Review of the NWMO Copper Corrosion Program

NWMO-TR-2016-11 **August 2016**

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ABSTRACT

Title: **Review of the NWMO Copper Corrosion Program**
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Abstract

Beginning in 2011, the Nuclear Waste Management Organization (NWMO) initiated a design change for their deep geological repository (DGR) system for the long-term storage of used nuclear fuel. In addition to significant changes to emplacement and clay buffer methods, a primary change was the adoption of a copper-coated used fuel container (UFC). To support this vessel, the NWMO initiated a series of copper corrosion related research programs, to compliment the many years of research that have been previously performed on copper for its use in DGRs. As much of this historic work has been previously reviewed [Scully & Edwards 2013], an emphasis within this current review was placed on the active copper corrosion programs, and the potential impacts of copper corrosion mechanisms to the copper-coated UFC. The review panel concluded that the NWMO has developed a well-integrated and world-leading research team to conduct this work, through a combination of academic institutions, industrial consultants and international collaborations. The research effort is extensive, and can be summarized in the following statements:

- The programs have been well designed to address the specific requirements of copper-coated UFCs in anticipation of the eventual licensing such a container. Future efforts and funding should remain within the existing topics: anoxic corrosion of copper; radiolysis related corrosion of copper; copper coating vs. wrought copper corrosion; localized corrosion of copper. Possible enhancements of research as proposed by the review team will fall into these categories.

- In addition to supporting the use of copper coatings, the programs are providing significant data for the generic use of copper as a DGR material within an eventual license application. Ongoing partnerships with other international organizations responsible for nuclear waste management have produced a mutually beneficial knowledge database that will continue to build confidence in this topic.

- The NWMO has developed a clear path forward with respect to continued research on copper corrosion as its proceeds to a site selection and the site-specific chemistry that will be produced in the future. The successful conclusion of the existing corrosion programs combined with the future programs that incorporate site-specific data are highly likely to support very long lifetime predictions for UFCs (i.e., 100,000 y), provided supporting assumptions with respect to geochemistry, environment, bentonite clay performance, as well as container/bentonite manufacturing can be substantiated.

Information from parallel research in microbial processes affecting DGRs was also provided, but was not the scope of this review. Nonetheless, it was clear that the NWMO microbial and corrosion programs are well integrated, and supportive of each other.

The review also focused on uncertainties within the prediction of copper corrosion, and a series of recommendations with respect to future work were derived. Using the same topic breakdowns as above, these are:

- Anoxic copper corrosion investigations should emphasize efforts for identifying the source and technical basis for hydrogen observed during experiments in pure water and brine. In addition, the effect of sulphide as a catalyst for anoxic corrosion should be specifically assessed;
- Radiolysis copper corrosion programs require an additional effort to integrate the experimental results that are providing enhanced understanding of mechanisms, etc., into applied results, such as rate laws or understanding of processes that contribute towards understanding the basis for estimating a corrosion allowance;
- Copper coating investigations should focus on ensuring a continuing characterization of samples that use the actual selected manufacturing processes, and the resultant corrosion behaviour as the NWMO develops a final manufacturing method. The technical basis for any differences in corrosion behavior between electrodeposited copper and wrought copper should be understood; this includes sulphide induced corrosion, radiolytic corrosion, and anoxic modes (i.e., any that contribute to the corrosion allowance calculation);
- Localized corrosion research should continue to define differences between active and passive conditions to ensure that corrosion via pitting does not occur. Long-term testing is encouraged.

An additional recommendation from this review is that:

- The internal corrosion program should include specific investigations with respect to the evolved hydrogen, and its eventual fate (i.e., sources and sinks) inside a used fuel container.

With respect to the related microbial programs not evaluated in this review, the NWMO is encouraged to conduct a future peer review, with the specific goals of assessing these programs, as well as their integration with the corrosion programs.

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1. INTRODUCTION

The Nuclear Waste Management Organization (NWMO) is responsible for designing and implementing the program for long-term nuclear waste management in Canada. A proposed concept for permanent storage of spent nuclear fuel involves use of a deep geological repository (DGR), within which multiple engineered barriers isolate the used fuel from the environment. Beginning in 2011, the NWMO initiated a design change for their DGR system. In addition to significant changes to emplacement and clay buffer methods, a primary change was the adoption of a copper-coated used fuel container (UFC). The previous reference UFC consisted of a two-part, steel-copper cylindrical vessel, consisting of an inner steel 100 mm thick structural and containment component, and an outer 25 mm thick wrought copper corrosion barrier. The new UFC design (denoted the 'Mark 2') instead utilizes a 3 mm integral copper coating on a fully welded cylindrical steel container with hemispherical heads. In addition to advantages in its structural integrity under pressure and some manufacturing considerations, the Mark 2 is also substantially shorter and lighter than its predecessor, which offers improved flexibility in handling.

To support this DGR concept and the new UFC design, the NWMO initiated a comprehensive proof test plan (PTP). The PTP outlines a program to verify that the design concept meets design requirements and to develop a formal body of knowledge that can be used to illustrate this proof to the regulator, NWMO Board of Directors, and the Canadian public. One important goal of the PTP is to demonstrate confidence that the Mark 2 UFC will safely contain nuclear waste for a minimum of 100,000 years. To build this necessary confidence, the NWMO has initiated a series of corrosion research programs that complement the many years of research that have been previously performed on copper corrosion for its use in DGRs. The goal of this report is to provide a critical review of these ongoing corrosion programs and to evaluate the likelihood that these programs will enable the NWMO to demonstrate confidence in the corrosion resistance of the Mark 2 UFC.

1.1 HISTORICAL COPPER CORROSION RESEARCH

On account of its known thermodynamic stability in anoxic conditions and relatively low cost compared to noble metal alternatives, copper has been widely studied as a corrosion resistant fuel canister material for DGR environments since its first consideration in 1978.[1] Studies have been conducted in low salinity environments ($[Cl]^- < 60\ g\ L^{-1}$), bentonite, and various mixed sulphate/chloride solutions.[2–24] Other studies have considered copper corrosion in sulphide solutions.[18–20,25–36] Previously reviewed NWMO studies have encompassed the uniform corrosion, localized corrosion including under-deposit corrosion, stress corrosion cracking, and microbiologically influenced corrosion (MIC) of copper.[6,37–45]

The primary purpose of the copper corrosion barrier is to ensure that the used fuel remains contained for at least 100,000 years by preventing exposure of the underlying steel to DGR water and thus preserving the UFC integrity. A prior NWMO report examined the minimum copper thickness requirement and assessed that over the first 1,000,000 years, 1.27 mm of copper was a sufficient thickness for protection against uniform corrosion under the proposed disposal scenario.[41] This allowance was based on maximum estimates of copper wall penetration of up to 0.17 mm from uniform copper corrosion,[4] 0.1 mm from under-deposit corrosion,[4] and 1 mm from MIC.[46,47] As indicated above, the revised NWMO UFC design has a 3 mm copper layer, which is significantly thinner than the previous reference design. Nonetheless, this coating is in excess of double the NWMO estimated corrosion allowance requirement.

Two primary objectives of the ongoing corrosion programs are to explore additional possible corrosion processes not included in the 2011 estimate and to build confidence in the NWMO corrosion allowance as it applies to copper coating.

The goal of this report is to provide an independent critical review of the NWMO corrosion programs and to assess the prospect that they will lead to a sufficiently confident corrosion allowance for a copper barrier layer in DGR conditions. As much of the historic work on copper corrosion has been previously reviewed,[44] the emphasis of the present review is on the active NWMO copper corrosion programs and whether these will address remaining issues surrounding corrosion mechanisms for the copper-coated UFC. These programs have been subdivided into five general categories: i) anoxic copper corrosion, ii) radiolysis-induced copper corrosion, iii) copper form: wrought vs coated via electrodeposition, iv) damaged coatings and galvanic corrosion, and v) localized copper corrosion. Parallel research into the possible effects of microbial processes on UFC corrosion, internal container corrosion, stress corrosion cracking, and the effects of glaciation on corrosion are also briefly summarized. Although these studies are outside the scope of the present review, their integration with the NWMO copper corrosion programs is discussed. Finally, the prospect that the NWMO corrosion programs will lead to a successful licence application is evaluated.

1.2 DESCRIPTION OF PTP PROGRAMS

1.2.1 Anoxic Corrosion

Corrosion in anoxic waters has been considered in three conditions: pure water, chloride solutions (brine), and sulphide solutions. This program considers all three and the final condition is complemented by an extensive microbiologically influenced corrosion (MIC) program discussed in section 1.3.1.

The previous review of the NWMO corrosion allowance highlighted that it does not include any contribution from the anoxic corrosion of copper in pure water.[41,44] Yet there is some question regarding the thermodynamics for the spontaneous corrosion of copper in anoxic pure water and whether such corrosion even occurs.[48–63] In particular, the nature of a hitherto unidentified H_xCuO_y surface species and the resulting equilibrium H_2 pressure remain unresolved.[1,53–56,58–60,62–66] These factors have historically prevented the assessment of an anoxic pure water corrosion allowance with any confidence. Indeed, it is unclear if such an allowance is even necessary. In response, the NWMO has initiated a program with the primary objective to assess the corrosion rates of copper containers in anoxic groundwaters. In addition to the pure water case, anoxic waters may also be categorized as chloride solutions (brine) or sulphide solutions.[44]

The anoxic exposure of copper to pure water and brine solutions was accompanied by the measurement of trace hydrogen, which, for these experiments, was presumed to be released via an anoxic corrosion mechanism. Where hydrogen was detected, equivalent corrosion rates were calculated, assuming one of the following overall electrochemical reactions are operative to produce Cu^+ (from the latter equation, $CuCl_2^-$ can also be produced):

$$Cu_{(s)} + H_2O_{(l)} \rightarrow CuOH_{(ads)} + \frac{1}{2}\,H_{2(g)} \qquad 1.1$$

$$Cu_{(s)} + H_2O_{(l)} + 3\,Cl^{-}_{(aq)} \rightarrow CuCl^{2-}_{3(aq)} + OH^{-}_{(aq)} + \frac{1}{2}\,H_{2(g)} \qquad 1.2$$

The reaction of copper with aqueous sulphide such as shown in Equation 1.3, has also been investigated in a variety of binary solutions that contained both chloride and sulphide anions (within the concentration ranges 5×10^{-5} M ≤ $[SH^{-}]$ ≤ 1×10^{-3} M and 0 M ≤ $[Cl^{-}]$ ≤ 5 M) for immersion times up to 4000 h. Such high chloride concentrations may be relevant to the groundwaters in a Canadian DGR site. The surface film thickness, composition, and morphology were determined using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) as a function of time to examine the film growth kinetics and mechanism. For instance, sulphidation may occur by the following half-cell reaction:

$$2\,Cu_{(s)} + SH^{-}_{(aq)} + H_2O_{(l)} \rightarrow Cu_2S_{(s)} + OH^{-}_{(aq)} + H_{2(g)} \qquad 1.3$$

The NWMO is in the early stages of a program to determine whether hydrogen sulphide accelerates copper corrosion for the mechanism presumed by Equations 1.1 and 1.2 (above) where new Cu(I) cations are produced, aided by fast water reduction on Cu_2S, but new SH^{-} is not supplied. This route is different than SH^{-} induced corrosion where a sulphide anion can corrode at most two copper atoms (Equation 1.3). This may occur, for instance, through the formation of highly active copper sulphide cathodic surfaces or through control of the electrochemical potential. The precise work program will evolve as the project progresses and results are generated.

Other variables continue to be investigated, such as water chemistry, hydrogen sulphide dose concentration, temperature, etc. The general approach of this program is to monitor copper corrosion by measuring the amount of hydrogen gas produced and assuming an overall electrochemical reaction involving anodic and cathodic half reactions such as shown above.

1.2.2 Radiolysis Corrosion

The concern has been raised that some radiolysis of the environment surrounding the UFC will occur, which may lead to container corrosion.[67–70] Moreover, the proposed UFC has significantly thinner walls than the previous reference design and will therefore provide less radiation shielding. Therefore, a series of projects are underway to determine the influence of γ-radiation on copper corrosion under the different stages of the repository conditions. These studies are as follows:

(i) Radiolysis modeling of the anticipated repository environments
(ii) Radiolytic corrosion of copper in humid gaseous environments
(iii) Corrosion of copper in nitric acid solutions
(iv) Radiolytic corrosion of copper in saline groundwater

The radiolysis modeling builds upon previously developed liquid- and vapour-phase water radiolysis models.[71–77] The model development in this program is focused on establishing a humid air radiolysis model (HARM) and a groundwater radiolysis model (GWRM). The model development activities include i) assembling a comprehensive list of reactions and corresponding kinetic parameters (g-values for radiolysis, rate constants for chemical); and ii) verifying that the models are properly coded into the commercial software package FACSIMILE. For example, HARM presently includes 730 chemical reactions, 25 primary radiolysis products, and 95 secondary species. Using these parameters and the necessary initial conditions (humidity, dose rate, chloride concentration, etc.), FACSIMILE numerically calculates the evolving concentrations of the various radiolysis products as a function of time.

The radiolytic corrosion processes in humid gas are being monitored using a variety of surface analysis techniques and, in saline groundwater, conventional electrochemical measurements. It has been shown previously that the type and extent of corrosion damage may depend not only on accumulated dose, but also on the dose rate.[67] To account for and examine this possible dose rate dependence, radiolytic corrosion experiments in this program utilize both high (~3 kGy h^{-1}) and low (0.29 Gy h^{-1}) dose rate γ-radiation sources.

The potential effects of radiolytically produced nitric acid on the corrosion of copper are being investigated by performing electrochemical and other corrosion experiments in solutions prepared with various concentrations of nitric acid and oxygen. To simulate condensed droplets, these tests are performed in a small cell to minimize the ratio of the solution volume to the copper electrode surface area.

1.2.3 Copper Form: Wrought vs. Coated

One key assumption for the NWMO program is that the properties and corrosion performance of the copper coatings are the same as the bulk copper samples for which the copper corrosion allowance was originally estimated.[41] To test this assumption, this program is evaluating the properties and corrosion performance of electrodeposited and cold spray copper coatings on an ASTM A516 grade 70 steel substrate.[78] For the cold spray coatings, both as-sprayed and annealed (350 °C, 1 h, argon) are being examined. As a reference point, these materials are being compared to phosphorus-doped, oxygen-free wrought copper provided by SKB.

The properties and characteristics under investigation include:

(i) Surface morphology (SEM/EDX)
(ii) Porosity at the surface and in the bulk (SEM/EDX and EBSD)
(iii) Presence and distribution of impurities (SEM/EDX, ToF-SIMS, and XRD)
(iv) Hardness (Knoop microhardness)
(v) Presence and distribution of microstrain (EBSD)

To compare the corrosion behaviour of the coatings and SKB wrought copper, standard electrochemical measurements were performed in anoxic 3 mol L^{-1} NaCl aqueous solution (E_{corr} and R_p). To simulate the transition from oxic to anoxic conditions in a repository, samples were exposed to an oxygen-purged solution for a period and then an argon-purged solution (a few ppm O_2). To accurately simulate long-term anoxic conditions, experiments were also performed in an anaerobic glove box (< 1 ppm O_2).

1.2.4 Damaged Coatings and Galvanic Corrosion

Although inspection procedures should prevent it, a through-coating defect within the copper coating would potentially be a highly damaging corrosion situation. In the short term, while conditions at the container surface are oxidizing, due to the presence of O_2 trapped on sealing the repository and/or the γ-radiolytic production of oxidants, this would render the underlying container susceptible to galvanic corrosion. In this scenario, the oxidant reduction is expected to occur on the coating and on the through-coating defect wall and would support steel corrosion at the base of the defect. Although oxidizing conditions, and the associated galvanic couple, are expected to persist for only a limited period, corrosion of the steel exposed at such a location could continue under anoxic conditions, and eventually lead to failure of the container.

A series of additional experiments has been initiated, in which defective coatings are simulated in inert resin layers on steel substrates by drilling through coatings to expose the underlying steel. These electrodes are then coupled through zero resistance ammeters to copper electrodes of known dimensions and the rate of the galvanic process monitored by measuring the coupled current. A range of electrochemical, spectroscopic and microscopic techniques are being used to characterize the evolution of conditions within the defect, and X-ray tomography is being used to directly observe the extent and distribution of corrosion damage at the defect location. These experiments enable the accumulation of relevant kinetic information and to specify how the relative cathode/anode areas will influence the rate of steel corrosion. The goals of this project are the following:

(i) To evaluate quantitatively the extent and distribution of corrosion damage as a function of the inventory of available oxidant anticipated within a repository.
(ii) To determine what the long-term consequences of such a defect will be once anoxic conditions are eventually established.
(iii) To determine whether the coating process influences the distribution of corrosion damage, in particular whether the copper/steel interface is susceptible to corrosion and possible debonding.
(iv) To accumulate a quantitative database that will enable specification of the chemical conditions prevailing within a corroding defect and use them to develop a model to predict the long-term corrosion rate.
(v) To use the direct observations from X-ray tomography as the basis for the evaluation of corrosion damage and for validation of the corrosion model.

1.2.5 Localized Copper Corrosion

Early waste container corrosion models implicitly assumed that localized corrosion, in the form of pitting, would occur and either included a pitting factor[79] or a conservative statistical analysis of pitting depths[9] using data recorded in unrelated exposure environments. However, more relevant studies and recent reviews indicate corrosion will be general leading to a roughening of the surface.[11,44,80] Yet the justification that this would be the case is considered incomplete. King and Lilja have considered the near-field environmental conditions and concluded that the conditions will not lead to passivation of the container surface and, hence, pitting will not occur.[81,82] Whereas such an analysis may provide sufficient evidence for the relatively thick-walled KBS-3 copper container (50 mm), greater certainty is required for the 3 mm of copper in the Mark 2 UFC design.

The goals of this project are to quantify the extent of any localized corrosion or surface roughening and to build confidence in the NWMO corrosion allowance. The overall approach involves both experimental and computational components and is designed in three stages:

(i) Determining whether the container surface will be passive or active in anticipated repository conditions
(ii) The development of models and the collection of input data
(iii) The assessment and quantification of the degree of damage to the container compared to the corrosion allowance

To determine whether active or passive conditions will occur, potentiodynamic polarization profiles were measured on copper in an extensive variety of solution conditions. Solution parameters included temperature, pH, chloride concentration, sulphate concentration, and carbonate concentration. From these results, active-passive (AP) maps were prepared and compared with the anticipated near-field environment during the early thermal transient. These near-field conditions were predicted by considering factors including the inventory of trapped O_2, the extent of O_2 consumption by processes other than container corrosion, the level of γ-radiation, the time- and spatial-dependent degree of saturation, and the inventory of chloride and sulphate anions from the clay and the groundwater.

In the passive regions, a larger inventory of critical potential values is being determined. In keeping with standard practice these potentials are the corrosion potential (E_{CORR}), the pitting breakdown potential (E_B) and the repassivation potential (E_{RP}). Pitting is only expected if $E_{CORR} > E_{RP}$. Since these values are expected to be statistically distributed a sufficiently large database of values will allow the probability of pitting to be expressed. For assessment of the likelihood of pitting of containers in the repository, models are being developed to predict the variation of E_{CORR} (along with the associated uncertainty) for evolving repository conditions.

1.3 CORROSION MECHANISMS AND PROGRAMS NOT CONSIDERED IN THIS REVIEW

The NWMO PTP includes several additional programs that are outside of the scope of the present report. These are briefly summarized below with some discussion of their integration with the above-described programs. They were not, however, subject to a detailed critical review here.

1.3.1 Microbiologically Influenced Corrosion

From the geosphere, it has been assumed by the NWMO that some microbiological activity will produce a small amount of soluble sulphide at remote distances, which will gradually make its way to the UFC. Because copper reacts with sulphide according to 1.4, this degradation mechanism is included in the corrosion allowance:

$$2Cu(s) + HS^{-}(aq) + H^{+}(aq) \rightarrow Cu_2S + H_2(g) \qquad 1.4$$

Although the bulk of the 1.27 mm corrosion allowance previously stated is dominated by a 1 mm microbiologically influenced corrosion (MIC) value,[41] review of the fundamental understanding of the relevant microbiological processes is better performed separately from this review. Nonetheless, some of the corrosion programs have been developed to consider the effect of sulphide on copper within the DGR. In particular to the proposed design of the DGR, modelling the transportation of sulphide to the UFC as a function of its shape and placement within bentonite buffer has been highlighted within this review.

1.3.2 Internal Container Corrosion

The total oxygen inventory in a sealed Mark 2 container is insufficient to cause penetration of the carbon steel by general corrosion. However, allowing for the possibility of trapped water in a failed used fuel bundle leading to localized corrosion does provide a potential mechanism for container failure. This possibility is being investigated by an internal container corrosion program. This program is examining the possibility of localized corrosion a) at the weld site where the cylindrical container is joined with the hemispherical head and b) on the bold surface. The influence of γ-radiation and solution parameters including pH, dissolved metal ion concentrations, and oxidant concentrations on these processes are also being considered. The experimental portion of this program includes coupon corrosion tests of steel welds, galvanic coupling experiments for steel electrodes with various gap spacing, and high dose rate γ-radiation exposure tests.

Exposure tests were performed on welded steel samples to investigate the possibility of crevice corrosion due to water trapped inside a container. No localized corrosion has been observed at the weld site: i.e., there was no evidence of crevice corrosion. Rather, corrosion progresses at a slower rate at the weld site than on the bold carbon steel surface. This is attributed to a different evolution of solution parameters at the weld site, which leads to faster formation of a uniform protective oxide layer. This accelerates the corrosion rate on the bold surface, but the galvanic effect is quite small. Detailed parametric studies to determine the evolution of carbon steel corrosion and the resulting evolution of solution parameters in different water volumes are ongoing.

1.3.3 Stress Corrosion Cracking

Within previous reviews, stress corrosion cracking (SCC) has been assessed, based on this mechanism's requirements of a combination of susceptible material, environment and external tensile stress threshold.[2,37,42–44,83] As copper is not particularly susceptible to SCC, there is not a wide range of agents available within a DGR capable of producing SCC. In principle, ammonia, nitrite, acetate and sulphide produced microbiologically are among this narrow range. However, tensile stresses are needed to cause stress corrosion cracking. For the Mark 2 container, the hemi-spherical heads are welded to the cylindrical body such the shape ensures that external stresses are 100% compressive in a DGR (i.e. tensile stresses do not exist). This situation is consistent throughout the UFC life; thus it may not be considered a degradation mechanism.

1.3.4 Effects of Glaciation Loading on Corrosion

In response to new research questions that were not considered when the PTP was originally written, the NWMO has recently initiated a new program to examine the joint effects of corrosion and glaciation events on container integrity. The overview of this early-stage program provides the review committee an opportunity to appreciate very much the NWMO's adaptability to new research questions and the approach it takes to initiating and implementing new programs. Since the research program itself is still in a preliminary stage, the experimental methods will not be discussed or reviewed here.

2. SUMMARY OF PTP PROGRAM FINDINGS

2.1 CORROSION MECHANISMS AND PROGRAMS IN THIS REVIEW

2.1.1 Anoxic Corrosion

The exposure experiments conducted in pure anoxic water on bare and oxidized copper wires at 30 to 50 °C produced hydrogen at or near the detection limit of the equivalent of < 0.1 nm y^{-1}. At 75 °C the majority of the cells produced hydrogen at a constant equivalent corrosion rate of ≤ 1 nm y^{-1} for many months. A temperature perturbation event caused a sudden increase in the hydrogen production rate, followed by a monotonic rate decay, which decreased to below the detection limit over a number of weeks. The concentration of copper in flushed solutions was one to two orders of magnitude less than would correspond to the detected hydrogen, and refreshing of the solution did not restart the hydrogen evolution, which would suggest that anoxic corrosion rates near 1 nm y^{-1} are significantly overestimated by hydrogen evolution measurements.

When these hydrogen evolution experiments were recently repeated in an improved cell for which the detection limit was enhanced, the initial calculated corrosion rate at 75 °C was slightly lower, at an equivalent to ≤ 0.22 nm y^{-1}. In this case, the equivalent rate decreased to below the detection limit of 0.02 nm y^{-1} in just 70 days. The origin of this discrepancy is currently under investigation, but may be linked with hydrogen outgassing (see below). Regardless, while there is an ongoing interest in conducting these experiments and furthering the understanding of this process, the impact of the process is expected to be insignificant to the safety of the container, because the maximum equivalent corrosion rate is already accounted for within the existing corrosion allowance.

Corrosion experiments were conducted in anoxic buffered brine solutions with chloride concentration ranging from 0.25 to 5 mol kg^{-1}. As in the case of pure water, corrosion at 30 ºC is below the detection limit of < 0.1 nm y^{-1}. For exposures conducted primarily at 75ºC, elevated temperature perturbations produced occasional corrosion rate increases. The highest recorded rate during one of these perturbations was 30 nm y^{-1} for one measurement interval (i.e. 2 weeks). Typical measurements ranged between 4 – 10 nm y^{-1}, but the cells eventually decreased below the detection limit within 600 days from the experiment start. Solution refreshing did restart the hydrogen production at a reduced rate in one cell and is progressing while the cell is at 50 ºC.

Literature data suggested the possibility that the detected hydrogen originated from copper outgassing rather than corrosion. It is not possible to rule out this possibility in the case of the pure water cells, as total hydrogen produced from a 2 y exposure is similar to the maximum solubility of hydrogen within copper. Moreover, pristine wire from the same manufacturer was heated in a N_2 environment and H_2 was detected at high temperature (> 350 °C). The total H_2 removed was comparable to the cumulative H_2 detected after 2 y corrosion in pure water. As noted above, this may demonstrate that the source of the hydrogen is not wholly attributable to corrosion, particularly for the pure water experiments. However, some of the brine cells produced 14 times more hydrogen than the worst case scenario of thermal charging at the extremely low rates noted. This suggests a continuing exploration of this topic is desirable to further refine the understanding of this hydrogen evolution process; although it should also be noted that the maximum corrosion from this process is well within the existing corrosion allowance.

In anoxic sulphide solutions, the Cu_2S morphology and film growth kinetics (parabolic vs. linear) were measured at various sulphide and chloride concentrations. From the results, three corrosion behavior categories are observed: i) compact film growth controlled by Cu(I) transport through the sulphide film (occurs at high [SH^-], low [Cl^-]), ii) semi-porous film growth controlled by sulphide transport in the film pores and in the bulk solution (moderate [SH^-], high [Cl^-]), and iii) porous film growth controlled by Cu(I) and/or sulphide transport in the porous film (low [SH^-], high [Cl^-]).

It is the reviewers' opinion that the corrosion generated by this mechanism will fall within the assumed corrosion allowance. Future work will examine the effect of trace amounts of sulphide anions (on the order of a few ppm or less) in chloride-free and high salinity brine solutions on the rate of copper corrosion and on any surface species formed. As part of this work, experiments will be performed in which cells are 'dosed' with H_2S/SH^- equivalent to some fraction of a monolayer of copper sulphide. The low sulphur coverage regime is of interest to examine a plausible range and address the issue of whether one sulphide atom corrodes more than 2 copper atoms. The effect of bicarbonate buffer solutions will also be investigated.

2.1.2 Radiolysis Corrosion

Preliminary findings from the model calculations have identified the main radiolytic products of dry air (O_3 and NO_x) and humid air (HNO_3). The model also provides insight into the production rate of oxidants as a function of time, dose rate, and relative humidity that will ultimately be incorporated into a comprehensive model for corrosion in the early repository conditions.

The groundwater radiolysis model has identified the initial production of H_2O_2, followed by slow conversion to progressively weaker oxidants with time ($HClO_x$, $1 \leq x \leq 3$). The model similarly provides insight into the production rate and steady-state concentrations of oxidants as a function of time, dose rate, and chloride concentration. These results will be incorporated into a model for a saturated DGR environment.

Humid-air low dose rate radiolysis corrosion experiments demonstrate that γ-radiation causes corrosion layers growth to spread laterally more quickly relative to non-irradiated samples where oxygen is supplied without limitation. In either case, there is no evidence of intergranular attack. It is hypothesized that radiation promotes water condensation and establishes a slightly more oxidizing environment, leading to observed differences in the corrosion behavior. Short-term corrosion experiments at high dose rates demonstrate that the γ-radiation leads to more uniform corrosion than non-irradiated exposure tests. The extent of radiolysis corrosion in O_2/N_2 atmosphere is more severe than in O_2/Ar, which supports the conclusion from the radiolysis model that nitric acid production occurs and motivates the nitric acid tests summarized below.

Copper corrosion during exposure to nitric acid solutions (10 mM $\leq HNO_3 \leq$ 150 mM) were monitored by measuring the solution pH. The pH-time profile is divided into three regions: i) constant proton consumption rate, ii) short-term pH plateau near the pK_a of HNO_2, and iii) long-term pH plateau at steady state. Replicate experiments were interrupted at these three stages for surface imaging, depth-profiling, and chemical analysis. At low pH, a surface roughening up to a few µm deep occurs. There is, however, no evidence of pit formation or intergranular attack and the roughening is likely due to grain-orientation-dependent corrosion kinetics. A systematic study of copper corrosion kinetics as a function of nitric acid concentration, dissolved oxygen concentration, pH, and the water depth is ongoing. Future work will also measure the dissolved copper content in solution and corrosion deposit thickness as functions of time. Rate laws will be established as a part of this work.

Coupon corrosion tests were performed in sealed vials as a function of chloride concentration in aerated and deaerated solutions, with and without γ-irradiation (3 kGy h^{-1}). Following these tests, samples were taken for surface imaging, cross-sectional imaging, and chemical analysis. The results indicate that the experimental conditions affect the corrosion layer growth rate and morphology. The results are complemented by electrochemical measurements in chemically simulated radiolysis environments (10 µM H_2O_2 or HOCl) that examine the combined effects of dose rate, pH, and temperature. Significantly, there is no evidence of localized corrosion from any of these tests. A systematic study on copper corrosion kinetics in concentrated chloride solutions as a function of H_2O_2 concentration, HOCl concentration, and γ-radiation dose is ongoing.

It is the reviewers' opinion that the corrosion generated by this mechanism will not be localized. The investigators are encouraged to continue their preliminary, but ongoing, work to establish rate laws and to determine if growth is parabolic or otherwise slows down with time. With this information, a case can be made for why and how this form of corrosion is anticipated to produce depth of penetrations within a corrosion allowance. Once the work here described has been completed, it is assessed that the current programs will lead to a confident maximum corrosion allowance estimate.

2.1.3 Copper Form: Wrought vs. Coated Corrosion

In general, the electrodeposited coating, cold spray coating, and SKB wrought copper samples exhibit similar corrosion behaviour. For anaerobic conditions, E_{corr} is stable within the range -375 to -380 mV_{SCE}. R_p initially decreased slightly and then increased by approximately one order of magnitude. Additional specimens were removed at intervals and analysed by optical microscopy, SEM, and Raman spectroscopy, and reveal that the electrode surfaces were decorated with small Cu_2S deposits, formed from trace sulphide impurities in the NaCl. Therefore, the initial decrease in R_p is attributed to the removal of the air-formed oxide layers and the gradual increase may be attributable to the formation of the insulating sulphide. Large E_{corr} variations observed during exposure to oxygenated solution are attributed to the formation and subsequent delamination of an atacamite corrosion layer. On switching to anoxic conditions, E_{corr} decreased to values similar to those observed in the anaerobic experiments, while R_p remained lower. This suggests a slightly higher corrosion rate, which may be due to the coupling of Cu(II) reduction and Cu(0) oxidation. These samples were similarly decorated with Cu_2S deposits. For the cold spray copper coating, there was minor damage along the particle boundaries following corrosion in oxygenated solution.

The results support the inclusion of decades of corrosion studies on wrought copper samples to model the corrosion behaviour of the NWMO copper coatings. To further build confidence in this approach, a more diverse range of corrosion studies is planned involving a combination of long-term exposure tests and shorter term electrochemically-accelerated experiments. It was recommended that the testing includes a somewhat broader range of exploration in terms of test methods, durations as well as types of corrosion as is ongoing in other aspects of the program to detect whether differences in corrosion behaviour emerge for any of the types of corrosion anticipated. Of particular importance is the progress of the damage accumulation and distribution at the coating/exposure solution interface, and whether corrosion can access, and then propagate more rapidly at internal defects in the coating (i.e., nanoporosity, void space, crystallographic grain boundaries). Since no single approach can unequivocally demonstrate how the corrosion front will propagate, a series of different approaches is being used:

(i) Electrochemically accelerated experiments under galvanostatic conditions
(ii) Corrosion experiments in anaerobic sulphide solutions
(iii) Long-term exposure experiments under anaerobic and aerobic conditions
(iv) Long-term corrosion tests with a layer of bentonite clay on the copper surface
(v) Potentiodynamic tests near active-passive boundaries to confirm the coating passivation behaviour matches that of wrought copper

It is the reviewers' opinion that the corrosion of the copper coating materials will fall within the assumed corrosion allowance for wrought copper.

2.1.4 Damaged Coatings and Galvanic Corrosion

Based on chemical surface analysis and electrochemical measurements, the chemical and electrochemical processes within a simulated defect have been determined for O_2-rich solutions and are summarized in Figure 2.1.[84]

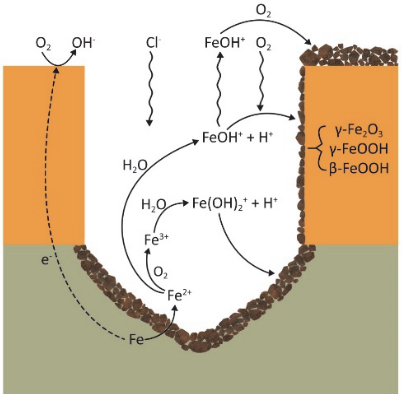

Figure 2.1: Schematic illustration of the chemistry inside a coating defect during corrosion in an O_2-purged 3 mol L^{-1} NaCl solution.[84]

The X-ray microtomography measurements show void spaces within the coating produced during coating development. A more detailed analysis of image slices confirms this porosity is not interlinked and does not threaten the coating integrity, although an allowance when defining a corrosion allowance should be considered if such porosity is observed in the optimized coatings (i.e., those to be used in production). The corrosion products are uniformly distributed on the exposed steel surface, indicating a minimal microstructural influence on the corrosion front and, at least within this exposure timescale, no localized corrosion. The presence of corrosion products along the copper/steel interface shows that the corrosion process propagates along this region and overcomes the bonding strength between the coating and the steel. Again, it is essential to note that the cold-spray coating process was far from optimized on this particular specimen. Additional studies show that the interface on electrodeposited coatings does not experience a similar corrosion process.

Presently, research is underway to follow the distribution of damage as a function of exposure time and oxygen concentration, including the anoxic condition. Since a very large number of image slices are recorded, the volume of metal loss can be measured, converted to a mass load and, via Faraday's law, to the inventory of consumed O_2. These experiments provide the required relationship to define the required damage function for a given solution environment. Future work is encouraged to continue to explore the nature of the cathodic reaction and a number of solution conditions, such as the effect of sulphide on galvanic corrosion.

The NWMO currently treats through-coating defects as failed containers in their safety scenario. Therefore, corrosion by this mechanism will not affect the assumed copper corrosion allowance. Nonetheless, this program will provide useful insight such as an accurate estimate of the time until container failure may occur.

2.1.5 Localized Copper Corrosion

Based on the NWMO's detailed analysis of the anticipated near-field environment during the period of localized corrosion susceptibility and the extensive active-passive (AP) maps, localized corrosion via conventional pitting is not expected. The expected range of near-field conditions (temperature, pH, chloride concentration, sulphate concentration, carbonate concentration) lies fully within the experimentally measured active region and is 2-3 pH units from the AP boundary. Passive corrosion conditions are therefore not anticipated in a DGR environment, making pitting corrosion unlikely.

This program will continue to refine the AP maps to further build confidence that passive conditions will not occur in a DGR. Efforts will continue to accurately measure the passivation parameters (E_{CORR}, E_B, E_{RP}). These results will be incorporated into a COMSOL model under development to prepare a statistical analysis of the probability for pit formation in DGR conditions. New experiments will be conducted in within the active region to determine how the roughness of the surface evolves with exposure time. These experiments will be conducted with and without bentonite clay layers and will provide the database required to develop a model based on the birth, growth and death of randomly distributed anodes and cathodes. In addition, the very slight roughening that has been observed previously for copper, for which there is a 0.1 mm corrosion allowance,[41] will be investigated using a multi-electrode array, among other methods. By defining discrete electrode regions, periods during which the individual electrodes support/undergo cathodic or anodic electrochemical events will be assessed, both for frequency and lifetime. Array tests on pitting susceptibility are also recommended to explore whether passivation can occur when the cathode is local during the period of O_2 consumption. These local cathodes could at least hypothetically alter the surface pH in such a way that passivation and subsequent pitting could occur. The potentiodynamic test involves an infinite cathode but it is remotely located. These efforts are expected to enhance the understanding of the empirical results noted above by providing a technical basis by which to understand roughening with time.

It is the reviewers’ opinion that the corrosion will fall within the assumed corrosion allowance.

3. RECOMMENDATIONS FROM REVIEWERS FOR PTP PROGRAM TOPICS

3.1 CORROSION MECHANISMS AND PROGRAMS IN THIS REVIEW

3.1.1 Anoxic Corrosion

The anoxic corrosion program includes a series of meticulous experiments performed over several years that will make valuable contributions to the fundamental knowledge of copper corrosion thermodynamics and kinetics. The researchers are encouraged to continue and expand current efforts to ascertain the presently unknown origin of the measured H_2 in these experiments. That is, it is important to determine whether H_2 is truly generated from the slow corrosion of copper or if it is introduced into the cell as pre-existing dissolved hydrogen at interstitial and trap sites in the copper wires. It is suggested to analyse hydrogen in copper samples before and after long-term tests by methods such as temperature-programmed desorption (TPD, even intentionally adding hydrogen by pre-charging in some samples) paired with the hydrogen-specific probe. Another way to be sure of the hydrogen source is the use of deuterium as a unique marker with D_2O, for instance. An important area to investigate is also whether low concentrations of sulphide may catalyse the corrosion of copper in anoxic solutions. The NWMO’s proposal to perform a series of long-term corrosion studies in dilute sulphide solutions has a high probability of addressing this issue.

In conjunction with the MIC research programs, there is a good prospect that through the continuation of these experiments, NWMO will confidently measure an upper limit for the corrosion allowance of anoxic corrosion in a DGR for the first 100,000 y.

3.1.2 Radiolysis Corrosion

Relative to the NWMO’s other corrosion programs, the radiolysis corrosion program is still at an early stage. Nonetheless, this program has already produced a large quantity of results and new findings that cover two main domains: humid atmospheres mainly and also aqueous solutions. These investigations are expected to provide fundamental insight into the radiolytic production of oxidants (H_2O_2, HNO_x, $HClO_x$, etc.) and the mechanism of corrosion for copper exposed to these chemical species.

It is apparent that the potential for radiolysis-induced corrosion of the copper layer is a significant issue that merits the further investigations outlined in the PTP. It is suggested that the largest challenge this program may face is the integration of modeling efforts with experimental results in a way that will lead to an accurate corrosion allowance determination. Such a model must be robust enough to handle the effects of changing DGR conditions with time, including temperature, humidity/saturation, and dose rate. It must also consider the heterogeneous nature of the copper-bentonite interface together with the international results.[67-68] The NWMO and its collaborators appear to recognize these challenges and have initiated relevant work that will be required to develop this model, such as dose rate calculations for the Mark 2 UFC as a function of time. It is therefore reasonable to anticipate that the continuation and expansion of the present radiolysis corrosion modeling and experimental programs will ultimately lead to sufficient insight for the NWMO to include an accurate radiolysis corrosion component in its copper corrosion allowance. The programs will contribute also to solve the influences of the dose rate versus the integrated dose on the radiolysis corrosion. Rate laws and transitions in corrosion processes will be important to elucidate.

3.1.3 Copper Form: Wrought vs. Coated

The results demonstrate that the corrosion performance of the copper coatings is quite similar to SKB wrought copper samples. Future work should continue to characterize electrodeposited and cold spray coatings, especially as NWMO and its partners further optimize the manufacturing methods. It is suggested to include more environments in the comparison between copper coatings and wrought copper, to deeply characterise the coatings (isotropy, porosity, impurities, stress, strain, etc.) and to include electrochemical measurements but also evolution of the corrosion interface, of damages with corrosion rates. Testing might be more broadly explored under different corrosion scenarios, e.g., sulphides, brines, etc. It is anticipated that this work will provide sufficient confidence to leverage the extensive body of corrosion studies on wrought copper for the NWMO copper corrosion allowance estimate.

3.1.4 Damaged Coatings and Galvanic Corrosion

The through-coating defect experiments are the first step in determining how the galvanic corrosion process will evolve as redox conditions change (*i.e.*, the availability of O_2 is reduced). This is an essential requirement if the process and the damages are to be modeled under repository conditions. Modelling galvanic corrosion involves basic electrochemical data including identifying and capturing effects of possible cathodic reactions. The NWMO is encouraged to pursue its plans to further characterize the cold spray coating porosity and to develop a statistical model for the formation of through-coating defects.

Future studies should consider the potential for hydrogen blistering and coating delamination, either from the radiation-induced absorption of hydrogen in the copper coating[70] corrosion products at the interface, or from hydrogen produced during internal container corrosion of the steel structural element.

3.1.5 Localized Copper Corrosion

The NWMO has conducted a thorough literature review and produced a detailed analysis of the possible conditions in which localized corrosion of the container may occur. Combined with extensive electrochemical measurements, it has already been demonstrated with reasonable confidence that the passive conditions necessary for localized corrosion will not occur in a DGR. The NWMO is nonetheless encouraged to continue the additional experimental and modeling programs outlined in the PTP, the successful execution of which will culminate with the preparation of a comprehensive statistical analysis of the probability for localized container corrosion in a DGR. In particular, the proposed use of close-spaced multi-electrode arrays is a promising approach to collecting the requisite statistically-relevant data for this analysis. This approach also places anodes and cathodes in close proximity as opposed to a polarization test where the cathodic reaction is remote and can identify composition–bulk pH combinations where the regions mapped via potentiostatic methods can be reconfirmed.[85,86]

By establishing a statistical analysis on the probability of localized corrosion and pit formation as well as the technical basis for roughening by moving clusters of anode and cathode sites, this program is anticipated to provide the necessary level of confidence for this component of the NWMO copper corrosion allowance.

3.2 CORROSION MECHANISMS AND PROGRAMS NOT CONSIDERED IN THIS REVIEW

Given that these programs were only summarily examined for this review, no comments are provided here on their prospects for contributing to a successful license application. However, some comments are made regarding how these programs will integrate and support the copper corrosion studies reviewed above.

3.2.1 Microbiologically Influenced Corrosion

The microbial programs appear to be well-considered, with respect to their integration into the corrosion work. It has to be remembered that the maximum estimate of copper wall penetration due to MIC is 1 mm while the estimates for all the other corrosion phenomena are of 0.27 mm. In future, the NWMO should consider performing peer-review of this work, including an assessment of its continued integration into the corrosion program.

3.2.2 Stress Corrosion Cracking

Previous reviews have suggested that stress corrosion cracking (SCC) is not a feasible mechanism, based on the absence of SCC agents for copper, and electrochemical conditions within the DGR environment. In addition, the Mark 2 container design of spherical heads and cylindrical body will be under compressive stress, not tensile stress, which enhances these arguments. However, should design elements change or environmental conditions differ at the site from the generic conditions expected the NWMO is encouraged to continue to provide evidence to support this understanding.

3.2.3 Internal Container Corrosion

The internal container corrosion program is complementary to the external copper corrosion research examined in this review. The radiolysis modeling components of the internal and external programs have considerable overlap and will support each other. It is recommended that the scope of the internal corrosion program be expanded to consider the possible evolution of hydrogen and its permeation to the copper-steel interface. Should such an event occur, hydrogen blistering and coating delamination could occur (section 3.1.4); the NWMO is encouraged to build evidence to demonstrate this is not likely.

3.2.4 Effect of Glaciation Loading on Corrosion

The overview of this early-stage program has provided the review team an opportunity to comment on how NWMO adapts to new research questions and initiates new programs in response. The general approach described demonstrates a balance between taking time to hold careful and detailed discussions with a variety of experts, and the flexibility to respond at an appropriately quick pace to a new research question. This provides insight into how the NWMO has built a robust, distributed network of corrosion research programs while staying focused on addressing the specific requirements of copper-coated UFCs in anticipation of the eventual licensing such a container. It is promising that this continued approach to building its corrosion research programs will satisfy the needs for licensing.

4. FURTHER DISCUSSION

4.1 Analogues

Based on the international feedback on the use of archeological or geological analogues for long-term prediction of corrosion, the review committee suggests to use or to continue to use these analogues to build confidence in the corrosion rates (some data already available), but also in the corrosion mechanisms that are observed on laboratory experiments and on these objects after long periods of exposure. As fuel container material analogues are naturally coupled with geological analogues, this approach offers the opportunity to consider important processes that may be coupled to the corrosion mechanisms (e.g. the fate of hydrogen produced via corrosion or radiolysis on microbial processes in a DGR). Thus, the NWMO is encouraged to further consider natural analogues for the entire repository system as their programs advance.

5. CONCLUSIONS

Since its formation in 2002, the NWMO has developed a well-integrated and world-leading research team to prepare a diverse body of experimental corrosion work, through a combination of academic institutions, industrial consultants and international collaborations. The research is conducted in a collaborative approach with considerable interaction between the NWMO and its research partners. The ongoing work in the programs described above reveals the NWMO’s commitment to understanding the corrosion of copper in UFCs, including all stages of its life in a deep geological repository. The evidence to date from these programs is that copper is not susceptible to corrosion mechanisms that will produce extensive localized damage, even when oxidation reactions are accelerated (i.e. via electrochemical or radiolysis means). Nonetheless, there is an ongoing commitment by NWMO to explore all of the above mechanisms, as well as any additional ones that may be discovered or postulated. As an example of this, NWMO has recently added a new program to the proof test plan in order to assess combinations of container ageing (i.e. corrosion) and glaciation (i.e. stress).

These programs are well designed and focused on addressing the specific requirements of copper-coated UFCs in anticipation of the eventual licensing such a container. Future efforts should remain within the existing topics: anoxic corrosion of copper; radiolysis related corrosion of copper; copper coating vs. wrought copper corrosion; localized corrosion of copper.

In addition to supporting the use of copper coatings, the programs are providing significant data for the generic use of copper as a DGR material within an eventual license application. Ongoing partnerships with other international organizations responsible for nuclear waste management have produced a mutually beneficial knowledge database that will continue to build confidence in this topic.

The NWMO has developed a clear path forward with respect to continued research on copper corrosion as it proceeds to a site selection and the site-specific chemistry that will be produced in the future. The existing corrosion programs combined with the future programs that incorporate site-specific data are highly likely to support very long lifetime predictions for UFCs (i.e., 100,000 y), provided supporting assumptions with respect to geochemistry, environment, bentonite clay performance, as well as container/bentonite manufacturing can be substantiated.

Parallel research in microbial processes affecting DGRs, internal container corrosion, stress corrosion cracking, and the initiation of a new program on the effects of glaciation on UFC corrosion was also provided, but was not within the scope of this review. Nonetheless, it was clear that these are well integrated with the corrosion programs, and that the NWMO programs in general are very supportive of each other.

In summary, the NWMO has established a comprehensive corrosion program that is world leading both in scope and quality. The NWMO is encouraged to proceed with its present direction with the suggestions above. Provided the continued success of the NWMO corrosion programs and detailed investigation of the suggestions in this report, the prospects of a successful license application appear very promising. It is emphasized that this assessment is based solely on the corrosion programs reviewed in this report, and makes no comment on the quality or direction of the other NWMO programs, such as siting, repository design, etc.

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