SKI Report 2006:11

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Engineered Barrier System – Assessment of the Corrosion Properties of Copper Canisters

Report from a Workshop at Lidingö, Sweden, April 27-29, 2005

Synthesis and extended abstract

Swedish Nuclear Power Inspectorate

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Foreword

The Swedish Nuclear Fuel and Waste Management Company (SKB) plans to submit applications for construction of an encapsulation plant and a deep repository for the geological disposal of spent nuclear fuel (SFL-2). SKI is preparing to review these license applications, and as part of its preparation, SKI is conducting a series of technical workshops on key aspects of the Engineered Barrier System (EBS) of the repository. This workshop concerns the assessment of the corrosion properties of copper canisters. Previous workshops have addressed the overall concept for long-term integrity of the EBS (SKI Report 2003:29), the manufacturing, testing and QA of the EBS (SKI Report 2004:26), the performance confirmation for the EBS (SKI Report 2004:49) and long-term stability of the buffer and the backfill (SKI Report 2005:48).

The goal for the ongoing review work in connection with the workshop series is to achieve a comprehensive overview of all aspects of SKB's EBS work prior to the handling of forthcoming license applications. This report aims to summarise the issues discussed at the copper corrosion workshop and to extract the essential viewpoints that have been expressed. The report is not a comprehensive record of all the discussions at the workshop and individual statements made by workshop participants should be regarded as opinions rather than proven facts. Results from the EBS workshops series will be used as one important basis in future review work.

This reports includes apart from the workshop synthesis, questions to SKB identified prior to the workshop, and extended abstracts for introductory presentations. In the preparation of this report a substantial part of the work has been done by Peter Robinson (Quintessa Limited).

Contents

1 Introduction

The long-term safety of a future spent-fuel repository in Sweden relies on the long-term isolation that is provided by the copper canister embedded within a low permeability clay barrier (SKBF 1983, SKB 1999a, SKB 2004). This can be regarded as the primary safety function for the KBS-3 design concept. In performance assessment (PA), considerable attention also has to be devoted to other safety features such as slow radionuclide release and subsequent retardation provided by the engineered barrier system (EBS) and the geosphere. This is to demonstrate that safety does not depend on any one particular isolation function.

In the evaluation of the various mechanisms that could compromise the canister integrity, it is important to acknowledge that the bentonite-clay buffer serves a key role in physically protecting the copper canister, and that the properties of the near-field rock and tunnel backfill in turn affect the buffer. It is therefore essential to integrate the analysis of the functions of these components, rather than analyse them one at the time. Moreover, the Thermal, Hydraulic, Mechanical and Chemical (THMC) processes that may affect canister integrity are in many cases strongly coupled. One must therefore adopt an integrated approach covering both the components and the processes. The expected long lifetime of the canister itself may to some extent mitigate the potential adverse impact of many coupled processes on the radionuclide release performance because the strong initial gradients that drive coupled processes dissipate within the first thousand years following repository closure. These processes do, however, have an impact on canister integrity both in the short and long term. Two areas that are probably most crucial for canister integrity are:

- The corrosion behaviour of the canister influenced by the groundwater chemistry coupled with the extremely low hydraulic conductivity of the buffer.
- The mechanical integrity of the canister and buffer under THMC coupled processes in the bentonite-rock system.

These topics were discussed at a workshop held in November 2002 (SKI, 2003). This was the first of a series of workshops organised by SKI looking at different aspects of the EBS. Subsequent workshops focused on manufacturing issues (SKI, 2004a), long-term experiments (SKI, 2004b) and the long-term behaviour of the buffer and backfill (SKI, 2005).

The Swedish programme for a spent-fuel repository is now close to the licensing phase, with a few years before submittal of license applications for construction of an encapsulation plant and subsequently for the construction of a repository for spent fuel. The Swedish Nuclear Fuel and Waste Management Company (SKB) has suggested a time frame, based on the time needed for the required development of the barrier-, system components, and the ongoing site investigations in the Östhammar and Oskarshamn municipalities. The Swedish Nuclear Power Inspectorate (SKI) and the Swedish Radiation Protection Authority (SSI) need to be prepared for the future reviews of these license applications, which include a performance assessment (PA) related to long-term safety. The workshop series plays an important role in this preparation, as part of a comprehensive strategy that SKI will use to prepare for future license applications from SKB. This strategy is discussed in Sections 5.1 to 5.6 of SKI (2002).

Since the first workshop, SKB has continued to develop the safety case by undertaking further experimental and modelling work. The Interim SR-Can safety assessment report has also been produced (SKB, 2004). This again emphasises the primary safety function of the copper canister – that it should prevent radionuclide release over the full 1 million year assessment time frame. Two workshops in 2005 and 2006 will look in more detail at the issues of copper corrosion and mechanical integrity.

This report is a synthesis of the discussions that took place at the first of these workshops, which was held in Sweden in April 2005.

The report sets out the objectives and format of the workshop in Section 2. Section 3 provides a high-level overview of processes that need to be taken into account. In Section 4, the types of argument that are made in a safety assessment are described in a general way. Section 5 gives a more detailed description of the important threats to canister integrity and reviews SKB's approach for demonstration of the containment phase. In Section 6, the key issues for different time periods in the evolution of the EBS are brought together. Section 7 discusses the implications for design and manufacture of the canisters and Section 8 presents overall conclusions from the workshop.

Several appendices provide more details of the workshop – Appendix A lists the participants, Appendix B lists the questions that were provided to SKB ahead of the workshop, and Appendix C provides extended abstracts of the presentations made by SKI's experts at the workshop.

2 Workshop structure

2.1 Objectives

Given the emphasis on the primary safety function of the canister, the objectives of the workshop were to:

- identify critical issues for the demonstration of the long-term integrity of the canister for spent nuclear fuel, especially with regard to what must be addressed by a licence application in 2008;
- evaluate SKB's latest work on copper corrosion (see King et al., 2001 and updated by subsequent work);
- review and discuss SKB's ongoing and planned research activities within the copper corrosion area;
- suggest further work that would be appropriate for SKI as a preparation for the review of documents supporting the application for the encapsulation plant and subsequent application for a repository for spent nuclear fuel.

In order to meet these objectives, all the various corrosion mechanisms for a copper canister were discussed, including:

- general corrosion;
- localised corrosion;
- whisker growth;
- stress corrosion cracking;
- microbial induced corrosion;
- radiolytic induced corrosion.

As well as the corrosion mechanisms, the transport of reactants towards and corrosion products away from the canister surface was discussed as was the geochemical environment near the canister. Consideration was given both to detailed experimental and modelling studies and to the way these will be represented in the safety assessment.

2.2 Workshop format

The workshop was attended by SKI and SSI staff and external experts covering the full range of issues (see Appendix A for a list of participants).

On the first day, the experts independent from SKB were invited to give presentations covering the background for each of the issues, including their current understanding of SKB's approach to the topic (Appendix C gives extended abstracts of these presentations). The participants split into two working groups, one covering detailed process issues and the other focusing on their treatment in safety assessment. These groups discussed the list of question that had been provided to SKB ahead of the workshop (see Appendix B) and a list of supplementary questions was prepared.

On the second day, SKB and their consultants participated in order to give presentations addressing the list of questions provided. This was followed by an informal hearing with SKB, drawing on the supplementary questions that had been prepared.

In a final session on the third day, the participants discussed the responses that SKB had given, in preparation for the production of this synthesis report. The report has been developed on the basis of the workshop discussions with additional material provided by the participants after the workshop.

It is intended that this report should give a clear overview of the issues involved and that it will be useful for SKI in their reviews of SKB licence applications. Viewpoints presented in this report are those of one or several workshop participants and do not necessarily coincide with those of SKI.

3 The canister in an evolving EBS

Figure 1 shows the dimensions of the canister and deposition hole as well as indicating the relevant features in the EBS (Engineered Barrier System). The canister itself has a minimum 50 mm thickness of copper on the outside. Inside is an iron insert containing the spent fuel bundles.

This section gives a high level discussion of the way the canister and its environment evolve following emplacement. The types of processes of interest are introduced and the way the canister is expected to evolve is described. This will form the background for a subsequent detailed description of the various threats to canister integrity. Note that the workshop and this report focus almost exclusively on the vertical emplacement option. Some mention is made of the option of horizontal emplacement, but if SKB were to switch to this design it would be necessary to re-examine all the issues.

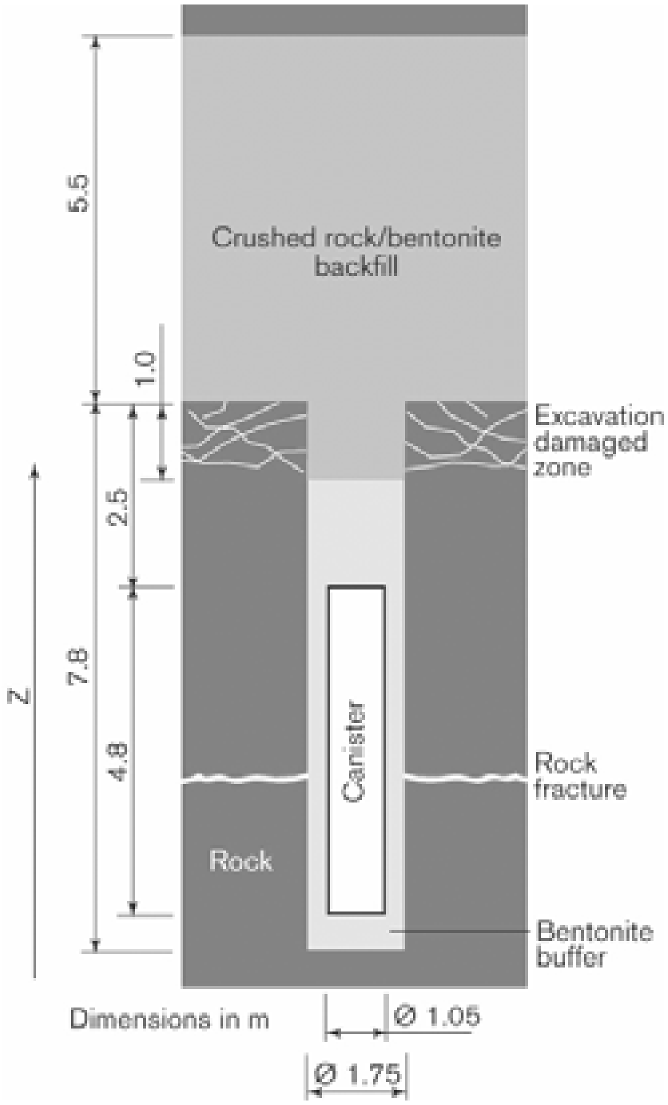


Figure 1. The canister in the EBS (after Hedin, 2004)

While it is intact, the canister provides complete isolation of the radionuclides in the spent fuel. If a canister should fail, other safety barriers come into effect and so the canister is not the sole barrier. It is, however, the primary barrier and its integrity is therefore a key issue in any safety assessment. It should be noted that the regulatory requirements do not insist on presence of such a barrier for long-term isolation in the canister – this is a design decision taken by SKB. Moreover, the regulations are not specific about the time period over which complete isolation of the fuel must be assured – SKB have adopted the design requirement that no known corrosion processes should result in canister failure within at least 100 000 years (Werme, 1998).

Consequently, any loss of integrity of the copper canister would be of key interest. In the current context the focus is on chemical rather than mechanical processes. Another workshop early in 2006 address the mechanical issues. Stress corrosion cracking, where chemical and mechanical aspects act in consort, is included within the scope of the current workshop.

3.1 Corrosion mechanisms

In general, loss of integrity of the copper canister involves an actual loss of copper from the outside of the canister as a result of some reactant reaching the copper and reacting with it to form some soluble species which can be transported away. Such an attack might be general, involving a loss of copper from much or the entire canister surface, or localised, involving loss from only a small part of the surface. Stress corrosion cracking (SCC) could lead to a loss of integrity without a bulk loss of copper, since it can result in small cracks through the copper under particular conditions.

There is also some possibility of corrosion from the inside of the canister, although the fact that the canister is sealed limits the supply of reactants for this.

The design minimum thickness of the copper is 50 mm. If this design target were not met then the degree of corrosion necessary for loss of integrity would be reduced. The most likely location for such problems is the weld, where the canister lid is attached. SKB have stated that the fabrication and inspection process will ensure that no more than 1 canister in 1000 would have a minimum copper thickness at the weld of less than 15 mm. The topic of quality assurance during fabrication was discussed at an earlier workshop (SKI, 2004a).

Metal corrosion is widely studied and types of corrosion are classified by their physical characteristics. Although the same types of physical consequences arise, the detailed electrochemistry of any particular combination of metal and reactant is complex. Nonetheless, some general principles are clear and a key issue for demonstrating the integrity of copper is to show that these apply.

It is worth nothing that the average rate of corrosion required to breach a 50 mm thick copper layer in one million years is 50 nm/y and that detecting such rates experimentally is challenging. The basis for assessment of such slow rates must therefore be an understanding of corrosion mechanisms, rather than empirical measurements.

General corrosion occurs when there is an adequate supply of reactants that can reach the copper surface. A build up of corrosion products might prevent this, so it is necessary for corrosion to proceed either that these are porous (non-protective) or that they are soluble and so do not build up. In a heterogeneous system, general corrosion may occur over a limited area where favourable conditions exist and reactants are most easily accessible.

Pitting corrosion occurs when there is a protective layer of corrosion product over most of the surface, with small breaks in it. This allows a separation of anodic and cathodic reactions and rapid corrosion can occur at the breaks, leading to pits. If the reactions in the pits are such as to maintain the appropriate local conditions then the pits can become significant. Pitting corrosion is strongly controlled by the electrochemical potential as well as requiring particular chemical species to be present. The standard EN ISO 8044 defines pitting corrosion as “localized corrosion resulting in pits, i.e. cavities extending from the surface into the metal”.

In some cases, pitting corrosion is initiated but the pits are not sustained. New pits are constantly formed and the result is like general corrosion but with a rough corrosion profile. Another type of localised corrosion is due to surface deposits and is termed under-deposit or crevice corrosion. In the under-deposit case, corrosion happens because the area under the deposit is anodic to the bare surface. The driving force is oxygen (or other oxidant) concentration difference. The standard EN ISO 8044 defines deposit corrosion (not under-deposit) as “localized corrosion associated with, and taking place under, or immediately around, a deposit of corrosion products or other substance”.

Stress corrosion cracking is linked to pitting. The electrochemical conditions required are similar to those for pitting corrosion. In the appropriate conditions a pit can act as a focus for tensile stresses and as an crack initiation site. As the crack lengthens, and in given conditions, the local chemical dissolution is maintained enabling the process to continue.

Microbes do not cause corrosion directly, but can act to convert otherwise benign components of the system into reactants. Sulphate-reducing bacteria (SRBs) are common in Swedish ground waters and can be expected to be present. They produce sulphide, which is the main general reactant for copper corrosion under reducing conditions.

3.2 Evolution of the EBS

The overall environment around the canister is, of course, not fixed. The EBS goes through a series of phases in terms of the chemical environment. Physical aspects also evolve, either independently or coupled to the chemical evolution. Thus, in order to understand the potential corrosion mechanisms that might be important through the one million year time period covered by safety assessment, it is necessary to consider how the entire EBS and near-field bedrock conditions evolve.

Prior to the time of deposition of a canister in its deposition hole in the floor of a repository tunnel, the tunnel will have been open for some time. Thus the rock surrounding the tunnel will have desaturated and oxygen will have reacted with minerals near fractures or the tunnel wall.

When a canister is placed into a deposition hole, along with its bentonite buffer (in blocks) its outside surface will be close to room temperature. The buffer will not be fully saturated to allow swelling of the buffer after emplacement. There is a small gap between the bentonite and the canister. Soon after canister and buffer emplacement, the length of tunnel above the deposition hole will be backfilled. Details of the backfill material are yet to be finalised by SKB but it is anticipated that clay or a crushed rock and bentonite mixture will be used.

The temperature at the edge of the canister and in the buffer will rise. Water will begin to re-enter the region around the deposition hole and the tunnel. When water reaches the bentonite it will begin to swell. Water may enter from the tunnel or Excavation Damaged Zone (EDZ) above the canister, or from a fracture crossing the deposition hole at some location, or, most likely, from several directions.

As water enters, air must be driven out of the pore space. Oxygen may be consumed in reactions with the canister, bentonite and rock. The resaturation of the buffer may take from a few years to a few decades or even longer depending on the amount of mobile water in the bedrock. During this period, parts of the buffer may be close to being fully saturated while others will have decreased water content. The unsaturated parts may have high levels of water vapour. The fate of microbes near the canister is an essential aspect of the corrosion analysis. They may succumb to temperature changes and to the pressure of the swelling bentonite – this is a topic that will be discussed in detail later in this report.

Eventually, resaturation will be complete and all the oxygen will have been driven out or consumed. The system will become reducing (and corrosion is only possible if reactants other than oxygen are present, such as HS^-). The temperature gradually falls back to ambient. This state is expected to last for most of the one million year time period covered by safety assessment. In this state, there may be a gradual alteration of the buffer due to interactions with flowing groundwater in the near-field rock leading to changing buffer properties. This could change the rate of supply of reactants and the rate at which corrosion products can be transported away. The swelling pressure may reduce.

In very long time scales, climate changes will have an impact on environmental conditions at repository depth. The most significant include permafrost and glacial events. The deglaciation stage may be particularly significant for the conditions at depth, since it might lead to faulting, and dilute glacial melt water intrusion to repository depth.

4 Approach to making a safety assessment

In a safety assessment arguments must be presented to demonstrate that the system will behave satisfactorily. Although the copper canister is not the only safety barrier in the system, SKB plans to demonstrate that canisters will under normal circumstances remain intact for at least 100 000 years and possibly also up to the full assessment time scale of one million years.

SKB will not argue that copper corrosion does not occur. Rather, they will attempt to demonstrate that the degree of corrosion is not a threat to the integrity of a 50 mm thick copper canister (raising the issue of how to measure a corrosion rate less than 50 nm/year). Thus, they will identify potential processes that lead to corrosion and attempt to show that none of them (individually or collectively) could reasonably be anticipated to lead to significant corrosion.

The types of argument that can be made can be classified as: dismiss, bound, realistic analysis, probabilistic analysis. In short,

- dismissing a process is sensible if it can be shown that it can never happen in the repository or that its effect is trivial, e.g. using thermodynamic calculations;
- bounding a process is sensible if the process is complex, but by using unrealistically extreme parameter values, often in a simple model (e.g. based on mass balance or transfer resistance) its effect can be shown to be less than a tolerable degree;
- realistic modelling is sensible when there is sufficient understanding to try to actually predict what will happen in the repository;
- probabilistic modelling is sensible when there is sufficient understanding to develop a model but there is uncertainty (or variability) in the parameters.

Behind the final arguments presented in a safety assessment, there will be more detailed work, both experimental and modelling. Some of this will be specific to the SKB repository while some will be from more general literature on related studies.

The most important supporting work will be the development of an understanding of how a particular process operates and how it links to other processes. Such understanding is crucial in long-term assessments because of the inevitable need to extrapolate from small-scale short-term experiments. It will rarely be possible to demonstrate directly how a process will operate in the repository in an experiment, although analogues can go some way towards this end. Neither will it be possible to demonstrate how a process will operate in the repository by modelling alone. SKB have undertaken analogue work (e.g. Milodowski et al, 2002) but this was not mentioned in their presentations and it is unclear how this will be used to support the safety case.

Ideally, one would like to have experimental support, understanding and detailed modelling behind each argument. It is also important to be careful not to take a lack of evidence for something as if it is evidence against. Some processes may occur too slowly to be seen experimentally or may require rather precise conditions.

In some cases, one may believe that an argument is true without quite having sufficient evidence to back this up. A “what-if” calculation can then be useful in showing the implications of being unable to sustain the argument.

The most common approaches used by SKB to date for issues in copper corrosion are to dismiss or bound. Sometimes the bounding argument leads to a trivial result, which then makes it equivalent to dismissing.

Arguments to dismiss a process are generally made on the basis that it is sufficiently well understood that a set of prerequisites can be identified. It is then argued that one or more of these prerequisites cannot occur in the repository. Examples of arguments to dismiss have been presented for various forms of localised corrosion. Particular care must be taken in making these exclusion arguments to recognise the potential for heterogeneous conditions – the fact that a prerequisite is not met on average is not a sufficient argument, it must not be met anywhere at any time.

Bounding arguments are generally easy to make as they often rely on a very simple model. This strength can also be a weakness since the model may be overly simple. For example, when a mass balance argument is used then the target area for damage is crucial – the average loss rate is not important but the maximum local rate is the key issue.

5 Processes and features related to canister copper corrosion

In Section 3, a general overview was given of the processes of interest for corrosion and for the development of the environment in which corrosion can occur. The arguments that SKB will put forward for this essentially take the form of analyses of potential threats to the canister integrity. The aim is to dismiss each threat through a combination of experimental demonstration and understanding. The types of arguments that can be made were discussed in Section 4.

By a threat, we mean a process or feature that can directly or indirectly lead to a loss of integrity or at least to a significant contribution to such. Each threat must be addressed and treated in some appropriate way in a safety assessment.

In this section, we list some specific threats and discuss them in some detail. The list of threats forms the basis on which SKB's presentations at the workshop were discussed. The conclusions reached through those discussions are included here. Table 1 lists the threats and indicates the times during the evolution of the EBS when they may be relevant. Mechanical effects are not considered here except where explicitly linked to corrosion as in stress corrosion cracking.

Table 1. Threats to be considered for the evaluation of canister corrosion.

Threat	**Time frame in EBS evolution of main relevance**	**Description**
Oxygen	Initial phase and possibly glacial	Rapid reaction of oxygen with copper with formation of copper oxides
Chloride	Throughout	Complexation with copper ions
Sulphide	Throughout	Reaction with copper by reduction of water and formation of copper sulphides
Nitrogen compounds	Initial phase	Ammonia and nitrite are along with acetate most important agents facilitating stress corrosion cracking Nitric acid is an aggressive reactant formed by radiolysis in the interior of the canister
Microbes	Throughout	Microbes catalyse otherwise relatively slow inorganic processes, such as consumption of oxygen and reduction of sulphate
Surface salt	Resaturation phase	Evaporation of water on canister surface leading to accumulation of salt deposits in micro-environments on the canister surface
Sulphide whiskers	Reducing phase	Rapid formation of whiskers on copper surfaces during pitting corrosion
General corrosion	Oxygenated phase (by O_2) Reducing phase (by HS^-)	Uniform thinning of the canister wall
Pitting corrosion	Initial and resaturation phases	Localised attack with persistent pits under oxidizing conditions. Also general rough corrosion caused by unstable pit formation. Uneven swelling of bentonite might lead to under-deposit corrosion.
Stress corrosion cracking	Initial phase and possibly glacial	Cracking at tensile parts of canister wall
Radiolysis and radiation influenced corrosion	Initial phase	Creation of locally oxidizing conditions due to gamma radiation field
Galvanic coupling	Early inside canister and after canister failure	Different potentials for iron and copper in presence of water lead to corrosion. Earth currents leading to external corrosion
Environmentally controlled creep	Throughout	Corrosion might influence creep and result in creep failure

5.1 Oxygen

The presence of oxygen during the handling and deposition of a canister as well as during the early phase of repository evolution will lead to some copper corrosion. SKB stated that corrosion rates with unlimited oxygen in a high temperature humid atmosphere could be as great as 100-300 μm/year. However, a normal corrosion rate in oxygenated natural waters is a few micrometer/year (1 μm/year means that the canister is penetrated in 50 000 years). The corrosion during the handling stages with unlimited oxygen access need to be addressed with a well justified corrosion rate in air at temperatures around 90°C. Under expected conditions of more limited oxygen access within the repository (e.g. a smaller amount of oxygen compared to approx. 8 ppm O_2 for groundwater in equilibrium with air) corrosion rates are expected to be lower.

SKB's analysis of corrosion by oxygen after canister emplacement is based on mass-balance arguments rather than corrosion rates. Since the sealing of deposition holes and tunnels will probably restrict the oxygen access after disposal, total amount of corrosion by oxygen will depend on the amount left in tunnels after the sealing stage. It can be conservatively assumed that all this oxygen reacts with copper (other reductants of oxygen in the bentonite and bedrock are in reality likely to be more accessible than the copper). The available amount of oxygen for each canister needs to be bounded as part of this argument. The basis for an estimated amount of 30 m^3 O_2 (SKB 1999b, Section 3.7.5) appears to be an equal allocation of air in the tunnel system to each canister. This volume of oxygen corresponds to about 1220 mol O_2. The following conversion to cuprous oxide is assumed:

$$2Cu + \frac{1}{2}O_2(g) \rightarrow Cu_2O$$

A conservatively assumed consumption of all oxygen by oxidation to Cu(I) would correspond to about 2 mm of corrosion of the canister wall. This corrosion during the oxidizing phase is in reality likely to form a cuprous/cupric oxide film on the copper surface of a canister (Cu_2O/CuO). Presence of such a film may influence the subsequent corrosion behaviour of the canister (pitting corrosion and SCC) and its role and subsequent fate must be understood. Especially, the persistence of such a film after establishment of reducing conditions needs to be analysed.

The workshop participants agreed that SKB's approach for handling the oxidizing phase seemed reasonable, but wished to have a more detailed justification for the amount of oxygen allocated for each canister. There is a lot of additional oxygen potentially available in the open parts of the repository during long time periods (after sealing of deposition tunnels) and the arguments as to why this cannot reach the canisters needs to be clearly stated. It may be that the bounding argument in this case cannot be sustained and that a more realistic assessment of the fate of oxygen during this phase will be needed, e.g. by considering oxygen diffusion and rates for various processes which may contribute to oxygen consumption.

The workshop participants felt that SKB need to better justify how corrosion would be distributed on the canister surfaces during the early phase. In this oxidizing environment, pitting corrosion may be correlated with surface defects. Even in a case when pitting corrosion could be ruled out, there is no apparent reason to believe that the corrosion would be exactly uniform across the canister. The distribution of corrosion needs to be taken into account – for example between the lid and the sides, but also near block boundaries in the bentonite buffer where the oxygen might enter.

5.2 Chloride

Chloride forms strong complexes with Cu(I) and therefore facilitates mass-transfer limited corrosion near the canister-bentonite interface. Figure 2 shows a conceptual model for general corrosion of copper, which focus the role of chloride and kinetic redox processes in an oxic environment. General and localised corrosion of copper will be much decreased when the oxygen is being depleted. General corrosion may to some extent be decrease with increasing chloride concentrations even if oxygen is present, which may be related to the kinetics of the copper redox speciation and the Cu(II) sorption on bentonite (King et al, 2001).

The chloride concentration will initially be low and determined by the bentonite pore-water. Subsequent inflow of the surrounding groundwater with reasonably well-known composition will tend to increase the chloride content in the near field (commonly measured concentrations at repository depth are up to 5000 mg/l for coastal sites). In extremely long time-scales, the chloride content can vary greatly due to climate evolution with possible occurrences of very high and very low levels. The safety assessment must therefore be able to account for canister corrosion in a wide range of chloride concentrations.

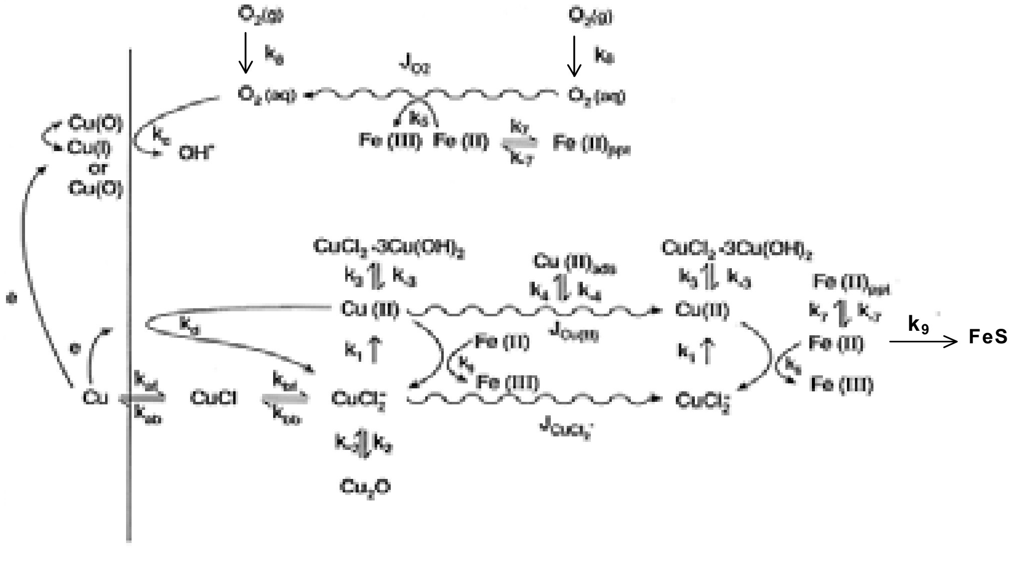


Figure 2. Schematic illustration of processes involved in the corrosion of copper in saline O_2-containing groundwater (King et al, 2001).

Pitting corrosion of copper in the presence of chloride has many practical implications such as use of copper pipes and is therefore reasonably well investigated and understood (see Pourbaix, Appendix C). Localised corrosion of copper is generally considered to be promoted by chloride. It has been shown also that the propagation of pitting of copper is impossible below a certain potential. This potential does not depend much on the bulk chloride concentration. Anoxic conditions most probably lead to such low potentials, where pit propagation in not possible. Long-term tests have shown that large amounts of chloride ions may promote active dissolution rather than localised corrosion. It has been suggested that canister exposed to saline groundwater will be more exposed to general corrosion and less susceptible to stress corrosion cracking.

The general corrosion of copper in saline environments could in the absence of oxygen proceed by reduction of protons according to:

$$Cu(s) + H^+ + nCl^- \rightarrow \tfrac{1}{2}H_2(aq) + CuCl_n^{(1-n)}$$

There is a lack of experimental data relevant for this mechanism, but thermodynamic calculations suggest that this reaction would only be significant for very high concentrations combined with unrealistically low pH values. SKB will therefore argue that it can be dismissed. Considering that it may not be possible to rule out scenarios that include highly saline groundwater in contact with canisters, more experimental work might be needed to support the evaluation of this corrosion mechanism.

It has been suggested that high chloride concentrations could be produced by a “percolator effect” and this needs to be addressed. Indeed, in the Ophélie experiment in Belgium about 1 g/l chloride was observed when bentonite blocks were saturated with a simulated groundwater. This was attributed to “percolation”: even when the chloride content of the bentonite is small, the percolating water becomes more and more concentrated.

5.3 Sulphide

Dissolved sulphide is perhaps the most essential reactant for copper canisters, since it continues to be relevant for the long-term reducing phase after depletion of available oxygen. The reaction proceeds by reduction of water and formation of sulphide minerals more stable than elemental copper under expected repository conditions, such as chalcocite, Cu_2S, and covellite CuS:

$$2Cu(s) + HS^- + H^+ \rightarrow Cu_2S(s) + H_2(g)$$

General corrosion with the accessibility of dissolved sulphide as the rate-limiting factor has been suggested as the main corrosion mechanism of copper canisters in previous safety assessments (SKB, 1999a). The low concentrations of dissolved sulphide encountered under relevant groundwater conditions were found to be of a key factor for the conclusion that this corrosion mechanism will not seriously jeopardise the long-term integrity of the KBS-3 barrier system. It is doubtful whether a Cu_2S-surface film formed on the canister surface would be sufficiently protective to play a role in the safety assessment timescale.

SKB reported that more recent modelling results suggest that only sulphide present in the buffer (mainly as an impurity in the form of pyrite, FeS_2) would react with the copper canister. This reaction would proceed until all buffer sulphide was depleted. If sulphide concentrations are controlled by pyrite solubility, the average general corrosion would be less than 1 mm during the period covered by safety assessment of 1 million years. However, corrosion at the lid surface would be faster (Hedin, 2004). After depletion of available buffer sulphide, SKB suggested that continuing corrosion by sulphide from the groundwater would always be slower.

Workshop participants were doubtful whether pyrite could always be assumed to exhibit effective solubility control of dissolved sulphide within the buffer. It has to be considered that groundwater may be oversaturated with respect to pyrite and that HS^- concentrations may be closer to equilibrium with meta-stable pyrrhotite (FeS). Moreover, the significance of other sulphide minerals (e.g. Fe_3S_4), polysulfides, dissolved H_2S (g) and sulphur of intermediate redox state ($S_4O_6^{2-}$, $S_2O_3^{2-}$, SO_3^{2-}) need to be assessed and separately described in future safety assessment work. SKB is recommended to in more detail investigate the importance of various forms of sulphide in the groundwater, e.g. by utilising information from the ongoing site investigations.

The suitability of placing a sulphide source (e.g. MX-80 containing sulphide sulphur of about 0.3%) directly adjacent to copper canisters was debated among workshop participants. In this context, it should also be recognised that the reduction capacity of the bentonite sulphide source makes a significant contribution to the potential for oxygen consumption within the repository. In order to assess these two contradicting aspects of the buffer sulphide content, characterisation of bentonite sulphide sulphur and other possible reducing minerals will be essential, especially since the content of trace constituents may vary considerably.

The workshop participants suggested that SKB's conceptual and mathematical model for general corrosion by sulphide should be reviewed in detail as part of future safety assessment reviews (and especially the justification for the assumed maximum corrosion rates 7 times faster than the average rate; Hedin, 2004).

5.4 Nitrogen compounds

The nitrogen compounds nitrite (NO_2^-) and ammonia (NH_4^+) are together with acetate (CH_3COO^-) the only known agents which promote stress corrosion cracking (SCC) in the repository environment. The concentrations of these species are under normal circumstances expected to be low in the repository environment, but it may be difficult to rule out local spots with sufficiently high concentrations. These may originate from residual material from construction and operation, in addition to the natural traces of nitrogen compounds. It should also be considered that concentration of these species may also be influenced by microbial processes.

The workshop participants expressed the view that uncertainties connected with concentrations of ammonia seemed to be more significant than those for nitrite or acetate. Although considered an unlikely failure mechanism for copper canisters, it may be hard to rule out SCC based on SCC agent concentration. Moreover, it must be considered that all the mechanisms involved in SCC are not yet well understood and that other unknown SCC agents could exist. SKB is therefore recommended to consider what-if calculations including SCC canister failure. Additional analysis of other factors affecting SCC might also be needed (e.g. stress, crack growth rate, temperature).

Nitric acid is an aggressive reactant but SKB argues that it cannot be formed in significant quantities. The most likely mechanism for the formation of nitric acid is via gamma irradiation of humid air and radiolysis. With SKB's increased assumption of the maximum amount of water that may be present in a canister, there is potential for a non-trivial amount of nitric acid to be created if nitrogen is present. For this reason, SKB have modified the encapsulation design to ensure a nitrogen-free atmosphere.

The amount of nitric acid that can be formed outside the canister has been estimated by scoping calculations and is too small to have any significant impact (SKB, 1999b).

5.5 Microbes

Microbes may have highly significant geochemical effects in the repository environment due to their ability to catalyse otherwise kinetically slow redox-processes. Work by Pedersen and co-workers has shown that microbes are much more active in the deep bedrock than previously assumed (Pedersen, 1993). Microbes will survive even in extreme environments (e.g. radiation, high temperatures), but their activity is dependent on sources of energy, carbon, nutrients as well as a sufficient quantity of water. As pointed out by Hallberg (Appendix C), in spite of recent progress our understanding of microbes is still limited since research has only covered a small fraction of all existing microbial populations.

Field investigations have shown that microbes may under certain conditions be able to consume oxygen at a faster rate than inorganic processes (e.g. Banwart, 1995). If this assertion can be supported to a sufficient extent, microbial activity may be used as a beneficial process in safety assessment. If accounted for it could reduce the initial time period with canister corrosion by oxygen. However, microbial activity by sulphate reducing bacteria may increase the availability of sulphides in the repository environment and therefore promote copper corrosion by formation of copper sulphide (see Section 5.3). A third role of microbes, which has been analysed within the Canadian repository programme, is their influence on concentrations of nitrogen containing SCC agents.

SKB have performed a series of experiments to look at microbe survival in simulated repository conditions. The activity of sulphate reducing bacteria (SRB) was measured in bentonite samples by using radioactive sulphate ($^{35}SO_4^{2-}$). Microbial activity was shown to decrease with increasing bentonite density, swelling pressure and temperature. Measured rates of Cu_2S production imply a microbial induced corrosion rate of less than 1 mm for the full safety assessment period of 10^6 years for a bentonite density of 2 g cm^{-3}. This work is still ongoing and will be used as a basis for handling of SRBs in the SR-Can safety assessment. SKB will argue from the results of this experimental work that the temperature, low water activity and swelling pressure in the early phase are sufficient to limit microbial activity and that the small pore size ensures that new microbes cannot enter the bentonite later.

The detrimental role of the SRBs is to increase availability of sulphide by utilising a more rapid mass transfer rate of sulphate (since sulphate is available in higher concentrations). The reduction of sulphate, catalysed by sulphate-reducing bacteria, is the key control. The overall reaction can be written as:

$$SO_4^{2-} + CH_4 + H^+ \rightarrow HS^- + CO_2 + 2H_2O$$

The corrosion rate is therefore ultimately limited either by the supply rate of sulphate or by the supply of methane to the bacteria. In addition, it might be limited by the rate at which sulphide can be transported to the canister.

A key issue is therefore how close to the canister the microbes can be active. At early times microbes could e.g. be active in the slot between the canister and the buffer. However, more relevant is their longer-term survival after the sealing of this slot by buffer swelling. As long as the buffer density and swelling pressure remains constant, pore spaces may be too small for any movement of microbes. There is a need to address whether or not localised populations of bacteria could survive near the canister surface and lead to a localised attack at some subsequent stage. If this can happen then it is difficult to construct arguments based solely on mass balance.

Hallberg (see Appendix C) reviews the current SKB approach which suggests that microbes cannot survive inside the bentonite or at the canister surface. He is of the opinion that ruling out microbes completely for the full safety assessment period may be too optimistic – they have many survival mechanisms, some not completely understood, which mean that they may survive in a dormant state to become active again if conditions become more favourable. SKB is recommended to be careful in the interpretation of microbial viability from small-scale lab experiments, since microbes cultivated during an exponential growth phase can be expected to be sensitive to environmental conditions. They may therefore appear more fragile during experiments as compared to in-situ conditions.

The workshop participants recommended that SKB should analyse how important their assertion of zero microbial activity in the buffer could be, given that microbial activity will under repository conditions be dependent on whole range of other factors (energy supply, carbon source, nutrients etc.). An example of this is what would be the consequence of sulphate reduction being limited by the available carbon sources for microbes rather than microbial viability in general. Recent work by Liu and Neretnieks (2004) to some extent addresses this issue.

5.6 Surface salt

SKB raises the issue of water boiling on the canister surface leaving a salt deposit. This might allow formation of a microenvironment under this deposit that could be a site for corrosion. This possibility is used as a reason for limiting the maximum temperature at the canister surface to 90°C (SKB, 2004).

It was felt that the explanation offered by SKB currently in SKB (2004) was not clear and that an improved discussion was required in SR-Can.

5.7 Sulphide whiskers

Hermansson (see Appendix C) reports the observation of whiskers growing on the surface of copper in the presence of constant concentrations of sulphide. These whiskers form rapidly over a period of just a few days during lab experiments in small vessel kept in glove boxes with a nitrogen atmosphere. Whisker formation is associated with a rapid rise in electrochemical potential in the experiment. They are composed of copper oxides and sulphides, with oxide in the layer closest to the copper surface. Examination of the copper surfaces after termination of the experiments suggests that whisker formation is related to position of localised surface attack. Thus, there is a potential for localised attack by whisker formation that needs to be considered. Hermansson recommends further study of the phenomenon in similar experiments also including bentonite.

SKB have reviewed the Hermansson work and concluded that the processes seen are most likely a consequence of contamination by oxygen. Even if best endeavours have been taken to work in an oxygen free environment it is notoriously difficult to achieve this in laboratory experiments. Oxygen contamination in the experiments by Hermansson and Gillén are most likely manifested by an increase in the corrosion potential and a colour change indicating the presence of Cu(II). In the repository environment, the corrosion potential is expected to decrease monotonically and to remain at a negative value indefinitely. SKB argues that the whiskers are a consequence of pitting corrosion rather than the cause for it. If the explanation of oxygen contamination is accepted, then this type of mechanism would only be possible in the simultaneous presence of sulphide and oxygen. Nevertheless, the experiments show that only minute concentration of oxygen would be needed for whisker growth. SKB further suggests that whiskers would in any case not occur in the presence of bentonite.

SKB is currently in collaboration with POSIVA performing similar experiments on copper corrosion in the presence of sulphide at the University of Western Ontario. A conclusion based on experiments conducted so far is that control of the atmosphere within experiments is of crucial importance for experimental results.

5.8 General corrosion

General corrosion depends on the rate of electrochemical reactions, formation of surface films and mass transfer rates. The result is a uniform thinning of the metal thickness. General corrosion of copper will occur to some extent both under oxidizing and reducing conditions, even if copper is usually assumed to be resistant to corrosion in an oxygen free environment. Aromaa (see Appendix C) states that uniform corrosion occurs in the atmosphere and in the presence of drinking water or seawater with rates up to 50 μm/year in extreme cases, with more usual corrosion rates being 1-5 μm/year (see Section 5.1).

General corrosion of copper in oxygen tends to decrease with increasing pH and alkalinity and results in cuprous/cupric oxide films, which will tend to gradually reduce the corrosion rate. The limited degree of general corrosion under reducing conditions is a result of the presence of small amounts of sulphide in the pore-water close to the copper surface. The sulphide corrosion of copper is accompanied by hydrogen formation (see Section 5.2).

Measurement of corrosion rates during experiments and application of those rates in safety assessment is a problem due to the long time scales involved. A corrosion rate of 1 µm/year will penetrate the canister in 50 000 years, while corrosion rates in this range are in other contexts often considered not to be significant. A corrosion rate of 50 nm/year means a corrosion current density 5 nA/cm^2. Modern electrochemical equipment is capable of measuring such low currents but in many cases electric noise and background currents from the electrolyte impurities produce higher currents. It can therefore be questioned if SKB can verify that no corrosion reaction will happen based on this approach. The use of thermodynamic calculations will provide a basis for excluding some reactions, but kinetic data would still be needed for reactions that cannot be excluded on thermodynamic grounds. Some experimental data has been presented (King et al, 2001), but the variation between different tests can be orders of magnitudes. For this reason, it is problematic to incorporate kinetic data in corrosion models for long-term safety assessment. Clearly, it would be beneficial to find suitable natural analogues.

SKB's handling of general corrosion in the forthcoming SR-Can safety assessment will be based on transport rates and simple mass balance calculations, with all reaction rates conservatively neglected. The three main sources of reactants will be considered: 1) initially entrapped oxygen, 2) sulphide from pyrite in bentonite, 3) sulphide in groundwater. Preliminary calculations suggest that the accumulated corrosion from these sources would be much less than the total canister thickness of 50 mm. However, the total initial copper coverage would at some spots on the canister surface be smaller than 50 mm due to the presence of weld defects such as cracks. SKB have made a preliminary assumption that one canister in a thousand has a coverage randomly distributed between 0 and 15 mm (with a uniform probability density). These conditions suggest that general corrosion could not be ruled out as a corrosion process causing canister failure, but that the probability of failure would be less than one defective canister (of 4500 in total) for 10^6 years. Future work includes the incorporation of more realistic distribution of weld defects, extension to a fully probabilistic framework and a more comprehensive evaluation of other relevant input data.

Future postglacial climate states will most likely include periods of elevated groundwater recharge. For conditions of very high flow rates, the rates of oxygen scavenging reactions in the bedrock may not be sufficient to prevent oxygen from reaching the repository depth (Guimerà et al, 1999). To account for this possibility, SKB presented preliminary calculations based on general corrosion, which showed that a copper canister would just barely be penetrated after 10^6 years, even with the unrealistic assumption that oxygen consumption by the bedrock is completely ignored with full oxygen availability during the entire period.

The workshop participants suggested a need for a more comprehensive review of SKB's model for general corrosion of copper canisters, which should involve computational issues as well as supporting assumptions and data. The following factors deserve special attention:

- Environmental conditions, especially sources of reactants and sinks of reaction products (sulphide and oxygen)
- Microbial activity and the role of sulphate reducing bacteria in various parts of the system
- Implications of realistic weld defects

- Uneven distribution of general corrosion on a macroscopic scale due to mass transfer effects.

SKB's analysis of sources of sulphide and oxygen seemed incomplete at the time of the workshop. It is presently difficult to assess whether or not all assumptions and selection of data are conservative. SKB is recommended to more fully describe the environmental factors and their expected variability, e.g. sulphide chemistry of relevant groundwater types and bentonite composition.

From the point of view of available reactants, the most critical factor in SKB's assessment seems to be the assertion that microbial viability will be zero within the buffer for the full assessment period. SKB is therefore recommended to include a thorough assessment of this aspect of the buffer performance in SR-Can. Moreover, it would be useful to analyse the consequences of microbial sulphate reduction within the buffer even if there is a sound basis for assuming that such microbial activity should not take place. If sulphide is only produced by SRBs in the groundwater outside the bentonite then consequences for the canister lifetime would be more limited. This case has recently been analysed by Liu and Neretnieks (2004).

5.9 Pitting corrosion

Pitting corrosion is usually related to formation of non-continuous, non-protective surface films. The essential film properties are affected by the chemical conditions and the film growth rate. A pH in the interval 7.2-9.0 and high alkalinity are favourable conditions for avoiding pitting corrosion of copper, whereas high chloride and sulphate may aggravate pitting corrosion. Classically pitting corrosion is extremely localised corrosion due to cathode-anode separation on a small scale. In such cases, deviating acidic chemical conditions exist within the microenvironment of the pits. The progressive pitting corrosion can be autocatalytic – i.e. the process is self-sustaining and the rate will not necessarily decrease as a function of time.

Pourbaix (see Appendix C) reviews the current state of knowledge in the area of pitting corrosion. He points out some differences between SKB's views about localised corrosion (e.g. Taxén, 2002) and CEBELCOR views, e.g. that important mechanisms of the "occluded cell" have been underestimated in SKB's studies. SKB is recommended to review utilised criteria for pitting corrosion based on these differences. At a more basic level, there is a consensus on key aspects of pitting corrosion, e.g. concerning the existence of a critical potential below which pits do not grow. The latter is of key concern for a KBS-3 type of repository in which anoxic conditions are expected to be established some years after the sealing of tunnels. Pitting corrosion in the presence of chloride has been studied extensively, since it is of importance for the corrosion of copper pipes in certain types of water. However, there is less information about pitting corrosion in the presence of sulphide.

SKB presented an experimental study of copper corrosion under simulated repository conditions during the early oxidizing phase. Examination of the corroding surface suggests that no classical pitting had taken place, since there appear to be no permanent separation of anodic and cathodic sites. Rather, it is under-deposit corrosion, which arises when pits start, but die and then start elsewhere. As is shown in Figure 3, the

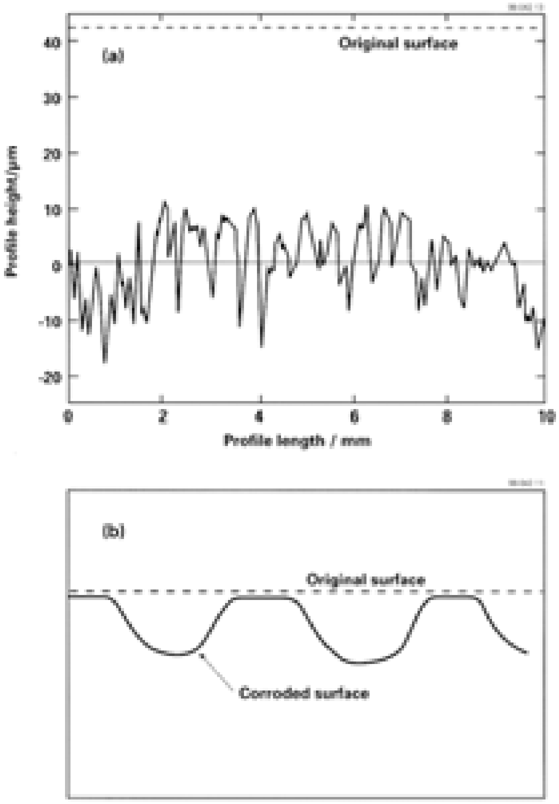


Figure 3. Comparison of surface profiles expected for pitting and under-deposit corrosion. The picture at the top a) shows the expected corrosion behavior of KBS-3 canisters in oxidizing conditions with a small pit-depth in relation to the overall corrosion, which is contrary to a typical pitting corrosion profile b) (source: SKB workshop presentation).

effect is to get a rough surface but with a general corrosion behaviour. Various analyses have been performed and the conclusion is drawn that overall corrosion depths are limited to a few tens of µm. It is important to be able to explain these observations, since under-deposit corrosion is a mechanism that under unfavourable circumstances can lead to penetration of potable water pipes in few months.

The maximum pitting factor is 1.45 in these experiments, while a pitting factor between 2 and 5 have been used in previous safety assessments. However, the use of a pitting factor (maximum penetration depth divided by average penetration depth) to characterise pitting or under-deposit corrosion does not seem particularly helpful in the situations of interest – there is an inverse correlation between the pit depths and the overall degree of corrosion. The pitting factor will typically decrease with increasing depth of corrosion. It is simpler to consider the average penetration depth due to roughening and the additional penetration depth caused by pitting.

SKB presented various approaches for predicting localised corrosion on copper canisters:

- Pitting factor approach
- Extreme-value analysis of pit-depth data
- Comparison between corrosion potential (E_{corr}) and the pitting breakdown potential (E_b)
- Stochastic under-deposit corrosion model

The two former approaches can be regarded as very conservative, since they do not account for the possibility of pit death but rather assume that pits propagate indefinitely. Regarding the third approach, SKB's predictions of the corrosion potential suggest that it will initially be higher than the pitting breakdown potential E_b, but eventually the potential will stabilise at least 250 mV below (see Figure 4). At present, there is apparently no relevant application of the final approach, i.e. the stochastic under-deposit corrosion model.

The workshop participants agreed that pitting corrosion most likely could be ruled out for the long term reducing phase of the repository evolution. However, the determination of the pitting breakdown potential and of the threshold potential for pit propagation for different water compositions is less clear. There is a need for the understanding of the electrochemical controls in this work – at present some of the explanations seem implausible. It is debatable whether the threshold potential coincides with the Cu_2O/CuO equilibrium potential. Moreover, it would be helpful if the mechanisms that may be involved in localised corrosion within a chemical environment including both sulphide and chloride would be further analysed.

To avoid confusion in the discussion of corrosion potentials consistent use of reference electrodes in diagrams (e.g. SCE (Saturated Calomel Electrode) or SHE (Standard Hydrogen Electrode)) should be used.

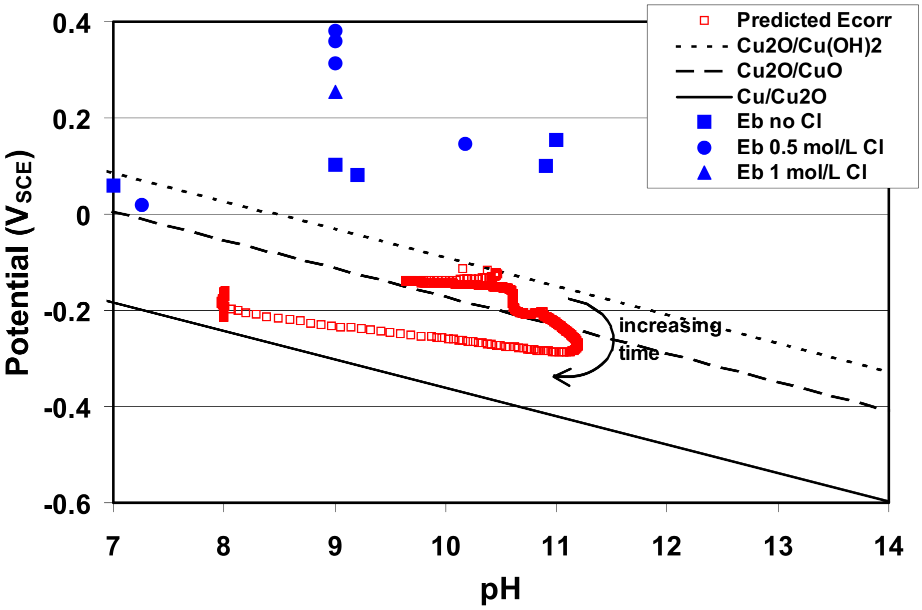


Figure 4. Predicted evolution of the corrosion potential with time. The comparison with the pitting breakdown potential is made by assuming that it coincides with the Cu_2O/CuO equilibrium potential line. The corrosion potential is initially above the Cu_2O/CuO equilibrium potential line but stabilises well below for subsequent stages (source: SKB workshop presentation).

5.10 Stress corrosion cracking

The occurrence of stress corrosion cracking (SCC) is dependent on three particular circumstances: tensile stresses (external loads or residual stresses); a susceptible material; and an aggressive chemical environment (King et al, 2001). All of these three circumstances could in principle be fulfilled for an emplaced KBS-3 copper canister, so SCC cannot be considered as a completely infeasible failure mechanism. There are three known agents that promote stress corrosion cracking: nitrite (NO_2^-), acetate (CH_3COO^-) and ammonia (NH_4^+; see 5.4). According to available knowledge, at least one of them needs to be available in sufficient concentrations. In addition, SKB suggests that the corrosion potential and pH must be such that formation of a Cu_2O/CuO film is thermodynamically feasible (similar criterion as used for the handling of pitting corrosion; see 5.9). In other words, SKB do not expect SCC to occur once reducing conditions has been established within the repository environment. Other factors include high chloride concentrations, which are claimed to have an inhibitive effect (presumably due to its influence on film stability). In addition the initially elevated canister temperature will reduce SCC susceptibility, due to increased general corrosion and an increased threshold potential . In King et al (2001), it is suggested, as an additional argument against SCC, that the creep behaviour of the copper canister will tend to relieve the crack-tip stresses before any extensive SCC.

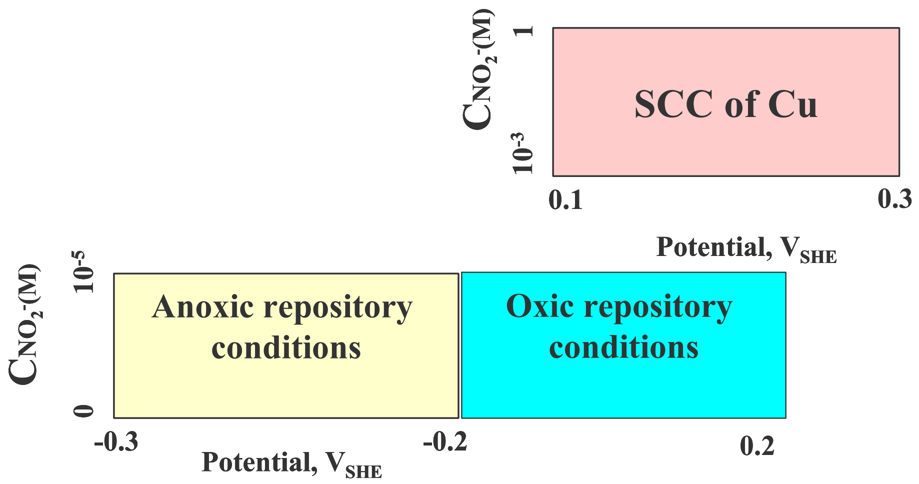
Saario (see Appendix C) discusses the crack growth rate and exclusion approaches for handling SCC in safety assessment. The first approach would involve concluding by measurement that the crack growth rate is too slow to cause canister failure. The problem here is that crack growth rate can only be measured down to about 10^{-8} mm/s, while a precision down to 10^{-12} mm/s would be required for being able to confidently ruling out SCC for the entire safety assessment period of 10^6 years. Indeed, if SCC were measurable in the laboratory it could compromise canister integrity in a few hundred years. For this reason Saario suggests application of the second “exclusion principle” approach. This involves the plotting of all available SCC data in a SCC agent concentration – potential diagram.

Figure 5 shows “exclusion principle” plots for nitrite and ammonia. No overlap suggests that SCC can probably be excluded provided that sufficient data is available. However, an overlap suggests that SCC need to be considered in more detail through further experimental studies and/or in safety assessment. The results in figure 5 suggest that SCC is only possible in the early oxygenated phase and that ammonia is the most significant complexing agent. A more detailed analysis of other factors affecting SCC would thus be needed, as well as more detailed studies concerning the sources and reactions involving ammonia in the repository environment.

SKB acknowledge that tensile stresses will be present in some parts of the canister and so this does not form part of the argument. However, SKB intends to dismiss the possibility of SCC in safety assessment based on the primary criterion of sufficiently low redox (which is related to the Cu_2O/CuO film stability) as well as low SCC agent concentrations (ammonia, nitrite, acetate). Moreover, additional arguments in support of neglecting SCC include unfavourable temperature and chloride concentrations for SCC.

Workshop participants agreed that SCC seemed to be an unlikely failure mode for copper canisters, but suggested that the data and mechanistic understanding which provides the basis for ruling out SCC should be further scrutinised. Moreover, the sources and reactions affecting ammonia concentrations may need to be assessed in greater detail.

a)



b)

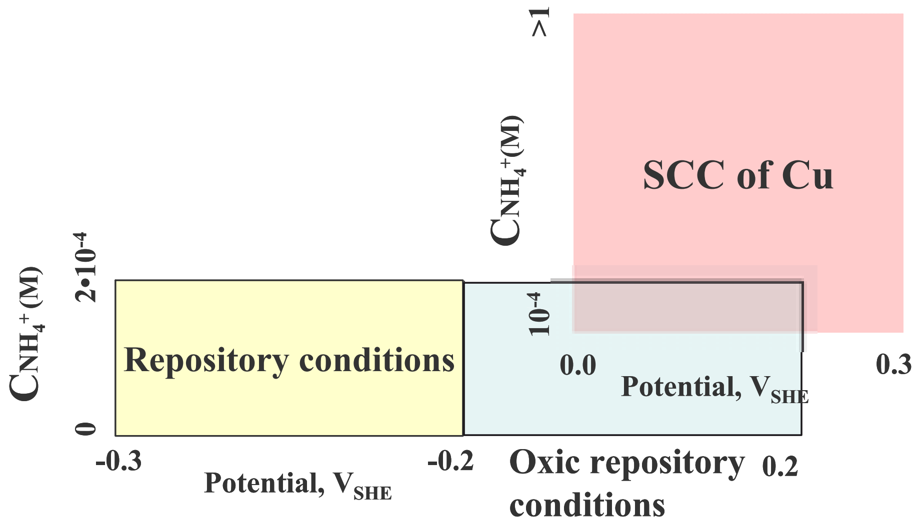


Figure 5. Assessment of likelihood of stress corrosion cracking (SCC) for a) nitrite and b) ammonia by application of the exclusion principle (Saario, see Abstract C). These figures show the concentration of SCC agent (Y-axis) plotted against potential (X-axis). In figure b) there is an overlap between the areas of possible SCC and the repository conditions, which suggest that SCC with ammonia needs to be further studied.

5.11 Radiolysis and radiation influenced corrosion

Radiolysis produces oxidants and reductants (ions and radicals) in radiation fields, e.g. due to decomposition of water molecules. Because reductants such as hydrogen are relatively inert and mobile, oxidizing conditions may develop in local environments. This can occur inside the canister or just outside through the effects of gamma energy mainly from decay of ^{137}Cs, which must be considered in the analysis of canister integrity. SKB suggests that the period of appreciably elevated dose rates coincides with the initially oxidizing phase in the repository environment.

Kyllönen (see Appendix C) points out that special consideration needs to be given to the outer surface of the copper where electrons generated in the copper provide a significant contribution to the dose. Attenuation calculations have been conducted using the MCNP 4C code. The results suggest that the dose just adjacent to the copper surface is considerably elevated compared to the dose in the bulk water phase. SKB suggested that the total energy available for radiolysis is the most important entity and that this would not be critically dependent on surface effects.

SKB have studied the effect of gamma radiation on copper and cast iron corrosion. Copper corrosion was studied in dose rates ranging from 13 Gy/h to 1000 Gy/h. At the lower range, which is the most relevant for the expected conditions, corrosion of copper was proceeding at a lower rate compared to conditions without radiation. Analysis of Cu-profiles indicated that irradiation promoted the formation of Cu(I)-species rather than Cu(II). SKB suggests that the reduction in corrosion rates may be explained by a more protective surface film formed on the samples exposed to gamma radiation. In any case, the radiation dose is relatively short lived and the net effect seems to be of low significance.

SKB have also studied radiation-induced corrosion of cast iron under reducing conditions, relevant for the interior of a canister. Experiments were conducted in doses of 11 Gy/h and 300 Gy/h with temperatures of 30°C and 50°C. SKB concludes that the cast iron corrosion rate is increased by 10-30 times due to the radiation fields (Smart and Rance, 2005). For repository conditions, the average effect would be small considering that corrosion will anyway be limited by the small amounts of available water within each canister. However, the potential for local effects may need to be further analysed. SKB now consider that up to 600 g of water may be present in each canister, based on an assumption of one failed fuel pin per canister. The main corrosion product during the experiments was magnetite, but there were also higher oxidation state oxyhydroxides for the highest dose rates.

5.12 Galvanic corrosion

Galvanic corrosion within the canister due to the simultaneous presence of the iron and copper components in contact is a potential corrosion mechanism, which has to be addressed. Nevertheless, since the galvanic coupling is mainly relevant when the integrity of a canister has been lost anyway, galvanic corrosion needs to be considered when addressing the continued evolution after canister failure. SKB reported recent experimental work on galvanic corrosion with bullet shaped electrodes of iron and copper (Smart et al, 2005). Although galvanic corrosion rates were initially higher, deaeration led to a pronounced decrease in the corrosion rate of iron. The corrosion rates of iron in deaerated conditions were not significantly different from those measured in the absence of galvanic coupling. This will form the basis of an argument to dismiss the process.

An issue of the galvanic corrosion of copper due to natural or man made earth currents was raised. SKB are currently looking at this issue in the context of the Forsmark site, which is close to the earthing point of a power line. The possible impact of earth currents will be discussed in the SR-Can report. It was noted that the horizontal emplacement option would be more susceptible to such effects due to the extended line of conducting material.

Another point to consider here is that the canister will be in an electric field. Even though the canister dimensions are so small that macrocells will not be produced, the surface potential of the canister may change from its normal corrosion potential value. This can affect reaction rates and formation of surface films.

5.13 Environmentally assisted creep

Creep is similar to SCC in that creep rates at relevant conditions have so far been considered too low to be measured experimentally. Contrary to SCC it is known that the copper shell will be subjected to creep, and the small gap between the shell and the insert will eventually be closed by this process. Creep could possibly contribute to material fracture. From other material-environment combinations it is known that corrosion may markedly increase the creep rate. However, this issue was not covered at the workshop.

6 Issues in each phase

The relevance of processes and features discussed in the previous section varies during the time evolution of a repository. Some issues only need to be addressed for a relatively short period e.g. some years after the emplacement of a canister (e.g. oxygenated phase or period with elevated temperature), while other issues will mainly be of relevance for the up to one million years time scale addressed in safety assessment. The purpose of this section is to group canister corrosion issues and viewpoints raised at the workshop according to their relation to the time axis.

6.1 The oxygenated phase

Oxygen will be present in the repository environment during operations and for a period after sealing of tunnels. Since oxygen could contribute significantly to canister corrosion, the workshop participants had the view that SKB need to provide a more defensible and detailed analysis of the amounts of oxygen that could react with copper. SKB's present approach is to present a bounding calculation for the total amount of oxygen and not to model different reactions that may consume oxygen in any detail. A consequence of this approach is that output of the analysis can only be a bound on total corrosion in this phase. Although this may be an appropriate strategy for this issue, there may be a need for a complementary mechanistic modelling effort, which could illustrate the significance of various oxygen consuming reactions. Moreover, there is a need to justify and bound the target area for corrosion. An evenly distributed corrosion cannot be assumed without justification.

The availability of oxygen during the operation phase will contribute to the presence of biomass from microbial processes and sources of ferric iron. Microbial processes need to be analysed and understood for the oxygenated phase. A contact between groundwater and atmospheric CO_2 will also affect the chemical environment. Ammonia in sweat, urine and residues from explosives may locally increase concentrations in comparison with the original groundwater composition.

Localised corrosion has to be addressed in detail for the oxygenated phase. There is a need for a demonstration as to whether localised corrosion (deep penetration on limited areas) can occur or not during the oxygenated phase. The experiments shown by Fraser King were regarded as important in that respect. However, the participants thought there is a need to demonstrate that the corrosion profile in reality will be similar to those experiments, i.e. roughening without real pitting. More arguments are needed to demonstrate this. One such argument would be to show and explain that Cu cannot passivate in contact with saturated bentonite.

6.2 The resaturation and thermal phase

The resaturation phase includes the closure of any available pore-space near the canister. This evolution is of considerable relevance for SKB's assertion that no SRB microbial activity will occur within the buffer, which depends on a sufficiently low water activity and microbes being crushed due to the high swelling pressure of a homogenously saturated buffer. It is important that open pore-space will not be available adjacent to the canister surface, since biofilm formation on the canister may be particularly detrimental for canister integrity. Workshop participants suggested that microbes might be able to survive in larger pores of the buffer, e.g. near buffer impurities, or on rough surfaces.

The thermal gradient may cause mineral precipitation and accumulation of salts near the canister surface, such as those with retrograde solubility behaviours (e.g. gypsum). It was pointed out that if this cannot be ruled out then possible effects on canister corrosion would need to be evaluated. Such an evaluation needs to consider the types and amounts of salt accumulation that can be expected based on experiments and modelling work.

Workshop participants suggested that the various stages of the repository evolution should be described at some level of detail even if there is no immediate threat to canister integrity during the particular stage under consideration. Description of the evolution of one phase may be helpful in understanding the initial conditions for subsequent phases – e.g. roles of surface films on a canister, importance of alteration of buffer density or other buffer properties. There is a need for THMC modelling work to support such a description of the various stages of repository evolution.

6.3 The reducing phase

The workshop participants felt that the key factor for the reducing phase is sulphide availability. It was felt that SKB had not addressed various sources of sulphide as comprehensively as could be expected. However, basic thermodynamic solubility arguments, mass transfer calculations and the data from characterisation of sulphides in the bedrock, and buffer bentonite as well as sulphide chemistry of relevant groundwater should be able to fill in the gaps. As pointed out earlier, the most sensitive assumption in SKB's handling of sulphide corrosion appears to be the assertion of zero microbial activity in the buffer. Other arguments that may be used to support limited but not zero microbial activity should be assessed.

Chloride is another important groundwater component for the analysis of the long-term canister corrosion behaviour. The assessment of corrosion should be able to handle a wide range of chloride content, since it appears to be very difficult to provide robust upper and lower limits.

6.4 Glacial related events

Glacial effects on the repository may include an increased probability of earthquakes and movement of the rockmass (e.g. post glacial faulting), as well as intrusion of dilute possibly oxygenated glacial meltwater. Even if a faulting event would not cause canister failure, shear slip along a fracture plane intersecting a deposition hole may affect canister geometry and stress conditions of relevance for the corrosion analysis. Oxygenated melt water could possibly reach repository depth and enter the repository environment via fractures or tunnels. Implications for the canister corrosion such as localised corrosion need to be addressed, at least if it is not possible to confidently rule out the re-establishment of oxidizing conditions at repository depth. The possibility of permafrost at or near the repository level must also be considered.

6.5 Other events or issues

It was suggested that the size of the individual canisters are probably not large enough for effects of earth currents to be worrying. Earth currents and differences in soil composition at long distance have been reported to cause corrosion problems for pipelines extending several km. However, canister would be discretely distributed and not contacting each other, which is a different case.

7 Implications for design and manufacturing

A component of the design basis for the KBS-3 concept is that the copper has been selected because of its corrosion resistance in the expected repository environment. According to SKB's specifications, no know corrosion processes should lead to a canister life time less than 100 000 years (Werme, 1998). Calculations suggest that the thickness of 50 mm for the outer copper layer should be sufficient for the canister to survive for considerably more than one million years (SKB, 1999a). In fact the choice of this thickness is based on manufacturing and handling considerations rather than from the corrosion requirements.

It was suggested that efforts to avoid grease on the canister surfaces would be worthwhile. Aging may result in the formation of carboxylic acid, which is corrosive to copper. Grease may under heating in reducing conditions (e.g. during arc welding) produce graphite, which is nobler than copper and would consequently accelerate corrosion.

The quality of the sealing weld and the spot on the canister with the thinnest coverage of copper will have to be considered in future canister corrosion studies. This aspect should essentially determine the canister lifetime from a corrosion point of view.

There are no critical corrosion issues brought up at the workshop that seemed to be significantly affected by the selection of either the KBS-3 vertical or the horizontal emplacement option. However, a separate review of the issues connected with the horizontal emplacement option could be needed, since SKB's present work has mainly focussed on the vertical emplacement option.

8 Conclusions and discussion

A general impression from literature studies, presentations by workshop participants and the informal hearing with SKB is that there is in general a strong basis for the handling of copper corrosion in safety assessment. Work has been ongoing in the area for many decades and there appears to be a consensus on several key aspects of corrosion, such as the existence of a threshold potential for localised corrosion. This is of key importance for the assessment of corrosion under repository conditions.

Localised corrosion has to be evaluated for the initial oxygenated phase. There is a need for SKB to demonstrate that the corrosion profile in reality will be similar to those of small scale experiments, i.e. roughening without real pitting. There is also a need for SKB to develop a better and more transparent basis for assessing how much oxygen can be available during the early oxygenated phase. Regarding stress corrosion cracking, there is a need for a consistent and possibly more detailed explanation either why it can be completely disregarded, or accounted for by probabilistic methods.

Copper is normally assumed to be resistant to corrosion in oxygen free environments. However, this is not correct for the extremely long time period of one million years covered by SKB's safety assessment. Copper will react with sulphide by reduction of water. This reaction is the basis for SKB's performance assessment model for copper corrosion (Hedin, 2004). The key aspect of this model is the availability of sulphide. SKB may need to address in more detail the availability of sulphide from the groundwater and the buffer bentonite and its speciation and solubility behaviour. However, the most sensitive assumption in SKB's modelling appears to be the assumption of zero microbial activity in the buffer throughout the assessment time scale of 10^6 years. A detailed justification of this assumption is needed and possibly also "what-if" calculations to illustrate consequences if this assumption turns out not to be valid at some stage during the repository evolution. Workshop participants suggested a need for SKI to review SKB's canister corrosion model in more detail as part of future safety assessment reviews (calculations, assumptions and data). Additional experimental work might be needed for the assessment of copper corrosion in high chloride environments and with simultaneous presence of chloride and sulphide.

It is essential that altogether consistent facts, understanding and models are used when developing an argument. Any inconsistency regarding these three aspects (facts, understanding, models) needs to be identified. An example would be if thermodynamic data and theoretical calculations suggest that corrosion will not happen, while kinetic data (experimental results) suggest a significant corrosion rate.

For future safety assessments, SKB is recommended to use a consistent template for the handling of different corrosion mechanisms even if their final treatment will be quite different. This may include e.g. an extended application of the exclusion principle (as applied for stress corrosion cracking, see Figure 5) and/or application of the decision tree approach (as applied for stress corrosion cracking in the Canadian programme). However, it should be noted that the reliability of the exclusion principle depends on the quantity and quality of information on which it is based, and that more explicit criteria might be needed to support the decision tree approach.

There is also a need for a well structured approach to handling uncertainties. Examples include those that can be characterised as variability (welding defects, sulphide content of groundwater and bentonite) and as lack of knowledge (e.g. microbial viability, the existence of an unidentified groundwater component affecting corrosion or an unknown corrosion mechanism). A suitable combination of a probabilistic application of the main copper corrosion model, well supported calculation cases with mechanistic models and possibly a selection of what-if calculations could provide a good coverage of all corrosion processes and their uncertainties.

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Appendix A: Participants

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Appendix B: Questions asked of SKB

This list of questions was provided to SKB ahead of the workshop.

1. Local corrosion – mechanism for pitting
Which are the prerequisites for pits to occur and pitting corrosion to proceed ? Which are the uncertainties still present regarding the mechanism ? Can the mechanism, and in that case how, be proven not to be a problem ?

2. Local corrosion – formation of whiskers
It has been proven that sulphide whiskers can be formed on copper in a sulphidic environment (Hermansson et al., 2001; Hermansson and Gillén, 2004). Two types of whisker could be distinguished, with different types of "roots". The whiskers consist of different strata (innermost oxides, and outermost sulphides etc) and are very fragile.
The growth mechanism has proven to be very fast – is there a possibility that the same mechanism may operate under repository conditions ? Can it, and in that case, how, be proven not to be a problem ?

3. Microbial assisted corrosion
Which mechanism is most important for limiting the life support for sulphate reducing bacteria in the bentonite, low water activity or small porosity (mechanical pressure)?
How can SKB ensure that there are no other strains of similar bacteria able to endure conditions in the buffer? Are these limiting conditions corroborated by evidence from other microbiological research? Will any bacteria suffer from these effects even with unlimited supply of nutrients? Will SKB be able to show that no biofilms of sulphate reducing bacteria will be formed at the copper-bentonite interface? How will the effect of any deteriorated bentonite (erosion, smectite conversion, reduced swelling pressure etc) be treated with regard to microbial survival ?

4. Radiation induced corrosion effects
What will be the effects of radiolysis both inside and outside the copper canister ? On what levels is it necessary to investigate special interface effects, e.g. due to secondary photons ? Will any corrosion effect be general or local ? Can these mechanisms, and in that case how, be proven not to be a problem ?

5. Stress corrosion cracking
In what "performance window" of the three necessary factors (stress, potential, environment) can stress corrosion cracking on copper occur ? How is that "window" compared to the repository situation ? How will the repository environment after water ingress differ from undisturbed groundwater, e.g. in regard of the human introduction of ammonia ? If SCC would occur, how would it affect the local stress distribution?
Specifically, would it replace the compressive stress at the inner part of the wall by a tensile stress thus enabling a penetrating crack?
If the SCC cannot be totally ruled out, how will it be treated in the performance assessment ?

6. Corrosion and mechanical load together
Which other effects of combined chemical and mechanical "loads" could exist and need to be treated? One case is simultaneous loading (except SCC, is there a possibility for

other combinations of outer stress and corrosion) ? What happens if the canister is first corroded and then is exposed to outer mechanical load ? And the reverse, first loaded (creep, with possible wall thinning) and then subject to corrosion attack ? Will uneven swelling of the bentonite influence the corrosion ?

7. Galvanic couplings

Galvanic effects has been mentioned now and then since the KBS-3 concept was presented. Which galvanic effects need to be considered, and are they treated in the performance assessment ? The most obvious example is the coupling between the iron and the copper in the case of a penetrated copper shell - the degradation of the canister as a barrier as well as the effect of such degradation on other barriers. Another coupling would be between copper canisters and "currents in the earth" – how will such phenomena be treated ?

8. Corrosion in PA modelling

Which corrosion mechanisms will explicitly be treated in the performance assessment, and which will be disregarded ? What are the arguments to disregard mechanisms ?
What kind of models will be used ? How does these models differ from earlier assessments ?
Examples of situations to be treated in PA:
- possibility for hydrogen formation at high chloride concentration
- corrosion by initial oxygen
- glacial meltwater, with oxidizing conditions
- sulphide corrosion

9. Corrosion as a basis for design requirements

In the SKI regulations it is recommended that certain scenarios should be employed for derivation of design basis for the barrier system. How will any design basis for corrosion resistance be derived ? What are the critical cases and scenarios? How will the behaviour of the surrounding barrier system be considered in this analysis (e.g., properties and changes in bentonite and rock). What models and calculations will be used?

Be aware list (no presentation is asked for, but the questions may come up for discussion):
- difference in prerequisites or mechanisms between vertical or horizontal deposition of canister
- difference between bulk material and welded material
- impact of discontinuities on the copper surface on corrosion
- acceptance criteria with respect to corrosion resistance

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Appendix C: Extended abstracts

Copper corrosion in soil and natural water

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1 Environments

1.1 Soil

Several important variables have been identified that have an influence on corrosion rates in soil; these include water, degree of aeration, pH, redox potential, resistivity, soluble ionic species (salts), and microbiological activity. The soil as a corrosive environment is probably of greater complexity than any other environment. Corrosion in soil follows aqueous electrochemical mechanism, but the conditions in the soil can range from 'atmospheric' to completely immersed. Which conditions prevail depends on the compactness of the soil and the water content. Moisture retained within a soil is largely held within the capillaries and pores of the soil.

Variation in soil composition or structure can result in different environments acting on different parts of the same metal surface, and this can give rise to electrical potential differences at the metal/soil interface. This will result in predominantly cathodic or predominantly anodic areas, and the consequent passage of charge through the metal and through the soil. Differences in oxygen concentration, or differences in acidity or salt concentrations may give rise to corrosion cells. The distance of the separation of the anodic and cathodic areas can range from very small to metres or more. The conductivity of the soil is important as this can be rate controlling; a high conductivity will be conducive of a high corrosion rate.

Copper is usually resistant to various soils. The corrosion rates are usually 2-20 µm/year. Rather severe corrosion and pitting is possible in soils with high salt contents: sulfides, organic sulfur compounds, ammonia or ammonium salts or with high acidity and poor aeration. Camitz and Vinka (Korrosionsinstitutet 2003) report that after 5 to 7 years exposure in different soils, the maximum uniform corrosion was 4 µm/year. Nine of 66 test panels showed uniform corrosion rate higher than 0.5 µm/year. The maximum local corrosion was 30 µm/year. Twelve of the 66 test panels showed a local corrosion higher than 10 µm/year. No pronounced pitting was found such as that occurs inside copper water tubes. Both the uniform and the local corrosion were in most cases higher above the groundwater table than below it. The results are applicable to real copper structures in soil such as e.g. copper grounding electrodes and copper pipes.

Microbes can increase copper corrosion rate in soils. Increased cathodic reaction rate (cathodic depolarization), selective leaching, underdeposit corrosion, and differential aeration cells have been cited as MIC mechanisms for copper alloys. Corrosive products produced by microbes include carbon dioxide, hydrogen sulfide and other sulfur compounds, ammonia, and organic and inorganic acids.

1.2 Drinking water

Fresh waters are less corrosive towards copper than seawater, and copper is widely used for distributing cold and hot waters. Corrosion processes on copper take place at the copper-water interface and form cuprite. At the cuprite-water interface, cuprite usually reacts electrochemically to form malachite and tenorite above pH 7.0. In most water compositions, corrosion does not directly liberate copper or copper compounds to water.

General corrosion of copper in drinking water is slow. A copper pipe is said to corrode slowly when the rate of corrosion is uniform and equal to 0.4 μm/year. The piping is expected to last tens of years. Pitting corrosion in drinking water can lead to leaks in few weeks. Pitting corrosion and uniform corrosion do not usually occur simultaneously.

The European Union directive 98/83/EY for quality of water for human consumption has some maximum values that are based on health effects, but do have influence on corrosivity:

- Aluminium 200 μg/l
- Ammonium 0.50 mg/l
- Chloride 250 mg/l
- Conductivity 2500 μS/cm, $T = 25$ °C.
- Hydrogen ion concentration, $pH = 6.5$-9.5
- Sulfate 250 mg/l

In relation to pH, conductivity, chloride and sulfate concentration it is stated that the water shall not be corrosive.

The Finnish “Application guide to the decree concerning water for household consumption” (2000) has guidelines based on experience for minimizing corrosion in drinking water:

- $pH > 7.5$
- Alkalinity over 0.6 mval/l (HCO_3^- concentration)
- Calcium over 10 mg/l (0.25 mmol/l)
- Oxygen over 2 mg/l
- $HCO_3/(SO_4+Cl) \geq 1.5$ (equivalent ratio)

This composition is a compromise to control corrosion of both ferrous and non-ferrous metals used in the distribution system.

A compilation of Finnish and Swedish instructions to prevent copper corrosion gives following parameters:

- pH 7.2-9.0
- Chloride less than 50 mg/l
- Maximum temperature 65 ºC
- Calcium concentration more than 0.6 mmol/l (corresponds to about 25 mg/l Ca)
- Flow rate higher than 0.3 m/s, but less than1.5 m/s to prevent erosion corrosion.
- Bicarbonate/sulfate ratio HCO_3^-/SO_4^{2-} more than 1 (concentrations in mg/l).
- Al, Fe and Mn all less than 0.1 mg/l to prevent deposits.

To prevent pitting corrosion of type II and III the following parameters are included :

- Bicarbonate/chloride ratio HCO_3^-/Cl^- as high as possible, concentrations in mg/l.
- Alkalinity minimum 70 mg/l, but less than 300 mg/l HCO_3^-.

1.3 Seawater

The concentration of dissolved materials in the sea varies greatly with location and time because rivers dilute seawater, rain, or melting ice, and seawater can be concentrated by evaporation. The most important properties of seawater are

- Constant ratios of the concentrations of the major constituents worldwide
- High salt concentration, mainly sodium chloride
- High electrical conductivity
- Relatively high and constant pH
- Buffering capacity
- Solubility for oxygen and carbon dioxide
- The presence of organic compounds and biological life, to be further distinguished as microfouling (e.g., bacteria, slime) and macrofouling (e.g., seaweed, mussels, barnacles, and many kinds of animals or fish)

Although copper is a noble metal, the main reason for its satisfactory performance in a seawater application is that a protective film of cuprous oxide forms directly on the metal surface. Often products deposit on top of this film and may contribute to the protection. These may be cupric oxychloride, cupric hydroxide, or basic copper carbonate and calcareous materials. Owing to the buffering properties of seawater, the rate of formation of cuprous oxide in seawater solution is lower, and the rate of generation of cuprous complexes (and thus the general dissolution rate) is higher than in the NaCl solution. Polluted seawater often has hydrogen sulfide or other sulfides present. The copper sulfide film formed on the metal surface in polluted seawater is more noble than the corrosion film developed in clean seawater. If there are breaks in the sulfide film, local attack is stimulated greatly by the large area of active cathode.

When water speeds are low and deposits settle on the surface (particularly at water speeds below about 1 m/s), pitting of copper and copper alloys can happen by differential aeration effects. In seawater systems such attack may occur under dead barnacles or shellfish, the decomposing organic matter assisting corrosion. Pitting is most likely to occur in polluted in-shore waters, particularly when hydrogen sulphide is present. In such contaminated waters non-protective sulphide scales are formed and these tend to stimulate attack.

Copper corrodes typically at rates varying from 10 to 50 μm/year in shallow and deep-ocean environments. Copper is also used as antifouling material in seawater. Copper can be metallic copper or cupric oxide. The corrosion rate of copper above which the amount of released copper ions is sufficient to avoid biological activity has been estimated as 0.02 g/m^2h that corresponds to 20 μm/year.

2 Corrosion forms

In natural environments the common forms of copper corrosion are uniform corrosion and pitting. In soils and under fouling in seawater microbes can have an effect on corrosion. Crevice corrosion can happen in constructions with tight joints.

2.1 Uniform corrosion

In atmosphere estimates of the annual corrosion rate of naturally patinated copper that has developed a green patina have shown rates between 0.2 and 0.3 µm/y. Compared with atmospheric patina, the layer of corrosion products formed under immersion in seawater provides a poor protection to the metal. In aqueous environment the inner layer of cuprite is formed by large octahedral crystals, which form a porous and permeable structure facilitating the corrosion process of the base metal. The outer layer of basic cupric chlorides also form a porous structure.

General corrosion has been seen in soft acidic drinking water when:

- pH < 6,7
- Free CO_2 > 15 mg/l
- Bicarbonate hardness < 0.54 mmol/l (< 3 °dH)
- Alkalinity < 1.0 mmol/l

Some drinking waters continuously dissolve copper. Factors that favour this action are high free carbon dioxide, chloride and sulphate contents, low hardness, and increase of temperature. The corrosion is general and the resulting thinning is so slight that the useful life of the pipe or component is virtually unaffected. Uniform corrosion does not usually lead to failure but it can produce “blue water” or “green water” and when it does, this is readily detected by consumers. Blue water is the result of corrosion and its subsequent release of copper in the form of insoluble salts or minerals such as brochantite and posnjakite, to the water. When the concentration of dissolved copper sulfate in water is larger than 5 mg/L the water becomes blue, and this situation should not be confused with the “blue water” caused by the presence of solids in the water.

2.2 Pitting

Pitting corrosion requires a passive film of Cu_2O and/or $Cu(OH)_2$, chloride ions, and corrosion potential higher than the potential of pit initiation. Pitting requires that the protective film turns to non-continuous. Pit propagation requires supply of oxidant (O_2, Cu^{2+}), separation of the anodic and cathodic reactions (by corrosion products covering the pit), and small anode to cathode surface area ratio.

Copper pitting is the primary cause of copper tube failure in potable water lines, and characteristics and some mechanisms that propagate copper pitting have been identified. Three types of pitting can be distinguished for copper. Type 1 occurs on annealed or half-hard tubes in cold tap water, caused by a continuous carbon film formed on the inner tube surface during bright annealing. Type 2 occurs on hard drawn tubes in hot tap water of low pH (<7.4) and low (< 1) $[HCO_3^-]/[SO_4^{2-}]$ ratio. Type 3 occurs on both hard and annealed tubes in cold tap water of high pH, with low salt concentration.

Type 1 pitting occurs in hard or moderately hard waters and is favored by water with high sulfate content. Failures occur most rapidly in water of fairly low chloride content. Pitting occurs when carbon residues, which arise from the breakdown of lubricants during bright annealing, are present. Type 1 pitting occurs in cold hard waters, with high conductivity, high alkalinity, high sulfate concentration, low total organic carbon and micro-organisms. These characteristics are usually associated with well waters. The pits are spherical and covered by several films. The original one is a cuprous oxide film, the second to be formed is cuprous chloride and the third is composed of copper salts, most commonly malachite.

Type 2 pitting occurs in water with $pH<7.4$ and at temperatures >60°C. Water that causes pitting has a relatively low HCO_3^- content (<l00 mg/L), whereas no pitting occurs in water with a higher HCO_3^- concentration (100-300 mg/L). The SO_4^{2-} concentration is 15-40 mg/L. At higher HCO_3^- concentrations, a protective basic copper carbonate forms. In carbonate and sulphate containing water, a basic copper sulfate crust forms that covers the pit mouth and creates an occluded cell.

Type 3 pitting corrosion occurs in soft, cold water of low conductivity, low alkalinity and high pH. In Sweden the most damages were in water with $pH = 8.8$, HCO_3^- concentration around 40 mg/L and SO_4^{2-} concentration around 15 mg/L. The pits are wide and shallow and have two films, the first one consists of cuprous oxide and the second one of brochantite and/or malachite. The reason of Type 3 pitting corrosion has been suggested to be rapid growth of Cu_2O layer that forms as large crystals leaving well conductive pores.

Types 1 and 3 result in pits with approximately hemispherical shapes whereas type 2 results in pits with irregular shape. Type 3 differs from type 1 and 2 in that several small pits may be concentrated in a relatively small area.

2.3 Crevice corrosion

A higher concentration of metal ions tends to form on a crevice, whereas any copper ions formed outside the crevice are swept away by the current. Under these circumstances, local attack takes place on the copper just outside the crevice. Cuprous oxide is less stable than cupric oxide. In crevices cupric oxide forms on the interphase with the solution, while between the cupric oxide and the metal there is cuprous oxide.

2.4 MIC

If anaerobic bacteria, especially sulphate-reducing bacteria, grow under a deposit, microbially influenced corrosion (MIC) may occur as a number of tiny pits under a nodule of corrosion product, and is thus sometimes called pepper-pot corrosion. Microbial growth and, hence, MIC is most likely at temperatures of 25-55 °C. Microbially influenced corrosion and other cases of under-deposit corrosion are more likely in stagnant or very slow flowing water.

3 Surface films

In atmosphere the copper patina typically consists of two distinct layers, a 5-10 µm layer of essentially continuous cuprite (Cu_2O) against the copper base metal and an external, porous layer of 5-40 µm of basic copper sulphate, brochantite ($Cu_4SO_4(OH)_5$) or basic copper chloride, atacamite ($Cu_2Cl(OH)_3$). Brochantite patinas are more common, however atacamite is found in marine patinas.

When copper objects corrode in water that is sufficiently oxidizing and near neutral, in the absence of bacteria the first copper corrosion product is cuprite (Cu_2O) that forms epitaxially as a product of the direct reaction of copper with dissolved O_2. Cuprite has a high electrical conductivity and permits transport of copper ions through the cuprite layers, allowing the copper ions to dissolve in water and reprecipitate. If the water chemistry approximates that of seawater, copper ions reprecipitate as botallackite ($Cu_2(OH)_3Cl$), which can convert in minutes or hours to either paratacamite or atacamite (alternate crystal structures of botallackite), depending on local water chemistry. Paratacamite is the more common form.

If the water contains little Cl^- but is in equilibrium with the atmosphere with regard to carbonate species, basic copper carbonate malachite ($Cu_2CO_3(OH)_2$) will form. A direct solid-state transformation of cuprite to malachite is possible, while a transformation to a hydroxychloride mineral would require dissolution and precipitation. Malachite and hydroxychloride minerals normally precipitate from solution. If both Cl^- and carbonate species are lacking, tenorite (CuO) is produced. In water with sulfides corrosion products could be cuprous oxide, Cu_2O and brochantite $CuSO_4.3Cu(OH)_2.H_2O$.

Copper alloys are also subject to sulfide-induced corrosion by SRB within a biofilm. Under these circumstances chalcocite Cu_2S forms easily, covellite CuS less easily. The corrosion layer may contain other sulfides buried under other corrosion products and the poor adherence and mechanical properties of the sulfides make these layers nonprotective. The presence of iron ions in solution can lead to the formation of a layer of chalcopyrite ($CuFeS_2$).

MICROBIAL INDUCED CORROSION
Rolf Hallberg

General aspects on bacteria.

Bacteria can be found in almost all type of environments. The species diversity is large and their distribution scattered. Below a temperature of 120 C the most important limitation is the availability of water, which can be expressed as water activity (a_w, see below).
Bacteria form nisches and biofilms where they create optimal conditions for growth and activity. We can thus not use overall redox and pH conditions to exclude the activity of certain bacteria. Microbiologists believe that we may have catalogued 1% of all types of bacteria in natural and man-made environments. The one we have catalogued are those we can cultivate in the laboratory. When we count the numbers of viable bacteria in a natural environment or sometimes even in the lab.experiments we seldom get representative numbers of those that are attached to solid material. A very large number is attached as this conserves energy compared to mingle around.

Can bacteria survive and be active in the bentonite surrounding the Cu-canister?

In the modelling of copper canister corrosion Liu and Neretnieks (2004) state "The water activity is low enough to exclude all bacteria that do not form spores." This statement is based on findings reported by Pedersen and co-workers. The bentonite will reach the planned full compaction density of 2g cm^{-3} (5Mpa), and have a water content of around 26%. The water activity (a_w) is low, probably around 0.92.

a_w is related to the water concentration through an activity coefficient times the mole fraction of water in the system (%RH/100).

There are many factors regulating the activity of bacteria but water is probably **the factor.** Bacterial cells are membrane bound bags of water. In the compacted bentonite the bacteria are exposed to a process of desiccation. Potts (1994) has published a thorough review, "Desiccation tolerance of Prokaryotes", on the subject with 433 references. Many of his statements are worth taking into consideration before we exclude the bacterial activity in the bentonite. Especially in the long time perspective, which according to SR 97 is one million years. I will here list some citations from Potts paper.

There are numerous biophysical and physiological components that contribute to, interact in, and require consideration with respect to desiccation tolerance.
The anhydrobiotic cell is more than simply a collection of dried components.
The lipid biosynthetic machinery, as well as the proteins required for the uptake and phosphorylation of glycerol and the uptake of sulphate remains functional during desiccation.
A film provides the largest surface area for rewetting, and a film with a clay envelope, especially montmorillonite, may protect bacteria from excessive desiccation.
Cells that express desiccation tolerance undergo drying at much lower water potentials, and it would appear that they must withstand the most extensive perturbations of V_b (quantity of bound water) for their various cellular constituents over the long term - the absolute lower limit beyond which no reactivation can occur is unknown.

The water potential of a system is proportional to a constant times the absolute temperature and a_w. The term represents the work involved in moving 1 mole of water from some point in *a system to a pool of pure water at atmospheric pressure and at the same temperature as the system under consideration*

The sensitivities of soil bacteria to relatively small negative water potentials have been attributed to the restriction of movement as the soil water drained. *Pseudomonas a.* requires water-filled pores 1 to 1.5 μm in diameter or larger to move readily in soil, so it is easy to understand how a matric deficit could influence viability if the latter is dependent on motility. ... not all cells in a population respond in a similar fashion to a water deficit. The physiological status of the cell at the time of drying, and the time of the drying event, seem to be potential sources of this variation in sensitivity.
Studies suggest that cells in the stationary phase are structurally, physiologically, and functionally distinct from those in the log phase. Stationary-phase cells of *E. coli* show a marked enhancement of resistance to air drying, ...
Surface structures of *Desulfurococcus mobilis*, another archaebacterium, have an unusual protein lattice at the surface, providing almost an exoskeleton, that has been speculated to afford protection from water stress.
Bacteria respond to desiccation by channelling energy and nutrients into polysaccharide production. For example, *Pseudomonas sp.* contains more EPS (extracellular polysaccharides) than protein when desiccated.
What is remarkable about desiccation tolerance is not what is known but what is not known. .... ecological studies, for the most part, include a good deal of phenomenological and anecdotal observations that shed little light on the mechanism of desiccation tolerance.

The joints between the bentonite packages and between the bentonite and the canister will allow the bacteria to form biofilms, including EPS, where they can tolerate desiccation and have enough space for mobility in case they seek for nutrients. The SRB (sulphate-reducing bacteria) are motile by means of a polar flagellum. Masurat and Pedersen, report. Observed that SRB were present in a dormant state in the commercial bentonite tested. The dormant SRB produced hydrogen sulphide after activation by groundwater and in the presence of added carbon sources.
At the present state there are no evidences that can allow us to exclude the activity of bacteria in the bentonite barrier.

Will the redox environment of the repository stay anoxic during 1 million years?

Liu and Neretnieks, 2004, state that during the period of glaciation, groundwater containing high concentrations of oxygen might penetrate into the depth of the repository. The duration of those periods is in the order of a few hundred years and can be considered as instantaneous and these events are deemed not to cause significant corrosion.
The duration of a glaciation is about 100000 years, and the interglacial periods, like the one we have now, last for about 10000 years. During the last million years, the Baltic shield has experienced at least 8 glaciations. Oxygen may penetrate into the bedrock during a glaciation but I do not know to what depth and to what extent. There may be observations from the polar regions that will allow us to make some conclusions on that subject. The presence of oxygen is an important factor for pitting corrosion to take place. The concentration of oxygen necessary to create pitting corrosion can be debated. Hardy and Bown (1984) suggested that the most aggressive conditions associated with SRB were those, which were not entirely anaerobic, but where small quantities of oxygen might be present from time to time. My own observations from studies of bronze canons from 'Kronan' showed that the most severe corrosion had taken place at the interface between the anoxic and oxic environment. To create an anode/cathode system you need a combination of both. These results and those of Zhu et

al., 1994 show that SRB can survive and contribute to metal corrosion problems in environments with the presence of oxygen. The total time needed for construction and operation of the repository will probably be about 40 years. During that time oxygen will be introduced into the repository. For how long times will the oxygen that is trapped in the repository be available for pitting corrosion processes? (300 years, Wersin et al., 1994). This together with a high probability that about 90% of the time, the repository will be subject to glacial conditions, means that oxic conditions will be prevailing during which, there is a high risk for pitting corrosion.

SRB exists in nature as components of consortia of organisms. Hamilton (1985) states that these consortia often take the form of biofilms and allow for the creation of anaerobic microenvironments within a bulk aerobic environment. It has been estimated that when a biofilm of aerobic or facultative bacteria and their associated EPS reaches a thickness of 10-25 μm, then conditions at the base of the biofilm will be anaerobic. Other estimates suggest that in most natural biofilms the depth required for anaerobiosis may be closer to 100 μm. That is to say that even within aerobic environments, thin bacterial slime growth, or biofilm, can generate ideal conditions for the growth of the obligately anaerobic sulphate-reducing bacteria, with all the attendant problems of sulphide production and corrosion.

During the interglacial time anoxic conditions is the most plausible and it seems to be a consensus that pitting corrosion can be excluded. Liu and Neretnieks (2004) have modelled the general corrosion of a canister where water is entering the repository from a horizontal fracture in the ambient rock. They base their transport processes on the vague argument that "Inside the bentonite buffer, no bacteria are assumed to exist or be active." They continue "Corroding species like sulphide will be transported only by molecular diffusion through the bentonite buffer to the canister surface." They do not take into consideration the possibility of biofilms on the canister surface. They conclude "This means that in this example 41% of the produced sulphide enters the clay, and the rest is carried away by the water. During 10^5 years a general corrosion opposite the fracture would be 2.45 mm." If we extrapolate this to 10^6 years it would correspond to 24.5 mm. If all sulphide reaches the canister surface 60 mm is a more appropriate number.

Energy, carbon and sulphate source for SRB.

Bacteria can use hydrogen as an energy source. Nikitinsky (1907) suggested from field observations that certain sulphate-reducing bacteria oxidized hydrogen. However, it was not until 1931 that Stephenson and Strickland established the utilization of molecular hydrogen by SRB. Sisler and ZoBell, 1950, give an excellent review of the subject. Hydrogen can escape from the lower part of the crust to the surface through fissures in the basement. There are many small pits in the bottom sediments of the Stockholm archipelago. These are created by gas leakages from below. Presently I do not have excess to analytical data from these gases but they contain hydrogen as well as methane. Methane is used as carbon source by SRB, which was documented by Cappenberg 1974 in several papers, eg. Cappenberg and Prins, 1974. Liu and Neretnieks, have in their model used methane as carbon and energy source, and applied a value of 1 mol m^{-3}. Finish data show, according to Liu and Neretnieks, concentrations that are one magnitude higher. Why is not the higher concentration used in the model? Data on hydrogen and methane concentrations should be sampled in the rock fracture where the gases are transported. This is the place where we should expect the highest concentrations and if it coincides with the canister it would be the most conservative number of a model.

The worse scenario - a conceptual model.

A vertical fracture in the rock is created in the middle of a canister repository and passes along the surface of the canister. Hydrogen and methane are transported from the lower part of the crust along the fracture to the top of the rock where it is mixed with the surface environment.
SRB attach to the surface of the canister where gypsum has precipitated at an early state from diffusion of sulphate to the warm surface of the canister (Tr-00-22. page vi. Precipitation, mainly gypsum, takes place on the copper tube in the warmest section. Increase of minerals, mainly gypsum, in the innermost millimetres of the bentonite in the warmest 2m section.). Gypsum is reduced by SRB, which is documented in the literature. I have myself isolated SRB that could use gypsum as a sulphate source. The scenario takes place during a glacial period and oxygen is penetrating to the repository. All necessary factors are fulfilled for pitting corrosion to start. With time the pitting penetrates the canister and radionuclides escape to the fracture where they are attached to small particles and transported with gas bubbles to the surface. Bingo!

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STUDSVIK NUCLEAR AB
Corrosion and Water Chemistry
Hans-Peter Hermansson

SKI workshop
April 27-29, 2005
Extended Abstract

Formation of whiskers on copper – experimental results

A series of projects on copper corrosion has been performed at Studsvik on commission by SKI [1-6]. The work has been focused on general and localised corrosion of copper in the repository environment.

The work started with a thorough compilation and up-date of literature data. A selection of a “working environment”, defining the chemical parameters and their ranges of variation was made from literature and discussions with SKI and later on used as a fundament for planning of experiments. Solutions mostly containing sulphide, chloride and carbonate at different concentrations were selected and cylindrical copper samples were exposed mostly at a low E_h.

At the simultaneous presence of sulfide and chloride a very complicated surface film was formed on the copper surface. In several cases of environment the growth of copper containing whiskers or needles was observed on top of a substrate surface film. As whiskers could indicate an underlying localized attack on the copper metal, specific care was taken to find evidence of such attacks. The nature of layers and whiskers and their chemical phases was investigated by applying SEM-EDS, XRD, Raman Spectroscopy and optical microscopy. An example of layer and whisker morphology is shown in Figure 1 [5].

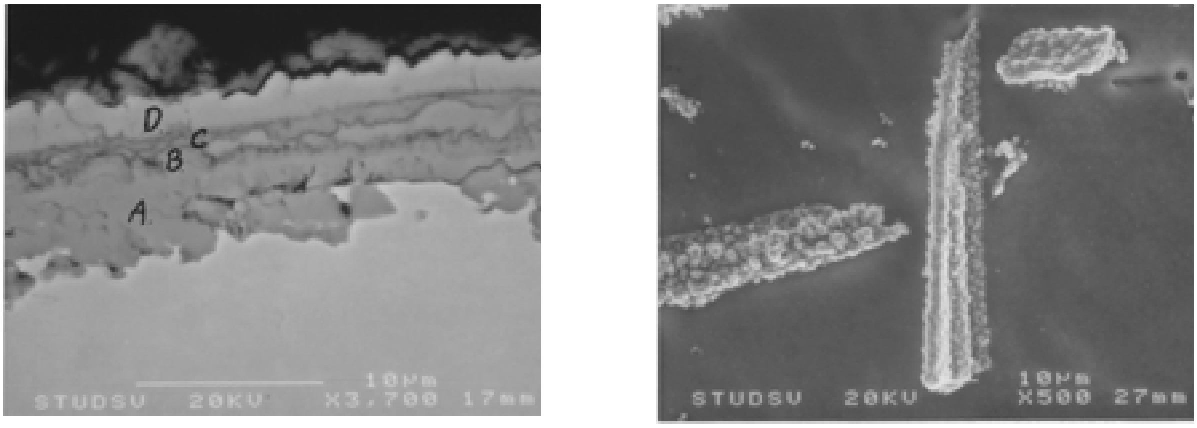

Figure 1 Morphology of layer and whisker growth on copper. A-D in the left hand picture denote differently composed strata in the layer. Parts of whiskers are shown in the right hand picture.

The concentration of sulfur seems to increase outwards in the layered structure and the outer layers shown in the left hand picture of Figure 1 consist mainly of copper sulfides. A multitude of very easily detached and fragile whiskers or needle-shaped growth forms was often found on the surface. An example is shown in the right hand side of Figure 1. A whisker seems to have a core of copper sulfide. The concentration of sulfide increases from the root to the top part of the whisker. There are often straight dendritic, flanged edges along the sides of the whiskers rich in copper oxide and carbonate. The composition of a whisker is thus very complex. A similar stratification as found in the corrosion layer is also present in a whisker but with a concentric, cylindrical geometry.

The whiskers are either of a larger diameter (roughly > 1 mm) or a smaller diameter (roughly < 0.1 mm). They are localized to specific areas of the surface. The larger are situated close to the bottom rim of the cylinder and the smaller on the inside of the surfaces. As already notified, all of them are very fragile and extremely easily detached, especially when the system is perturbated as in the process of sampling. Because of this it was very difficult to correlate the positioning of whiskers with obvious roots or substrate areas in the underlying copper metal.

Several techniques were therefore tried to find such a correlation and finally an optical method for the registration and positioning of whisker growth was developed. Whiskers and substrates were observed with a video camera throughout an experiment. It proved to be a successful means to coordinate whisker position and to link it with the morphology and also with the type of attack on the copper metal surface beneath a whisker root. Examples of results are shown in the following figures taken from [6].

Figure 2 Positioning of whiskers to their substrates using optical methods.

The root parts of the whiskers growing on the bottom part of the copper cylinder shown in the video picture to the right in Figure 2 could be related to areas of attack shown in the left hand photograph. Those areas could in turn be correlated to different kinds of whisker roots in the corrosion product layer that remained after descaling the outer parts.

After further descaling, extended areas of small diameter whisker roots could be positioned and an example is shown in Figure 3. In turn, one single root out of such an area is shown in Figure 4. After removal of the whole corrosion product layer the underlying localized attack is demonstrated in Figure 5. Thus, the whisker roots could finally be correlated to localized attacks in the underlying copper metal.

As previously indicated, the sulfide contents of the corrosion product layers are increasing going out in the layer from the metal. However, close to the metal oxide phases are prevailing. Phases as CuS, Cu_2S, CuO and Cu_2O have all been detected by LRS in different parts of layers and whiskers, but also several other phases depending on the related environment.

Figure 3 LOM photograph taken in an area with small whisker roots.
The horizontal length of the picture covers 2.5 mm.

Figure 4 Raman microscope picture of a small whisker root.
The picture height is 300 µm.

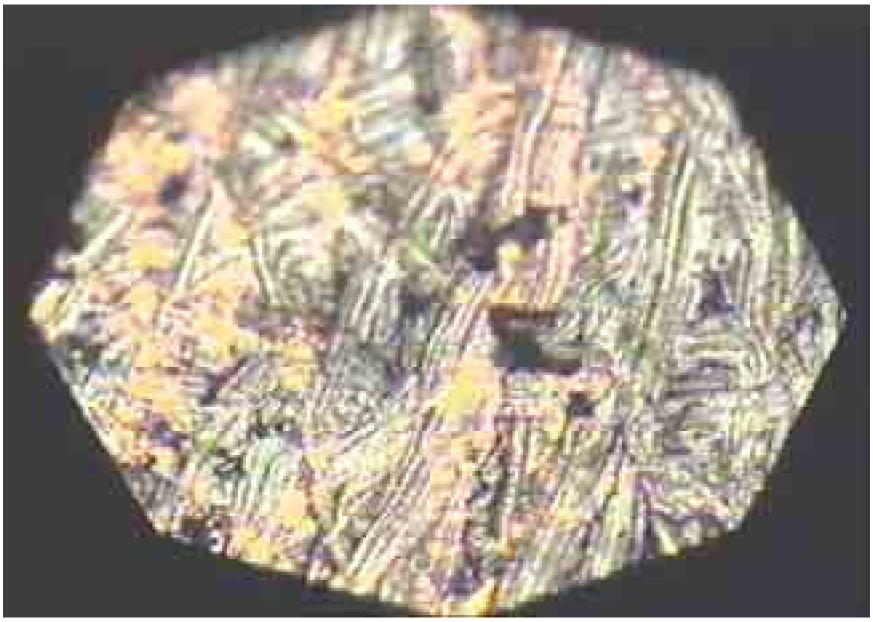

Figure 5 Raman microscope picture from the same area as in Figure 4 after removal of the whole layer. The picture height is 300 µm.

Some conclusions of this study:

- By combining the results from the optical methods it has been possible to distinguish two kinds of whiskers and their roots with small and large diameters respectively.
- The roots have in turn been correlated to specific areas on the underlying metal surface.
- It has been demonstrated that there is a localized attack on the metal surface beneath a small diameter whisker root.
- This correlation is less clear for the large diameter whiskers.
- The results could have an implication on the integrity of the copper lining of the waste canister as there is probably a localized attack going on when small diameter whiskers grow.
- The seriousness of such an attack should be discussed and could be evaluated for example by studying the ability of whiskers to grow on copper in a strict repository environment.

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2004-05-11
J. Kyllönen

MCNP simulations of spent fuel canister

CONCLUSIONS

- Simple attenuation calculations closely correspond to results from MC-simulations (Table 2 and Figure 1).
- No (<1E-15) 100 keV photons from the radiation source are emitted from the Cu-surface (Table 2).
- 0,2% of 662 keV photons from the radiation source are emitted from the Cu-surface (Table 2 and Figure 1).
- 3% of 2 MeV photons from the radiation source are emitted from the Cu-surface (Table 2 and Figure 1).
- With the utilised simple geometry and 1,8E15 Bq/(metric ton) gives a dose-rate in the aqueous phase of about 100 mGy/h.
- The photon-fluence on the copper surface is dominated by the primary energy, and a majority of the scattered photons have energy in the range 100-300 keV (Figure 3 and 4).
- The energy-spectra of the scattered photons exhibit a small degree of variation through the material (Figure 3 and 4).
- The dose in the interface between the aqueous phase and the copper surface is 10-100 times higher than in the bulk aqueous phase for the energies 100 and 662 keV photons, respectively (Figure 5).

MODEL RUNS

Run 1

Fuel_INP och Fuel_outp. A cylindrical source composed of UO_2(s) with a radius of r=12 cm and length of 3 m, encapsulated with 5 cm of Fe, 5 cm of Cu and 5 cm of water. Two sampling-volumes have been used for each material. Electron transport not permitted within the UO_2(s) core and within the Fe insert.

Run 2

Simulation of interface between Cu and H_2O exposed to 662 keV photons from the Cu-side.

Run 3

Simulation of interface between Cu and H_2O exposed to 100 keV photons from the Cu-side.

Run 4

Same as Run 1 but with 100 keV photons. None of them escape through the Fe-layer.

Run 5

Same as Run 1 but with 2 MeV photons.

SIMPLE ATTENUATION CALCULATIONS

Table 1. Attenuation Coefficients

Material	100 keV	662 keV	2 MeV
Fe (cm2/g)	0,3717	0,0739	0,0427
Cu (cm2/g)	0,4585	0,0731	0,0421

Table 2. Exponential attenuation of primary photons.

Material	100 keV	662 keV	2 MeV
5 cm Fe	4,75E-7	0,055	0,186
5 cm Cu	1,2E-9	0,038	0,152
Fe + Cu	5,7E-16	2,1E-3	0,028

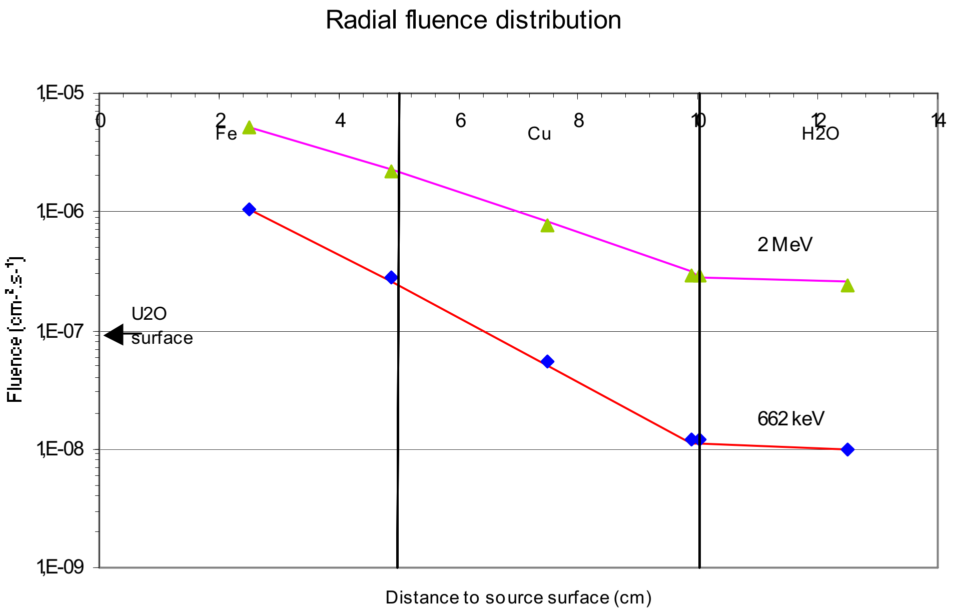

Figure 1. Fluence as a function of radial distance from the UO_2 surface. The lines correspond to the calculated theoretical attenuation of the primary photon fluence. The dots correspond to the MCNP simulations.

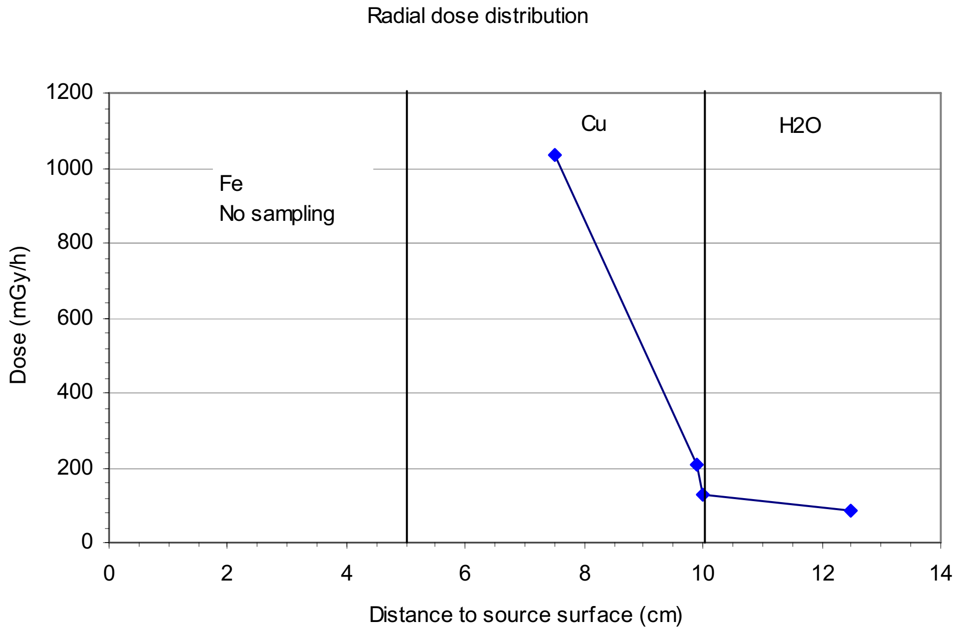

Figure 2. Absorbed dose as a function of radial distance from the UO_2 surface, 662 keV. Calculated with 1,8E15 Bq /(metric ton). No sampling has been done within the Fe.

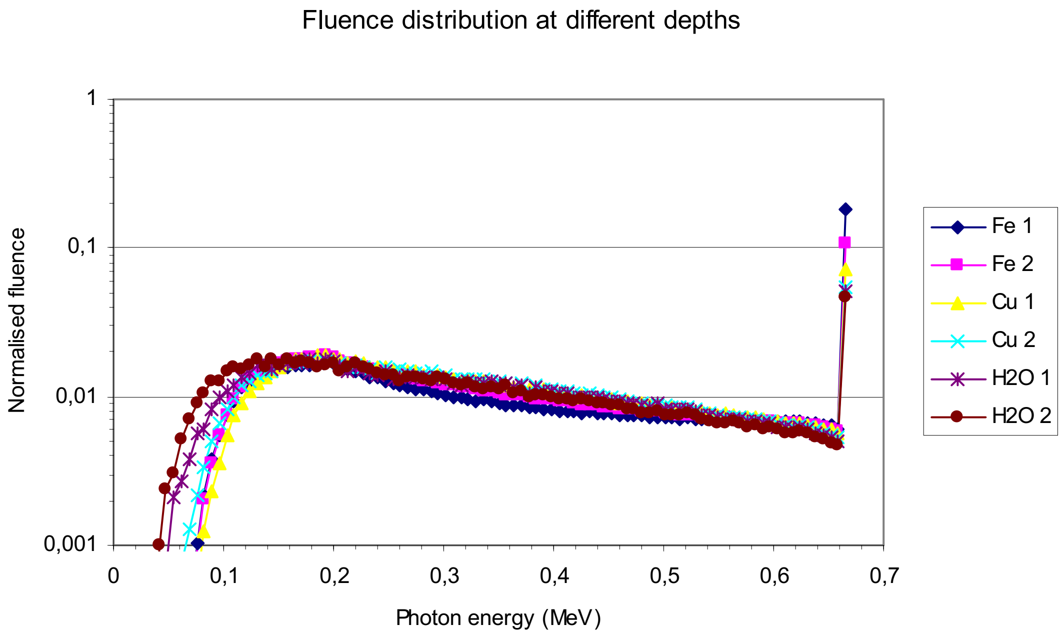

Figure 3. Energy distribution at different depth (corresponds to the dots in Figure 1) for 662 keV primary photons. The curves are normalised.

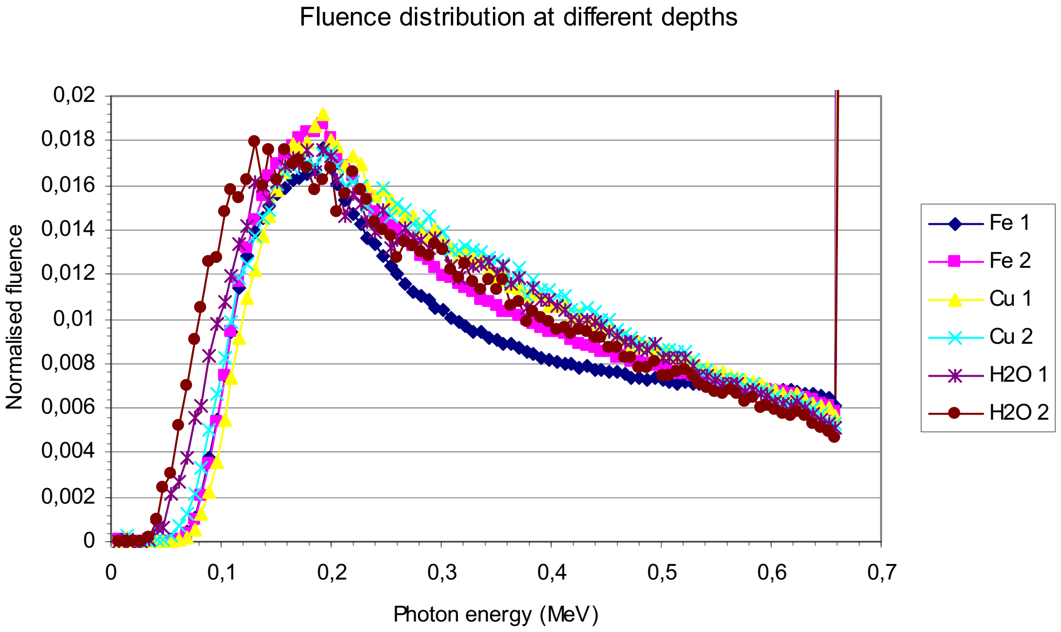

Figure 4. Same as figure 3 except for the more detailed scale.

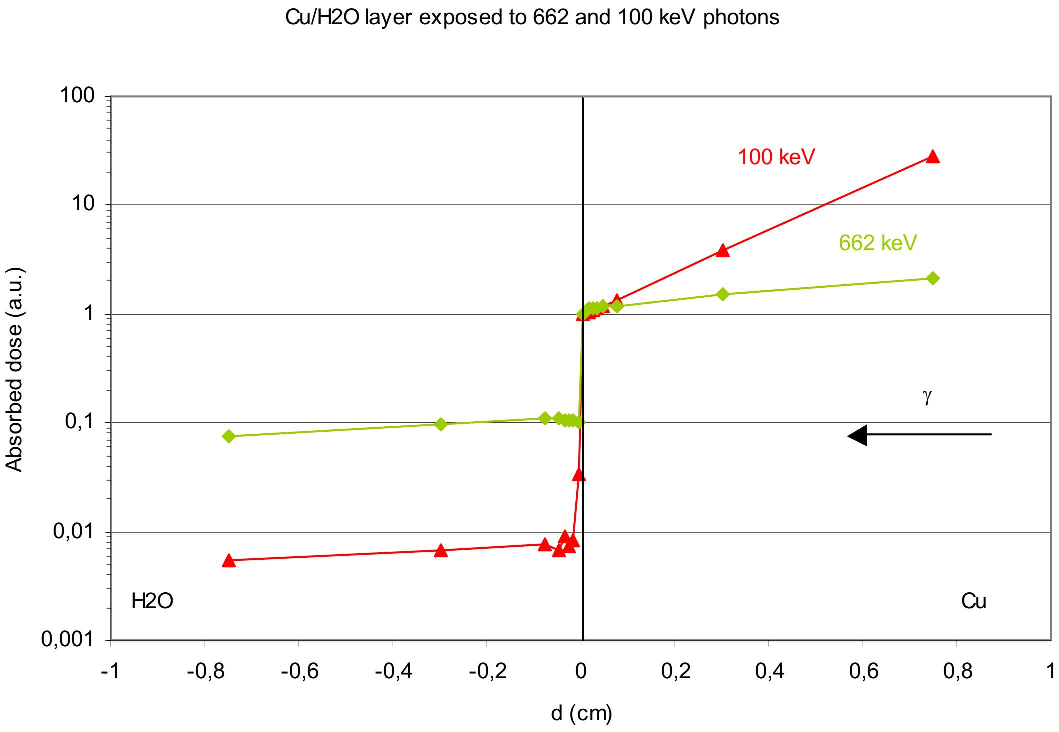

Figure 5. Dose around the Cu and water interface for different photon energies emitted toward the Cu at 1 cm inside of the interface.

SKI workshop on Copper corrosion, Stockholm, April 27-29, 2005.

Overview of localised corrosion of copper : long term evolution

by Antoine Pourbaix, CEBELCOR.

Summary

Various models and mechanisms for copper pitting in the presence of chloride have been proposed, in SKB studies and elsewhere. These different approaches are reviewed here.

Although the differences are real, there is a consensus on some keypoints. One of those is the existence of a critical potential (or « protection potential ») below which pits do not grow.

The values of this critical potential are reviewed and their meaning is detailed in terms of thermodynamic data.

The pitting processes in the presence of ions other than chloride are less known and, in fact, have been little studied. There are some strong evidence that such mechanisms in the presence of reducible or oxidisable sulphur species (sulphate, thiosulphate and especially sulphide) may be largely different from those in chloride solutions. A detailed study (theoretical and experimental) of such mechanisms is recommended.

The future of initially active pits, when anoxy is progressively installed, is analysed, based on theoretical grounds. Here also, an experimental study is recommended to verify and quantify the mechanistic predictions.

Some other more practical recommendations are underlined, for example about the danger of remainings of grease on the canisters.

Table of content

1. Outline

This presentation has two main objectives :
- analyse the various approaches of copper pitting and analyse their consequences,
- describe the transition between aerated and anoxic conditions and analyse in more details the future of copper pits under anoxic conditions.

These two items are expected to provide additional robustness to the long term prediction of the localised corrosion of copper. There is also an attempt to identify all parameters and side effects that could alter or modify the corrosion processes of copper.

2. Localised corrosion of copper : pitting, crevice, scc

Pitting of copper has been extensively studied in connection with premature failures of tap water pipes in the 1950s. Several types of pitting were identified :

Type I is the most widespread in tap water copper pipes. It is observed on annealed tubes in cold hard water with a high bicarbonate, high conductivity and high mineral content (these are often well waters). Solid CuCl and cuprous oxide are present in type I pits, covered with atacamite (a chloride cupric salt) and brochantite (a carbonate cupric salt) in their advanced stages. The surface films outside pits are malachite on top of the initially formed cuprous oxide. The approximate penetration rate of the pits is 1 mm in less than 1 y [1,2]

Type II occurs in soft surface water, rich in CO_2 and O_2, slightly acidic, aggressive to $CaCO_3$, in cold and hot water [2,3]. The major products in pits are cuprous oxide, capped with blackish cuprous oxide and copper sulphate. Outside pite : cuprous and cupric oxide, atacamite and brochantite, often covered by silt. Manganese in the water enhances type II pitting. Approximate penetration rate : 1 mm in 8 y [1,2].

Type III is observed in cold, soft or mildly hard water, with a low conductivity, low bicarbonate, low chloride, silicious, high pH (above 7.2) and high O_2. Type III pits contain Cu_2O on top of CuCl. Surface films are brochantite and cuprous oxide. Pits are wide and shallow. Dissolved copper in the tap water (up to 40 mg/L) is more a problem than perforation in house-life time span [1,2].

Other types of localised corrosion :
- stress corrosion cracking, scc : it is often reported that pure copper is immune to scc. However, ammonia, nitrite and acetate are mentioned as possible causes of scc for pure copper [15]. Scc is dealt with in another presentation at this workshop.
- crevice corrosion is generally less severe for copper, compared to other metals (such as C-steel, stainless steel) [5].
- MIC is an important issue that is also addressed elsewhere in this workshop. Surface films (possibly formed by exopolymers) may suppress the well known inhibiting effect of copper on bacterial growth. They may also create local anoxy and subsequent S^{--} formation [2]. Another type of MIC is called « pepperpot » corrosion. Like type I pitting, it has cuprous oxide and cuprous chloride in pits and cupric oxide between pits.

3. Previous studies on pitting of copper in chloride solution

Type I pitting, the most widespread and the most threatening type of copper pitting, was extensively studied in connection with perforation of copper pipes for tap water. The pioneer work of Campbell [6] and May [7] showed in the early fifities that type I pits contain solid CuCl, and is often associated with a carbonaceous film on the surface of the tube. After an extensive research for INCRA (International Copper Research Association) in 1963-1965, CEBELCOR described in detail the pitting process and the conditions for the growth or the stifling of pits [8-11] : a continous cuprous oxide film is formed during the early days of exposure then, in hard or midly hard water, malachite is formed, first as a discontinous deposit. This malachite deposit somehow isolates some areas more than others from the free access of dissolved oxygen and so creates an « occluded corrosion cell ». A flow of local current becomes thus possible between these isolated areas and the rest of the surface. These local currents were already observed by May [7] and he noticed that the current direction was sometimes reversed.

The occluded cell is created by an acidification process and by the relative occlusion due to the malachite deposits. The initial step of copper corrosion produces some small amount of cuprous ion Cu^+. This ion is not stable in neutral water and tends to hydrolyse to a more stable form such as Cu_2O :

$$2\ Cu^+ + H_2O \rightarrow Cu_2O + 2\ H^+ \qquad (1)$$

This hydrolysis reaction produces acid and, as a result, more dissolved cuprous ion Cu+ is formed. When the solubility of Cu_2O is reached for the actual pH value, corrosion of metallic copper

$$Cu \rightarrow Cu^+ + e^- \qquad (2)$$

and reaction (1) occur again, with more acidification. The reduction reaction (reduction of oxygen) that balances the oxidation reaction (2) occurs more on the surfaces that are exposed to the aerated bulk water than inside the occluded cell.

Therefore, as it is now well known, the simple fact that local deposits form a barrier to the access of dissolved oxygen creates discrete sites that develop acid conditions and become active pits.

Consequent to this, pits are becoming more and more acid, their concentration in dissolved copper (Cu^+, Cu^{++}) increases, the positive charges in the pit solution are balanced by migration and diffusion of the most mobile anion (most often the chloride ion), thus the pit becomes more and more concentrated in chloride, until CuCl precipitates, instead of Cu_2O. When the potential of the open surfaces outside the pits is higher than the potential in the pit, the local pitting corrosion process proceeds at an accelerated rate. If, for any reason, the potential outside the pits is equal or lower than the potential in the pit, the local current flow is reversed (as was occasionally observed by May) and the pits stifle.

Lucey suggested another mechanism for copper pit formation [12]: dissolved oxygen is reduced on the outer surface of the cuprous oxide film originally present. This outer surface of the Cu_2O film acts as a cathode. Metallic copper is corroding underneath this Cu_2O film, generally as dissolved cuprous chloride $CuCl_2^-$. When the process goes on, the dissolved curpous chloride precipitates as solid CuCl under the Cu_2O film. And when the chloride concentration decreases due to the precipitation of CuCl, other copper salts start to precipitate.

Pitting corrosion of copper is approached in still another manner in SKB studies [13] : similar to the Lucey model, SKB considers that the reduction of oxygen occurs essentially on Cu_2O and not on the cupric oxide CuO. And, similar to the CEBELCOR views, SKB considers that there is a critical potential above which pits can grow. But the reason given is that the acidifying reactions work at a sufficient rate only above this potential. If this critical potential is higher than the equilibrium potential between Cu_2O and CuO potential, pitting will not occur. The pH for which this Cu_2O/CuO equilibrium potential is calculated is probably the pH in the pit, although it is not clear in the paper. For a given bulk water composition, the study calculates the critical potential for pitting and the maximum potential that Cu_2O can sustain. The comparison of the two gives a criterion for the pit growth and an idea of the severity of pitting.

Although the ideas in this study are interesting and the models are refined, we feel that basic and important mechanisms of the occluded cell mechanisms of localised corrosion are somewhat underestimated in this study, compared to the importance given to some estimated kinetic values.

In fact, the composition of the bulk solution and the pit solution are drastically different : in the pit, Cu_2O is formed by precipitation of the soluble copper ions (mostly Cu^+ and Cu^{++}, and also $CuCl_2^-$ in the more advanced stage) and not by direct oxidation of metallic copper, as considered in [13]. Cu_2O in the pit is a secondary corrosion products, it is highly porous and not at all protective. The acid in the pit is not formed by direct oxidation of Cu into Cu_2O, but by hydrolysis of soluble cuprous species. The corrosion potential of Cu in the pit is significantly lower than the Cu/Cu_2O equilibrium potential for the pH in the pit ; it is the determined by the equilibrium potential between Cu and the soluble ions Cu^+, Cu^{++}, $CuCl_2^-$. This potential depends more on the concentration of these ions than on the pH in the pit.

From a series of experimental results, we see that reduction of oxygen also occurs, at least to some extent, on surfaces covered with cupric salts (malachite etc.) and not only on cuprous oxide Cu_2O [8,9]. However, more work on this would be welcome.

From the above comments, it is possible and probable that the calculated criteria for pitting corrosion might be inadequate. See section 4, below.

4. Steady state conditions in copper pits in chloride solutions

If we know the exact conditions in copper pits (potential, pH, copper concentration, chloride concentration…), then we can determine a criterion for the stifling of pits and, if this criterion is not satisfied, we can indicate the exact conditions (pH, concentrations etc.) in which the corrosion rate should be determined experimentally.

This exercise was made by CEBELCOR in 1965 [10].

Figure 1 is the original picture (1963) of a cross section through a type I copper pit. At the bottom, there is white cuprous chloride CuCl, over which there is porous and reddish cuprous oxide Cu_2O. The pit is convered by the green malachite $CuCO_3.Cu(OH)_2$ and with some$CaCO_3$.

This shows that the porous cuprous oxide is a secondary corrosion product (formed by precipitation of copper ions) and that the pit is filled not with the bulk water but with a solution saturated in both CuCl and Cu_2O.

Figure 2 is a E-pH stablity diagram for the system Cu-Cl-H_2O, for 10^{-2} g.ion/L chloride which corresponds to a solution saturated in CuCl [14]. This shows that CuCl is stable only is acid conditions. By the way, historically, the sequence that led to the development of the « occluded corrosion cell » theory for localised corrosion was the following : copper pits were found to contain solid CuCl, diagrams were calculated for the system Cu-Cl-H_2O and showed that CuCl is stable only in acid solutions, then the acidification was explained by the corrosion and hydrolysis reactions presented above, and the corresponding increase in chloride concentration as well as the role of the potential on the local current flow and on corrosion or redeposition was demonstrated experimentally.

Coming back to figure 2, the only point where Cu, Cu_2O and CuCl are stable at the same time is indicated by a black circle. The potential is +270 mV_{she} and the pH is 3.5. Under certain assumptions (if activity equals concentration and if thermodynamic data are correct), the total dissolved copper concentration is $10^{-2.43}$ (234 ppm), of which $10^{-2.44}$ Cu^{++}, $10^{-3.37}$ $CuCl_2^-$ and $10^{-4.31}$ Cu^+ and the total chloride concentration is $10^{-2.12}$ (270 ppm), of which $10^{-2.17}$ Cl^- and $10^{-3.07}$ $CuCl_2^-$.
The simple criterion for copper pitting in chloride solution is thus : if the potential inside the pit is higher than +270 mV_{she} (ot +20 mV_{sce}), pits will grow, and they will stifle if the potential is below that value. Potential inside pits are not easy to measure ; therefore, it is convenient to correlate it to a potential measured outside the pit, by adding some diffusion potential which is often between 80 and 150 mV, depending on the size of the pit and of the curvature of the surface. The critical potential for pitting measured with a reference electrode placed outside the pit thus becomes +350 to +420 mV_{she} (or +100 to +170 mV_{sce}).

This closely corresponds to the separation between pitting and no pitting observed in practice and in laboratory experiments [10].

The SKB study [13] has another approach to determine the critical potential for pitting, and this was discussed in section 3 above. However, the values obtained are not too different : in most of the cases considered in the study [13], the critical pitting potential is between +100 and +240 mV_{she} (measured in the pit). For a rather similar water, CEBELCOR gives a slightly more conservative criterion of +270 mV_{she} (also in the pit) [8].

These critical pitting potentials must be compared to the actual potential during storage. We still lack data the in situ potentials. The underground laboratory at Äspö has apparently not yet provided such data [15]. At this time, some laboratory data are available : after one month in compacted bentonite, the potential of copper is between -130 and -80 mV_{she} [16]. This suggests that pit growth is impossible in those conditions.

The question was raised as to whether the critical pitting potential for copper depends on the chloride concentration or the pH of the bulk water. According to the occluded corrosion cell mechanism, the final conditions in the pit (potential, pH, dissolved copper and chloride concentrations) are determined by the solubility of CuCl and not by the composition of the bulk solution. This is consistent with the theory and practical observations on the critical potential for pitting propagation (also called « protection potential » or repassivation potential ») for other metals such as C-steel, stainless steels, titanium etc. [17].

5. Pitting of copper in solutions containing other ions than chloride

Copper pitting can also occur in the presence of other ions such as bicarbonate, sulphate and ferric ions. The cases of thiosulphate and sulphide also deserve to be considered.

To our knowledge, mechanistic studies on those cases are little developed or even absent. Still, a basic understanding of mechanisms of localised corrosion in these media is needed.

The sulphur compounds (sulphate, thiosulphate and sulphide) deserve a special attention because they will be present at some time in the repository and because the mechanisms of localised corrosion in these media have specific features. Copper sulphate is much more soluble and acidic than cuprous chloride and could thus act as a pitting promotor. This is the opposite situation compared to iron, where ferrous sulphate is less soluble than ferrous chloride and acts as an inhibitor against chloride pitting. Also, the non oxidising conditions prevailing in pits could change sulphate to sulphide, at least in the presence of microbial catalysts.
If sulphide is initially present in a slightly alkaline bulk water, HS^- will change to dissolved or gaseous H_2S in acid pits. The localised corrosion processes of copper in the presence of sulphide alone or in a mixture of chloride and sulphide are probably much different from those in chloride alone, and they need to be analysed by a mechanistic study. The same need was underlined before for other materials (C-steel, stainless steels).

Such a mechanistic study would solve the debated question as to whether copper can undergo localised corrosion in the presence of sulphide, as is mentioned in some SKB and canadian studies.

6. Transition from aeration to anoxy

The major driving force of localised corrosion is the reduction of oxygen.

It is expected that anoxic conditions will be reestablished after some time in the repository. It is thus important to analyse the evolution of active pits, when oxygen is progressively depleted. This is approached in section 7, below.

7. Evolution of pits when anoxy is established

The discussion below considers the case of chloride pitting. Others cases (sulphate, sulphide) would need further study.

The initial stage is an active pit is represented in figure 3 in a E-pH stability diagram by a black circle showing the occluded pit in a CuCl saturated solution. The vertical elongated zone in figure 3 shows the pH and the mixed potential on the surfaces surrounding the pits, exposed to the dilute bulk solution.
The « protection potential » zone is the critical potential defined earlier.

In oxidising conditions and when the pit is active, the mixed potential is above this « protection potential ». This potential is rather high (+350 to +420 mV_{she}). Indeed, most copper pits are observed when copper is coupled to more noble material, such as graphite, gold, platinum, rhodium etc. [9].

When oxygen is progessively depleted, the mixed potential decreases rapidly below the critical protection potential and the propagation of pitting corrosion is stopped. In the longer term, the mixed potential drops further, first down to the cupric oxide or cupric salt/Cu_2O equilibrium potential until all cupric salts are reduced, then further down to the Cu_2O/Cu equilibrium potential if reducing species are present and are able to reduce Cu_2O.

When an active pit which is initially saturated in CuCl ceases to propagate, the chloride and copper ions will slowly diffuse out of the pit, due to the concentration gradient. Progressively, the conditions in the pit will move from the black circle in figure 3 towards the right hand side, along the line Cu/Cu_2O, with an increase of pH and a decrease of the copper and chloride concentration. In the end, the pit will see the same conditions as the rest of the surface and further corrosion will either come to a complete stop or become slow and uniform.

The process described above is based on the interpretation of thermodynamic stability diagrams and on previous experimental studies conducted on iron [11]. Considering the use of copper canisters in deep geological repositories, it would be useful to conduct similar studies on copper, to verify the future of active pits under anoxic conditions. Such a study would provide details on the final potentials under full anoxy and on the influence of earlier active pits on the surface profile of copper.

8. Conclusions

The mechanims of copper pitting in the presence of chloride have been extensively studied and are now well known. Several approaches of these mechanisms have been compared (kinetics, mass transport, thermodynamics). As a result, the existence of a critical potential (or « protection potential ») below which pits do not grow is confirmed and quantified. The value of this critical protection potential is rather high (+270 mVshe in the pit, or +420 mV_{she} measured outside the pit).

The anoxic stage of the disposal will result in a deactivation of the pits. The trends for the conditions inside previously active pits has been described from mechanistic consideration, but further experimental studies on this deactivation process are recommended, for verification.

It is felt that there is still a field of uncertainty when sulphate, thiosulphate and sulphide are considered. The mechanisms of localised corrosion of copper in the presence of these ions is certainly largely different from those in chloride solution. As for other materials considered elsewhere for long term disposal (such as stainless steel), a study of the specific mechanisms of localised corrosion, in particular in the presence of sulphide, is recommended.

Other more practical recommendations directly derive from the this presentation : all remainings of grease must be avoided. Grease can oxidise to carboxylic acid by aging and oxidation, and carboxylic acid are corrosive to copper. Grease could also change to graphite if brought at high temperature under an inert atmosphere, which could happen during the welding process.

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Figure 1 : Cross section of a type I copper pit in Brussels tap water

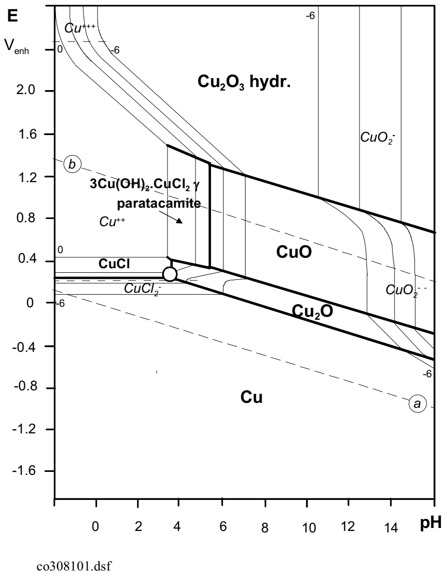

Figure 2 : Cu-Cl-H_2O for 10^{-2} g.ion/L chloride Cl^- [14]

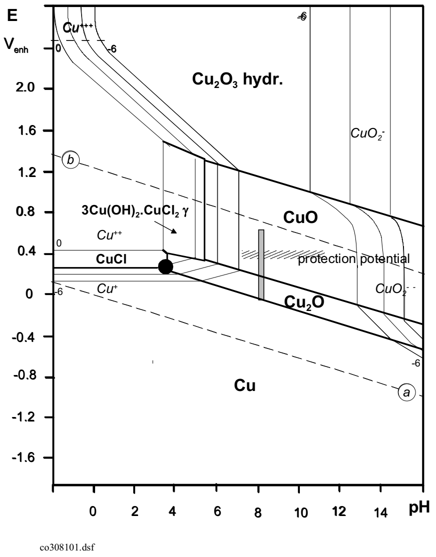

Figure 3 : Stability diagram for Cu-Cl-H_2O, with indication of the conditions in a CuCl saturated pit, on the open surfaces surrounding the pits and of the protection potential.

Extended abstract
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2 June, 2005

Methods for investigating stress corrosion cracking on copper

Presentation to the SKI EBS Workshop on Copper Corrosion, April 27, 2005

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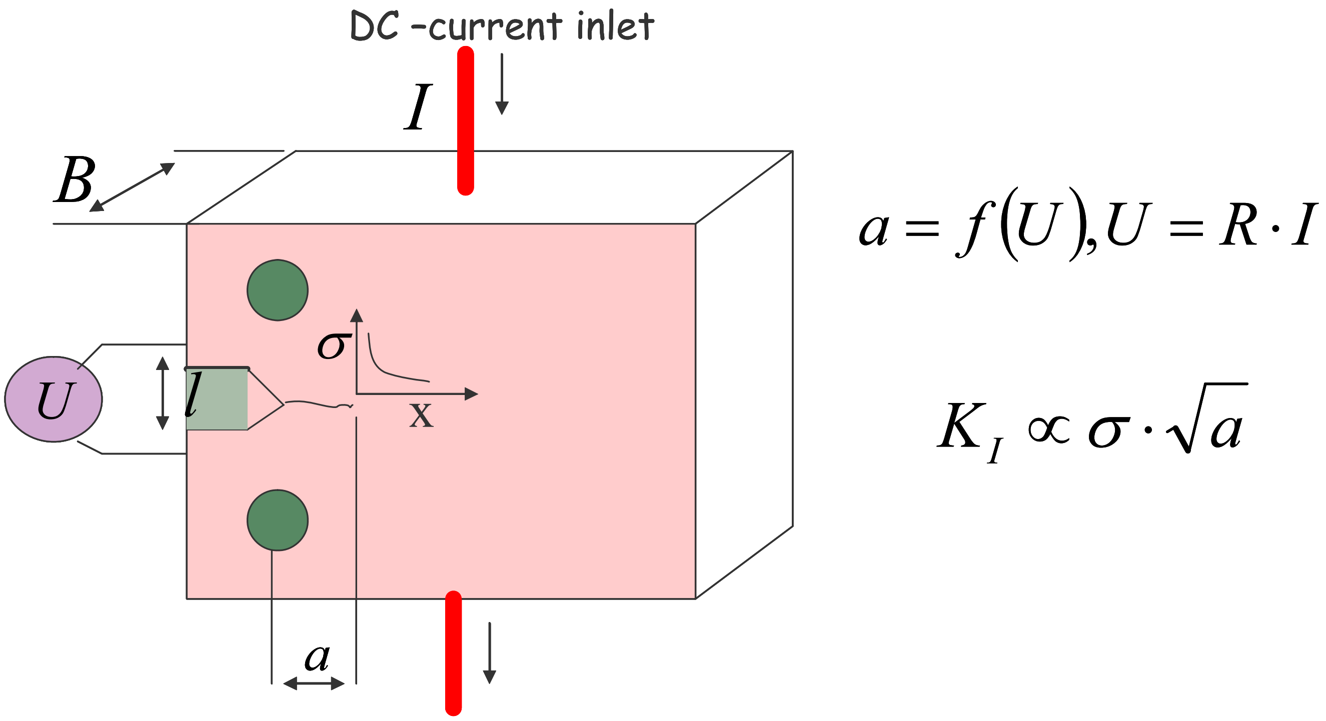
Stress corrosion cracking is a potential failure mechanism of the copper canister. Based on the earlier studies it is known [1] that SCC in pure copper

- occurs exclusively in the presence of a surface film
- is promoted by complexing agents such as NO_2^-, NH_4^+, $CH_3CO_2^-$ etc.
- occurs only in presence of dynamic straining.

Susceptibility to SCC can be studied in several ways. One possibility is to perform crack growth tests with large fracture mechanical specimens. Such tests are useful in the sense that by varying experimentally controllable parameters, i.e. stress intensity, concentration of chemicals, or electrode potential one may be able to determine minimum/maximum levels in these parameters that give rise to SCC.



$$a = f(U), U = R \cdot I$$

$$K_I \propto \sigma \cdot \sqrt{a}$$

Figure 1. Schematic showing the arrangement for crack growth rate measurement.

Fig. 1 shows a typical arrangement for crack growth rate measurement using a potential drop (PD) technique. In such an arrangement the resolution of crack length is largely determined by the noise in the electrical systems, which is in the range of ±1 μV, resulting in a minimum measurable growth rate in the range 10^{-8} to 10^{-9} mm/s. For the copper canister case one should be able to measure reliably crack growth rates at least two to three orders of magnitude lower than these. Thus, although in a certain crack growth rate measurement of copper one may see no crack growth (in a typical maximum test period of one month) this could not necessarily be taken as a proof that crack growth does not occur in a longer term.

Another possibility to study SCC is to use slow strain rate test (SSRT) which gives a more on-off type understanding of the susceptibility of copper to SCC in a given environment. In a slow strain rate test a tensile specimen is slowly strained to fracture in the environment of interest. Typically a strain rate of 10^{-6} s^{-1} to 10^{-7} s^{-1} is used, resulting in a test time from about a week to two months. Possible susceptibility to SCC is seen as a reduced strain (or more precisely elongation) needed to fracture the specimen. The SSRT is always complemented with a scanning electron microscope (SEM) investigation of the fracture surface. This is to verify whether any fracture morphological details typical to SCC can be found on the fracture surface.

A third experimental way to study susceptibility to SCC is to use voltammetry. Potentiokinetic polarisation curves have been successfully used to predict the susceptibility of brass to SCC in acetate, tartrate, formate and hydroxide [1]. This method is based on the assumption that the SCC of brass in these environments propagates via the anodic dissolution mechanism. In such a case the passivation properties of the crack walls (dominating during a slow sweep rate test) versus the passivation properties of the crack tip (dominating during a fast sweep rate test) are expected to be remarkably different within the range of potentials in which the material is susceptible to SCC.

The main target in SCC research with any technique would be to determine the limiting values for the critical parameters and to reveal the mechanism of SCC. The limiting values looked for include the critical concentration of the harmful species, the range of potentials in which the particular species has been found to cause SCC and the threshold stress level required for SCC to occur. These parameter values can then be compared with the corresponding values known to prevail in the final disposal vault in order to decide whether SCC is a real concern or not. This is the reasoning behind the Exclusion Principle approach introduced recently [2]. For this approach to be valid enough SCC data has to be known, including the influence of all three key parameters, i.e. stress, concentrations and potential.

As an example of the application of the Exclusion Principle, Fig. 2 shows the case of NO_2^- and copper. There is no overlap for the NO_2^- concentration – potential window where it is known that copper is susceptible to SCC and those of the repository conditions. Thus, the possibility of SCC can be excluded in this case. However, as shown in Fig. 3 for the case of NH_3, there is an overlap of the known SCC conditions and the repository conditions during the oxic period. This case needs further more detailed experimental and modelling studies to prove that SCC does not pose a problem for the canister integrity.

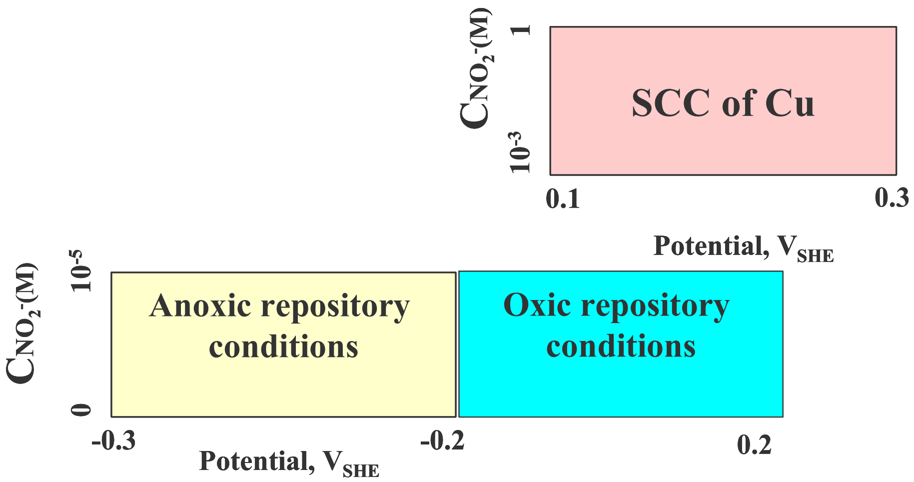


Figure 2. An example of the application of the Exclusion Principle for SCC of copper in presence of NO_2^-.

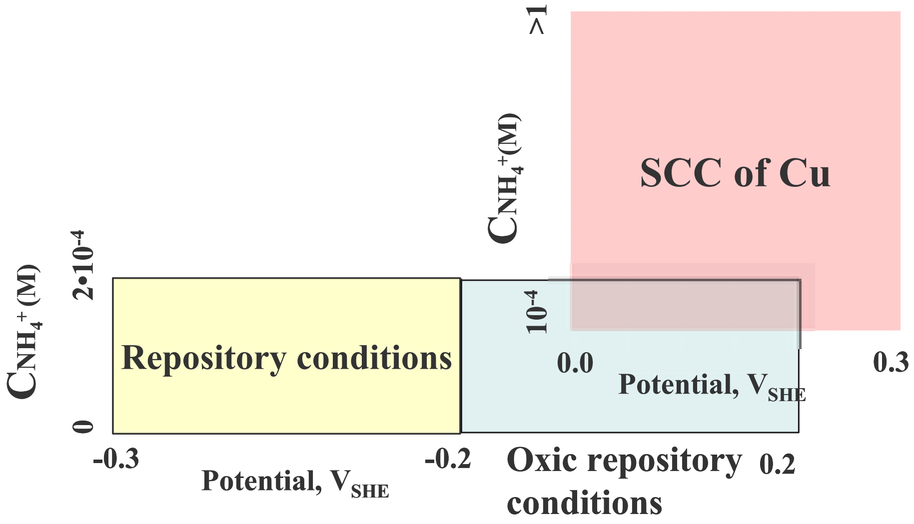


Figure 3. An example of the application of the Exclusion Principle for SCC of copper in presence of NH_3.

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