water inflow vary between the deposition holes. Consideration must also be taken when carrying out the theoretical analysis and experimental runs on the following aspects:

- The water inflow at one or more cracks in the bedrock in connection with a deposition hole. What happens when there are no such cracks?
- The formation of cracks in the bedrock when the transportation tunnels in the repository are blasted
- Inflow of water in the emplacement holes; will the water come from the rock at the bottom or on the sides or from the deposition tunnels above the holes?

3.2 Evaporation of groundwater

A bottom plate of bentonite is placed in each deposition hole. The copper canisters are subsequently placed on this bentonite plate. Finally, bentonite is added to fill the gap between the bedrock and the canisters.

Groundwater will flow from the cracks in the surrounding bedrock into the deposition holes. This water will after a certain period of time come in contact with the hot copper surfaces resulting in an evaporation of the water. What happens at the evaporation of water and how much of the vaporized groundwater will condense and where? SKB consider that each deposition hole is a hermetically sealed system and vaporized ground water can not penetrate into the

overlying deposition tunnels and water saturate the bentonite present in the tunnels. Is there some experimental support for this assumption?

3.3 Salt concentration in the bentonite placed in the deposition holes

Sena et al have presented a model for the flow of water from the granite wall of the deposition holes towards the canisters during the initial period, when the water saturation of the bentonite takes place; see Figure 2 below (SKB TR-10-59, page 13). Remarkably, the model does not consider that there is an air gap between the copper canister and bentonite.

According to the model water evaporates at the water front and water vapour diffuses through a bentonite zone towards the hot canister that is in the opposite of the heat flow. It is likely that mass transport is opposite to that described in the figure and that the water vapour diffuses to the waterfront, and then condenses. The effect of these reactions is that the salts dissolved in the water are transported towards the canisters and is precipitated in the bentonite, when the water is evaporated.

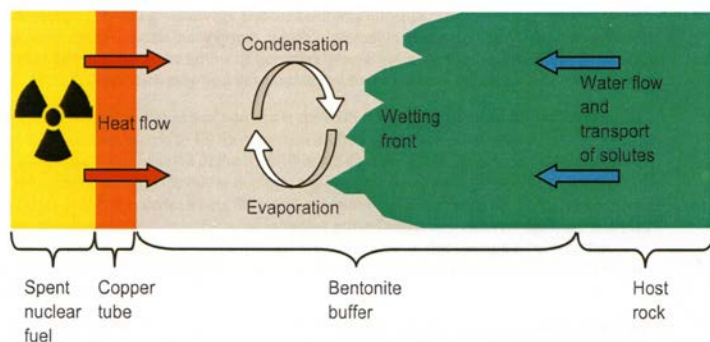


Figure 2-1. Sketch of a vertical cross section of the near-field of a KBS-3 repository showing the thermo-hydraulic and transport processes that are believed to occur during the saturation period of the bentonite buffer.

Figure 2. Sena et al, SKB TR-10-59, page 13.

There will thus be evaporation and condensation of water vapour in a zone in the bentonite. Some of the water vapour will escape into the air gap between the canister and the bentonite and through cracks in the bentonite (see Figure 3 below from Atkins, 2009, SKB R-09-29) into the deposition tunnels above the deposition holes. SKB have introduced a completely unrealistic assumption that has not been verified experimentally, that all the deposition holes are hermetically sealed in the 100 to 1000's year period that it takes to water saturate the bentonite in the tunnels and deposition holes.

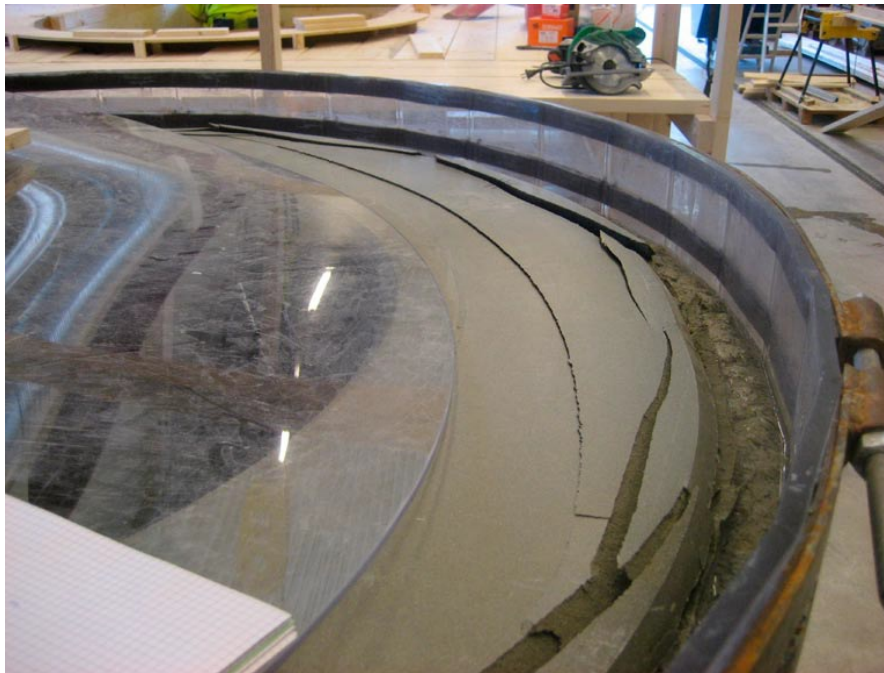


Figure 3. Large cracks in the ring after 48 h (Åberg 2009, SKB R-09-29).

Evaporation of the incoming ground water results in precipitation of salts in the bentonite, in the gap between the copper canister and the bentonite and also on the copper surfaces. Sena et al, 2010, (SKB TR-10-59) have not considered the fact that the evaporation of groundwater can lead to enrichment of salt in the deposition holes. They refer to the LOT experiment A2 (Karnland et al. SKB TR-09-29). This is completely irrelevant in this case as the experiment LOT A2 was carried out during a time which is very short in this regard – 6 years – and with artificially water-saturated bentonite.

It is most important to determine how this salt enrichment in the bentonite takes place due to water vapour leaving the system and to which extent the salt enrichment affect the material and functional properties the bentonite.

3.4 Copper corrosion caused by precipitation of salts on the copper surfaces

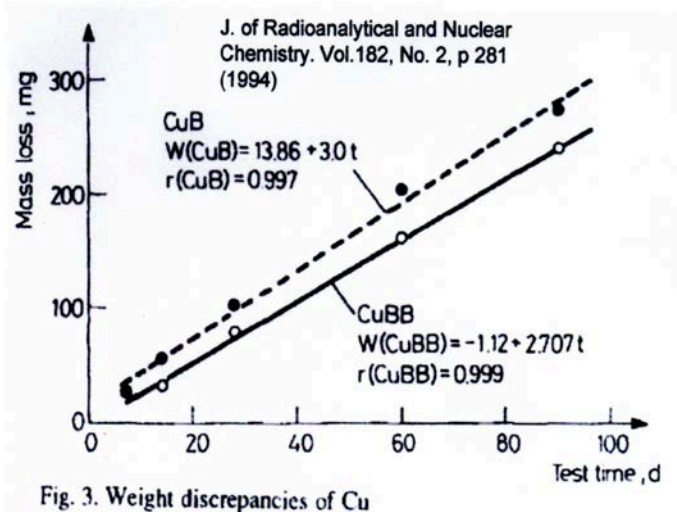
Evaporation of groundwater will also lead to precipitation of hygroscopic salt crystals on the copper surfaces. These will then be completely or partially covered with a salt layer. In the case where the surfaces are only partially covered, there is a risk for formation of local galvanic cells. Corrosion is usually high when hot metals coated with salt are exposed in a high humidity environment.

SKB have chosen to exclude this corrosion mechanism in the safety analysis and indicate that the corrosion caused by salt precipitates does not occur. One reason for this standpoint is that SKB did not detect any salt precipitates on the copper surfaces in the LOT experiments.

However, this is entirely as expected as these experiments were carried out with water-saturated bentonite, during a relatively short time and with a large supply of water. Salt precipitates will almost certainly be obtained in the bentonite and on the copper surfaces during the initial period of some 1000 years when the bentonite is not water saturated.

3.5 Copper Corrosion caused by elevated salinity in the deposition holes

Evaporation of the water that flows into the deposition holes leads directly also to an enrichment of dissolved salts in the water found in the deposition holes with chloride, sulphide or sulphate ions. Even if only a very limited portion of the incoming water evaporates and leaves the deposition holes, this leads to an increase in salinity of the water. Elevated contents of chloride ions in water are known to strongly corroded copper see Figure 4 below.



Corrosion of copper (>99.99%) at oxygen free exposure in autoclave in brine with 14% Cl⁻ at 90°C. Linear corrosion rate about 100 μm/year.

Figure 4. Szakalos P. (2009)

SKB have chosen to based SR-Site on the assumption that each deposition hole is hermetically sealed for up to some thousand years and until the tunnels are filled with water. SKB also claims that when the deposition holes are closed, there can be no air leakage into the holes or flow of water vapour from the deposition holes. SKB has not yet proved this assumption by means of any experiments.

3.6 Corrosion test of copper placed in water-saturated bentonite

SKB have in recent years determined experimentally that the copper corrosion proceeded in LOT and Minican projects at a rate of 1-20 microns/year. This rate is 10,000 to 100,000 times higher than the theoretically calculated based on the assumption that the rate determining step is sulphide corrosion, see SKB TR-10-66 page 45.

Karnland et al (SKB TR-09-29) specify in the summary on page 4 "the measured corrosion rate of metallic copper is consistent with results from previous experiments and by modelling."

Rosborg estimate further in Appendix 3, in the same report that the corrosion rate was less than 0.5 microns/year when the reaction temperature was 30 °C, page 145.

Both Karnland et al and Rosborg must be well aware of the fact that this information is wrong and misleading. It is evident from the report SKB TR-09-29 that copper dissolves in the water and copper ions diffuse into the bentonite where the copper is precipitated, in part as copper sulphide. Elevated copper levels were measured in the bentonite at a distance of up to 20 mm from the copper pipe. Rosborg observed also that the copper, from the samples, had penetrated the bentonite to a depth of 500 microns perpendicularly from the copper surface. Rosborg also determined the content of copper in the bentonite as a function of the distance from the copper surface, see Figure 5.

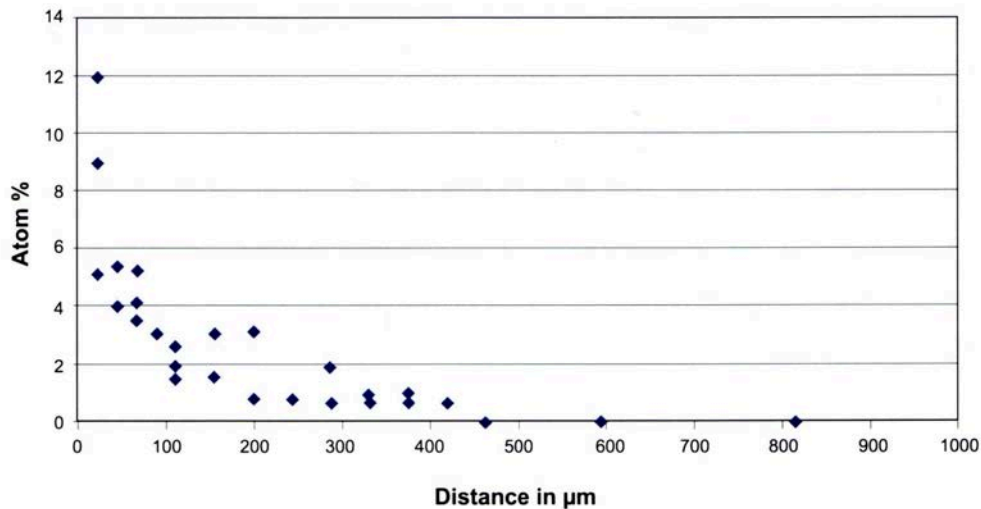


Figure A3-3. Copper profile in bentonite next to copper coupon A230H.

Figure 5. Karnland et al (SKB TR-09-29), precipitation of copper in the bentonite.

Karnland et al and Rosborg are well aware of the corrosion mechanism in which copper dissolves in water and then precipitates in the bentonite. Despite this, these authors did not consider this mechanism, when they calculated the overall copper corrosion rate but just indicate it to be less than 0.5 microns year.

An estimate based on the copper concentrations in the bentonite; see Figure 6 below gives an actual corrosion rate of 10 - 20 microns/year. It must be obvious even to Karnland et al and Rosborg that the corrosion rate must be much greater than 0.5 microns/year when such high levels of copper are found in the bentonite as shown in Figure 5. See further below under section 3.7.

SKB now claim that LOT-and Minican-trials due to oxygen leakage took place under aerobic conditions, i.e. in water containing dissolved oxygen. However, it is clear from the electrode potential measurements at the Minican experiments and direct measurement of the oxygen content of the water that the conditions were anoxic (Smart et al. SKB TR-09-20).

The copper corrosion rate and the electrode potential of the copper canisters were measured electrochemically and simultaneously in the Minican experiments. The copper canisters were placed in water saturated bentonite under anoxic conditions. The results showed that the copper canisters corroded with a few microns/year under anoxic conditions.

As the measurements of corrosion rate and the electrode potential were made simultaneously, the results can only be interpreted as the true *copper corrosion rate when the metal is placed in water-saturated bentonite and under anoxic conditions*. SKB's statement that the corrosion was caused by leakage of oxygen or from oxygen present in the bentonite at the test start is thus incorrect.

King et al 2010 (SKB TR-10-67) chose not to mention the results of Minican experiments in section 5.2.6 In-situ experiments.

SKB have indicated in their safety analysis and in a number of reports that the oxygen dissolved in the water in the deposition holes will be consumed in a short period of time, around 5 days to a few weeks, once the bentonite is water saturated (Hedin, SKB TR-10-46, page 103, 106). SKB claim at the same time that the reason for the high rate of corrosion of copper in some long-term experiments such as LOT and Minican experiments is due to the presence of dissolved oxygen. What is the cause of this discrepancy and what is the experimental evidence that oxygen was present?

3.7 Corrosion by dissolution of copper in the ground water and precipitation in the bentonite

SKB have found, in several corrosion experiments with copper samples placed in water-saturated bentonite, high levels of copper in the bentonite in a zone of a few centimetres from the copper surface. These results were obtained after a few years of exposure of the copper. The amount of copper precipitated in the bentonite can be converted to a corrosion rate of 10 - 20 microns/year over a 6 year period in the LOT 2 trials, which is a very high corrosion rate, see Figure 6. This corrosion mechanism have been considered only to a limited degree of SKB and are not included, for example in the compilation of corrosion mechanisms that affect the life time of the copper canisters (SKB TR-10-66 page 45 and Figure 6-1, Hedin, SKB TR-10-46, SR-Site, Part II, page 428, Figure 10-88 and SKB TR-11-01).

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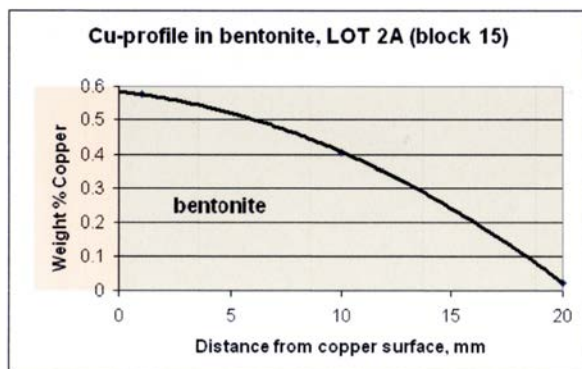
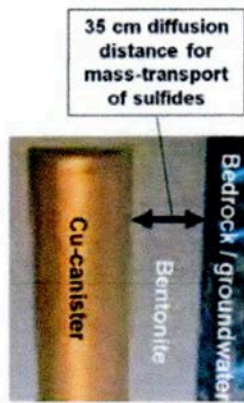


Figure 6. Szakalos P. (2009)

Figure 7 shows that copper dissolves in the ground water, after which the copper ions diffuse into the surrounding bentonite and finally become dispersed in the bentonite. Chemical analysis of the bentonite showed high levels of copper in the bentonite zone closest to the copper. The thickness of this zone was a few centimetres. Corresponding results of copper precipitates in the bentonite have probably also been found in prototype repository trials. SKB ought to theoretically and experimentally study how this corrosion mechanism influences the life of the copper canisters. The results SKB hitherto have published show that the bentonite accelerates the dissolution of copper and that the precipitation of copper in the bentonite may affect its functional properties.

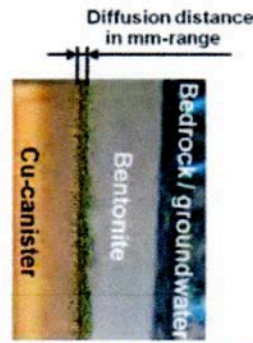
The KBS-3 model:



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

P. Szakalos and S. Seetharaman

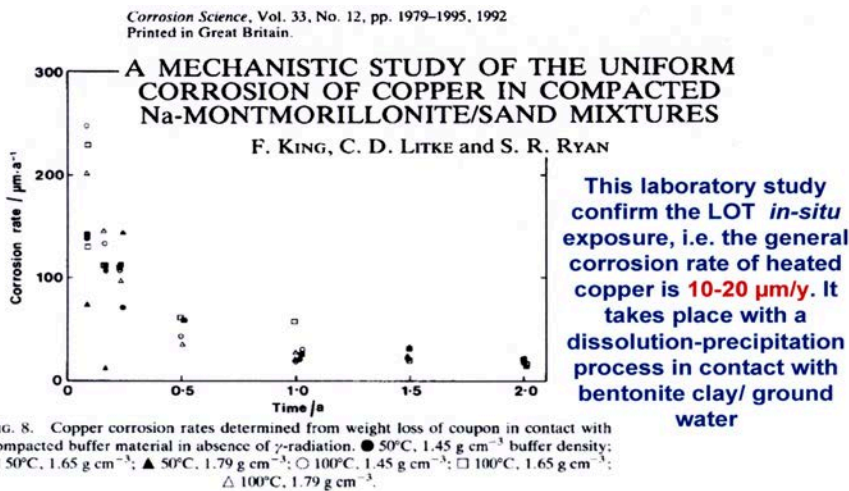
Reality:



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

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

Similar results have also been published by King et al (1992). See Figure 8. Corrosion rates were measured in this study of approximately 20 microns/year after 2 years of exposure. It is surprising that SKB is not taking this corrosion mechanism in consideration in the safety analysis.



On page 1991, it was concluded that " O_2 -transport was not rate-limiting" and that the corrosion took place with a dissolution-precipitation process; "Precipitation of copper inevitably occurred in all of the tests, with usually more than half of the total copper corroded being in the form of precipitate rather than being sorbed on the clay".

Figure 8. Szakalos P. (2009)

3.8 Corrosion of copper due to radiation (radiolysis)

After the bentonite has become saturated with water, the radiation from the canisters causes radiolysis of water and formation of oxidants and hydrogen. This phenomenon is also likely to occur during the initial period from the time the canisters are placed in the deposition holes until complete water saturation is achieved.

King et al (SKB TR-10-67) and Hedin (see page 110, SKB TR-10-46) state the following regarding corrosion caused by radiolysis:

"The experiments were performed in aerated and de-aerated solutions and the corrosion rates were about a factor of four lower in the presence of radiation. / King and Litke 1987 / attributed this to the more protective nature of the surface film formed in irradiated solutions. Available

information shows that there is no evidence for enhanced corrosion rates caused by gamma radiation. On the contrary, at least for the dosage rates in the range of 10-100 Gy / h, the experimental data seem to indicate a lower corrosion rate in the presence of radiation / King et al. 2010 / . "

SKB has therefore chosen to theoretically estimate the maximum corrosion attack on the copper canisters due to radiolysis of water to about 10 microns in 1 million years.

This assessment should be compared with experimental results from a recent survey of Björkbacka et al (2012) see the photographs below, Figure 9. The report and photographs show that "gamma radiation causes significant corrosion of metallic copper in anoxic aqueous solution". Furthermore, it was found that the radiation resulted in a significantly higher content of copper dissolved in the aqueous solution compared with the reference sample. The radiation dosage used by Björkbacka et al were in the same range amounting from 10 to 100 Gy/h as in the earlier experiments carried out by King et al.

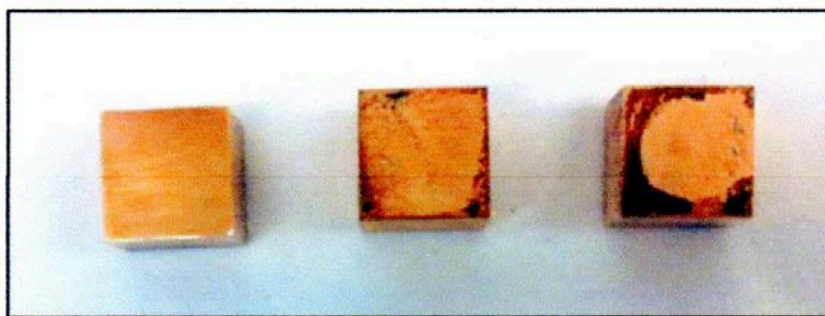


Figure 1. Photography of an experimental set of copper cubes. The cube to the left in the photography is the non-irradiated reference sample. The cube in the middle has received a total dose of 62 kGy while the cube to the right has received a total dose of 129 kGy. The irradiated copper cubes are more corroded than their reference sample.

Figure 9. Björkbacka et al (2012)

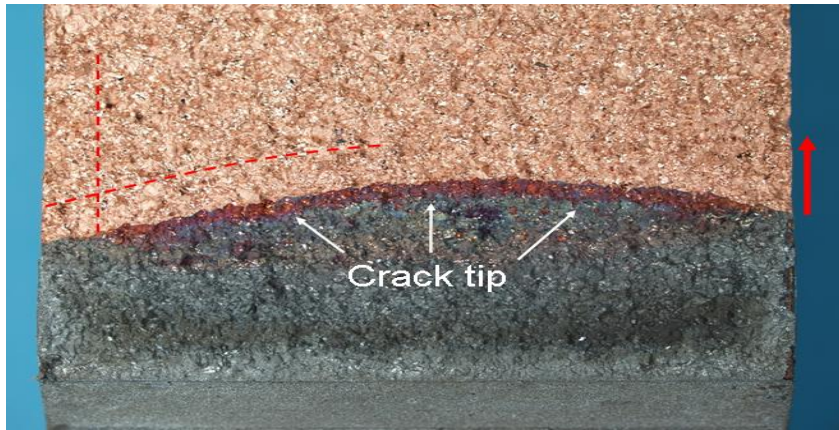
This shows that SKB's and King's assessment of the significance of this corrosion mechanism is most probably wrong. There is a need for much more experimental results on corrosion of copper due to radiation, i.e. radiolysis of water. Gaseous copper corrosion must also be studied by the wet gas mixture (water vapour, nitrogen, etc.) during the initial period of a few thousands years before the bentonite is water saturated.

3.9 Sulphur embrittlement

Ari-Lahti et al. from VTT, Finland, stated in a recent report (Int. Conf. Brugges, Belgium, 2010) the following (Ari-Lahti et al., 2010, page 4);

"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 20a% 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."

The results Ari-Lahti et al. reports are brand new, very important and describe a new embrittlement mechanism for copper that is sulphur embrittlement, see Figure 10.



Surface of Cu OFP specimen after a three week exposure to groundwater with 100 mg/l sulphide. The dashed red lines indicate lines along which local area SEM/EDS analyses were made with roughly one millimetre distance.

Figure 10. Arilahti et al. 2010

The authors of the report have found that:

- Mass transfer of sulphur from the groundwater to the copper metal is taken place at high rate when the concentration is 100 - 200 mg of sulphide per litre of groundwater
- The diffusion of sulphur into the copper is very fast even at room temperature with a rate of over 1 mm/week
- The sulphur forms copper sulphide precipitates in the copper grain boundaries
- The copper sulphide precipitates appear to embrittle the copper metal

It is vital that SKB closely follow this work, which also needs to be complemented with extensive mechanical testing of specimens with diffused sulphur in the copper grain boundaries.

3.10 Hydrogen embrittlement and hydrogen sickness

SKB have initiated some research on hydrogen absorption of pure copper, (Martinsson et al., 2008). These authors state that hydrogen can be released due to corrosion of the cast iron insert inside the copper canister and absorbed by the copper canisters. This can happen if the copper canisters break and the ground water react with the cast iron. Another possibility is the reaction between residual water remaining within the canisters and the cast iron.

Martinsson et al (2008) does not mention that hydrogen can be transferred directly to the copper when it is corroded and by earth currents, although these mechanisms are of greater importance to the repository situation.

The presence of hydrogen in the copper can generate "hydrogen sickness", and hydrogen embrittlement. The hydrogen reacts at hydrogen sickness with inclusions of copper oxides. The oxides are reduced to metallic copper during the formation of water vapour, which is precipitated in the grain boundaries, on the surfaces of the inclusions and in the cracks, resulting in that the copper become brittle.

High contents of atomic hydrogen in copper can also be introduced electrochemically. This results in hydrogen embrittlement of copper, similar to the well-known phenomena resulting in hydrogen embrittlement of high strength steel. This mechanism does not involve the formation of water vapour in the copper or steel. Hydrogen embrittlement of copper has been described by Nakahara et al (1988).

The copper used in the manufacture of the canisters has very low oxygen content, whereby the risk of hydrogen sickness is very low. However, the welds formed by friction stir welding operations contain high levels of oxides and these are located in strings, which is particularly unfavourable. It is thus important to consider the risk of hydrogen sickness in the welds.

Martinsson et al (2008) have conducted various experiments comprising introduction of hydrogen in copper both by thermal and electrochemical methods. Two different copper materials were used in the experiments - copper foil and cylindrical specimens of OFP copper. No analysis was reported for the two materials.

Very high levels of hydrogen could be introduced electrochemically in the two samples of copper foil (62 ppm and 248 ppm). Very low levels were, however, obtained when the rods of OFP copper was electrochemically charged and amounting to less than 3.5 ppm. The reason for these discrepancies is probably problems with the experimental technique and not due to any differences between the copper alloys as the authors indicate.

It is essential for the safety of the repository the risk is eliminated for hydrogen embrittlement due to electrochemical charging of copper with atomic hydrogen. It is important that SKB conduct experiments to evaluate this risk and in such a way that the tests are relevant of the conditions at the repository in Forsmark. The risk of hydrogen embrittlement must be determined experimentally. This means that mechanical testing must be carried out in an aqueous solution under static load and during long time and with simultaneous charging of the hydrogen atoms in the copper by an electrochemical method.

The chemical composition of the aqueous solution should correspond to the composition that exists in Forsmark taking into consideration the increase of salt content due to evaporation of water as discussed under Section 3.5. Martinsson et al (2008) suggest that assessment of the risk of hydrogen embrittlement shall be carried out through creep test in air. This method is obviously not relevant here.

3.11 Creep ductility

Prof. Kjell Pettersson has on behalf of SSM completed an evaluation of SKB's research efforts on the creep ductility of phosphorous-alloyed copper (see report SSM 2012:13). The following conclusions were presented in this report;

"SKB has presented insufficient evidence to justify their position that the OFP copper has an adequate creep ductility during long term storage. Their large body of experiments only serves to prove that the creep ductility is sufficient for much shorter time spans than the intended storage times. There is a clear need for a credible theory of creep brittleness of OFP copper which will permit extrapolations to long term storage. The theory presented by SKB does not in its present state permit credible extrapolations. Alternatively SKB needs to find an explanation to the effect of phosphorus on the creep ductility and that it ensures the absence of creep brittleness in OFP copper."

It is important that this matter be investigated further.

3.12 General copper embrittlement

See paragraph 3:09 to 3:12. Copper capsules will be exposed to several different embrittlement mechanisms. SKB have chosen in the safety analysis only to consider two of them separately. It is essential that the SKB can present experimental results showing the risk of brittle fracture when these mechanisms interact. The analysis should include the combination of stress corrosion cracking and embrittlement.

3.13 Friction stir welding

Savolainen et al (2008) have shown that large amounts of copper oxide are formed at the friction welding operation of the lid and the bottom to the cylindrical part of the canister. It is well known that high levels of copper oxide in metallic copper promote the formation of hydrogen sickness. How has SKB studied the risk of hydrogen sickness of the friction welded parts? Has this been taken into account in the SR-Site?

3.14 Stray current corrosion

It is well known that significant stray currents are formed from the power line cables located in Forsmark. Two high voltage direct current cables are going between Forsmark and Rauma in Finland. The cables are called Fenno-Skan 1 and Fenno-Skan 2. Fenno-Skan 1 was installed many years ago (1989) and is monopolar. Fenno-Skan 2 is newly installed and bipolar.

Hedin states on page 121 in the report SKB TR-10-46 that:

"As a result of the HVDC cable located 30 km north of the Forsmark site (the Fenno-Scan cable), man-made earth currents are a potential source of enhanced corrosion. Indications of such corrosion have been seen on stainless steel logging equipment used in the Forsmark site investigation /Nissen et al. 2005 /."

Hedin calls thus the clear evidence that exists on severe corrosion attacks caused by stray currents *only indications*. See the following two pictures from Nissen et al SKB P-05-265. The authors of the latter report state that these cases of severe corrosion, both pitting (Fig. 11) and crevice corrosion (Figure 12), on the stainless steel SS2343 (so-called acid-proof stainless steel) were caused by stray currents in the rock from the monopolar high-voltage cable between Sweden and Finland.

The equipment was intended for chemical analysis of the groundwater in Forsmark and was placed in a borehole having a depth 360 m. Hedin mentions further that the distance between the HVDC cable and plant in Forsmark is 30 km.

This is misinformation, as the distance between high voltage cable and the proposed repository is only 2 km.



Figure 2-3. Pitting corrosion on the outside of the chemical analysing equipment.

Figure 11. Pitting of stainless steel SS2343 after 10 days of exposure in a borehole. Forsmark. SKB report P-05-265.



Figure 2-9. Details with crevice corrosion inside the chemical analysing equipment.

Figure 12. Crevice corrosion of stainless steel SS2343 after 10 days of exposure in a borehole. Forsmark . SKB report P-05-265.

It is also very remarkable that Hedin (SKB TR-10-46) do not mention these corrosion attacks, which occurred after a very short time (10 day) exposure. Hedin has further not communicated that corresponding corrosion caused by stray currents also was obtained in a bore hole in Laxemar, Oskarshamn at a depth of 970 m. A literature search was made of the reports published by SKB to get more information on corrosion problems in the bedrock in Laxemar due to stray currents.

It seems that this vital information has not been reported, at least not in SKB public reports. It is therefore possible that the corrosion problems encountered in Laxemar and caused by stray currents in the rock is only publicly mentioned in Appendix 3 to SKB P-05-265. The authors of this report further recommended that direct corrosion tests were conducted to clarify the problem of corrosion of copper canisters through stray currents. SKB has not made any experimental attempt to clarify issues regarding copper corrosion and stray currents. Hedin has instead carried out a theoretical argument on pages 121-126 in TR-10-46 ending with the conclusion that the copper canisters can not corrode due to stray currents. SKB has not verified the hypothesis with experimental results. Further, Hedin states on page 125 of the report TR-10-46:

"Further, it is only HCDC cables operated in monopolar mode that can cause currents through the earth. The cables could be operated in bipolar mode, with a separate cable to lead the current back."

This information is directly inaccurate, misleading and is different from what Fingrid OYJ states on their homepage regarding the transfer of power from Sweden. Fingrid OYJ own the national grid in Finland and all significant foreign power supply connecting systems. The company states in the information from Powering Finland (www.fingrid.fi) regarding corrosion caused by stray currents that; *"Bipolar operation reduces corrosion to about one fifth of the present level"*.

Furthermore, Hedin mention in SKB Report TR-10-46 that stray current corrosion can not occur in anoxic environment (page 126). This statement should be compared with what is stated in SKB Report P-05-265 on page 43 regarding confirmed crevice corrosion and pitting of stainless steel equipment in the borehole KLX03A, Laxemar;

"This type of corrosion was unexpected in the oxygen-free environment at 970 m "

How have these attacks been reported? How will the SKB in the future, evaluate the risk of copper corrosion caused by stray currents?

3.17 Stress Corrosion

Taniguchi et al have found that pure copper is susceptible to stress corrosion in anaerobic synthetic seawater containing sulphide ions from sodium sulphide. The authors estimate that the threshold for initiation of stress corrosion cracking was in the range 0.005-0.01M sodium sulphide at 80 °C. Concentrations exceeding this threshold value generate according to Taniguchi et al stress corrosion cracking.

SKB dismiss the potential risk for stress corrosion of copper canisters on the basis that this threshold value is higher than that of SKB calculated content of sulphide ions in the water contained in the deposition holes. SKB have then not taken account that the salt content may increase dramatically in the ground water by evaporation, see above section 3.2 and 3.3.

King et al write on page 134 of the report SKB TR-10-67 that:

"In addition to there being a low probability of SCC during the initial warm, aerobic period, there is no evidence to suggest that cracking can be sustained during the long-term anaerobic phase in the absence of oxidants or due to the presence of sulphide."

This reasoning is curious. King excludes thus the risk of any stress corrosion cracking as, according to him, there is no evidence that this corrosion mechanism exists under the conditions that prevail in the repository. The reverse would be more logical i.e. that there is evidence that stress corrosion can not occur under current conditions. King et al acknowledge that there may be stress corrosion if there is an enrichment of for example sulphide ions in the deposition holes by evaporation of water.

4. CONCLUSIONS

SKB's methodology is questionable as it sometimes exhibits a lack of good scientific practice and serious shortcomings in the implementation and evaluation of experimental trials. There is a severe lack of information missing in several important areas.

There is an urgent need for additional information and studies on:

- How long is the period until the bentonite is saturated
- What happens when the ground water in the deposition holes is evaporated
- Precipitation of salts in the bentonite
- Precipitation of salts on the copper surfaces

SKB has not or only inadequately considered the following mechanisms of corrosion of copper caused by:

- Hygroscopic precipitates of salt on copper surfaces
- Increased salinity in the deposition holes
- Dissolution of copper in the ground water and precipitation in the bentonite
- Corrosion caused by radiolysis
- Stray current corrosion

SKB have also neglected to take into account the atmospheric corrosion during the period when the bentonite is not saturated with water. Furthermore it is important to consider interaction between different corrosion mechanisms. SKB have not or only very inadequately treated the following embrittlement mechanisms for copper:

- Sulphur embrittlement
- Lack of creep ductility
- Hydrogen embrittlement and hydrogen sickness
- Stress corrosion

SKB have not given due consideration to potential interaction between different embrittlement mechanisms.

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