

Status of Corrosion Studies for Copper Used Fuel Containers Under Low Salinity Conditions

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ABSTRACT

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Abstract

Copper has been studied as a corrosion resistant material for used fuel containers in the Canadian nuclear waste management program. Over the past 20 years, many studies have been carried out on the corrosion behaviour of copper under anticipated low salinity conditions (< 60 g/L [Cl⁻]) that could be found in a deep geological repository in crystalline rock. The subject of copper corrosion has also been extensively studied in the Swedish and Finnish nuclear waste management programs as copper is also specified in their canister designs. This report summarizes the state of understanding of the long-term behaviour of copper under low salinity conditions from these studies and what the implications are for the predicted service life of the container in a deep geological repository. The key findings include:

- Copper will corrode under atmospheric conditions (at a relative humidity > 50-70%) and the rate and mechanism of corrosion will be affected by the presence of atmospheric contaminants.
- A copper used fuel container in a deep geological repository will experience an initial short period of uniform corrosion leading to some surface roughening under aerobic conditions, but once long-term anaerobic conditions are established, it will become thermodynamically stable in the absence of sulphide.
- Stress corrosion cracking on a copper used fuel container is unlikely due to the lack of:
 - (i) the required threshold concentration of stress corrosion cracking agents;
 - (ii) a suitable interfacial pH, and
 - (iii) the required corrosion potential on the copper surface. The elevated Cl⁻ and initially the elevated temperature will also lower the probability of stress corrosion cracking.
- Microbiologically influenced corrosion is expected to be controllable through the use of compacted bentonite to suppress microbial activity in the near field.

The knowledge gained over the past 20 years from studies on the corrosion of copper has allowed predictions of the lifetime of a copper used fuel container in a deep geological repository. Under low salinity groundwater conditions, a realistic estimate of copper corrosion from all processes is about 1.27 mm in 1 million years in a deep geological repository.

Therefore, the lifetime of a copper used fuel container is expected to exceed 1 million years in a deep geological repository in crystalline rock. This finding is consistent with the predicted container lifetime for the Swedish deep geological repository in crystalline rock.

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1. INTRODUCTION

The Nuclear Waste Management Organization (NWMO) is studying various corrosion resistant materials, including copper, for the long-term containment and isolation of used nuclear fuel in a deep geological repository. Copper has been considered as a possible corrosion barrier material for a used fuel container since copper has been shown to be thermodynamically stable in the anoxic conditions anticipated in a deep geological repository. Over the past 20 years, extensive experimental and modelling work has been carried out in Canada and internationally to study the long-term corrosion behaviour of a copper container in postulated repository environments with low salinity groundwater (< 100 g/L total dissolved solids or < 60 g/L [Cl⁻]) (King et al. 2010). Experimental studies have focussed on uniform corrosion, stress corrosion cracking (SCC) and microbiologically-influenced corrosion (MIC). Modelling studies have addressed uniform and localized corrosion (i.e., in the form of under-deposit corrosion), SCC, MIC, and predictions of the evolution of environmental conditions within a deep geological repository.

This report summarizes the state of knowledge on copper corrosion under low salinity.

2. COPPER USED FUEL CONTAINER

The NWMO's current reference design for a copper container is a dual-vessel comprising an outer oxygen-free phosphorus-doped (OFP) copper corrosion-barrier vessel, an inner steel load-bearing vessel and interior baskets for holding the used fuel bundles (Figure 1).

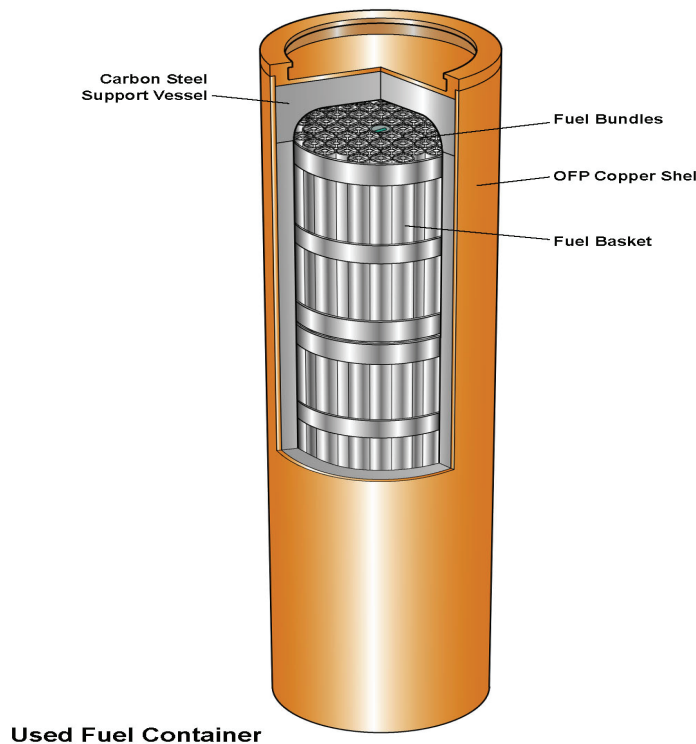


Figure 1: Conceptual Design of a Copper Used Fuel Container.

The OFP copper shell (typically ~ 25 to 50 mm thick) was developed in the Swedish national radioactive waste management program and is, essentially, oxygen-free copper (equivalent to UNS C10100) with the additional compositional requirements of some tens of ppm oxygen, 30-100 ppm phosphorus, < 0.6 ppm hydrogen, and < 12 ppm sulphur (SKB 2010). The phosphorus addition and the sulphur content are to obtain the required creep ductility. The hydrogen content is to avoid embrittlement during the manufacturing process. The oxygen content is to avoid corrosion coupled to grain boundary corrosion.

Various used fuel container designs and container welding methods are being evaluated by the NWMO as part of the Adaptive Phased Management Technical Program for long-term management of Canada's used nuclear fuel.

3. POSSIBLE CORROSION MECHANISMS OF COPPER

An extensive experimental and modelling program has been performed in Canada over the past 20 years on the potential corrosion of copper in a deep geological repository. Experimental research has focussed on uniform corrosion, SCC and MIC. Corrosion modelling has evaluated uniform and pitting corrosion, SCC, and MIC based on anticipated repository environments and their evolution with time. A list of studies conducted in the Canadian copper corrosion program is tabulated in Appendix A.

Overall, these studies conclude that a copper used fuel container in a deep geological repository will be primarily subject to general corrosion. The degree of localized attack (pitting), MIC and SCC will be negligible and can be controlled using sound engineering design and practice. All forms of corrosion will be stifled as the repository environment becomes anoxic. The various corrosion mechanisms are discussed in more detail in the following sections.

3.1 UNIFORM CORROSION

Copper would corrode in dry air via reaction 1. The rate of copper oxidation in dry air at temperatures below 150°C is of the order of nm/y (King and Watson, 2010), and, therefore, effectively negligible.

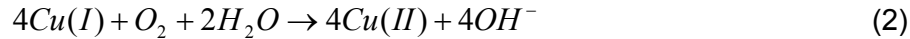


The uniform corrosion of copper (Cu) in the environment in a deep geological repository has been extensively studied and the corrosion mechanism is well understood. The corrosion behaviour of copper in oxygen (O₂) containing chloride (Cl⁻) environments has been well studied. King and Kolar (2000) have proposed a detailed reaction mechanism to account for the various electrochemical, chemical, redox, adsorption/desorption, precipitation/dissolution, and mass transport processes involved in the corrosion process in compacted bentonite. The behaviour of copper over a range of chloride concentrations has also been evaluated experimentally (King et al. 1997b). Kinetic rate constants, equilibrium constants and other thermodynamic parameters required for modelling are available (King 2008).

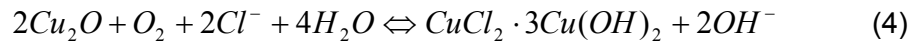
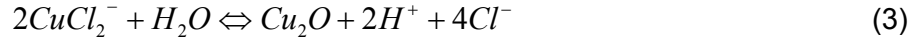
Copper would corrode in O₂ containing Cl⁻ solutions and under atmospheric conditions providing the relative humidity is above that required to form a thin surface water film (approximately 50 to 70% RH) (King et al. 2001, King et al. 2010). The rate of corrosion will depend on the presence

of atmospheric contaminants, such as SO₂, NO₂, and CO₂ (Leygraf and Graedel 2000). The water film acts as an electrolyte to support electrochemical reactions and the dissolved impurities will further enhance the corrosion process. For instance, the SO₂ forms HSO₃⁻ and can be oxidised to sulphate by oxidants in the air. The NO₂ can be absorbed in the water film as HNO₃.

Copper dissolves in Cl⁻ environments as the cuprous (Cu(I)) complex ion CuCl₂⁻. The anodic dissolution is coupled to the cathodic reduction of an oxidant, either dissolved O₂ or Cu²⁺. Cupric species are produced by homogeneous oxidation of Cu(I) by O₂ (Reaction 2).



Both Cu(I) and Cu(II) can precipitate as Cu₂O and CuCl₂·3Cu(OH)₂, respectively (Reactions 3 and 4). The duplex corrosion product layer would comprise an inner layer of Cu₂O and an outer layer of basic Cu(II) salts such as CuCl₂·3Cu(OH)₂ or Cu₂CO₃(OH)₂ depending on the specific composition of the pore water.



The precipitated surface film blocks surface electrochemical reactions and does not sustain the permanent separation of anodic and cathodic reactions that would be required for localized corrosion to occur. As the repository environment becomes anaerobic, the CuCl₂·3Cu(OH)₂ layer dissolves with further corrosion supported by the cathodic reduction of Cu(II).

In the absence of oxygen, corrosion would require reaction with water to produce hydrogen gas (H₂):



or



Known thermodynamic relationships (Pourbaix 1974) indicate that reaction 5 should not occur and that the corrosion product in reaction 6 has not been shown to be stable. Therefore, reactions 5 and 6 are considered very improbable in water. Under anaerobic conditions, copper corrosion accompanied by the evolution of H₂ does occur in the presence of sulphide (Reaction 7) (King et al. 2001, 2010).



Recently, it has been claimed that reactions 5 and 6 are thermodynamically possible. Gunnar Hultqvist and Peter Szakálos from the Royal Institute of Technology (Sweden) have published experimental results they claim indicates that copper can corrode in pure, oxygen-free water, which, if true, would have implications to the predicted container lifetimes (Szakálos et al. 2007). Their research claims that hydrogen ions are reduced in the anaerobic corrosion process to form hydrogen atoms. The hydrogen atoms can then either combine to form

hydrogen gas (H_2) or be absorbed into the metallic copper. This absorption into the metal can embrittle the copper. Such a claim would challenge the safety case of copper used fuel containers in a deep geological repository and the Swedish National Council organized an expert review to assess the issue of copper stability.

After a thorough assessment of the available experimental data by the expert review panel, the technical experts concluded that the experimental results interpreted by Hultqvist and Szakálos and claimed to show that copper oxidizes spontaneously in oxygen-free water by the reduction of protons, is not supported by the second law of thermodynamics and conflicts with accepted knowledge and experience (Swedish National Council Nuclear Waste Report 2010). The panel stated that it was necessary to demonstrate that the proposed corrosion product was thermodynamically stable before it could be justifiably claimed that copper could corrode in oxygen and sulphide-free water. Attempts to reproduce the reported observations (Szakálos et al. 2007) have not been successful (King 2010, King and Lilja 2011). At the current time, there is no evidence that water will oxidize copper. This suggests that copper corrosion would cease in a deep geological repository in the absence of oxygen and sulphide.

NWMO will continue to monitor this copper corrosion issue and respond to any developments that may affect the safety case of a deep geological repository.

In Canada, the prospect that highly saline groundwater could be encountered in a deep geological repository in sedimentary rock requires additional research to assess whether water may act as an oxidant in high salinity environments. The effect of salinity on the corrosion behaviour of copper is often estimated based on thermodynamic equilibrium expressions. However, most available thermodynamic parameters are generally reliable only up to chloride concentrations of ~ 2 mol/L of chloride. Thermodynamic data (i.e., equilibrium constants, activity coefficients) for solutions containing high concentrations of chloride, as seen in sedimentary rock formation (as high as 5 mol/L), are limited. In addition, most thermodynamic parameters are determined at 25°C and estimates of the thermodynamic data at other temperatures are frequently associated with an extrapolation error. The need to extrapolate to both high temperatures and high chloride concentrations requires better data.

Overall, the uniform corrosion behaviour of copper in conditions expected for a deep geological repository in crystalline rock is well understood. Both the mechanism of copper corrosion in oxygen-containing chloride (< 2 mol/L) and kinetic and thermodynamic parameters required for modelling are available. For the higher saline concentrations anticipated in sedimentary rock groundwater, the use of the existing thermodynamic data for high chloride concentrations at elevated temperature in order to determine if H_2O can act as an oxidant for copper involves some uncertainty.

An experimental program is being carried out by the NMWO to evaluate the anaerobic corrosion behaviour of copper under high-salinity conditions (i.e., about 5 to 6 molar chloride), which are typically found in sedimentary rock formations in Canada. The experiments would be used to identify conditions (if any) under which hydrogen may evolve from copper in the high-salinity solutions. A custom-designed pressure gauge system and a solid state hydrogen sensor would be used to detect hydrogen evolution during the experiments. The findings would be used to assess whether water could act as an oxidant for copper under the high-salinity repository conditions, which are expected in a deep geological repository in sedimentary rock in Canada.

3.2 LOCALIZED CORROSION

The extent of localized corrosion (pitting) of a copper used fuel container has been assessed using extreme-value analysis of literature pit-depth data (King and Leneveu 1992) and by comparison of predicted corrosion potential (E_{corr}) values to published breakdown and re-passivation potential data (King et al. 2001). In addition, studies designed to specifically examine the surface profile of copper corroded in groundwater-saturated, compacted buffer materials were carried out (Litke et al. 1992). Results showed that the copper will only undergo a form of surface roughening as a result of the non-permanent separation of anodic and cathodic processes. Evaluations of the distribution of precipitated corrosion products and surface morphology on the coupon surface (i.e., distribution of peaks and valleys on the surface) indicated an “under-deposit” corrosion. A mechanism to account for the observed surface profile, which involved the periodic separation of anodic and cathodic processes through the formation of temporary occluded cells has since been proposed (King and Kolar 2000).

Brennenstuhl et al. (2002a) carried out experiments to assess the possibility of localized corrosion of copper for the situation in which there are differences in the flux of O_2 to different parts of the container surface, for example, in the case where bentonite blocks of different density might be used around the container. In this situation, the (semi-) permanent spatial separation of anodic and cathodic processes is possible. It was shown that the localized corrosion rates would decrease with decreasing oxygen concentration and decreasing container surface temperature. The corroded copper surface showed only general corrosion with minor surface roughening and no distinct pitting. It was concluded that the rate and extent of localized corrosion in a deep geological repository would be very small since there will only be a limited supply of oxygen in a deep geological repository. It was expected that the corrosion products on the container surface would further limit the rate and extent of localized corrosion.

The long-term localized corrosion behaviour of copper has also been extensively studied in the Swedish / Finnish nuclear waste management programs. They predicted the depth of localised corrosion based on pitting factors and an analysis of empirical pitting data from archaeological artifacts subject to long-term burial in natural environments (Bresle et al. 1983, Swedish Corrosion Institute 1983, Werme et al. 1992). Extreme-value statistics have also been applied to estimate the maximum pit depth on a container as a function of exposure time in the repository. Taxen (1991) developed a pit propagation model for reducing conditions assuming the pit growth was limited by the transport of HS^- to the Cu surface.

Based on these various measurements and models, it was generally agreed that a Cu container in a deep geological repository will not undergo classical pitting corrosion, but only a surface roughening or under-deposit corrosion (King 2005b, King et al. 2010). Corrosion occurs under deposits on the surface, with the resultant temporary spatial separation of the anodic and cathodic sites accounting for the roughened surface. Surface roughening, or under-deposit corrosion, may add a maximum of 0.1 mm to the depth of general corrosion (King 2005b).

3.3 STRESS CORROSION CRACKING (SCC)

The occurrence of SCC requires a susceptible metal to be exposed to sufficient tensile stress and an active SCC agent. Copper is known to be susceptible to SCC in environments containing ammonia, nitrite ions, acetate, or, possibly, high concentrations of sulphide (King et

al. 2001, Taniguchi and Kawasaki 2008). Studies focussed on SCC have concluded that the SCC of copper requires the formation of a thin oxide or tarnish film (Ikeda and King 2001). When this film does not form, SCC is not observed.

While SCC agents are not normally found in natural groundwater, they could be introduced by either mining activities or microbial activity. Numerous tests have, therefore, been performed to assess the SCC behaviour of copper in nitrite-, ammonia- and acetate-containing environments (Ikeda and Litke 2000, Ikeda et al. 2004, Litke and Ikeda 2006, Litke and Ikeda 2011). Results indicate that copper SCC susceptibility would decrease with decreasing concentrations of the SCC agents. These studies also suggest a threshold concentration level for each agent below which SCC would not occur. Also observed in these studies is the inhibiting effect of chloride on copper SCC in nitrite, ammonia and acetate environments, the SCC susceptibility decreasing with increasing chloride concentration. The ability of chloride to inhibit SCC susceptibility also appears to be enhanced by elevated temperatures, as exhibited in tests conducted at 100 to 130°C (in nitrite only and nitrite/chloride solutions). This effect can be attributed to the ability of chloride ions to promote general dissolution of copper, which results in more uniform corrosion at the expense of the formation of the required thin oxide film.

Surface defects on the used fuel container surface can act as stress concentrators (notch-like defects) or stress intensifiers (crack-like defects) and may increase the probability of crack initiation or growth, respectively. King (2004) has performed a literature review and engineering analyses to assess the effect of surface discontinuities on the initiation and propagation of localised corrosion and SCC of copper welds. The findings indicate no evidence that weld discontinuities would adversely affect the localized corrosion and SCC behaviour of copper containers. The predicted service life of the containers is not affected by the presence of the surface discontinuities.

A number of mechanisms have been proposed for the SCC of copper, including film-rupture / anodic dissolution, tarnish rupture, film-induced cleavage, and surface mobility mechanisms (Ikeda and King 2001, King 1996a, King et al. 2001). Taking into account the pre-requisites for crack initiation and crack growth, King and Kolar (2004) have defined a conceptual SCC model for copper containers in a repository based on predicting whether the necessary environmental conditions will exist or co-exist. The model is mechanistically based and defines various absolute and conditional criteria for SCC. This model also addresses each of the environmental parameters that control the initiation and growth of SCC.

Research results have suggested SCC under aerobic conditions in a deep geological repository is unlikely as the pre-requisite conditions of corrosion potential, interfacial pH, and concentration of SCC agent do not exist simultaneously at the container surface (King and Newman 2010, King et al. 2010). According to mechanistic arguments, there is also no evidence to indicate that SCC of copper is possible under anaerobic conditions at the sulphide levels expected at the container surface (King and Newman 2010). Based on the nature of the repository environment, SCC does not appear to be a threat to the integrity of a copper UFC.

Despite the low risk of SCC on copper, suitable engineering procedures can be effectively applied to further minimize the probability of SCC. For instance; (i) the level of airborne ammonia and nitrite formed during blasting operations can be controlled to below the threshold concentration in order to preclude the possibility of cracking; (ii) the residual tensile stress following container shell and bottom manufacturing can be thermally relieved; and (iii) the residual stress on the final closure weld can be controlled and/or reduced using a suitable

welding technique. It is nevertheless good engineering practice to perform a post-weld stress relief of the final closure weld, regardless of the apparent SCC susceptibility of the material. The introduction of a surface compressive stress has proven to be an effective way of preventing the initiation of SCC on various industrial structures. Ambient temperature techniques, such as laser peening and low plasticity burnishing have been developed in the Yucca Mountain Project for this purpose (DOE 2008).

3.4 MICROBIOLOGICALLY INFLUENCED CORROSION (MIC)

Similar to other engineering materials, copper is susceptible to microbiologically influenced corrosion (MIC) (Little et al. 1991). Microbial metabolic by-products may affect the SCC behaviour of copper as microbial activity may form SCC agents, namely ammonia, nitrite, and acetate ions (King et al. 2002, 2003, 2004). Ammonia and nitrite are produced (and also consumed) by different types of microbe as part of the nitrogen cycle. Acetate is produced by the fermentation of organic molecules. Another species often considered is HS^- produced by the reduction of sulphate by sulphate-reducing bacteria (SRB). This last reaction occurs under anaerobic conditions and requires the presence of simple organic molecules or H_2 as electron acceptors (King et al. 2004). Without the formation of biofilms on the container surface, the only form of MIC possible is that due to the diffusion of remotely-produced metabolic by-products through the bentonite to the container surface. Sulphide ions produced at a location away from the container surface must diffuse through the bentonite sealing materials to have any effect on container corrosion. The corrosion rate is, therefore, limited by the rate of diffusion of sulphide (HS^-) to the container surface, a continued supply of which is required to sustain MIC.

The Canadian microbial experimental program has demonstrated that a water activity of ≤ 0.96 in a bentonite buffer can effectively suppress the microbial activity, which can be achieved by a minimum bentonite dry density of 1.6 Mg/m^3 (Stroes-Gascoyne et al. 2006, 2007) or a minimum pore-water salinity of 60 g NaCl/L (Stroes-Gascoyne and Hamon 2008). It has also been shown that microbial activity would be suppressed in a bentonite buffer system with swelling pressure of $\geq 2 \text{ MPa}$ (Masurat et al. 2007).

A reactive-transport corrosion model to predict the extent of MIC of copper containers has also been developed in the Canadian corrosion program (King and Kolar 2006, King et al. 2002, 2003 and 2004). This model (King and Kolar 2006) indicates that microbial activity in the repository will not result in shorter container lifetimes. The amount of sulphide ions provided by the microbial reduction of sulphate that reach the container surface is predicted to be insignificant over a million year timeframe. The amount of nitrite and acetate ions, both of which are associated with SCC of copper, are similarly insignificant. Although a higher maximum concentration of ammonia (another known SCC agent) of $\sim 10^{-6} \text{ mol.dm}^{-3}$ is predicted at the container surface, cracking is unlikely because of the relatively low concentration and because ammonia is only formed after all oxidants in the repository have been consumed.

4. COPPER CORROSION ALLOWANCE

Lifetime assessments have been performed for copper UFCs in various national nuclear waste management programs. In all cases, the corrosion processes considered in the assessments have been uniform corrosion, localized corrosion, SCC, and MIC.

Corrosion modelling of the Canadian copper container began in 1996 as part of AECL's Second Case Study. An early version of the Copper Corrosion Model (CCM) estimated the maximum depth of copper wall loss caused by uniform corrosion to be 0.011 mm (King et al. 1996). This estimate was based on the prediction that only a fraction of the initially trapped O₂ will support copper corrosion, the remainder being consumed by reaction with iron minerals in the sealing material. Although the process was considered unlikely, the depth of pitting corrosion was predicted based on a statistical extreme-value analysis of literature pit depth data. The maximum pit depth was conservatively estimated to be 6 mm after 1 million years. Stress corrosion cracking was not considered because of the limited period of tensile stress, the absence of SCC agents, the lack of oxidant during the anoxic phase, and the inhibitive effects of chloride ions in the pore water. Microbial activity was considered possible, but to be of limited impact. Based on the assumption that sulphate-reducing bacteria activity would occur in the host rock near the borehole and would, conservatively, produce a continuous concentration of 3 ppm of hydrogen sulphide, the corrosion rate was estimated at 1 nm.a⁻¹ and the corrosion allowance for MIC was estimated to be 1 mm after 1 million years (King and Stroes-Gascoyne 1995, King 1996b).

In 2005, a preliminary estimate of the lifetime of copper containers in a deep geological repository in a sedimentary rock formation was performed (King 2005b). This assessment yielded a maximum depth of uniform corrosion of 0.17 mm based on the initial oxygen inventory (102 moles per container) in the repository. The revised uniform corrosion allowance also did not take credit for the consumption of oxygen by microbial activity and by reaction with Fe(II) minerals. For localized corrosion, a 0.1 mm pit depth is predicted based on the argument that localized corrosion occurs as surface roughening in the form of under-deposit corrosion rather than distinct pitting (King 2005b). Recent reviews have generally agreed that this surface roughening argument is more realistic since the container will not undergo pitting corrosion and considered the previous 6 mm estimate to be overly conservative (King and Watson 2010, Landolt et al. 2009). SCC remains excluded in this recent assessment for similar reasons to those used previously, which include the absence of SCC agents and the inhibitive effects of chloride ions. The corrosion allowance for MIC remains at the 1 mm depth.

Therefore, the total wall loss due to copper corrosion after 1 million years is realistically predicted to be about 1.27 mm (i.e., 0.17 mm (uniform corrosion) + 0.1 mm (under-deposit corrosion) + 1 mm (MIC)).

5. CONCLUSIONS

Research work over the past 20 years has established a good understanding of the long-term performance of copper used fuel containers in a deep geological repository in a low salinity crystalline rock environment. A work program specifically designed to study the long-term stability of copper and copper oxides in a high salinity environment, which could be encountered in a deep sedimentary rock repository, is currently being planned.

In the low salinity environments anticipated in crystalline rock groundwater (i.e., < 2 mol/L), copper will begin to corrode under early atmospheric conditions provided the relative humidity is above ~ 50-70%. The rate and mechanism of corrosion will be affected by the presence of atmospheric contaminants such as SO₂ and NO₂. With time, as the repository environment evolves, the copper container will experience an initial aerobic period of uniform corrosion and some form of surface roughening, before establishing a long-term condition of thermodynamic

stability. Uniform corrosion is associated with active copper dissolution in the presence of chloride, which causes the copper container to corrode uniformly, thereby avoiding localized corrosion. Stress corrosion cracking (SCC) on the copper container is considered unlikely due to the lack of the pre-requisite conditions for SCC, namely, the required threshold concentration of SCC agents, a suitable interfacial pH, and the required corrosion potential on the copper surface. Microbiologically influenced corrosion (MIC) of copper will be controlled by the use of compacted bentonite around the copper container to suppress microbial activity in the near field.

Although there have been claims that water acts as an oxidant for copper, the available evidence is not compelling and attempts to reproduce the observations have not been successful. At the current time, therefore, there is no evidence that water oxidises copper. It is expected that corrosion of a copper container in a deep geological repository would cease in the absence of oxygen and sulphide.

The knowledge gained over the past 20 years from studies on the corrosion of copper has allowed improved and more realistic predictions to be made for the lifetime of a copper container in a deep geological repository. Under low salinity groundwater conditions, a realistic estimate of the total extent of copper corrosion from all processes is a loss of wall thickness of about 1.27 mm in 1 million years.

Therefore, the lifetime of a copper used fuel container is expected to exceed 1 million years in a deep geological repository in crystalline rock. This finding is consistent with the predicted container lifetime for the Swedish deep geological repository in crystalline rock (King et al. 2010).

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APPENDIX A: STUDIES OF THE CORROSION MECHANISMS OF COPPER

Studied Topic	Reference
<p>Uniform Corrosion</p> <ul style="list-style-type: none"> ▪ Environmental conditions of a deep geological repository and an overview of corrosion behaviour of copper ▪ Copper corrosion in synthetic groundwater ▪ Anodic dissolution of Cu in Cl⁻ solutions ▪ Cathodic reduction of O₂ and the effect of surface films ▪ Dissolution behaviour of CuCl₂·3Cu(OH)₂ and Cu₂O ▪ Effect of mass transport, [Cl⁻] and [O₂] on E_{CORR} ▪ Effect of HS⁻ on the E_{CORR} and simulation of the evolution of E_{CORR} in a repository ▪ Corrosion behaviour of Cu in bentonite, measurements of corrosion rate and the nature of corrosion products ▪ Measurements of sorption of Cu(II) on bentonite ▪ Creep behaviour of oxygen free OFP copper ▪ Effect of γ-radiation on the corrosion of Cu ▪ Copper corrosion model 	<p>Johnson et al. 1996 King et al. 1994 King 2005a King 2005b King 2006 King and Kolar 1995 King and Kolar 1997a King and Kolar 1997b McMurray et al. 2003 Oscarson and Dixon 1989 Quigley 1984 King and Litke 1987 King and Litke 1989a b King et al. 1995a, b King and Kolar 2000 King et al. 1995c King et al. 1995d King and Stroes-Gascoyne 1997</p> <p>King et al. 1992 Litke et al. 1992 King et al. 1997b Graham et al. 1997 Ryan and King 1994 Ho 2000 Shoesmith and King 1999 King 1996b King and Kolar 1996a King and Kolar 1996b King and Kolar 1997a King and Kolar 2000 King and Kolar 2006 King 2008</p>
<p>Localized Corrosion</p> <ul style="list-style-type: none"> ▪ Under-deposit corrosion studies ▪ Microstructural characterization of OFP-doped copper 	<p>Brennenstuhl et al. 2002a Brennenstuhl et al. 2002b</p>

APPENDIX A (cont'd)

Studied Topic	Reference
<p>Stress Corrosion Cracking SCC</p> <ul style="list-style-type: none">▪ Stress corrosion cracking of a copper container in a deep geological repository ▪ Effect of nitrite and ammonia on SCC of OFP copper ▪ SCC of Cu in acetate solutions▪ Copper corrosion model for SCC ▪ Anodic dissolution of Cu in Cl⁻/SO₄²⁻, Cl⁻/NH₃ solutions	<p>King 1996a King et al. 1999a King et al. 1999b King et al. 1999c King and Kolar 2005 Ikeda and King 2001 King et al. 1997 Ikeda and Litke 2000 Litke and Ikeda 2011 Ikeda and Litke 2007 Ikeda et al. 2004 Litke and Ikeda 2006 King 2001 King and Kolar 2004 King and Tang 1998 King et al. 1997a</p>
<p>Microbiologically Influenced Corrosion (MIC)</p> <ul style="list-style-type: none">▪ MIC of a copper UFC ▪ Copper corrosion model for MIC ▪ Effects of dry density and salinity of bentonite	<p>King 1996c King and Stroes-Gascoyne 1997 King et al. 2003 King et al. 2002 King et al. 2004 Stroes-Gascoyne et al. 2006</p>