

Review of the NWMO Copper Corrosion Allowance

NWMO TR-2013-04

May 2013

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ABSTRACT

Title: Review of the NWMO Copper Corrosion Allowance
Report No.: NWMO TR-2013-04
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Abstract

Within this review, NWMO expectations for uniform, microbially induced, underdeposit, pitting corrosions and stress corrosion cracking of thin copper layers in deep geological repositories were examined. The focus was on issues that might call into question or alter the NWMO corrosion allowance depth of 1.27 mm in approximately 1 million years, a value that has been found to be appropriate within this review given current knowledge. This summary highlights the main findings from a critical review of both NWMO documentation and the broader literature.

Current experimental evidence for spontaneous copper corrosion in O₂ free waters has not been corroborated by multiple investigators and there is also a lack of agreement regarding equilibrium hydrogen partial pressures for copper corrosion [Cu \rightleftharpoons Cu(I) + e⁻] in DGR environments without oxygen. Although this issue is not completely resolved, there are compelling reasons to accept that these uncertainties should not affect the corrosion allowance because even after considering reasonable expectations for equilibrium Cu(I) and hydrogen partial pressures in the available data, spontaneous corrosion should essentially cease after a short period of time due to establishment of equilibrium H₂ partial pressures and mass transport limitations in the thick bentonite layer. Additional experiments could confirm thermodynamic (and mass transport) predictions of conditions where spontaneous corrosion processes cease.

There is also evidence to support concern for spontaneous copper corrosion in oxygen free situations at high Cl⁻ concentrations, elevated temperature and at low Cu⁺ levels, and each of these conditions may exist at some point over a Canadian DGR lifetime. These conditions should be further explored to better define if and when spontaneous corrosion occurs, and what mass transport reactions control rates. If slow molecular hydrogen transport controls these rates also then corrosion rates are likely very low. The likely transition from spontaneity to non-spontaneity upon changes in certain parameters could in theory be experimentally confirmed.

Assuming that O₂ free uniform corrosion is spontaneous, kinetic models have been developed for formation of CuOH in pure water and Cu₂S in sulfide containing environments. These kinetic models for spontaneous uniform corrosion rates rely on strong arguments for mass transport control and low HS⁻ levels supplied by microbial processes. Should these conditions prevail, rates will be kinetically slow and should cease based on thermodynamic arguments. Alternative rate limiting factors have been discussed.

Underdeposit corrosion depths appear to have been adequately represented for the short time period when corrosion is dominated by oxygen, but this issue could be further explored for conditions that might tend to produce more permanent anodes, such as that caused by non-uniform sulfide diffusion towards the canister or hydrogen gas diffusion away from the canister. In principle, one stress corrosion cracking (SCC) mechanism involving HS⁻ may be possible under anoxic conditions but mitigating factors such as limited HS⁻ concentrations in bentonite, mass transport limited HS⁻ transport to crack tips, and sequestration of sulfide suggest that it should not be considered in corrosion allowance to date.

Taken together, this review concludes that the NWMO Corrosion Allowance of 1.27 mm in approximately 1 million years is appropriate. To complement this finding, research related activities that will build confidence and further explore the validity of key assumptions have been suggested.

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1. INTRODUCTION

1.1 BACKGROUND

The Canadian nuclear waste management program is under development by the Nuclear Waste Management Organization (NWMO). A proposed concept for permanent storage of spent nuclear fuel involves use of a deep geological repository (DGR), within which multiple engineered barriers contain and isolate the used fuel from the environment. The current reference used fuel container (UFC) consists of a two-part, steel-copper vessel, for which the inner steel 100 mm component will provide structural support and containment, and the outer 25 mm copper casing will provide a corrosion barrier. The copper layer would be further isolated from moderately saline groundwater of Crystalline Rock (CR) or highly saline groundwater in Sedimentary Rock (SR) in the DGR by a thick (> 30 cm) layer of bentonite clay^[1-14].

Copper has been studied as a corrosion resistant fuel canister material for over 30 years since initial considerations by the Swedish Corrosion Institute in 1978^[15]. Programs are underway in Sweden, Finland and Japan amongst other places. Copper has been considered because of its suspected thermodynamic immunity to spontaneous corrosion in anoxic oxygen free water relevant to DGR and relatively low cost compared to noble metal alternatives. Studies have been conducted in low salinity environments (e.g., <60 g/L [Cl⁻]), bentonite and various mixtures of solutions containing Cl⁻ and SO₄²⁻^[7, 8, 10, 16-37]. Other studies have considered HS⁻^[32, 35, 38-49]. Studies through NWMO have focused on uniform corrosion, localized corrosion including underdeposit corrosion, stress corrosion cracking, and microbially induced corrosion (MIC)^[2-14].

As indicated above, the NWMO reference design considers a dual vessel comprised of outer oxygen free phosphorous-doped copper over inner steel. However, to overcome manufacturing challenges associated with producing 2-component UFCs (i.e. machining tolerances of less than 1 mm for up to a 4 m length), NWMO is exploring coating and cladding technologies, which would allow copper to be applied to the steel during fabrication. In principle, such an operation would allow copper to be applied to any thickness, rather than being defined by manufacturing processes, as per the reference design (i.e., 25 mm). Accordingly, in this review, a conceptual ~3 mm of electrodeposited, thermal or cold sprayed copper coating is under consideration; although NWMO has not yet defined a minimum coating thickness.

The purpose of the copper corrosion barriers is to 1) ensure the container remains intact for up to one million years, and 2) to prevent exposure of the underlying steel waste vessel to groundwater in the DGR. Both of these goals will be achieved if the copper barrier is not penetrated by corrosion over pertinent radionuclide half-lives. A prior NWMO report examined this issue, and estimated that corrosion would not penetrate the thin copper layer by more than 1.27 mm over a 1 million year time period under the proposed disposal scenario. The 1.27 mm corrosion allowance was based on estimates of copper wall penetration of up to 0.17 mm penetration from uniform copper corrosion, 0.1 mm from under-deposit corrosion and 1 mm from microbially influenced corrosion.

The current position of NWMO with respect to corrosion and the corrosion allowance calculated to date are summarized here as expressed in NWMO TR-2011-14 for “low salinity systems” (i.e. below approximately 100 g/L salinity, and $<60 \text{ g/L Cl}^-$) [11]. Within this document an anoxic corrosion allowance in O_2 free pure water is not considered; however, Newman has calculated corrosion rates of copper in anoxic Cl^- -containing water at 2-4 nm/yr (2-4 mm in 10^6 years) during anaerobic corrosion, as measured in “highly saline bulk solutions” (i.e., 350 mg/L salinity) [1, 3]. While these measurements are preliminary and are in the process of confirmation, and the rates were determined in the absence of a protective bentonite barrier in a DGR, some anoxic corrosion allowance may be necessary for highly saline SR ground waters. Corrosion leading to Cu(I) by a CuCl_n^- formation mechanism would be subject to thermodynamic limitations when the equilibrium partial pressure is reached and/or kinetic limitations if H_2 mass transport is the rate determining step. Initial uniform corrosion due to the mass balance with oxygen yields a corrosion penetration of 0.17 mm, but this is conservative given there is no credit taken for parallel consumption of the residual O_2 by Fe(II) and microbial activity rendering some O_2 unavailable for copper corrosion. As noted in NWMO-TR-2011-14, previous extreme value analysis of pitting conservatively estimated 6 mm in 10^6 years, but this value has now been estimated as a somewhat uniform 0.1 mm pit depth, based on arguments of surface roughening due to switchable anodes and cathodes rather than conventional pitting with small permanent anodes. SCC is not considered operative by either acetate, formate, nitrate or ammonia copper SCC mechanisms because threshold potentials and corrodant concentrations required are not reached [5, 6, 9, 11-13, 23, 50-52]. More recently stress management or low or non-existent tensile stresses have been added to the arguments against the possibility of SCC. A 1 mm corrosion allowance for MIC is also included to account for slow movement through bentonite of sulfides from the bentonite-rock interface where microbial activity may occur, to the container surface; it is presumed that the highly compacted bentonite will inhibit microbial growth closer to the container [15, 24]. The sum of these processes produces a corrosion depth of 1.27 mm in approximately 1 million years.

The goal of this report is to provide an independent critical review of corrosion literature reports (supplied by NWMO and obtained from other external sources), to assess the appropriateness of the 1.27 mm corrosion allowance. Results of this critical review are briefly summarized in separate sections that follow which examine uniform corrosion, pitting and under-deposit corrosion, stress corrosion cracking and MIC. After a brief discussion that synthesizes the overall review comments, conclusions are provided.

1.2 THE GROUND WATER AND NEAR CONTAINER ENVIRONMENT

The following ground water table was considered in the preliminary assessment. Table 1 shows a Cl^- level of as high as 199,000 mg/L and a sulfate level of as high as 1,100 mg/L [53-56]. Within the table, CR indicates crystalline rock formations, while SR refers to sedimentary rock formations. The sulfate level is noteworthy given the susceptibility of copper to sulfate induced pitting. The supply of sulfide by bacteria is enabled by sulfate reducing bacteria at the bentonite-rock interface and a very conservative value of 3 ppm is used to approximate a concentration

produced at steady state. Reducing conditions at a pH from 6.5 to 7.75 prevail under most crystalline, sedimentary and melt-water conditions. It is unclear whether the solutes present could form insoluble or partial soluble deposits that could promote underdeposit corrosion.

The presence of highly compacted bentonite (HCB) will have a significant impact on the nature of the environment in contact with the container. Some additional environmental considerations due to the effects of HCB on the near-field environment include the presence of calcite in the bentonite which is expected to buffer the pore-water pH in the range 7-8. Many bentonites contain pyrite and other ferrous minerals as impurities. Oxidation of these minerals will consume a fraction of the initial O₂ inventory. HCB prevents microbial activity in the near field. The HCB is emplaced with an initial degree of saturation of ~70%. Drying of the bentonite will also affect the rate of mass transport of species in the buffer, with gaseous species (O₂(g)) diffusing rapidly and dissolved species diffusing more slowly than under saturated conditions. In the long term (i.e., following equilibration of the pore water with the ground water), it can be expected that Cl⁻ will be the dominant anion in the pore water. Even prior to equilibration, Cl⁻ may dominate the pore-water composition due to the dissolution of halite impurities and the re-distribution of salts during the thermal transient. However, sulfate could be predominant during at least part of the initial anoxic period. An alkaline plume containing Al(OH)₃ as a potential detrimental deposit (from the grout used in closure applications) is not expected to interact with containers. These environmental conditions are considered below in this assessment [53-56].

Table 1. Reference Canadian Ground Waters Based on Data from References [53-56]

Rock Type	Crystalline				Sedimentary			Meltwater
Water Name	CR-50	CR-20	CR-10	CR-0	SR-300	SR-170	SR-20	RM-0
pH	7.5	7.5	7.5	7.5	6.5	6.5	6.5	7
Environment Type	Reducing	Reducing	Reducing	Oxidizing	Reducing	Reducing	Oxidizing	Reducing
Nominal Eh (mV)	-200	-200	-200	90	-200	-200	90	-200
Solutes (mg/L)								
Na	5100	3400	1900	75	43100	37400	4300	16
K	50	20	15	3	3600	1750	130	0.2
Ca	15000	4800	2130	40	57300	14700	1500	6
Mg	200	50	60	10	9900	3900	900	0.02
HCO ₃	10	25	70	230	40	60	330	30
SO ₄	800	800	1000	50	160	460	1100	6
Cl	34300	13800	6100	40	199500	97400	11300	6
Br		85		<1	2000	600	80	0.03
Sr	20	55	25	<1	900	480	30	0.2
Li		0.1		<1	10	10		
F		2.5	2	2	8	40		7
I		0.4		<1	90	90		
B		0.9		<1				
Si	15	3	5	5	<200	<200		7
Fe	1	2	1	2	50	47	50	0
NO ₃	50	<1	<1	<1	<10	<10		
PO ₄		0.2	<1	<1				
TDS	55500	23000	11300	455	317000	157000	20000	80
Reference	53	54	53	53	56	56	56	55

2. NWMO COPPER CORROSION ALLOWANCE: SUMMARY OF CRITICAL REVIEW

2.1 ISSUES RELEVANT TO THE NWMO CORROSION ALLOWANCE

The uniform, localized corrosion, under-deposit corrosion, stress corrosion cracking and microbial corrosion considered by NWMO to arrive at a corrosion allowance of 1.27 mm has been examined, with the objective of identifying key unresolved issues, research needs and knowledge gaps. In conjunction with the review of the NWMO reports cited here, there has been some consideration of the broader literature. Issues discussed include uniform corrosion, localized corrosion, under-deposit corrosion as well as stress corrosion cracking under the initial oxygenated and long term anoxic conditions.

2.2 UNIFORM CORROSION

2.2.1 UNIFORM CORROSION BACKGROUND

Uniform corrosion has been factored into the NWMO corrosion allowance in several ways for each period in the repository environment. These include conditions early after placement and closure when O₂ and Cu(II) are available for cathodic reduction prior to their depletion. This stage has been taken into consideration. Radiation induced corrosion is not considered operative due to thick container dimensions (e.g., 100 mm steel + 25 mm copper for the reference UFC). Should thinner walled UFCs be utilized, radiation effects should be reviewed. With the thick walled containers, the case may be made that the radiation product generation rates are too low to support general corrosion. The case is also made in the Canadian DGR that HS⁻ induced general corrosion is not extensive because the sulfide concentration will be too low. That is, naturally-occurring sulphide is not found in Canadian groundwaters; however, a very conservative value of 3 ppm or approximately 0.1 mM of HS⁻ has been used to account for sulphide that may be produced as a result of remote microbial metabolic processes occurring >30 cm from the container, leading to microbially influenced corrosion (MIC) ^[11]. Over one million years, a 1 mm corrosion allowance for MIC is included^[11].

2.2.2 UNIFORM CORROSION – THERMODYNAMIC CONSIDERATIONS

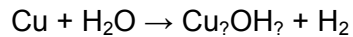
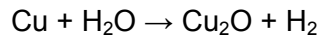
Corrosion in O₂ free waters has been considered by three processes (H₂O, Cl⁻, and HS⁻) as listed below. There is some question regarding the equilibrium partial H₂ pressure at which spontaneous corrosion of copper in O₂ free pure water ^[57-61] is no longer thermodynamically favored.

Anoxic Corrosion of Copper in the Presence of Pure Water

Corrosion under anoxic conditions in pure waters could occur spontaneously by the “Cu(I) compound formation mechanism.”



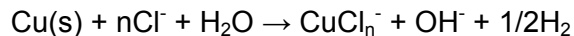
Macdonald has proposed a $f_{H_2}^{1/2} - C_{Cu(l)}$ relationship, that once exceeded by H_2 partial pressure or $Cu(l)$ or some combination, restored immunity^[60]. In other words O_2 free corrosion of copper is only spontaneous for very low hydrogen pressures and low $Cu(l)$ concentrations. In this regard there is no issue and no disagreement. The only unresolved issue is nature of the exact H_xCuO_y species and the resulting equilibrium H_2 pressure.^[15, 59, 60, 62-72] Two reactions are proposed.



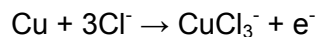
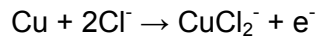
The former is the conventional corrosion reaction involving copper in water with an equilibrium pressure of 10^{-16} atm, while the latter is the Hultquist, Szakalos reaction mechanism with a H_2 partial pressure of 10^{-3} atm ^[73]. There is strong computation evidence ^[22] against H_xCuO_y formation but past and recent surface science methods have been used to support its existence ^[61, 65]. The theoretical equilibrium H_2 pressure for H_xCuO_y/Cu equilibrium should be further verified/confirmed experimentally ^[57, 61]. Another diagnostic would be to test the validity of the $f_{H_2}^{1/2} - C_{Cu(l)}$ relationship and associated corrosion domain diagrams to determine if corrosion becomes spontaneous when f_{H_2} or Cu^+ levels are lowered with respect to the proposed Szakalos thermodynamic equilibrium conditions^[60]. Once the f_{H_2} fugacity and Cu^+ concentrations reach certain levels, quasi-immunity may be restored depending on slow dihydrogen liquid phase transport rates and pressures below the hydraulic pressure such that hydrogen evolution does not occur ^[60].

Anoxic Corrosion of Copper in the Presence of Water and High Chloride Concentrations

Corrosion under anoxic conditions in pure waters could also occur spontaneously by the “*Cu-Cl species formation mechanism*.” The following is an example of one possible overall reaction:



The thermodynamic claim of immunity made is affected by the Cl^- concentration and pH assumed and the resulting assumed Cu-Cl complex formed. Two examples of Cu/ $Cu(l)$ half-cell reactions possible in Cl^- containing waters are:

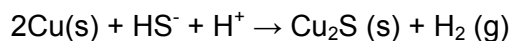
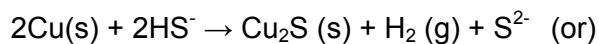


The Nernst potential for each of these anodic half-cell reaction decreases with increasing Cl^- concentration and temperature. Therefore, assertion of limits on Cl^- and pH need to consider the absolute upper bound of Cl^- activity possible that might form by some accumulation process such as discussed in TR-02-25 on p. 15 ^[30]. This concern was raised in a SSM Technical note

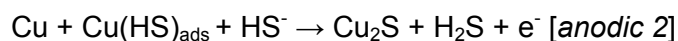
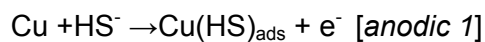
by Scully (Scully, SKB 2012)^[51] and this review also agrees that this work should be pursued especially in the NWMO case given the Cl⁻ concentrations possible. These conditions should be further explored to define under what conditions spontaneous corrosion occurs, at what rates, and by what rate limiting processes (e.g. H₂ diffusion) when high Cl⁻ concentrations are present in O₂ free water. Recent NWMO sponsored work initiated at the University of Toronto is in the preliminary stage to address these concerns^[1, 3]. Review of some of these project reports reveals that (a) the work is in early stages, (b) multiple types of analysis are not yet producing data to provide a quantitative correlation between surface/solution corrosion products and hydrogen, (c) measurement of copper corrosion rates by hydrogen pressurization should be confirmed by multiple parallel and redundant pressure measurements and independently through measurement of corrosion rates, for instance, by solution analysis. Additional diagnostic experiments are recommended in high Cl⁻, O₂ free waters to assess E_H, and account for both initial O₂ levels and H₂ produced without oxidation of copper. H₂ generation *without copper corrosion* has been predicted to be possible from Cu(II) originating from the pre-air formed film by either reduction of dissolved Cu(II) to form CuOH that then enables water reduction^[74, 75] or chemical conversion between preformed Cu(II) oxides and hydroxides in the presence of H₂O (Brite)^[22]. Experiments could also confirm thermodynamic predictions that spontaneous corrosion processes cease under certain conditions such as slight increases in hydrogen pressure. The likely transition from spontaneity to non-spontaneity upon changes in certain parameters could be experimentally confirmed. Newman has produced data suggesting rates of nm/year corrosion rates or ~mm over 10⁶ years in O₂ free Cl⁻ bulk solutions^[2, 3]. As indicated above, within the repository environment that is dominated by mass transport limitations, it appears likely that O₂ free corrosion will proceed at low rates and cease and, therefore, have limited effect on corrosion allowances taken into account.

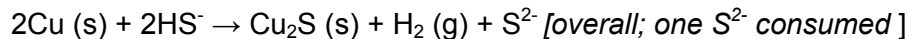
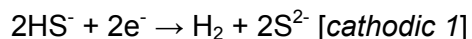
Anoxic Corrosion of Copper in the Presence of Water and Sulphides

In the case of HS⁻ presence from sulfate reducing bacteria, or other sources, mass transport limited HS⁻ induced corrosion of copper by the “Cu₂S formation mechanism” is considered as described in TR-10-66 on p. 14]^[76]:

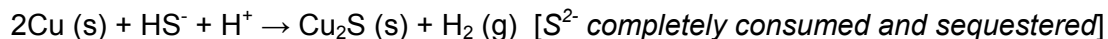


Although they are not found in currently anticipated DGR Canadian groundwaters, for the purpose of safety assessments sulfides are considered to exist at low concentrations (ca. 10⁻⁵ M)^[76-79], presumably formed by sulfate reducing bacteria and Fe(II) catalysis of sulfate reduction. The assumed reaction path described by Shoosmith and Smith is^[32, 33]:

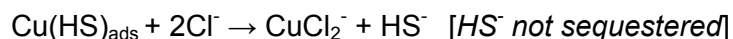




An alternative overall path is:



Parallel reaction paths that do not sequester HS^- (low HS^- , high Cl^- , O_2 free) should be thoroughly explored including the possibility of the following half-cell reaction suggested by Shoesmith^[33]:



In principle, and depending on the potential, this half cell reaction could be supported by water reduction and not rely on HS^- reduction as the only viable cathodic process. If this overall reaction were operative, HS^- would not be entirely consumed by Cu(I) formation. If Cl^- supply is relatively plentiful in ground water, would HS^- be regenerated by this reaction and allow additional dissolution of copper by a thermodynamically spontaneous Cu^{+1} oxidation process? It should be noted that Taxen has modeled CuCl_2^- transport limited corrosion controlled by either H_2 transport or CuCl_2^- movement away from the Cu interface and arrived at extremely low corrosion rates as pointed out in TR-10-66 on p. 85^[23]. However, this model has not been fully reviewed at the time of this report. The pathway reported for $\text{Cu} - \text{HS}^- - \text{Cl}^-$ was discounted using various other arguments. For instance, the extremely low chemical solubility of Cu_2S is taken to provide evidence that all S^{2-} will be sequestered by Cu^{+1} ; or that complete S^{2-} sequestering will occur^[33]. Another argument is that CuCl_2 or CuCl_2^- would not be thermodynamically stable at the potentials of Cu_2S formation. However, high Cl^- concentrations and temperatures coupled with uncertainty over mixed potentials makes exact conditions uncertain.

Therefore, corrosion experiments in mixed high Cl^- + dilute HS^- electrolytes at various H_2 partial pressures, and corrosion experiments before and after HS^- removal would strengthen these arguments. The case of low sulfur concentrations combined with high Cl^- or episodic HS^- dosing followed by exposure to high Cl^- concentrations could also be considered. The E-pH diagram for the Cu -adsorbed S^{2-} system showing formation of CuHS_{ads} but not solid sulfide compounds may be considered^[80]. Rotating ring disk (RRDE) studies that do not show evidence of extra Cu^+ release during S^{2-} corrosion are taken as evidence to support the view of complete Cu_xS sequestering, but these are very complicated experiments with low collection efficiencies. Therefore, they may deserve further reconsideration. Evidence in the literature is available that indicates high copper corrosion rates that persist upon the complete removal of $\text{Na}_2\text{S (aq)}$ or $\text{H}_2\text{S (g)}$ initially supplied from the corrosive environment^[42, 43, 81]. In the Edwards and Jacobs study, high corrosion rates on copper were obtained when Na_2S was removed but Cu_2S was smeared on clean samples^[42]. In the Freeman studies, copper coupons were placed in a sealed glass chamber and removed periodically for corrosion rate assessment^[81]. Corrosion continued for the 90 day total test period at the initial rate in presence of HS^- when the source of sulfides

was completely absent. Elevated rates of corrosion continued contrary to the HS^- sequestering assumption. In general, oxygen has been present in these studies; although some studies were in a sealed container where presumably some O_2 depletion occurred [81]. There are also a number of older papers such as regarding sulfide polluted seawater which will not be reviewed here [38-41, 45-47]. As indicated above, most of these studies were conducted in aerated environments and may not be relevant. However, it is well known that Cu_2S catalyzes ORR (the oxygen reduction reaction) to enhance copper corrosion. It is not clear whether HER (the hydrogen evolution reaction) is catalyzed by Cu_2S in an O_2 free situation and this possibility may be worth exploring because it could affect the corrosion allowance. In summary, the argument has been made that HS^- cannot catalyze anodic reactions in a regenerative mode and that no evidence is available that indicates Cu_2S catalyzes hydrogen evolution. If these key assumptions are confirmed then the existing corrosion allowance does not need to consider the issues raised.

2.2.3 UNIFORM CORROSION – KINETIC CONSIDERATIONS

Assuming that O_2 free uniform corrosion is thermodynamically spontaneous, corrosion rates are limited due to slow mass transport of hydrogen reaction products through the saturated bentonite and away from the copper surface. Models of these kinetic limitations indicate very low rates of copper corrosion under control of H_2 mass transport through saturated bentonite [82].

If the bentonite were to be unsaturated much higher rates of H_2 diffusion and associated copper corrosion are possible. The bentonite will be unsaturated for an unknown period of time after construction, and thereafter, would remain saturated unless H_2 partial pressures at the copper surface exceed the local hydrostatic pressure at 500 m depth (≈ 5 MPa or 50 atmospheres) [73]. As long as the equilibrium partial pressure of H_2 for the prevailing corrosion reaction is well below 1 atmosphere in the saturated bentonite after construction, or well below 50 atmospheres after construction and saturation of the bentonite and assuming 500 m depth of overlaying water, equilibrium pressures proposed by Hultquist of ~ 1 mbar ($\sim 10^{-3}$ atm) at 60-70°C do not threaten the assumption that saturated bentonite may become unsaturated as a result of gas generation. Kinetically, the threshold of 1 or 50 atmospheres is also conservative, given that much higher levels of supersaturation are necessary to initially nucleate bubbles in saturated water of fine pores [83, 84]. Much higher equilibrium pressures of H_2 (> 50 atm) would have to be achieved in the presence of hydrogen sulfide or other circumstances for this assumption to be violated.

The possibility of higher pressures could readily be tested by treating copper with sulfides and determining whether H_2 gas generation occurs despite high hydrostatic pressure, as can occur in the case of HER on iron in deep seawater simulations [85]. Additionally, a kinetic model for the O_2 free case of copper corrosion at elevated temperatures in high Cl^- could be developed as part of the Toronto work, so that the technical basis for a low corrosion rate can be better understood under anoxic conditions. In summary, these issues frame the current state of understanding of the O_2 free Cl^- and or HS^- general corrosion issues. However, until such time that any of these scenarios are confirmed, the present corrosion allowance should be used.

2.3 LOCALIZED AND PITTING CORROSION

Two periods were considered in this review based on the information provided ^[50].

- Viable mechanisms for penetration within the initial ~100 year period assuming presence of residual O₂ and Cu(II) reduction as possible cathodic reactions.
- Viable mechanisms and penetrations over the long term when the environment is O₂ and Cu(II) free.

During the oxic stage, it is logical to examine mechanisms of local corrosion viable in the presence of tarnish films such as anion induced pitting. In the latter case it is logical to search for local corrosion mechanisms that could operate under oxic or anaerobic conditions without oxide or hydroxide based tarnish or oxide films.

Several issues were considered regarding the handling of localized corrosion in these two stages. It is assumed that either pitting corrosion, or non-uniform general corrosion (and not crevice corrosion) is the relevant mode of attack to consider in the first stage. In this respect, the review agrees with the findings of NWMO that traditional pitting is unlikely. However, an open question concerns whether corrosion with moving anodes and cathodes is a form of anion induced pitting with non-permanent pit-like anodes or is relatively non uniform general corrosion due to something else such as a differential oxygen concentration cell ^[11, 15, 24, 26, 73, 86]. This may sound like a semantic argument but it is not. If the former is the case, then a valid concern exists over whether certain environmental factors (see under-deposits below) can shift conditions towards more permanent anodes. The general corrosion allowance approach is extremely supported in the latter case, but pit factor analysis and extreme value statistics would seem to be the approach of choice in the former case.

Most rapid copper corrosion failures in potable waters proceed via pitting, which occurs via an anion-induced oxide breakdown ^[87-96]. Local attack is driven by a concentration cell, in which a relatively large cathodic copper surface area is exposed to high levels of oxygen or a disinfectant such as chlorine (hypochlorous acid or hypochlorite) and a relatively small anodic area is screened from bulk water oxygen or disinfectant and/or harbors microbes such as sulfate reducing bacteria ^[95-97]. In this type of mechanism, comparison of mixed potential to threshold potentials (E_{pit} , E_r), stifling criteria such as anode starvation by oxygen depletion and Cu(II) reduction and pit factors and extreme value statistics are all valid approaches ^[51]. However, localized corrosion by this mechanism is generally regarded as unlikely due to reducing repository conditions after O₂ depletion and Cu(II) due to the prevalence of reducing conditions. Indeed E_h (SHE) values below -200 mV vs. SHE (-441 mV vs. SCE as indicated in Table 1) are far below any reported E_r values in mixed trace concentration sulfate + chloride environments investigated due to the detrimental effects of sulfate on copper pitting in potable waters. One method of assessing attack by anion induced localized corrosion is to compare the threshold potential for breakdown to the corrosion potential, E_{corr} . Comparison of E_r predictions from Cong in sulfate + chloride to the E_{corr} predictions of King and coworkers ^[98] yields several

hundred mV potential differences between the threshold potential and E_{corr} . Usually such a large difference is taken to indicate an extremely low or non-existent probability of attack^[51].

Another possible issue concerns the need to consider the effects of other potential oxidizers like peroxide generated by gamma radiolysis on localized corrosion processes. This concern differs from the issue of general corrosion. Here, the radiation chemistry concern is related to corrosion potential elevation not a mass balance. For thick walled copper over steel containers, this concern is not believed to be relevant^[99].

Another question is whether the pitting potential of copper and the distributions of anodes and cathode sites depend on combinations of high levels of Cl^- , HCO_3^- and SO_4^{2-} (Table 1). At issue is whether the large difference between E_{corr} and threshold potentials seen in Cl^- solutions might be altered in stage I. These species are all present in repository environments at intermediate to high levels especially compared to potable waters (Table 1). Saturation chemistries are unclear but high sulfate in the ground waters may or may not persist. King has conducted extensive studies of copper oxidation in Cl^- and mixed $\text{Cl}^-/\text{SO}_4^{2-}$ using a novel disk split ring electrode^[26]^[25]. He found that the general qualitative aspects such as Cu(I) formation at low potentials and Cu(II) formation at high potentials were similar. However, it is interesting to note that high levels of sulfate produced much higher disk currents (mA) compared to μA anodic reaction rates in Cl^- only solutions of the range from -0.2 to +0.4 V vs. SCE. This finding underscores the notion that SO_4^{2-} is quite a detrimental ion towards anodic dissolution of copper^[89]. The other significant aspect of this result is that E_{corr} should be lower in sulfate during the stage I period just as E_{pit} and E_r levels may be lower based on extrapolation of the empirical expressions of Cong and Sridhar and Cragolino to high sulfate levels^[34, 89, 90]. This is in agreement with the results of Cong where pH, Cl^- , HCO_3^- and SO_4^{2-} all affected the E_{corr} of copper, albeit in aerated solutions with disinfectant in his study^[90]. In summary, sulfate pitting may indeed be unlikely because of the high value of E_b and the difference between E_b and E_{corr} ^[99].

Anode cathode separation studies, pit factor and threshold potential treatments all could also consider effects of anion combinations such as Cl^- and SO_4^{2-} , as well as the hypothetical possibility of HS^- . There may be a need to explore possible long term anaerobic pitting mechanisms such as by HS^- pitting. The sulfide pitting mechanism has been suggested in the literature and elsewhere and the technical basis for why sulfide induced pitting can occur while in other cases, sulfidation is completely uniform is unclear^[35, 99]. However, it has been observed in a few cases and it is unclear whether aeration is needed (experience on pitting of copper and copper-nickel alloys in sulfide polluted seawater containing trace sulfides and high chlorides is a good example of pitting in high Cl^- low sulfide environments^[39-41, 45-47]). However, these solutions also contained a high oxygen content. Can such pitting occur under anoxic conditions? The important distinction here is that this is a remaining mode of pitting that might operate under reducing conditions without the need for an oxide film in the classical sense. However, this mode of pitting of copper is not understood and there are only a few references to previously published archival work. HS^- pitting was mentioned as a concern in TR-10-67 on p.101 and p. 105 as well as in TR-02-25 on pages 55-66 but the issue was not resolved^[30, 99]. Concerns regarding the anoxic period include the possibility of HS^- induced localized corrosion. An

extremely limited amount of data exists regarding both E_b and E_{corr} that would be applicable to this period and ground water chemistry. The declining E_{corr} with pH as shown in Figure 1 and improved passive film with pH are cited as reasons why this pitting should be dismissed such as stated in TR-10-67 on p.101^[99]. The strength of the passive film argument is not obvious since many materials pit and develop large PF particularly when well-passivated. Vasquez-Moll found $E_b = -0.74$ V SCE in $0.01 \text{ mol-dm}^{-3} \text{ HS}^-$ ^[35]. E_{corr} was found to be -0.95 V vs. SCE [TR-10-67; p. 82]^[99]. On this basis, the 200 mV potential difference between E_{corr} and E_b was argued to minimize the chance of pitting by an HS^- mechanism as described in TR-10-67 on p. 102^[99]. This type of difference is shown in Figure 2. However, a probabilistic treatment might suggest some finite risk of pitting under these conditions. This is especially the case because there is little understanding of what factors govern E_{corr} during this period or how local corrosion occurs in HS^- .

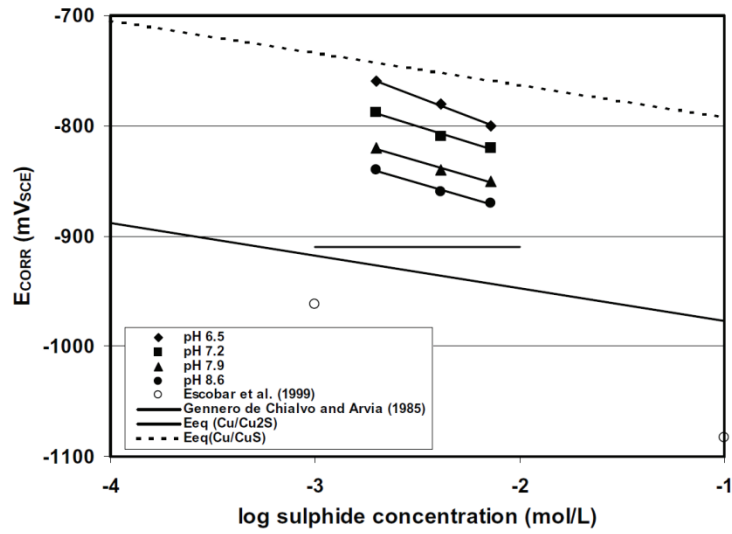


Figure 1: The dependence of E_{corr} on sulphide concentration as a function of pH. The equilibrium CuS and Cu₂S lines are indicated. [TR-02-25]

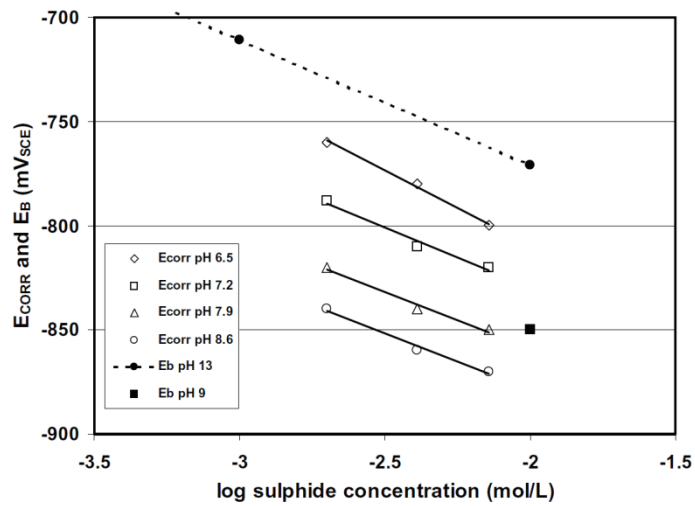


Figure 2: E_{corr} versus pitting potentials E_b in alkaline sulfide solutions [TR-02-25]

Taxen has modeled pit growth in HS^- and does obtain ~5 mm growth depths as covered in TR-10-67 on page 105^[99]. This model has not been applied to this review, but the mere fact that cm scale depths were obtained under anoxic conditions with HS^- should be cause for additional investigation. Not only is the mechanism of pitting poorly understood in HS^- (how does H_2O reduction occur on Cu_2S films and what is the localization mechanism that causes break down at Cu_xS defects?) but the empirical margin for risk is modest. For example, there is a lack of understanding on whether there is a statistical distribution of E_b during HS^- copper pitting. Given the current state of understanding, the probabilistic risk of pitting cannot be assessed. Clearly the need exists to explore E_b , E_r and E_{corr} under a broader range of repository relevant conditions such as at low sulfide concentrations and with the addition of other species such as sulfate. In summary, these factors might affect the corrosion allowance made for pitting in bentonite clay related underdeposit corrosion (0.1 mm corrosion depth; NWMO TR 2011-14) that was produced from movable anodes and cathodes^[11].

NWMO and contractors dismiss the HS^- pit mechanism based on the low concentration of sulfide that may be produced by microbial metabolism outside the bentonite zone^[21]. This is valid based on mass transport controlled pitting. A catalytic mechanism for HS^- pitting would need to be identified to raise significant concerns for HS^- pitting. If mass transport through fully saturated bentonite (eliminating gas phase transport of H_2S ^[62]), microbially produced sulfides, and full sulfide sequestering limited the reaction of copper (two Cu(I) ions per S^{2-} anion), it is hard to imagine sulfide pitting eroding confidence in the NWMO corrosion allowance. Another objection made towards HS^- catalyzed pitting calls into question the ability of sulfide to catalyze anodic reactions on copper based on (a) the extremely low solubility of Cu_2S (b) the concern that if HS^- was regeneratively involved in a catalytic process then the stable species of Cu(I) that could be formed and survive at such low potential besides Cu_2S is unclear. The suggestion is made that CuCl_2^- might be extremely unstable and might be reduced to Cu(0) at extremely negative potentials or Cu_2S would form leading to HS^- sequestering. However, inspection of E-pH diagram for $\text{Cu-Cl-H}_2\text{O}$ system assuming Cl^- total concentration of 5 M, various low Cu ion concentrations and 100°C assuming CuCl_3^{2-} formation suggest Cu-Cl species are stable at low enough potentials to sustain HS^- catalyzed corrosion where the eventual fate of the Cu(I) can indeed be in the form of a Cu-Cl species and at potentials consistent with pitting potentials seen on Cu in sulfides^[100]. A supporting finding is that Fe/FeS corrosion rates can be quite high under O_2 free conditions although the electrical properties of FeS and Cu_2S differ.

2.4 UNDER DEPOSIT CORROSION

Underdeposit corrosion should also be considered in light of the speculation that certain deposits may function as ion exchange membranes or to selectively allow anion transport^[92]. However, in this study, potable water was used and conditions were highly oxidizing not reducing. In limited work done in this area in the context of a waste site, an underdeposit cell demonstrated formation and corrosion at anodes under compressed bentonite clay (containing a variety of species including Al_2O_3) albeit under aerated conditions^[101]. These experiments were designed to address the effects of differences in O_2 flux through bentonite clay which is not

quite the focus of this report section. The data were misinterpreted by the authors who claim an absence of pitting (but much attack in a few cases). The rates of attack did decrease with declining oxygen levels and temperature. Precipitation was observed on the surface of copper coupons exposed to HCB under simulated repository conditions ^[24, 86]. In some cases, in addition to an underlying Cu_2O layer and an outer layer of atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$, King observed calcite crystals precipitated in a specific pattern, which when removed in acid, was mirrored in the underlying corroded surface. For this reason, NWMO and contractors sometime refer to the form of localized attack that we expect to occur as “under-deposit corrosion.”

The significance to a spent fuel container is that movement and exchange of anodes and cathodes may be suppressed when deposits are present to form more permanent anodes. The second concern is that pitting potentials can be formed at much less oxidizing potentials under deposits if they are ion selective towards detrimental ions. These phenomena could lead to (a) breakdown and (b) the formation of more permanent anodes such that both pit factor analysis and comparison of E_{corr} to E_r becomes more prudent than the uniform corrosion allowance used based on switchable anodes and cathodes.

King points out that the primary evidence for the NWMO treatment of localized corrosion without such formation of permanent anodes are profiles of the type shown ^[24, 86], which were obtained after stripping corrosion products from coupons exposed to simulated repository conditions, where deposits were formed. The profile used as primary evidence for moving anodes and cathodes results from an extended test (18 months) under conditions similar to those expected in the repository. A synthetic ground water solution containing both Cl^- and SO_4^{2-} (and HCO_3^-) was used, which was initially aerated. Precipitation of corrosion products and other mineral species clearly occurred. The bentonite (or, in this case a 50:50 mixture of sand and bentonite) was close to, but not fully saturated at the beginning of the test. This particular test was performed at 50°C , with others conducted at 100°C and 150°C . The depth of attack was only about $50\ \mu\text{m}$ perhaps due to a stifling of the anodic reaction documented for chloride even at orders of magnitude lower concentration than is encountered in either CR or SR groundwater ^[93, 94, 102]. Since the experimental data on roughening was collected for 18 months during which oxygen levels are near the maximum anticipated in the DGR, the collected data is conservative for the oxygenated portion of the canister lifetime. A corrosion mechanism was proposed based on precipitation of insulating CaCO_3 over cathodes and fracture of caps or cathode limited pit growth ^[20]. The proposed mechanism is purely conceptual and lacks direct experimental evidence ^[73].

The unresolved remaining issue concerning underdeposit attack is whether more permanent anodes could be sustained in the case of underdeposit corrosion without oxygen. Trace constituents can have a strong impact on the stability of anodes. For example, in the case of pitting (albeit in aerated environments with a disinfectant), the pitting factor varied considerably with precise details of the water chemistry for unknown reasons no doubt related to the number of surviving pits and the ability of the corrosion product to stabilize such sites ^[87]. It should be noted that copper pits repassivated in environments containing Cl^- and HCO_3^- due to the high resistance of malachite pit caps and filling with CuCl species ^[103, 104]. In contrast pits formed in

bentonite and to the copper surface, or 2) enhanced removal of possible copper corrosion reaction products [e.g. Cu^{+1} and H_2 (gas)] diffusing outward from the copper surface within the clay layer, via consumption or precipitation by microbes outside the clay layer. In both cases the rate of MIC attack is likely limited to that possible from transport of metabolites or reaction products inwards or outwards through the bentonite layer.

Such diffusion is extremely slow. Hydraulic conductivity through the bentonite layer is of the same order of magnitude or even lower than for intact concrete barriers ($\approx 10^{-12}$ m/sec), and for this reason bentonite clay barriers are used extensively in waste containment. The recent NWMO review properly indicates that water residence times in clay layers are on the order of millions of years and computer models estimating transport of corrosive metabolites (including sulfide) to the copper surface from the groundwater pose a negligible threat to a 1 mm corrosion allowance^[14, 21]. Considering all these factors and assuming the proper installation of a thick bentonite layer, the copper corrosion allowance of 1 mm copper is considered adequate for a 1 million year projected lifetime as long as no scenario exists for damage to the bentonite layer that would affect mass transport of aggressive anions (HS^-) to the copper surface or reaction products away from the surface (Cu^+ , possibly H_2).

Worfaardt also outline 6 recommendations for additional research^[14]. To the extent this research is completed, an even higher level of confidence could be applied to the assumptions outlined above, but the current level of confidence seems very high and the assumptions are reasonable.

2.6 STRESS CORROSION CRACKING

Stress corrosion cracking (SCC) under oxic conditions without HS^- appears to be unlikely by all conventional tarnish rupture mechanisms such as those caused by acetate, formate, nitrate/nitrite, or ammonia because (a) concentrations may be below thresholds levels seen in slow strain rate testing (SSRT) and (b) mixed potentials may be below the potential range associated with cracking^[12, 13, 50]. The only concern here is the potential non-conservative nature of SSRT conducted over days if slow incubation or crack growth is below detection limits. Moreover, another unresolved issue is the need to consider special oxidizers like peroxide from gamma radiolysis on SCC. These oxidizers are certainly not present in any concentrations that could affect mass balance centered determination of mass loss, but the question is whether the mixed potential is elevated coupled with an expanded window based on the non-conservative nature of the SSRT relative to long term sustained load crack growth rate testing monitored with a sensitive crack detection method. A strength of the current argument against SCC is that the tarnish rupture mechanisms can only operate in a somewhat oxidizing thermodynamically limited E-pH region by definition and, therefore, cannot occur once oxidizers are depleted.

The other important recommendation is to explore long term anaerobic SCC mechanisms. For instance, HS^- induced stress corrosion of copper under anoxic conditions does not require a passive film, can occur under anoxic conditions *at sulfide levels of 10^{-4} moles HS^- per liter*, and

would also enable secondary effects such as dissolution and hydrogen-induced vacancy injection^[106-122]. Classical hydrogen embrittlement^[106] is not considered to be of concern. However, the implications of hydrogen enhanced vacancy formation and subsequent SCC by the mechanism described by Airoka for ferrous and nickel based alloys in hot water should be considered further^[108, 109]. The vacancy injection-embrittlement SCC scenario under long term anoxic HS⁻ containing conditions should be investigated further to determine whether it represents a viable scenario for anoxic SCC. Furthermore, the role of corrosion-induced vacancy injection in supporting creep deformation at enhanced rates over “dry” thermally activated conditions might also be considered.

NWMO and associated supporting scientists agree but raise several concerns. First, the finding of Taniguchi, and Kawasaki have not been reproduced according to several investigators^[48]. NWMO also takes the position that this concern is more relevant for Swedish ground waters which contain natural HS⁻. Canadian ground waters (at possible repository locations) are anticipated to be largely naturally HS⁻ free; although a very conservative value of 3 ppm HS⁻ produced via microbial activity outside the bentonite has been considered. This HS⁻ must then be released from the biofilm and diffuse to the container surface according to King. King also takes the technical position that HS⁻ transport rates in bentonite will possibly be quite slow and that oxidized copper will readily sequester all HS⁻ given that Cu₂S solubility is extraordinarily low. The concern is that even more or less conservative SSRT tests (less conservative because they are incapable of detecting slow crack growth rates of relevance to repository time frames; more conservative because dynamic plastic strain is applied) are quite possibly drastically different from actual repository conditions given saturated bentonite with low HS⁻ concentrations and availability. The sulfide concentration at copper surfaces and crack tips might approach zero if supply is mass transport limited. Here, SCC crack tips might be extremely challenged towards the supply of HS⁻ necessary to sustain cracking. Therefore, the amount of sulfide reaching the container surface will be minimal and the interfacial [HS⁻] will be vanishingly small.

These arguments are solid but lack complete confirmation such as might be provided by long term SCC tests in bentonite clay with various amounts of HS⁻ and heat transfer. It is notable that there are many instances in the corrosion literature of bulk dilute environments containing an extremely low concentration of SCC agents yet still proven to be capable of enabling SCC. A notable example is ppm levels of Cl⁻ in high purity reactor waters used in nuclear power. There are similarities and differences. One notable difference here is that the extraordinary insolubility of sulfides ($K_{sp} = 3 \times 10^{-48}$ at 25 °C versus the moderate solubility of many metal chlorides) can lead to effective sequestering of HS⁻ with Cu(I) as Cu₂S to inhibit the process. Moreover, the vacancy condensation SCC mechanism requires at least moderate amounts of sustained dissolution to sustain metal damage via the vacancy coalescence process and subsequent inter ligament embrittlement^[48, 108, 109]. In other words, vacancy generation in this case would be coupled with and rely critically upon continued sulfide induced copper dissolution under repository anoxic conditions. The copper dissolution rate would be extremely slow if HS⁻ supply were mass transport limited through bentonite. The alternative argument would be Cu₂S induced

hydrogen generation, absorption and hydrogen induced vacancy generation by the mechanism of Fukai^[113, 114]. However, Cu₂S catalyzed hydrogen evolution has not been established.

3. DISCUSSION

A prior NWMO report examined the corrosion allowance of copper, and estimated that corrosion would not penetrate the thin copper layer by more than 1.27 mm over a 1 million year time period under the proposed disposal scenario. The 1.27 mm corrosion allowance was based on estimates of copper wall penetration of up to 0.17 mm penetration from uniform copper corrosion, 0.1 mm from under-deposit corrosion and 1 mm from microbially influenced corrosion (MIC).

Spontaneous corrosion in O₂ free water will be governed by the product $a_{\text{H}_2}^{1/2} a_{\text{Cu(I)}}$ ^[48, 60, 108, 109]. This situation ensures a very limited amount of corrosion before the product is exceeded and corrosion ceases in the absence of sulfides. The only controversial issue is the exact equilibrium hydrogen partial pressure in comparison to the hydraulic pressure. Since the equilibrium partial H₂ pressure for spontaneous corrosion of copper is likely well below the hydraulic pressure exerted on the spent fuel canister, then corrosion would readily become limited and the exact Cu(I) species and equilibrium pressure which depends on the Cu(I) identity becomes somewhat academic. Even in the presence of sulfides, low copper sulfide solubility leads to sulfide sequestering, and extremely low mass transport control of HS⁻ transport in MIC resistant bentonite assures very low corrosion rates. The only potential concerns for uniform corrosion would be the lack of bentonite saturation, and/or bentonite erosion, which would enable H₂ evolution by allowing its more rapid transport from the container. The other potential corrosion concern is unproven catalytic sulfide-induced corrosion of Cu by a catalytic regenerated adsorbed sulfide process coupled with stability of some other reaction product such as Cu-Cl species at low potentials. It might be argued that this corrosion would still be limited by liquid phase molecular hydrogen diffusion through saturated bentonite except that hydrogen fugacities, should 60-90 mV hydrogen overpotentials exist, can start to approach hydraulic pressures to enable corrosion with H₂ gas evolution. This scenario seems implausible but may deserve some further consideration.

Pitting by mechanisms seen in dilute Cl⁻ and SO₄²⁻ are only possible in the early stages of a DGR and may be cathode limited or starved. However, underdeposit corrosion and HS⁻ pitting in high Cl⁻ might be relevant during the long anoxic period. HS⁻ pitting also requires catalytic sulfide induced corrosion of Cu by a catalytic regenerated adsorbed sulfide process coupled with stability of some other reaction product such as Cu-Cl species at low potentials. It also requires HS⁻ pitting which is presently not well explained compared to uniform sulfidation. This scenario seems implausible but deserves some further future consideration. To date a general corrosion allowance based on underdeposit corrosion experiments in bentonite clay and Cl⁻ solutions where anodes and cathodes are movable is reasonable as long as 18 month experiments under aerated conditions are regarded to be conservative relative to 1 million year anaerobic exposures. The other requirement is that no other plausible environment such as Cl⁻

+ HS⁻ + SO₄²⁻ or some other deposit (i.e., Al₂O₃ from bentonite?) enables the establishment of more permanent anodes that can be supported by water reduction.

Enhanced corrosion by direct MIC is highly unlikely, but diffusion of aggressive constituents such as H₂S to the copper surface through the bentonite layer will enhance copper corrosion albeit slowly. The corrosion allowance of 1 mm is adequate as long as the bentonite layer remains intact.

SCC by any tarnish mechanism is unlikely because of a low concentration of SCC agents and low potentials outside of the tarnish E-pH range, but one HS⁻ induced SCC mechanism exists that might be mitigated by some of the same issues given above discussed previously in the context of HS⁻ general corrosion and pitting. Namely, insufficient dissolution would lead to insufficient vacancy formation and subsequently insufficient crack tip damage. Finally stress management to ensure compressive stresses may be another line of defense against this form of corrosion. For these reasons no corrosion allowance for SCC is necessary at this time. This issue should only be revisited should sulfide catalyzed copper corrosion be found to occur with hydrogen evolution.

4. CONCLUSIONS

The uniform, microbially induced, under-deposit and pit corrosion as well as stress corrosion cracking positions currently considered by NWMO have been examined. The focus was on issues that might affect the NWMO estimated corrosion allowance depth of 1.27 mm in approximately 1 million years. In conjunction with the review, there has been some consideration of the broader literature. This summary highlights the main review findings.

Current experimental evidence for spontaneous copper corrosion in O₂ free waters lacks corroborating diagnostics and broad consensus from multiple investigators regarding the exact equilibrium hydrogen partial pressure for Cu(I) oxidation in water. Therefore, it is the opinion of this review that the matter is unresolved. However, convincing and logical arguments have been made that the rate of corrosion should not affect the corrosion allowance, because spontaneous corrosion should cease once Cu(I) concentrations increase near the package or hydrogen gas pressures increase to modest levels. Additional confidence-building experiments could confirm thermodynamic predictions of conditions where spontaneous corrosion processes cease. There is also evidence to support the concern for spontaneous copper corrosion in oxygen free situations at high Cl⁻ concentrations, when low Cu cation concentrations and elevated temperatures are present. These conditions should be further explored to define under what conditions spontaneous corrosion occurs and what governs these corrosion rates. If slow molecular hydrogen transport controls these rates also then corrosion rates are likely very low. The likely transition from spontaneity to non-spontaneity corrosion upon changes in certain parameters such as hydrogen partial pressure could be experimentally confirmed.

Assuming that O₂ free uniform corrosion is spontaneous, kinetic models have been developed for formation of CuOH in pure water and Cu₂S in sulfide containing environments. These kinetic models for spontaneous uniform corrosion rates rely on strong arguments for mass transport control and low HS⁻ levels supplied by MIC. Should these conditions prevail, rates will be kinetically slow and should cease based on thermodynamic arguments. Alternative rate limiting factors are discussed.

Underdeposit corrosion depths appear to have been adequately represented as long as other conditions that produce more permanent anodes can be shown not to exist and as long as rates are limited by molecular hydrogen diffusion through saturated bentonite. One SCC mechanism possible under anoxic conditions exists but strong mitigating factors suggest that it should not be considered in the corrosion allowance to date.

Taken together, this review suggests that the NWMO corrosion allowance has been adequately described unless evidence changes key assumptions. However, hypothetical conditions for alternative scenarios have been described.

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