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Technical Note

2012:21

Initial Review Phase for SKB's Safety Assessment SR-Site: Corrosion of Copper

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SSM perspektiv

Bakgrund

Strålsäkerhetsmyndigheten (SSM) granskar Svensk Kärnbränslehantering AB:s (SKB) ansökningar enligt lagen (1984:3) om kärnteknisk verksamhet om uppförande, innehav och drift av ett slutförvar för använt kärnbränsle och av en inkapslingsanläggning. Som en del i granskningen ger SSM konsulter uppdrag för att inhämta information i avgränsade frågor. I SSM:s Technical note-serie rapporteras resultaten från dessa konsultuppdrag.

Projektets syfte

Syftet med detta granskningsuppdrag inom SSM:s inledande granskning är att beskriva hur SKB behandlat kopparkorrosion inom SR-site med avseende på den förväntade utvecklingen av miljö och då främst syrgasinnehåll i grundvattnet efter deponering av kapslar i slutförvaranläggningen. Baserat på författarnas kunskaper ska bedömning göras om SKB beskrivit de korrosionsmekanismer som kan ske för kopparkapslarna. Det huvudsakliga syftet inom denna inledande granskning av kopparkorrosion är att få en bred belysning av SR-site och underreferenser samt att identifiera eventuella behov av kompletterande information eller förtydliganden som SKB bör tillfoga ansökansunderlaget.

Författarnas sammanfattning

SKB:s redovisning av allmän korrosion, lokal korrosion samt spänningskorrosion har granskats med avsikt att identifiera olösta frågeställningar, kunskapsluckor, behov av kompletteringar och möjligheter. I samband med denna granskning av SKB rapporter som listas i bilaga 1 har även viss hänsyn tagits till övrig litteratur inom ämnesområdet. Denna sammanfattning belyser de viktigaste resultaten i granskningen av SKB:s inlämnade tillståndsansökan för slutförvaring av använt kärnbränsle inom korrosionsområdet.

Det experimentella beviset för spontan korrosion av koppar i O_2 fritt vatten saknar bekräftande analys och bred samstämmighet från flera forskargrupper. Av denna anledning är uppfattningen i denna granskning att frågan fortfarande inte är löst. Ytterligare experimentella undersökningar av kopparkorrosion i O_2 fritt vatten rekommenderas. Experiment kan även utformas för att bekräfta termodynamiska förutsägelser när spontan korrosion av koppar i rent vatten kan förväntas att avstanna. Det finns även bevis som stödjer att spontan kopparkorrosion kan ske i syrgasfria situationer vid en hög Cl^- koncentration och en samtidigt låg kopparjonkoncentration samt hög temperatur. Dessa betingelser bör undersökas ytterligares för att klart kunna definiera under vilka förutsättningar när spontan korrosion av koppar sker. Dessutom bör den övergången från spontan till icke spontan korrosion beroende på sammansättningsvariationer i den omgivande miljön experimentellt belysas.

Under antagande att allmän korrosion i O_2 haltiga miljöer är spontan har SKB utvecklat kinetiska modeller för bildande av CuOH i rent vatten och Cu_2S i sulfidhaltiga vatten. Dessa kinetiska modeller för att beskriva korrosionshastigheter för spontan allmän korrosion är icke-konservativa och bygger på principer som medför låga korrosionshastigheter. Antingen bör principerna för dessa modeller och antagenden underbyggas vidare eller annars bör den maximala korrosionshastigheten fastställas. Exempelvis är bildning av Cu_2S styrd av HS^- koncentrationen i grundvattnet tillsammans med restriktioner i masstransport.

Detta antagande utesluter alternativet att kopparkorrosion kan ske efter att HS^- konsumerats (eventuellt katalyserad av S^{2-} återbildning och återadsorption). Antagande att HS^- inte kan recirkuleras för att driva korrosionen ytterligare behöver beläggas.

För att bedöma risk för lokal korrosion av koppar jämför SKB gropfrätningspotentialen med korrosionspotentialen Ecorr. Tillförlitligheten med att använda gropfrätningspotentialen för att bedöma risk för lokal korrosion bedöms kunna ökas genom flera olika tillvägagångssätt. Ett sätt är att ta fram modeller som gör det möjligt att beskriva Ecorr som funktion av vattenkemi och fysikaliska förhållanden och dess utveckling på lång sikt. För närvarande är den Ecorr som används för bedömning av lokal korrosion av koppar i slutförvarsmiljö baserad på begränsade korta experimentella data eller på modelldata.

Ytterligare en fråga som inte tagits om hand är behovet att även använda inverkan av övriga oxidanter som exempelvis vätepeoxid som kan bildas från radiolys av gammstrålning på lokala korrosionsprocesser. Det bedöms även vara ett behov att ytterligare utöka kunskapen om initiering av gropfrätning, vilken idag baseras på potentialskillnaden Eb-Ecorr. För närvarande finns endast experimentellt underlag för hur denna potentialskillnad beror av isolerade förändringar av den kemiska sammansättningen exempelvis Cl-. Exempelvis bör analysen innefatta 1) att bestämma skillnaden mellan Eb-Ecorr för olika kombinationer av anjoner som Cl^- och SO_4^{2-} samt Cl^- och HS^-, 2) bedömning av den mer konservativa repassiveringspotentialen, samt 3) innehålla en bredare probabilistisk analys, för att ta fram ett bättre mer konsistent underlag att utesluta att initiering av gropfrätning kan ske.

För det fall sannolikheten för gropfrätning inte kan försummas bör undersökningar utföras för att förbättra uppskattning av gropfrätningskvot främst med avseende på små variationer i kemisk sammansättning på grundvattnet. Slutligen är uppfattningen att SKB även bör utföra mer studier om gropfrätning i koppar kan ske under syrgasfria förhållanden under närvaro av HS^-.

Spänningskorrosion (SCC) i grundvatten under syrgasrika förhållanden utan HS- verkar vara osannolikt baserat på kända mekanismer. En faktor som inte beaktats med avseende på SCC är emellertid inverkan av speciella oxidanter som peroxid vilken bildas vid gammaradiolys av vatten. En annan viktig rekommendation är att undersöka spänningskorrosionsmekanismer i grundvatten under syrgasfria förhållanden. Ett exempel på detta är HS^- inducerad spänningskorrosion av koppar i syrgasfria grundvatten vilken inte kräver närvaro av någon passivfilm och kan även sekundärt ge upphov till upplösning och väteinducerad vakansgenerering i koppar. Klassisk väteförsprödning bedöms inte vara något bekymmer. Däremot behöver konsekvensen av ökad vakansgenerering beroende på väte uppmärksammas.

Försprödning av koppar orsakad av vakansgenerering i koppar under syrgasfria förhållanden bör undersökas för att avgöra om denna mekanism är en verksam mekanism för SCC i syrgasfria grundvatten. Ytterligare en parameter som bör beaktas är inverkan av korrosionsinducerad vakansgenerering på krypdeformationshastigheter i jämförelse med ”torra” termiskt aktiverade krypmekanismer.

Projektinformation
Kontaktperson på SSM: Jan Linder
Diarienummer ramavtal: SSM2011-3399
Diarienummer avrop: SSM2011-4197
Aktivitetsnummer: 3030007-4003

SSM perspective

Background

The Swedish Radiation Safety Authority (SSM) reviews the Swedish Nuclear Fuel Company's (SKB) applications under the Act on Nuclear Activities (SFS 1984:3) for the construction and operation of a repository for spent nuclear fuel and for an encapsulation facility. As part of the review, SSM commissions consultants to carry out work in order to obtain information on specific issues. The results from the consultants' tasks are reported in SSM's Technical Note series.

Objectives of the project

In this review assignment, SKB's treatment of copper corrosion processes or mechanisms in SR-Site shall be reviewed both for the anticipated oxic and anoxic repository environments. The reviewer(s) shall consider if corrosion and corrosion mechanisms of the copper canisters in different possible evolutionary repository environments have been properly described. The objectives of this initial review phase in the area of copper corrosion is to achieve a broad coverage of SR-Site and its supporting references and in particular identify the need for complementary information and clarifications to be delivered by SKB.

Summary by the authors

The uniform and localized corrosion treatments as well as stress corrosion cracking positions currently considered by SKB have been examined with the objective of identifying key unresolved issues or gaps, needs and opportunities. In conjunction with the review of the SKB reports listed in Appendix 1, there has been some consideration of the broader literature. This summary highlights the main review findings.

Current experimental evidence for spontaneous copper corrosion in O_2 free waters lacks corroborating diagnostics and broad consensus from multiple investigators. Therefore, it is the opinion of this review that the matter is unresolved. Further diagnostic experiments are recommended in O_2 free waters. Experiments could also confirm thermodynamic predicts 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. The likely transition from spontaneity to non-spontaneity upon changes in certain parameters could be experimentally confirmed.

Assuming that O_2 uniform corrosion is spontaneous, kinetic models have been developed for formation of CuOH in pure water and Cu_2S in sulfide containing waters. These kinetic models for spontaneous uniform corrosion rates are non-conservative as currently composed and rely on key tenets that create low rates. Either evidence supporting these key tenets and assumptions should be strengthened or upper bound rates should also be established. For instance Cu_2S in sulfide containing waters restricts copper corrosion to rates governed by HS- concentration and mass transport. This assumption eliminates the option for copper corrosion after HS^- consumption (perhaps catalyzed by S^{-2} regeneration and re-adsorption). This assumption of HS^- sequestering could be strengthened.

Localized corrosion is treated by comparing the threshold potential for breakdown to the corrosion potential, E_{corr}. Such a threshold potential approach could be strengthened by several courses of action. One is the need to expand mixed potential theory models to enable definition of Ecorr as a function of water chemistry and physical conditions over the long term. Presently, E_{corr} for copper in repository situations is based on limited short term experimental data or model data under limited conditions. Another unresolved issue is the need to consider the effects of other oxidizers like peroxide generated by gamma radiolysis on localized corrosion processes.

There is also the need to expand the pitting initiation treatment based on assessment of the potential difference $E^{b-}E_{corr}$. Currently, this assessment is based on limited data for isolated species such as Cl^-. For instance, threshold potential treatments should also consider effects of anion combinations such as Cl^- and SO_4^{2}- as well as Cl^- and HS^-, consider more conservative repassivation potentials, and involve broader application of probabilistic treatments when necessary to enable a consistent basis for rejection of pitting initiation. If pitting probabilities are finite, studies should improve estimates of pit factors and be aware of subtle effects of chemistry on such pit factors. Finally, it is the opinion of this review that there is a need to explore possible long term anaerobic pitting mechanisms such as by HS^- pitting.

Stress corrosion cracking (SCC) under oxic conditions without HS^- appears to be unlikely by all mechanisms. However, an unresolved issue is the need to consider special oxidizers like peroxide from gamma radiolysis on SCC. 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, and would also enable secondary effects such as dissolution and hydrogen-induced vacancy injection. Classical hydrogen embrittlement is not considered to be of concern. However, the implications of hydrogen enhanced vacancy formation should be considered.

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 should also be considered.

Project information

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Content

1. Introduction

1.1. Background

On 16th March 2011 the Swedish Nuclear Fuel and Waste Management Company, SKB, submitted applications for licences to construct a spent nuclear fuel encapsulation facility in Oskarshamn and a repository for final disposal of the encapsulated fuel in Forsmark. SKB's applications are currently being reviewed by the Swedish Radiation Safety Authority, SSM, and the Land and Environmental Court in Stockholm. SSM's review is concerned with nuclear safety and radiation protection in the facilities in accordance with the Nuclear Activities Act. The Land and Environmental Court's review is concerned with compliance the Environmental Code.

The SR-Site safety assessment for the spent fuel repository is an important component of SKB's licence application and is a focus of SSM's review of the long term safety. SSM is undertaking a phased review SKB of the safety assessment involving an Acceptance Review, an Initial Review and a Main Review. Currently, the Initial Review Phase is being undertaken, where the overall objective is to identify requirements for complementary information and clarifications from SKB. In order to meet this objective, the review is aiming to achieve broad coverage of the SR-Site safety assessment and its supporting references. On completion of the Initial Review Phase, SSM will determine if the quality and comprehensiveness of the safety assessment is sufficient to warrant more detailed review in the Main Review Phase. The Main Review Phase will consist of a number of review tasks defined to address the uncertain and/or safety critical review issues identified in the Initial Review Phase as requiring more comprehensive review.

Due to the large scope and scientific breadth of the safety assessment, SSM has arranged for external experts to provide support in its review of the safety assessment. To this end, as part of SSM's review of engineered barrier performance for a KBS-3 repository for spent nuclear fuel, Galson Sciences Ltd (GSL) has been awarded a framework agreement with SSM concerned with copper corrosion. Prof. John Scully of the University of Virginia is subcontracted to GSL to support SSM's review under this framework agreement. Having established this framework agreement, SSM contracted GSL and Prof. Scully to review SKB's treatment of copper corrosion processes or mechanisms in SR-Site for oxic and anoxic repository environments. This Technical Note documents the results of the review of SKB's treatment of copper corrosion in the SR-Site safety assessment in support of SSM's Initial Review of SR-Site.

1.2. Objective

The objective of the review task is to consider if SKB has properly described and accounted for corrosion of copper canisters in different possible evolving repository environments in the assessment and mathematical modelling of copper canister performance.

1.3. Approach and Structure

This review assignment has considered the discussion of copper corrosion in the SR-Site Main Report (SKB, 2011a), the Fuel and Canister Process Report, the Data Report and the FEP Report, as well as a number of supporting documents that provide details of corrosion processes and their treatment in the safety assessment. The main review findings are presented in Section 2, covering SKB's treatment of uniform corrosion (Section 2.1), localized corrosion (Section 2.2) and stress corrosion cracking (Section 2.3). Recommendations to SSM arising from the review are presented in Section 3.

The Technical Note also includes three appendices. The first appendix records the SKB reports that have been reviewed in this work; the second appendix summarises the proposed requests for complementary information from SKB; and the third appendix lists proposed topics for further review in the Main Review Phase.

2. Main Review Findings

2.1. Uniform Corrosion Thermodynamics and Kinetic Processes

An open question concerns spontaneous corrosion of copper in O_2 free pure water (Hultquist 1986; Bojinov and Makela 2003; Szakalos et al. 2007; Becker and Hermansson 2011; Macdonald and Samin 2011). Uniform corrosion rates during the full saturated time period when O_2 free conditions have been established after repository closure have been considered by SKB using a corrosion allowance treatment. This approach has been applied to three processes which might be regarded as thermodynamically spontaneous or regarded as uncertain with regard to spontaneity. A few other aspects of the uniform corrosion scenario have been considered by SKB including corrosion during the aerobic period as well as during the anerobic period as a function of the ground water as a consequence of processes such as nuclear fuel decay.[1]

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

$$Cu(s) + H_2O(l) \rightarrow Cu(OH)\ (s) + 1/2H_2\ (g)$$

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:

$$Cu(s) + nCl^- + H_2O = CuCl_n^- + OH^- + 1/2H_2$$

The thermodynamic claim of immunity made by SKB is affected by the Cl^- concentration and pH assumed and the resulting assumed Cu-Cl complex formed.

In the case of HS^- presence from sulfate reducing bacteria, pyrite decomposition or other sources, mass transport limited HS^- induced corrosion of copper by the *"Cu_2S formation mechanism"* is considered as described in TR-10-66 on p. 14] (SKB 2010a):

$$2Cu(s) + 2HS^- \rightarrow Cu_2S\ (s) + H_2\ (g) + S^{2-} \quad \text{(or)}$$

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

There are several needs and gaps with regard to consideration of corrosion under anoxic conditions. Several unresolved or partially resolved issues were identified for further consideration concerning both uniform and localized corrosion. Concerns related to localized corrosion issues are addressed in section 2.2. Uniform corrosion rate processes in many cases have not been described by what in general would be the most conservative yet still realistic conditions. Instead non-conservative or slow conditions

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[1] Uniform corrosion rates estimated to arise as a result of nuclear reaction product formation are taken to be conservative as long as predictions of oxidizing species are at the upper bounds of the production rates possible.

have been considered in great detail. Unresolved issues are summarized here and then each issue is discussed in more detail below.

1. There is the need to (a) address needs and gaps associated with thermodynamics associated with each uniform Cu(I) formation mechanism. This includes the CuOH, Cu-Cl, and Cu-HS mechanisms. H_2O reduction leading to Cu^+, $CuCl_2^-$ or $CuCl_3^{2-}$ in low or nil HS^-/high Cl^- environments has been considered in several reports such as TR-10-67 on pages p. 52, p. 62 (Hermansson and Eriksson 1999; SKB 2010f). However, the current position is that at a pH > 4 and $Cl^- < 2M$, copper will not corrode spontaneously as mentioned in TR-10-67, section 5.2 and TR-02-25 on p. 13-15 (SKB 2002; SKB 2010f). This threshold for uniform corrosion in Cu-Cl systems needs to be better explained.
2. The corrosion rate expressions for the CuOH, Cu-Cl, and Cu-HS mechanisms are all considered to be limited by slow mass transport controlled process either towards or from the Cu interface. The key assumptions are that the following transport processes are slow: (CuOH formation; H_2 liquid phase transport, Cu-Cl formation; $CuCl_2^-$ liquid phase transport, and Cu-HS formation; HS^- liquid phase transport). However, there are unresolved issues regarding each of these assumptions compared to alternative fast transport paths.
3. There is need to expand corrosion kinetic descriptions to more realistic waters such as those containing mixtures of species such as both HS^- and Cl^-. Hence, the logical next step is development of hybrid models considering corrosion in copper-sulfide-chloride-(sulfate) systems by combined "HS^-" and "water reduction" under anoxic conditions.

Each uniform corrosion process is considered in greater detail below in this technical note.

2.1.1. Uniform Corrosion Thermodynamics and Kinetics in O_2 free pure water

Existence of Cu(OH) has been reported (Korzhavyi et al. 2012). However, corrosion of copper in O_2 free pure water has not yet been experimentally confirmed by multiple organizations, nor does consensus exist amongst independent investigators (Hultquist 1986; Hultquist 1987; Simpson and Schenk 1987; Eriksen et al. 1989; Hultquist et al. 1989; Hultquist 1995a; Hultquist 1995b; Hultquist 1995c; Hultquist 1996b; Hultquist 1996a; Bojinov and Makela 2003; Szakalos, Hultquist et al. 2007; Szakalos et al. 2008; Hultquist et al. 2009; Hultquist et al. 2010; Becker and Hermansson 2011; Hultquist et al. 2011; Korzhavyi, Soroka et al. 2012). Many diagnostics that would assist to either confirm or refute this process have not yet been conducted. The most obvious of these include multi-channel simultaneous information gathering such as a complete inventory of Cu in solution and on the surface in a non-reactive chamber that does not exchange species with the water, a complete inventory of H and H_2 (copper, chamber, Pd membrane, solution) and simultaneous O_2 and redox potential measurements. It is the opinion of this review that many of the anoxic, HS^- free, experiments conducted to date could be significantly improved with additional diagnostics to confirm or refute the spontaneity of this process.

In-situ film analysis, improved solution phase control (management of residual O_2) and post-corrosion analysis to inventory <u>all</u> reactants and products should be undertaken to confirm or refute the spontaneity of this process under verified O_2 free conditions. Enhanced study of H_2 production, transport, fate, mass balance and elimination of artifact effects such as possible H_2 production from the glass liner as reported in SSM 2011:34 should be undertaken (Becker and Hermansson 2011).

Even verification of corrosion rate measurement by the gas permeation method for a material with a known anoxic corrosion rate (e.g., zinc) could be undertaken to see if the corrosion rate can be determined accurately from the gas permeation method. The intention here is to use a material known to be readily corroded under anoxic conditions to test the corrosion rate measurement method.

Additional pressure gauge diagnostics independent of artifacts could verify thermodynamic principles such as non-spontaneous behavior at raised H_2 pressures which are soundly articulated (Macdonald and Samin 2011). The theoretical equilibrium H_2 pressure for H_xCuO_y/Cu equilibrium should be further verified/confirmed experimentally (Szakalos, Hultquist et al. 2007; Becker and Hermansson 2011)). Another diagnostic would be to test the validity of $fH_2^{1/2}$- $C_{Cu(I)}$ relationships in corrosion domain diagrams to determine if corrosion becomes spontaneous when f_{H2} or Cu^+ levels are changed with respect to thermodynamic equilibrium reaction coefficients (Macdonald and Samin 2011). Once f_{H2} fagacity and Cu^+ concentrations reach certain levels, quasi-immunity may be restored depending on transport rates (Macdonald and Samin 2011).

Regarding kinetics, it seems prudent to include consideration of corrosion kinetics under anoxic conditions in case this mode of corrosion should be proven to be thermodynamically spontaneous, and SKB has done this (SKB 2010a). One of the main assumptions of the O_2 free corrosion rate laws developed by SKB involves a key assumption that the corrosion rate is limited by dissolved H_2 (l) diffusion away from copper surfaces, whose liquid concentration is limited by the solubility of H_2 in water as discussed in TR-10-66 on pp 42-43 (SKB 2010a). Another key assumption seems to be that hydrogen recombination and evolution into the gas phase does not occur. It should be noted that this pathway for cathodic reaction dihydrogen reaction product removal to the gas phase (a) would enable rapid removal of H_2 from the copper surface eliminating the restriction of soluble H_2 transport on the overall coupled rate, (b) would continue until H_2 pressurization occurred to the point where corrosion was no longer thermodynamically possible as the reversible hydrogen potential became more negative than the presumed Cu/CuOH half cell reaction potential (Macdonald and Samin 2011)[2]. At a high level of examination, the assumption that liquid phase hydrogen diffusion occurs is non-conservative because it limits the rate of anoxic corrosion to liquid diffusion rates for H_2 away from the copper interface as discussed in TR-10-66 on pp 42-43 (SKB 2010a). One technical issue is what reference and precedence exists that such a phenomenon actually occurs in any other corrosion situation? For instance, corrosion or hydrogen production in deep water situations is not reported to be limited by H_2 (l) phase diffusion even in the presence of large hydrostatic pressures (note that hydrostatic pressure is not the same as hydrogen partial pressure but is merely the head pressure) which might be regarded to limit the hydrogen evolution reaction and H_2 gas bubble formation because of equilibrium pressure considerations. What references from the

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[2] The presence of multiple reaction products including CuOH may confound the identification of an exact hydrogen partial pressure which restores “quasi-immunity”.

literature of experiments can SKB provide that indicates unambiguously that H_2 (l) mass transport limits corrosion rate? SKB should provide such data from, for instance, controlled experiments at various relevant hydrostatic pressures and also consider literature data from deep water submergence.

In summary, the diagnostics suggested would not be terribly difficult experiments to conduct to confirm or refute spontaneity and rates and could be conducted over a few years.

2.1.2. Uniform Corrosion Thermodynamics in O_2 free water considering high Cl^- concentrations

It is reported that corrosion will not occur in oxygen free waters containing Cl^- at concentrations below 2 M and at pH greater than 4 and this is built into the copper canister safety case (SKB 2010a; SKB 2010f). The presumed basis for this assertion is the determination that the half cell reaction for Cu corrosion to form Cu(I) by a pathway leading to $CuCl_2^-$ formation or some other Cu-Cl^- species occurs at a potential more positive than the reduction of water or proton discharge half-cell reaction in the absence of O_2 as discussed in TR-10-67 on p. 52 (SKB 2010f). The following is an example of one possible overall reaction:

$$Cu(s) + nCl^- + H_2O = CuCl_n^- + OH^- + 1/2H_2$$

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

$$Cu + 2Cl^- = CuCl_2^- + e^-$$

$$Cu + 3Cl^- = CuCl_3^- + e^-$$

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 and the reason for assuming of 1 mol/Kg is unclear (SKB 2002)[3]. In addition, all relevant alternative Cu(I)-Cl^- species and their half cell reactions should also be considered. An example of the concern is shown below in Figures 1a and 1b from SKI Report 99:52 (Hermansson and Eriksson 1999). Low Cu cation concentrations coupled with high Cl^- levels and temperature would enable anoxic corrosion. The basis for excluding such data is not clear from review of TR-10-67 nor TR-02-25 (Hermansson and Eriksson 1999; SKB 2002; SKB 2010f).

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[3] The high pH assertion is made in connection with the bentonite clay.

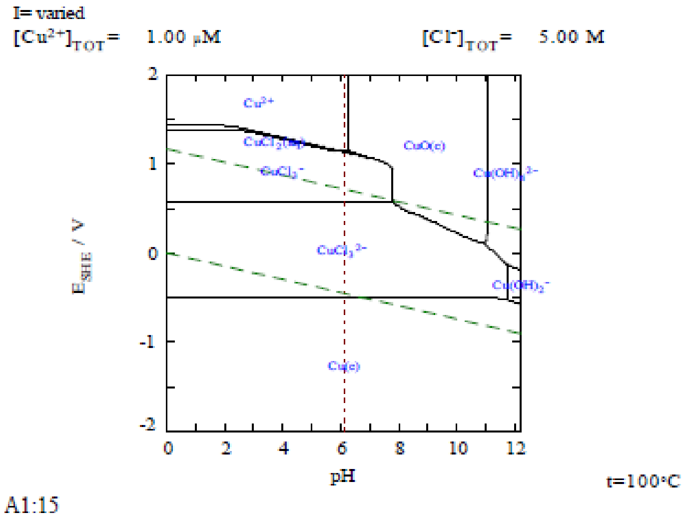

Figure 1a: E-pH diagram for Cu-Cl-H_2O system assuming Cl^- total concentration of 5 M, Cu^{+2} concentration of 1.00 μM and 100°C assuming $CuCl_3^{-2}$ formation. [From SKI 99:52]

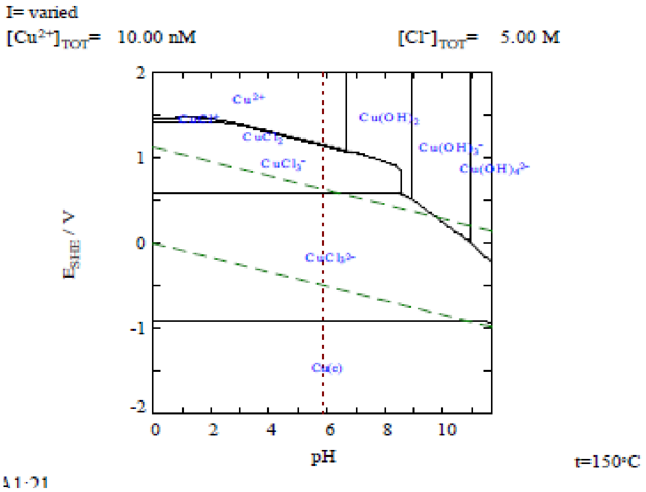

Figure 1b: E-pH diagram for Cu-Cl-H_2O system assuming Cl^- total concentration of 5 M, Cu^{+2} concentration of 10.00 nM and 150°C assuming $CuCl_3^{-2}$ formation. [from SKI 99:52]

2.1.3. Uniform Corrosion in O_2 free waters considering HS^-, and HS^- and Cl^-

Regarding kinetics, the other condition for anoxic corrosion involves corrosion rate definition in the presence of sulfides. Sulfides are known to form complexing species with copper which alter copper oxidation; specifically corrosion is thermodynamically spontaneous under Cu_xS formation conditions. SKB has considered this in detail [TR-10-66; TR-10-67; section 5.2.3; TR-02-25; section 4.3] (SKB 2002; SKB 2010a; SKB 2010f). One of the main issues for the O_2 free corrosion rate laws developed by SKB in the HS^- scenario involves a key assumption that the corrosion rate is limited by arrival of HS^- delivered to the copper surface to form Cu_xS (SKB 2010a). This process is assumed to be limited by liquid phase diffusion. Sulfides are considered to exist at low concentrations (ca. 10^{-5} M) mainly from decomposition of pyrite (SKB 2010a; SKB 2011a; SKB 2011b; SKB 2011c). Other sources of sulfides such as sulfate reducing bacteria and Fe(II) catalysis of sulfate reduction have also been considered. The assumed reaction path described by Shoesmith and Smith is (Smith et al. 2007a; Smith et al. 2007b):

$$Cu + HS^- \rightarrow Cu(HS)_{ads} + e^- \quad \text{[anodic 1]}$$

$$Cu + Cu(HS)_{ads} + HS^- \rightarrow Cu_2S + H_2S + e^- \quad \text{[anodic 2]}$$

$$2HS^- + 2e^- \rightarrow H_2 + 2S^{2-} \quad \text{[cathodic 1]}$$

$$2Cu\ (s) + 2HS^- \rightarrow Cu_2S\ (s) + H_2\ (g) + S^{2-} \quad \textit{[overall; one } S^{2-} \textit{ consumed]}$$

An alternative overall path is:

$$2Cu\ (s) + HS^- + H^+ \rightarrow Cu_2S\ (s) + H_2\ (g) \quad [S^{2-} \textit{ completely consumed and sequestered}]$$

Parallel reaction paths that do not sequester HS^- (low HS^-, high Cl^-, O_2 free) are not thoroughly explored including the possibility of the following half cell reaction suggested by Shoesmith (Smith, Wren et al. 2007b):

$$Cu(HS)_{ads} + 2Cl^- \rightarrow CuCl_2^- + HS^- \quad [HS^- \text{ not sequestered}]$$

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 was operative, HS^- would not be 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 rates as pointed out in TR-10-66 on p. 85 (SKB 2010f). However, this model has not been fully reviewed at the time of this report. The pathway reported for Cu - HS^- - Cl^- was discounted using various other arguments. For instance, the 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 (Smith, Wren et al. 2007b). However, a complete mass balance on corroding copper and sulfide concentration[4], a corrosion experiment in mixed electrolytes, 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 is not considered. The E-pH diagram from the Cu-adsorbed S^{-2} system showing formation of $CuHS_{ads}$ but not solid sulfide compounds is not considered (Protopopoff and Marcus 2003). 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 deserve more careful reconsideration. Besides being conducted in environments not representative of ground water, correct inventory of Cu(I) or $Cu(II)_{(aq)}$ is doubtful and complicated by S^{-2} interactions with the ring collector materials such as Pt or Ag. In contrast, evidence in the literature is available that indicates high copper corrosion rates that persist upon the complete removal of Na_2S (aq) or H_2S (g) initially supplied from the corrosive environment (Jacobs et al. 1998; Jacobs and Edwards 2000; Freeman 2011). 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 (Figure 2) (Jacobs and Edwards 2000).

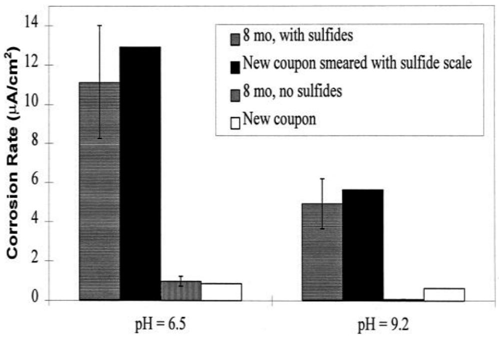

Figure 2: Corrosion rates of fresh copper coupons smeared with sulfide scale. Results are similar to the corrosion rate of coupons with 8 months of exposure to sulfides. Error bars indicate the 90% confidence interval. [Jacobs]

In the latter case, copper coupons were placed in a sealed glass chamber and removed periodically for corrosion rate assessment (Figure 3) (Freeman 2011). 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 (Figure 3). Corrosion continued in contradiction with the HS^- sequestering assumption. The former study was in a sealed container where presumably some O_2 depletion occurred. The latter was not. There are also a number of older papers such as regarding sulfide polluted seawater which will not be reviewed here (Syrett 1977; Gudas and Hack 1979b; Gudas and Hack 1979a; Syrett et

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[4] According to the SKB model, once all HS^- in a closed O_2 free system is consumed to form Cu_xS, all corrosion of Cu to form Cu(I) should stop and not a single Cu(I) cation should form by oxidation. Implicit in this assumption is that Cu adjacent to adsorbed HS^- and Cu_xS behaves thermodynamically as if the adsorbed proximate HS^- or Cu_xS does not exist.

al. 1979; Hack 1980; Syrett 1981; Eiselstein et al. 1983). It is well known that Cu_2S catalyzes ORR (the oxygen reduction reaction) to enhance copper corrosion. However, most of these studies were in conducted in aerated environments. It is not clear whether HER (the hydrogen evolution reaction) is catalyzed by Cu_2S in an O_2 free situation.

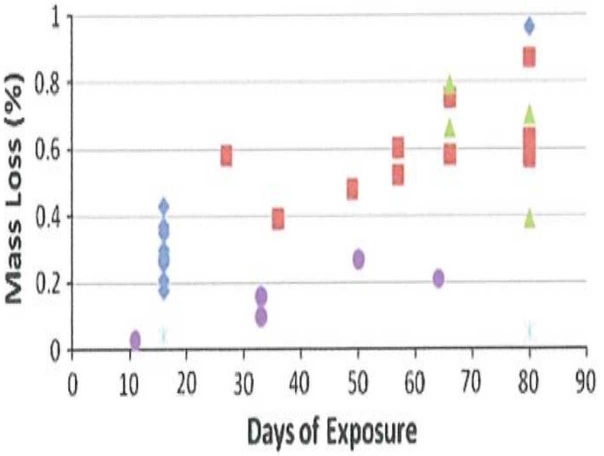

Figure 3: Gravimetric mass loss (all coupons acid washed prior to weighing) percent mass loss as a function of time (days). Diamond, constant exposure to Chinese Dry Wall (CDW) containing suflides as a H_2S source. Square 16 day exposure to the CDW as H_2S source then CDW removed and clean coupon attached; circle 0 days exposure then corroded coupon attached, six spoked asterisk; 0 days exposure to CDW as H_2S source. [Freeman]

SKB (2010a) implemented models of sulphide transport from the buffer to the canister surface to determine the rate of copper corrosion. The sulphide is assumed to arise as a result of dissolution of pyrite in the buffer. In the model, mass transport through the buffer is described using transport resistances based on the concept of equivalent flow rates. Transport resistances for transport from a fracture in the host rock to the buffer and from a spalling zone to the buffer are considered, with diffusion in the buffer. The equivalent flow rate from the fracture to the buffer is determined from discrete fracture network modelling. The transport resistance where a small area of buffer is exposed to flow from a fracture is represented by a thin band at the mouth of the fracture. This band is represented as a plug resistance extending into the buffer around the fracture intersection. Other geometric factors describe the equivalent flow rate in the spalling zone.

Description of this model would benefit from diagrams showing how the different components of transport resistance, such as the plug resistance, are represented. Also, a more detailed review of the model should be undertaken to understand the derivation and reliability of the transport resistance factors.

The model includes many derived geometric factors that lead to the distribution of the spread of corrosion attack on the canister surface. A more detailed three dimensional model of mass transfer in such a system would be informative and would support understanding of the corrosion of copper by sulphide from pyrite dissolution in the buffer.

In summary, several key assumptions in anoxic HS^- corrosion are currently not fully verified nor well supported by the literature. These may lead to non-conservative assumptions. The consequences are non-conservative estimates of corrosion rate. The key non-conservative assumptions and unresolved issues in the opinion of this review are as follows.

1. In the SKB treatment, HS^- transport associated with groundwater movement through a rock fracture that intersects the deposition hole is assumed to occur at the mid-height of copper canisters. This leads to a non-conservative estimate of rates based on slow HS^- transport using the Q_{eff} approach as discussed in point 3 [TR-10-66] (SKB 2010a).
2. This review has insufficient information in order to verify whether the Q_{eff} transport approach is conservative [TR-10-66] (SKB 2010a).
3. In the SKB treatment, HS^- transport is assumed to occur through the liquid phases assuming a fully saturated betonite clay situation [TR-10-66] (SKB 2010a). The ramification of this is that slow liquid phases transport will govern mass transport controlled rates. Alternatively, gas phase transport would lead to faster transport rates. It would seem that gas transport would be possible during any hot dry period as well as in situations where bentonite is not fully saturated with ground water. In these cases, it seems that H_2S in the gas phase may be transported rapidly to the copper interface. This scenario should be considered in the estimation of Cu-HS^- corrosion rates.
4. In the SKB treatment, HS^- is considered to be fully sequestered during the copper sulfidation process as discussed above (i.e., Cu_2S formation) [TR-10-66, TR-10-67] (SKB 2010a; SKB 2010f). In this assumption, only a maximum of two copper atoms can be corroded by a single S^{-2}. This is the least conservative assumption. It is further argued that Cu_2S growth is parabolic due to either HS^- diffusion in aqueous solution or formation of a protective Cu_2S film through which Cu^+ must be transported. Copper sulfides are not necessarily protective, may grow at linear rates and are known to spall. In a Shoesmith paper, linear growth is possible despite the fit to a parabolic expression. Moreover, voids are indicated (Smith, Wren et al. 2007b). If HS^- can activate copper towards corrosion due to water reduction, the possibility may exist that many copper atoms can be corroded by a single HS^- or S^{-2} anion, and this would be a more conservative position.
5. Mixed ground water chemistry and episodic or periodic sequential processes are not treated but represent realistic repository conditions. For instance, should the HS^- supply be interrupted or stopped and anoxic conditions persist, it follows from the present Cu-HS^- treatment and the asumptions made that no other pathway for Cu corrosion occurs spontaneously. This means that remaining copper atoms at canister surfaces revert back to the corrosion defining circumstances in O_2 free pure water (i.e., Cu(I)OH formation). SKB has not verified this key assumption.

Assumptions 1. and 2. will not be discussed further here except to say that higher corrosion rates may be possible. The higher rates would have to be evaluated to determine how or whether they affect the safety cases. In TR-10-66 on pp. 39-41, high HS^- concentrations and flow rates are considered but Cu^+ corrosion triggered by adsorbed HS^- that is not used up in the process is not considered (SKB 2010a). Taxen has considered $CuCl_2^-$ limited rates and reports an extremely low rate on TR-10-67 on p. 85 but this has not been reviewed in this technical note (SKB 2010f). Key assumption number 3. deserves further consideration. Also, the concern exists that HS^- is not used up and sequestered and is therefore not available for future corrosion. The assumption, although not well documented, seems to be that corrosion would stop completely if HS^- supply was interrupted. It is further argued that $CuCl_2^-$ formation in mixed HS^- + Cl^- environments is not possible although the complete argument is unsatisfactory. Basically, Cl^- induced corrosion of copper and HS^- induced corrosion of copper are treated as completely unrelated and separate processes that do not occur in the same environment nor at the same time (SKB 2010f). Mixed electrolytes are likely to exist at Forsmark, so the combined effects deserve consideration (SKB 2005; SKB 2010d; SKB 2010b; SKB 2011a; SKB 2011b; SKB 2011c).

In summary, the present analysis of HS^- corrosion rates may be non-conservative. A more conservative analysis would consider the possibility that multiple Cu^{+1} oxidation events could occur in mixed Cl^- - HS^- environments perhaps cataylzed by one HS^- radical perhaps triggered by HS^- adsorption, subsequent Cu^+ oxidation at reducing potentials, HS^- surface diffusion and HS^- re-adsorption (or, so called regeneration). This process might be coupled with water reduction and not rely entirely on HS^- reduction. However, a caveat is that $CuCl_2^-$ mass transport limited corrosion would need to be reviewed and this has not been done at the present time.

2.2. Localized Corrosion Processes

Copper canister corrosion analysis should consider viable local corrosion modes (pitting, SCC, under-deposit, miscellaneous). Two periods were considered in this preliminary review based on the information provided (SKB 2002; SKB 2010e; SKB 2010f).

- Viable mechanisms for penetration within the initial ~100 year period assuming presence of residual O_2 and Cu(II) reduction as a possible cathodic reactions.
- Viable mechanisms and penetrations over long term when the environment is O_2 and Cu(II) free.

Several unresolved or partially resolved issues were identified for further consideration concerning the handling of localized corrosion. It is assumed that pitting corrosion not crevice corrosion is the relevant mode of attack to consider. In this respect, the review agrees with the findings of SKB. However, the following issues remain for consideration on the topic of pitting corrosion. These issues may affect completeness at minimum and in the most conservative scenario where some pitting is conceded would either highlight the need for additional research to dismiss pit propagation as too low or alter the safety case.

1. The overall approach used to assess whether pitting is possible involves a threshold potential treatment where pit initiation is consider to be either “on” or “off” depending on how close the threshold potential, E_b is to the possible relevant reversible electrode potential reactions or mixed potentials that govern the potential of the copper surfaces (SKB 2002; SKB 2010f). Sufficient difference in voltage between these two potentials is taken as an indicator that

pit initiation is unlikely (SKB 2002; SKB 2010f). Currently, there is no consistent probabilistic approach to assess what voltage difference between these two potentials is necessary to reduce the probability of pitting corrosion to a negligible level such that pit initiation may be ignored.

2. The overall approach summarized above (1.) can be applied to both the oxic and anoxic periods. Further concerns regarding the oxic period include (i) the need to include the possible effects of mixtures of chemical species present in the repository environment on E_b in lieu of the current treatment which considers single aggressive species one by one in isolation of one another, (ii) the need to consider the role(s) and impact of possible deposits that do not function as a physical crevice but rather function as an ion exchange membrane enabling concentration of detrimental environments, (iii) the need to further consider nuclear processes such as gamma radiolysis of water and any related effects such as elevation in E_{corr} by the associated radicals and molecules thus developed, (iv) the need to develop a mixed potential model that predicts E_{corr} and E_b that can incorporate the chemical concentrations present, understands what model parameters are statistical distributed, and can anticipate statistical distributions of key potential values. After this is accomplished, the probabilistic risk of pitting corrosion could be properly assessed.
3. Concerns regarding the anoxic period include the possibility of HS^- induced localized corrosion during the long anoxic period under conditions dominated by formation of a Cu_2S film. An extremely limited amount of data exists regarding both E_b and E_{corr} during this period. Furthermore, there is little understanding of what governs E_{corr} during this period. Not only is the mechanism of pitting poorly understood but there is a lack of understanding on whether there is a statistical distribution of E_b. Given the current state of understanding, the probabilistic risk of pitting by HS^- cannot be assessed.
4. The present treatment of pitting corrosion also relies on the use of extreme value statistics or an uncertain application of pit factors (PF) to rationalize that local corrosion will only occur to a limited extent (e.g., 5:1 pit factor) compared to general corrosion. There is little basis for such assertions. Moreover, as discussed above, uniform corrosion is treated in a non-conservative manner and this weakness is then propagated into the local corrosion scenario if a PF is applied based on such a uniform corrosion rate. In cases where the risk of pitting assessed consistently by some sort of probabilistic analysis is not found to be very low, it may be prudent to rethink what pitting factors might actually exist in mixed environments instead of borrowing pit factors from other studies. Alternatively, it would be useful to develop a rational technical basis for pit stifling and/or repassivation. Otherwise, the technical basis is not strong to rationalize that pit depths are not a safety issue.

Each of these issues is discussed below in detail.

2.2.1. Overall approach

The overall approach to the treatment of localized corrosion phenomena under both oxic and anoxic conditions is based on the threshold type treatment where a critical breakdown potential E_b, a corrodant concentration as well as sometimes pH and temperature can be considered together to describe the threshold conditions for pit initiation. This type of threshold treatment is useful to create "domains of susceptibility." The expected conditions must exceed or meet the required conditions in terms of the threshold potential, corrodant concentration and temperature in order to enable localized corrosion initiation and stabilization[5]. Consider the break down potential, E_b. This "threshold" potential describes a critical potential for pitting and represents an "on/off" criterion for pitting. The overall approach is to compare E_b to the open circuit or corrosion potential, E_{corr}. This has been done extensively such as in TR-02-25 on p. 64-66 and in TR-67-10 on pages 89-91 and 104 (SKB 2002; SKB 2010f). If E_b is well above E_{corr} or other potentials which describe the mixed potential that the copper canister can realize, then pit initiation can be dismissed as an unlikely event.

E_b is dependent on the details concerning the material composition and microstructure, surface condition, and specific electrolyte species and concentrations. Unfortunately, E_b is also often technique dependent and slow upward potential scans or potential holds often yield lower values than those obtained in rapid upward potential scans. That is, the critical potential is measurement time sensitive. Moreover, E_b is often a statistically distributed parameter often reported through the use of a probability density function (Kehler et al. 2001). Cong has verified the existence of such statistical distributions of E_b in the case of copper in Cl^- - SO_4^{2-} - HCO_3^- environments (SKB 2002; Cong et al. 2009; Cong 2009; Cong and Scully 2010b; Cong and Scully 2010a; SKB 2010f). It should also be noted that E_r is often significantly below E_b as shown in Figure 4. Since E_r is more conservative and only moderately statistically distributed, it is often the most conservative potential to choose when considering potent-based thresholds.

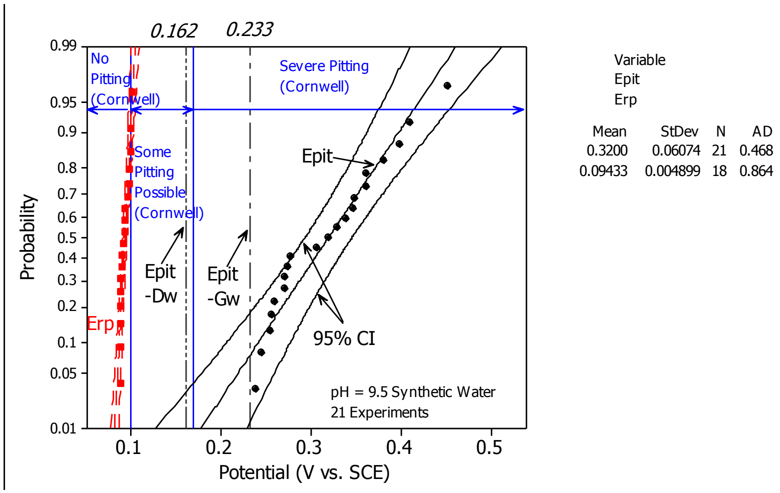

Figure 4: Statistical distribution of E_{pit} (E_b) and E_r from C11000 copper in pH = 9.5 deaerated Edwards synthetic water. Edwards synthetic water simulated the ionic constituents found at a water utility whose consumers experienced pitting problems. The freshly made synthetic water contained 34 mg/L alkalinity as HCO_3^-, 14 mg/L SO_4^{2-}, 20 mg/L Cl^-, and 17 mg/L Ca^{2+} added as reagent grade sodium or calcium salts to deionized water and had a measured conductivity of 148 μS/cm. The pH was 7.4. 95% CI (confidence interval) is plotted for both E_{pit} (E_b) and E_r. The mean pitting potentials for various waters are shown.

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[5] It should be noted that E_b has historically been associated loosely with a threshold potential for pitting "initiation" yet it is now clear that E_b is linked with localized corrosion stabilization where the local corrosion site becomes stable towards pit growth.

Given such a statistical distribution in E_b and E_r on copper albeit in a different electrolyte (drinking water), it is clear that the probability exists for E_b and E_r values somewhat lower than those obtained in a handful of tests reported in TR-10-67 on p. 100 and TR-02-25 on p.64-66 (Escalant.E and Kruger 1970; SKB 2002; SKB 2010f). There needs to be a methodology in place to decide when a probabilistic distribution is necessary. Figure 5 suggests one possible methodology. The use of a 100, 200 or 300 mV difference between E_{corr} and E_b can be debated. One justification is that E_r can be 200 mV below E_b as shown in Figure 4.

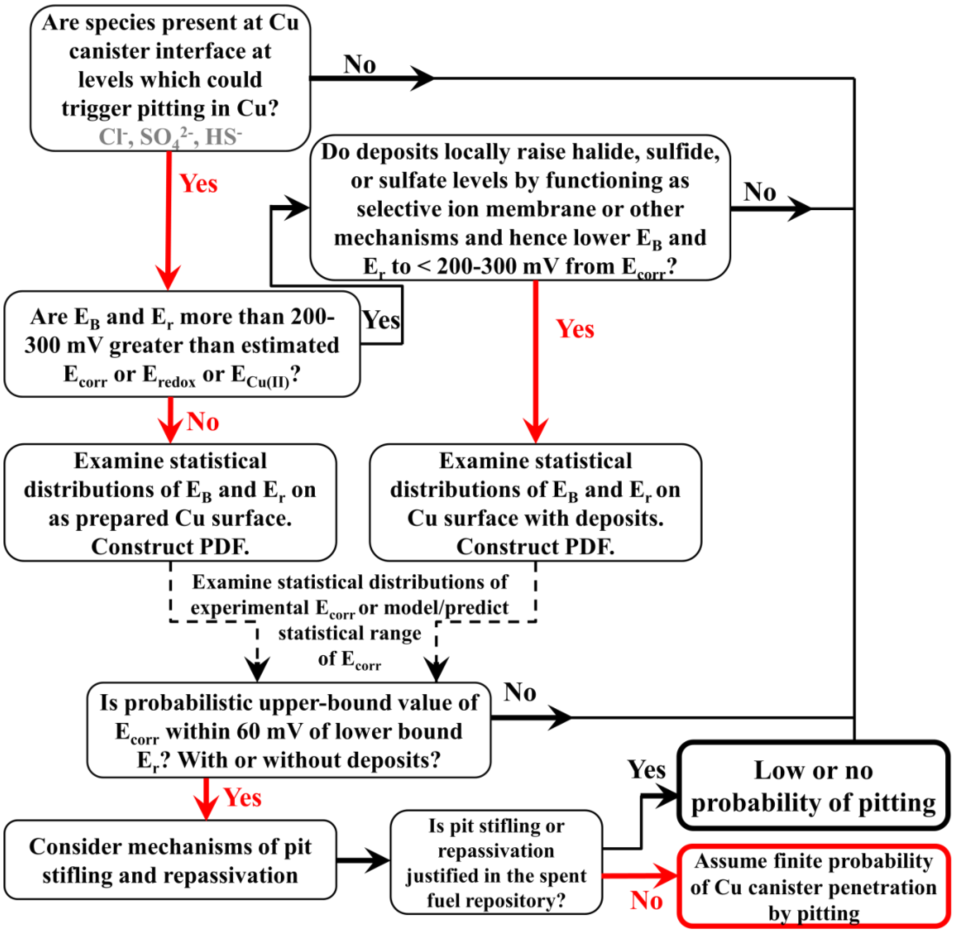

Figure 5: Suggested methodology to decide whether pitting corrosion should consider a probabilistic approach. The choice of a 200-300 mV potential difference for this decision can be debated.

2.2.2. E_b in mixed environments

Existing treatments by SKB consider the effects of Cl^- on E_b isolated from other salts except for a few reports which include pH or Cl^-/HCO_3^-. This material is reviewed in TR-10-67 in Figure 5-21, on p. 100, and in Figure 5-26 on p. 106. In Figure 5-28 [TR-10-67, Figure 5-28, p. 108] a 200 mV potential difference between E_b and the predicted

E_{corr} is reported but the environment contains only Cl^- and sometimes includes HCO_3^-. (SKB 2010f). Probabilistic treatments are lacking.

Therefore, the main unresolved issue during the oxic period includes the need to include the possible effects of mixtures of chemical species present in the repository environment on E_b in lieu of the current treatment which considers single aggressive species; mainly Cl^- with HCO_3^-. The relationship between E_b (E_{pit}) and water chemistry is complex as shown in Figures 6 and 7. Expressions have been developed to predict and express values for E_b as a function of mixed environmental solution chemistry (Sridhar and Cragnolino 1993; Cong, Michels et al. 2009; Cong 2009). E_b in mixed electrolytes should be compared to either the E_H, the redox potential of the possible cathodic reactions (i.e., Cu(II)/Cu(I)) or E_{corr} for the corroding Cu system under oxic or anoxic conditions. An important aspect of this comparison is the exact nature of the electrolyte chemistry. Sulfate is just as potent as a pit initiator as Cl^-, while HCO_3^- and pH are also very important factors (Sridhar and Cragnolino 1993; Cong, Michels et al. 2009; Cong 2009). The following data (Figures 6 and 7) consider the effects of Cl^-, HCO_3^-, pH and SO_4^{2-} on E_{pit} and E_r obtained in upward scans. Additional plots describe effects of sulfate with fixed Cl^- concentrations (Cong, Michels et al. 2009; Cong 2009). Two points are evident. $E_r << E_{pit}$ and both values depend critically on exact concentrations of chemical species and pH (Cong, Michels et al. 2009).

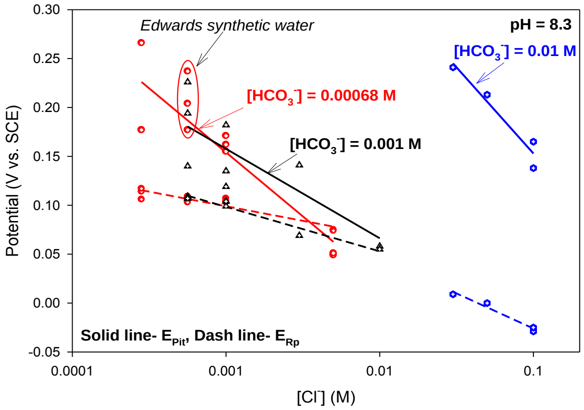

Figure 6: The effects of Cl^-, HCO_3^-, and pH on E_{pit} and E_r with the indicated molar concentrations. The Edwards solution contains SO_4^{2-}.

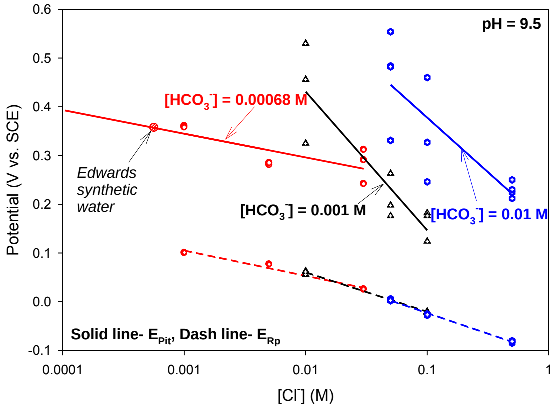

Figure 7: The effects of Cl^-, HCO_3^-, pH and SO_4^{2-} on E_{pit} and E_r in pH 9.5 waters with the indicated molar concentrations. The Edwards solution contains SO_4^{2-}.

In the work of Cong, empirical relationships developed based on the data reported above to describe E_b (E_{pit}) and E_r as a function of bulk solution chemistry input as molar concentrations were captured in analytical expressions (Cong, Michels et al. 2009; Cong 2009). While these exact expressions likely do not apply to Forsmark groundwaters, the combined effect of mixed electrolytes, pH and HCO_3^- is evident.

$$E_{Pit}(V_{SCE}) = 1.11 + 0.116 \cdot \log[OH^-] + 0.197 \cdot \log[HCO_3^-] - 0.130 \cdot \log([SO_4^{2-}] + [Cl^-])$$

$$E_{Rp}(V_{SCE}) = -0.0925 + 0.00373 \cdot \log[OH^-] - 0.0139 \cdot \log[HCO_3^-] - 0.0566 \cdot \log[Cl^-]$$

The Forsmark ground water contains SO_4^{2-} albeit at much lower concentrations than Cl^- (SKB 2005; SKB 2010c; SKB 2010d; SKB 2011a; SKB 2011b; SKB 2011c). The effect of such mixed environments on E_b and E_r should be considered. Sulfate + chloride should be considered together along with the other species present in relevant ground waters. If the potential difference between E_r and E_{corr} are less than 200 mV, a probabilistic analysis as described in Figure 5 or similar should be considered.

2.2.3. The possible role of deposits as detrimental ion exchange membranes that lower E_b.

Under-deposit localized corrosion is only mentioned briefly and apparently has only been conducted in swollen bentonite analogs such as in TR-10-67 on p. 98 (SKB 2010f). The studies reported during the period of release of the cementitious plume considers the effects of pH [TR-02-25, p. 62-66] (SKB 2002). This section of the SKB work considers the point that the Cu_2O/CuO equilibrium potential decreases with increasing pH. The interpretation is that the potential difference between E_b and E_{corr} becomes larger at high pH thus rendering pitting corrosion less likely in the presence of an alkaline plume.

Other concerns regarding pitting during the oxic period include the need to consider the role(s) and impact of possible deposits that do not just function as physical crevices but rather function as some sort of ion exchange membrane or preferential ion transport membrane that enables concentration of detrimental environments that could lower E_b or E_r. The categories of materials worth considering include deposits from bentonite, precipitation of chemicals from ground waters as well as from the cementitious plume. One example is Al^{+3} from calcium alumino-silicates such as in concrete. The example shown below was investigated under fairly oxidizing conditions in an unpublished study but the point is that some sort of functional deposit may lower threshold potentialsfor localized corrosion below those observed under an inert crevice former such as Delrin^{TM} placed over a copper surface (Cong 2012). Figure 8 shows that spatially resolved E_{pit} from a multi-electrode array (equivalent to E_b as expressed in TR-10-67) is reduced in dilute HCO_3^- + Cl^- + SO_4^{2-} solutions when a deposited $Al(OH)_3$ gel is present (Cong 2009). Figure 9, expressed as a cumulative probability distribution, shows that the effect of the deposit is statistically significant with a reduction in E_{pit} by about 300 mV relative to the openly exposed surface (Cong 2009).

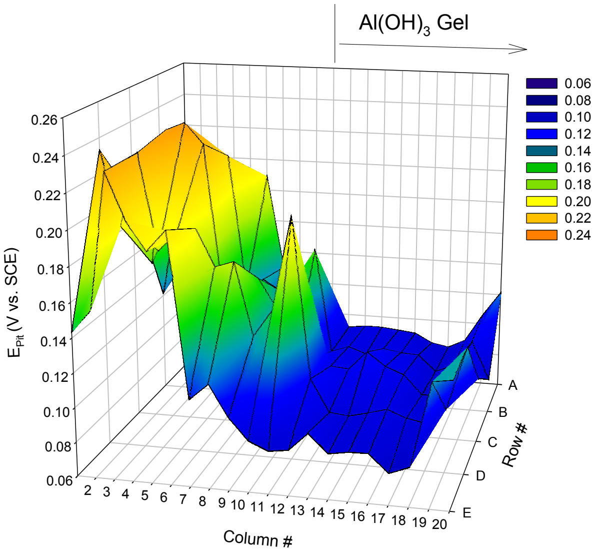

Figure 8: Position dependent pitting potentials on a C11000 copper multi-electrode array as a function of Al(OH)$_3$ gel position in Edward's synthetic drinking water (ESDW) with Cl$^-$, SO$_4^{2-}$ and HCO$_3^-$.

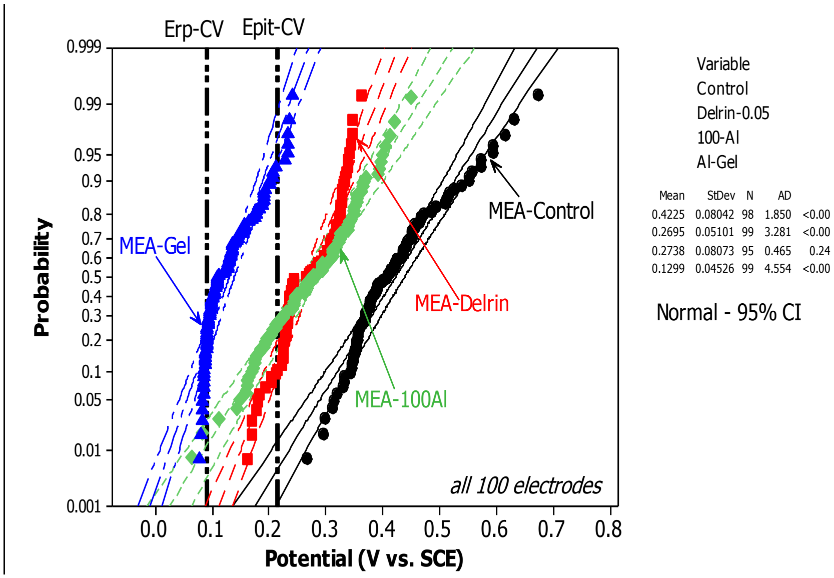

Figure 9: Cumulative probability of obtaining a given pitting potential on a 100 electrode C11000 copper array (MEA) as a function of crevice former type. Delrin (inert crevice former), 100Al – 100 wppm of Al^{+3} added to solution, gel- Al(OH)$_3$ deposit, control – no crevice.

The exact circumstances discussed above may not apply to copper canisters in bentonite clay but the point is that prudence would dictate that under-deposit pitting type attack be considered more thoroughly. Moreover, if the difference between E_{corr} and E_b is less than 200 mV, then a probabilistic treatment with a probability density function using a methodology such as presented in Figure 5 should be considered. This would strengthen the position that pitting does not occur or point to the need for further analysis.

2.2.4. HS$^-$ induced pitting corrosion under O_2 free conditions

In the absence of an oxidant such as O_2, a radiolysis product, or Cu(II), Cl$^-$ pitting may indeed be unlikely because of the high value of E_b and the difference between E_b and E_{corr} (SKB 2010f). 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 (SKB 2002; SKB 2010f). Concerns regarding the anoxic period include the possibility of HS$^-$ induced localized corrosion during the long anoxic period. 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 10 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 (SKB 2010f). 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 mol-dm^{-3} HS$^-$(Vasquez Moll et al. 1985). E_{corr}~ was found to be 0.95 V SCE [TR-10-67; p. 82] (SKB 2010f). 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 (SKB 2010f). This type of difference is shown in Figure 11. However, a probabilistic treatment as suggested in Figures 4, and 8 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$^-$.

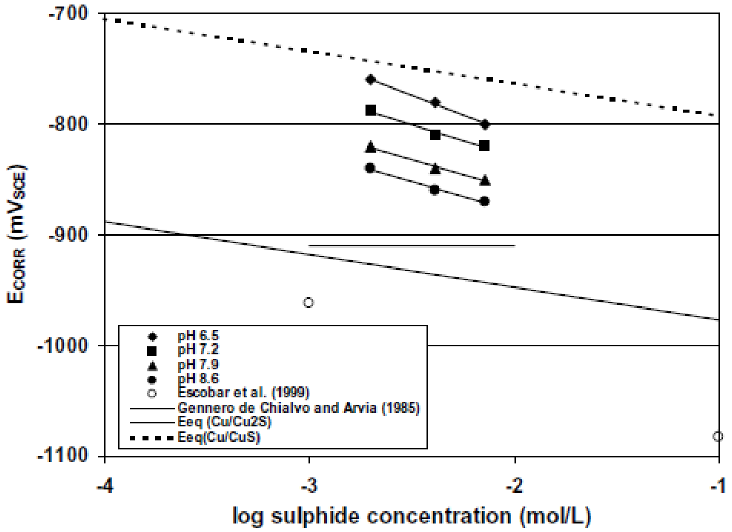

Figure 10: The dependence of E_{corr} on sulfide concentration as a function of pH. The equilibrium CuS and Cu_2S lines are indicated. [TR-02-25]

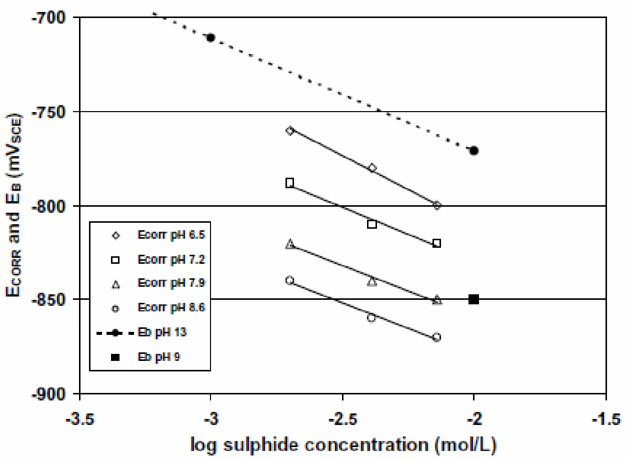

Figure 11: E_{corr} versus pitting potentials E_b in alkaline sulfide solutions [TR-02-25]

Taxen has modeled pit growth in HS^- and does obtain ~5 mm growth depths as covered in TR-10-67 on page 105(SKB 2010f). This model has not been reviewed during this preliminary 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. 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 sulfide concentrations, various pH levels, and with the addition of other species such as Cl^-.

2.2.5. Pit Factor Analysis

Pitting factor (PF) analysis may only be necessary under conditions where the probability of pitting is finite (see Figure 5). In these cases one approach may be to compare expected pit depths to the uniform dissolution depths to determine whether pits formed by such analysis can approach high aspect ratios. The next step would be to try to understand aspect ratio evolution over long times. The current SKB analysis for PF lacks a strong fundamental foundation and does not recognize that somewhat minor changes in environmental chemistry could significantly impact the pit factor observed on copper in other waters such as drinking water. The bases for these differences are unclear. Current analysis [TR-10-67, p. 97-98, pp. 107-108] is limited to a few exposure conditions where copper coupons were exposed to wetted compacted buffer material (SKB 2010f).

PF analysis was also conducted on lab studies, artifacts, and in other field studies. However, these cases were likely influenced by pit stifling or pit death as a part of the phenomena occurring (SKB 2010f). Pits may have died while uniform corrosion continued. The net effect might tend to minimize the PF. In one extreme scenario, the pit factor obtained this way would return to 1 if uniform corrosion did not occur in repassivated pits at the same rates as on exposed surfaces but continued on external surfaces. When samples are analyzed long after pits died the pit factor may be minimzed. A conservative PF of 25 was rationalized to be as low as 5 [TR-10-67, p 107] using this approach (SKB 2010f). If this situation prevails in the repository it may prove that there is no concern for pitting. However, it seems the pit factor should be considered in relevant cases where growing pit might survive for long times not in cases where pit repassivation occurs readily compared to the total time frame of the measurement. If pit death can separately be shown to occur readily that would be a big contribution to the use of copper in spent fuel repositories. However, the PF in cases where long lived pits might prevail needs to be considered separately from that.

The other issue is that PF may depend strongly on environment details. In one example pitting corrosion of copper was studied in synthetic potable waters known as Edwards Synthetic Drinking Water (ESDW) (Cong 2009; Cong and Scully 2010b; Cong and Scully 2010a; SKB 2010f). The PF of metastable pits was studied in freely corroding pitting experiments albeit with Cl_2 added as an oxidizer. Copper electrode arrays were used to compare pit events with general corrosion. The PF increases with pH from 7 to 9 in ESDW and it was most severe at pH 9 for reasons not well understood. When the pH was further increased to 10, pitting corrosion was significantly reduced. Figure 12 shows a cumulative probability plot for assumed hemispherical pit size as a function of pH in ESDW and Table 1 reports a PF (Cong and Scully 2010b; Cong and Scully 2010a). Unfortunately, pits where only grown for short time periods and are of small radii. The important point to be made here is that the factors controlling the variation in pit factor, pit growth rate, and formation of champion pits likely depend critically on ground water chemistry details and are at present rather unclear. It could be that solutions which are more passivating subsequently allow any pits that do form to develop a greater PF unless the chemistry changes lower the probability of pitting.

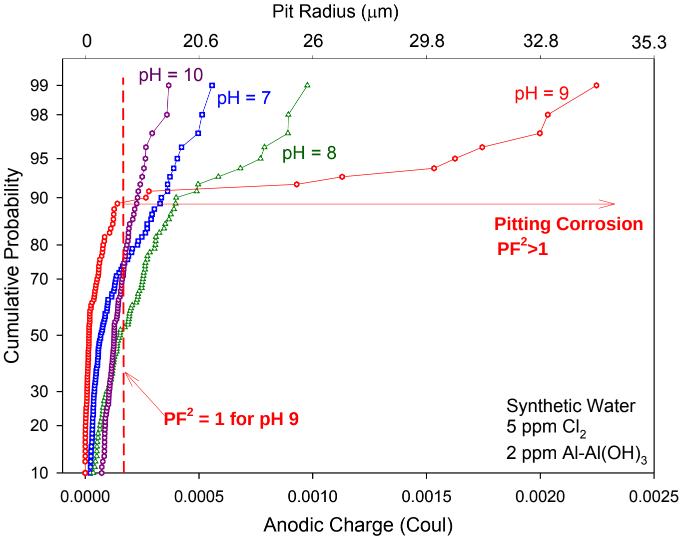

Figure 12: Cumulative probability of obtaining a pitting event of a given radius at E_{corr} as a function of pH in Edwards synthetic water ESDW with Al deposits.

The other aspect of the current SKB treatment of pitting depth was to utilize extreme value statistics [TR-10-67, p. 108] (SKB 2010f). Limited field data were fitted to extreme value expressions. One parameter was a function of time. This analysis showed that the maximum pit depth was only 7.6 mm after 10^6 years but the environment and electrochemical conditions were not specified. Therefore, one unresolved issue is that such analysis must be obtained over time for a range of relevant environments and the time progression understood both mechanistically and statistically. How the reported extrapolations of relatively short term data (The Romanoff study referred to in the report included over tens of years of exposure time) to extremely long times such as 10^6 years were achieved is unclear. In summary, the current SKB treatment of pit depths, PF and deepest pits is (a) based on limited data, (b) involves extrapolations to extremely long times without an understanding of the governing processes and (c) does not consider PF variations over relevant water chemistry variations.

Table 1: Total Anodic Charge and Pitting Factor Analysis

pH	7	8	9^a	9^b	10^a	10^b
$E_{max}(V_{SCE})$	0.069	0.078	0.112	0.096	0.587	0.669
Q_{max}(mC)	0.878	1.054	2.741	1.780	0.400	1.265
PF^2	5.3	4.8	15.8	10.5	1	2.5

2.3. Stress Corrosion Cracking

Copper canister corrosion should consider all the viable local corrosion modes (pitting, SCC, under-deposit, miscellaneous). Two periods were considered in this preliminary review:

- Viable SCC mechanisms for corrosion penetration within the initial ~100 year period assuming presence of residual O_2 and Cu(II) reduction as a possible cathodic reaction.
- Viable SCC mechanisms for corrosion penetration over long term when the environment is O_2 and Cu(II) free.

2.3.1. Overall Approach to SCC

The overall approach to the treatment of stress corrosion cracking (SCC) phenomena under both oxic and anoxic conditions is based on comparing the required SCC conditions for various SCC mechanisms versus those expected [TR-10-04, p 3] [TR-10-67; p. 114] (SKB 2010e; SKB 2010f). When considering experimental data, this treatment goes further to involve consideration of a threshold type treatment where a critical potential, corrodant concentration and other factors such as stress can be considered together to describe the threshold required conditions which enable SCC by various mechanisms [TR-10-04; p. 37] (SKB 2010e). This type of threshold treatment can be used to create "domains of susceptibility" based on the need to equal or exceed the threshold potential, corrodant concentration, stress, and temperature in order to enable SCC such as described in TR-10-67 on p. 116 and pages 129-130 (SKB 2010f). Consider the critical potential for SCC. This "threshold" potential describes the electrochemical threshold for SCC and can be taken effectively as an "on/off" criterion for SCC. One approach is to compare this potential to E_{corr}. If the threshold potential is well above the open circuit potential or any other rational potential which can describe the oxidizing potential or mixed potential that the copper canister can realize, then SCC can be dismissed as an unlikely event. Another potential of significance during SCC in tarnish rupture and film induced cleavage mechanisms is the need to reach the potential and pH associated with the Cu_2O/CuO equilibrium line [TR-10-67, p. 130] (SKB 2010f). This need exists regardless of whether ammonia, acetate or nitrate containing solutions were considered to cause SCC because a common factor is the existence of an oxide or tarnish. This potential is not dependent on the details concerning the material composition and microstructure nor surface condition but does depend on the specific electrolyte pH.

2.3.2. Unresolved Issues in SCC

Unresolved issues concerning SCC include:

1. The need for probabilistic treatments should expected conditions be near the known required conditions for each SCC mechanism. This information can be revealed by detailed comparisons such as in TR-10-04 and TR-10-67 (SKB 2010e; SKB 2010f).
2. Consideration of whether SCC is rendered more favorable under the oxidizing conditions created by gamma radiolysis should be checked.

3. SCC under anoxic conditions by a combination of HS^- induced SCC and the vacancy injection - embrittlement mechanism should be reviewed in light of emerging data.
4. Effects of vacancy injection and hydrogen induced vacancy formation (corrosion-induced vacancy formation) on thermally activated creep should also be reviewed in light of emerging data.
5. The prospects for solid metal embrittlement by an as-yet unknown lead accumulation mechanism should also be reviewed.

Each of these unresolved issues is addressed below.

2.3.3. Need for probabilistic treatment should “expected” conditions by near “required” conditions for SCC

Stress corrosion cracking (SCC) mechanisms under oxic conditions is [TR-10-04] unlikely. However, this position could be strengthened with stronger probabilistic support showing whether the gap between expected conditions and threshold conditions for SCC is wide as in the case of pitting (SKB 2010e). Unfortunately, it is recognized that SCC tests are time consuming and production of replicates is more difficult than in the case of pitting. It is the opinion of this review that SCC events during the oxic period are likely to be rare not only because of the likely large difference in potential between E_{corr} and oxide or tarnish formation potentials that must be exceeded to enable tarnish rupture or film induced cleavage type SCC to occur but due to fact that many other conditions must be simultaneously met in order to enable SCC. In other words, many factors such as the necessary SSC chemical agent concentration, temperature, high tensile stress state and dynamic strain must all be established and maintained in order for crack growth, if any, to occur. The difficultly in establishing all of these conditions simultaneously renders SCC under oxidizing conditions rather unlikely. Therefore, any circumstances that have the potential to reduce this gap between expected and required conditions should be examined.

2.3.4. SCC under oxidizing conditions created by radiolysis

Another unresolved issue is the need to consider the effects of special oxidizing radicals and molecules like O_2, H_2O_2, O_2^- and HNO_3 produced from gamma radiolysis of pure water on SCC. In Cl^- waters, additional oxidizers like Cl_2, and ClO^- may be produced. The analysis of corrosion induced by radiation effects considers specifically the effect on uniform corrosion and results appear to be restricted to waters of low salinity [TR-10-67, pp. 135-137] (SKB 2010f). Little is stated about either pitting or SCC (SKB 2010f). Little effect on E_{corr} was reported which tends to argue against a special effect of these species on SCC from the threshold perspective (SKB 2010f). The only unresolved issue would be to reconsider this effect in mixed electrolytes with high Cl^- levels pertinent to Forsmark ground waters (SKB 2005).

2.3.5. SCC under anoxic conditions with HS^-

The other important recommendation is to explore long term anaerobic SCC mechanisms that do not require oxidized corrosion products (Taniguchi and Kawasaki 2008). For instance HS^- induced stress corrosion of copper under anoxic conditions does not require a passive film, can occur under anoxic conditions, and would enable secondary effects such as vacancy and hydrogen injection (Taniguchi and Kawasaki 2008). This mechanism is considered in previous reports but is dismissed as being unlikely although Newman does point out the Aaltonen mechanisms should be considered in connection with a sulfide film [TR-10-67; pp. 130-132] [TR-10-04; p. 28] (SKB 2010e; SKB 2010f).

2.3.6. SCC under anoxic conditions by the vacancy injection - embrittlement mechanism

A combination of the SCC process proposed by Taniguchi and Aaltonen as well as recently by Hanninen should be explored further to determine whether the required conditions overlap with the expected conditions (Aaltonen et al. 1998; Aaltonen et al. 2004; SKB 2010e; SKB 2010f; Yagodzinskyy et al. 2010). Hence, the vacancy injection-embrittlement scenario as proposed for stainless steels but in the case of copper under long term anoxic HS^- containing conditions should be investigated further to determine whether it represents a viable scenario for anoxic SCC (Aaltonen, Jagodzinski et al. 1998; Aaltonen, Nevdacha et al. 2004; Arioka et al. 2010; SKB 2010e; SKB 2010f; Yagodzinskyy, Saukkonen et al. 2010; Arioka et al. 2011). This is necessary since many of the attributes for anoxic SCC are present such as HS^- and recent emerging information from different independent sources supports the view that all the attributes are present that could enable such a SCC mechanism on copper. Classical hydrogen embrittlement is not considered to be of concern. However, the implications of hydrogen enhanced vacancy formation in connection with the vacancy/embrittlement mechanism should be considered (Suzuki and Itoh 1984; Zurek 1987; Davanas and Solomon 1990; Unigovski et al. 2005; Wolski and Laporte 2008; Arioka, Miyamoto et al. 2010; Yagodzinskyy, Saukkonen et al. 2010; Arioka, Yamada et al. 2011).

The background is as follows. In this process, the conceptual framework is that dissolution and hydrogen ingress promote vacancy formation. Secondly, cavity formation by vacancy condensation occurs prior to brittle crack advance. Thirdly, cavities form a brittle crack path and ductile rupture of constrained ligaments between cavities might create a scenario for embrittlement. This process has been studied by Arioka at the Institute of Nuclear Safety, Japan, who has reported extensively on the role of cavities in crack advance in creep and SCC in steels and Ni-base alloys 600 and 690, albeit over the temperature range from 280 to 360°C. To briefly summarize these results (Arioka, Miyamoto et al. 2010; Arioka, Yamada et al. 2011):

- SCC crack growth (da/dt) occurs by SCC in waters and can be correlated with enhanced cavity densities near crack tips.
- There is a similar activation energy in the thermal dependence for both crack growth and vacancy condensation.
- More vacancies are created by exposure in water (SCC) and upon hydrogen precharging.

- Vacancies form along crack path and may serve as crack nuclei or enable strain localization or some other damage mechanism.

According to Fukai, hydrogen promotes super-abundant vacancy formation in many FCC materials (Fukai et al. 2001a; Fukai et al. 2001b; Fukai 2003; Fukai et al. 2003). McLellan and Gibala have shown that the vacancy formation energy is lowered by hydrogen-vacancy trapping by energy equal to the trap binding energy (Mclellan and Angel 1995; Counts et al. 2010; Counts et al. 2011). Other vacancy formation processes include formation of cold work induced vacancy formation and vacancy injection by high temperature oxidation and aqueous dissolution.

Regarding the application of this phenomenon to copper, Aaltonen in 1998 and 2003 as well as Jagodzinski in 2000, reported vacancy injection during dissolution in Cu during SCC in nitrate solutions (Jagodzinski et al. 2000). Taniguchi in 2008 reported SCC of Cu in Na_2S under anaerobic conditions but did not investigate specifically for vacancies (Taniguchi and Kawasaki 2008). Putting these two independent observations together, the question is whether vacancy injection can occur in copper under anaerobic sulfide conditions. Both dissolution and hydrogen production mechanisms are verified under O_2 free anaerobic conditions in the presence of HS^-:

$$2Cu\ (s) + 2HS^- \rightarrow Cu_2S\ (s) + H_2\ (g) + S^{2-}\quad \text{(or)}$$

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

There is no need for an adherent tarnishing film which is necessary to support the film rupture, tarnish rupture and film induced cleavage mechanisms. There is the requirement for vacancy injection which has been reported during dissolution in copper (Aaltonen – 1998, 2003) (Aaltonen, Jagodzinski et al. 1998; Aaltonen, Nevdacha et al. 2004). H-vacancy interactions are also reported in copper (Gibala, Fukai) (Fukai, Haraguchi et al. 2001a; Fukai, Shizuku et al. 2001b; Fukai 2003; Fukai, Mizutani et al. 2003; Counts, Wolverton et al. 2010; Counts, Wolverton et al. 2011) and this aspect is not considered in current treatments by SKB [TR-10-67, p. 130-131] [TR-10-04, pp. 28-30] (Fukai, Haraguchi et al. 2001a; Fukai, Shizuku et al. 2001b; Fukai 2003; Fukai, Mizutani et al. 2003; Counts, Wolverton et al. 2010; SKB 2010e; SKB 2010f; Counts, Wolverton et al. 2011). It should be emphasized that in this scenario classical hydrogen embrittlement is not considered to be a chief concern. Instead, the implications of hydrogen enhanced vacancy formation should be considered as a part of this overall process. The preliminary requirements have been met under the expected conditions. All other SCC mechanisms require potentials near the Cu_2O/CuO equilibrium potential except the surface mobility and this mechanism (TR-10-04) (SKB 2010e). There is sustained load and high temperatures for extended time periods. Slow anoxic dissolution of copper is possible along with hydrogen production, possible hydrogen ingress and vacancy formation. Therefore, it should be determined whether this SCC mechanism is relevant to copper canister SCC over the long term anaerobic period.

Criticisms of the vacancy formation-injection argument are more directly applicable to corrosion enhanced creep (to be discussed below). The dissolution induced vacancy formation depth may be limited by the slow self diffusion rate of copper, but during SCC the fracture process zone is within micrometers or less of the crack tip (Bowden and Balluffi 1969). In summary, the possibility of SCC by the vacancy/embrittlement mechanism should be considered further in light of this emerging information.

2.3.7. Effects of vacancy injection and hydrogen induced vacancy formation on creep

The vacancy injection mechanism enhanced by aqueous dissolution and/or hydrogen absorption may also impact thermally activated creep deformation. The ramification of this secondary effect is to produce creep rates that become enhanced over “dry” thermally activated creep. The dissolution induced vacancy formation depth may be limited by the slow self diffusion rate of copper which calls in to question any role of corrosion-induced vacancy injection in global creep processes occurring over copper canisters (Bowden and Balluffi 1969). However, hydrogen transport would eventually enable hydrogen penetration through 5 cm of copper over long times ($D_H= 10^{-9}$ cm^2/sec at room temperature) (Sakamoto 1982). It is recognized that hydrogen has a low solubility in copper. However, the hydrogen-vacancy trap might be stable over unfavorable interstitial lattice sites. Thus, the hydrogen-enhanced vacancy formation mechanism could operate in copper canisters. Given these pieces of information for and against this, further consideration should be given to the possibility of a vacancy concentration enhanced by hydrogen in creep modeling. Enhancements in creep rate, if any, should either be factored into existing environment independent creep treatments and models or the technical basis for their dismissal should be developed.

2.3.8. Solid Metal Embrittlement

Selected elements may embrittle copper by a solid metal embrittlement mechanism (Kolman 2005) (Monzen et al. 2002; Monzen et al. 2004; Liu et al. 2005; Wolski and Laporte 2008; Laporte and Mortensen 2009; SKB 2010e; Zhevnenko et al. 2011). The elements present in repository ground waters are listed in Table 2. The severity of embrittlement increases when copper is alloyed with aluminum and zinc. Hg, Li, Pb, Cd, Sb, Sn, Bi, Ga and Th are reported to embrittle copper. Embrittlement occurs in both tension and fatigue and varies with grain size and strain rate. Ga embrittles copper at 156 to 250°C (313 to 480 °F). The required and expected conditions at Forsmark do not match because the Hg and Pb concentrations are very low (Table 2) and a spontaneous electrochemical path for Li^+ cation reduction is not feasible even under reducing anoxic HS^- conditions (SKB 2005; SKB 2011a; SKB 2011b; SKB 2011c).

Therefore, the only unresolved issue is whether there is an accumulation mechanism for Pb on copper canisters that could operate in the repository scenario. A technological precedent for this does exist since trace amounts of Pb are found to accumulate at the crack tips of metals in nuclear reactor environments involving high purity waters (Staehle and Gorman 2003; Staehle and Gorman 2004b; Staehle and Gorman 2004a).

Table 2: Water chemical parameters analysed in the main and extended programs

Program	Parameters analysed in laboratory	Field measurements
Main program	Nutrients (Tot-P, PO_4-P, Tot-N, NH_4-N, NO_2+NO_3-N), TOC, DOC, DIC, POP, PON POC, pH, Alkalinity, Electrical Conductivity, Cations (Na, K, Ca, Mf, Si,, Li, Sr), anions (Cl, SO_4, F, Br), S_{tot}, Chlorphylis (a and c), Phenophytin, Dissolved oxygen, HS^-	Water temperature, Dissolved oxygen, pH, Salinity, Electrical conductivity, Light penetration, Turbidity, Water flow, Water depth, Water transparency
Extended Program in Streams	As main program + Cations (Fe, Mn) Anions (I), environmental metals (Al, As, Ba, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, V, Zn), Nutrients (NO_2, NO_3), Fe(II), Fe_{tot}, ^3H, ^{37}Cl, Deuterium, d^{18}O, ^{10}B, ^{87} Sr, ^{34}S, ^{13}C, PMC	As main program
Extended Program in lakes and at coastal sites	As extended program in streams + Lanthanides (Sc, Rb, Y, Zr, I, Sb, Cs, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, U, Th), Chlorophylis (a and c), Pheophytin, Isotopes of U, Th, Ra and Rn	As main program

2.4. Copper Corrosion FEPs

SKB's analysis and handling of FEPs (features, events and processes) has included the establishment of the SR-Site FEP Database (SKB, 2010c). The database includes the SR-Site FEP catalogue, which contains all FEPs that are considered in the SR-Site safety assessment, as well as the results of audits against other FEP databases. The FEP Database provides only brief high level descriptions of how these FEPs are handled in the SR-Site safety assessment. More detailed discussion of each FEP is provided in the Fuel and Canister Process Report (SKB, 2010d). The following observations are made regarding FEP *C11 Corrosion of copper canister*:

- The Fuel and Canister Process Report (SKB, 2010d, p103) includes some discussion of the potential for impacts or scraping of the canister surface during handling to result in locally cold worked areas that could stimulate corrosion. The report cites research on this topic which concludes that the corrosion rate of copper increases with an increase in plastic strain. However, the report provides no conclusions with regard to the effects on a copper canister. The FEP catalogue simply indicates that corrosion effects on cold worked material are neglected due to small consequences.
- In the FEP catalogue, the Main Report (SKB, 2011b, p418) and the Fuel and Canister Process Report (SKB, 2010d, p102) it is stated that copper corrosion processes would only be marginally affected by the changes in temperature expected in the repository. SKB (2010d, p108) notes that localised corrosion is affected by temperature and the degree of corrosion should decrease as temperature decreases. However,

there is no detailed discussion of the sensitivity of corrosion processes to temperature or whether the approach taken is cautious with respect to temperature effects.

- In the FEP Catalogue it is noted that a hole in the copper canister could be closed due to clogging from iron corrosion products, but it is stated that this process is not discussed because the probability of it occurring cannot be assessed. However, some discussion of this process and any experiments being undertaken that could support its understanding would be beneficial, because it could support arguments regarding the cautious treatment of the effects of canister corrosion in the safety assessment.
- The FEP Catalogue also notes that some volatile fission products are corrosive, but that such affects would be negligible. For example, it is noted that iodine would corrode less than 100 g of Cu, but no reference to this calculation is provided. The SR Site safety assessment reports do not discuss the potential for fission products to affect copper corrosion if released from fuel assemblies in the canister.

3. Recommendations to SSM

Current experimental evidence for spontaneous copper corrosion in O_2 free waters lacks corroborating diagnostics and broad consensus from multiple investigators. Therefore, it is the opinion of this review that the matter is unresolved. Further diagnostic experiments to resolve the issue of spontaneous copper corrosion are recommended in O_2 free waters. Experiments should also be conducted with and without Cl^- and controlled additions of Cu^+ with many diagnostics and multiple parallel types of data acquisition to confirm or refute spontaneous corrosion in O_2 free water. Experiments could also 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 should be further explored to define under what conditions they exist and over what repository time “quasi-immunity” would occur. The technical basis for why or under what circumstances this mode of corrosion will not be spontaneous should be strengthened. This is because it is also clear that O_2 free pure water corrosion of copper and O_2 free corrosion of Cu in high Cl^- waters can become non-spontaneous at certain temperatures, pH levels, hydrogen fugacities and copper cation concentrations. However, the likely transition from spontaneity to non-spontaneity under such changes in these parameters has not been experimentally confirmed.

Assuming that O_2 uniform corrosion is spontaneous, kinetic models have been developed for formation of CuOH in pure water, Cu-Cl species in $Cu-Cl^-$ waters and Cu_2S in sulfide containing waters. These kinetic models for spontaneous uniform corrosion rates are non-conservative as currently composed and rely on key tenets that ensure low rates. Either evidence supporting these key tenets and assumptions should be strengthened or upper bound rates should be established. For instance, limited dissolved H_2 solubility coupled with corrosion controlled by H_2 liquid phase diffusion in absence of H_2 gaseas evolution in pure O_2 free water establishes non-conservative or lower bound CuOH corrosion rates. Moreover, HS^- mass transport control of copper corrosion in O_2 free waters by HS^- reduction assumes no parallel cathodic reduction reactions such as water reduction and no allowed copper oxidation without Cu-S formation. These assumptions are key because they restrict copper corrosion to rates governed by HS^- concentrations and liquid phase mass transport and eliminate any option for copper corrosion after HS^- consumption (such as by S^{-2} regeneration and re-adsorption). This assumption of HS^- sequestering could be strengthened. It should be recognized that such assumptions non-conservatively establish lower bound corrosion rates.

Localized corrosion is treated using the common criterion where threshold potential for breakdown is compared to the corrosion potential, E_{corr} to make a determination regarding the risk of pit initiation. Such a threshold potential approach could be strengthened by several courses of action. One is the need to expand mixed potential theory models to enable definition of E_{corr} as a function of all relevant water chemistry and physical conditions over the long term. Presently, E_{corr} for copper in repository situations is based on limited short term experimental data. Another unresolved issue is the need to consider the effects of other oxidizers like peroxide generated by gamma radiolysis on localized corrosion processes. There is also the need to expand pitting estimations limited to the potential difference E_b-E_{corr} based on limited data for isolated species such as Cl^-. For instance, threshold potential treatments should also consider effects of combined anions such as combinations of Cl^-, HCO_3^- and SO_4^{2-} as well as for Cl^- and HS^-, consider repassivation potentials, consider deposits and involve broader application of probabilistic treatments when necessary to enable a consistent basis for rejection versus consideration of pitting. A decision making flow chart to consistently determine when and when a probabilistic treatment of pitting is necessary is suggested. If pit initiation probabilities are finite, studies should improve pit factor definitions and be aware of subtle effects of chemistry on such pit factors. Finally, it is the opinion of this review that there is a need to explore possible long term anaerobic pitting mechanisms such as by HS^- pitting that cannot be dismissed based on the lack of oxidants since water reduction could support such local corrosion processes.

Stress corrosion cracking (SCC) mechanisms under oxic conditions appear to be unlikely as the expected conditions differ from the required conditions by a considerable amount. However, as in the case of pitting, this position could be strengthened with stronger probabilistic support showing the gap between expected conditions and threshold conditions for SCC. It is the opinion of this review that SCC events during the oxic period are likely to be rare not only because of the likely large differences between E_{corr} and oxide or tarnish formation potentials that must be exceeded to enable tarnish rupture based SCC mechanisms to occur but because many other conditions must be simultaneously satisfied to enable SCC. SSC chemical agent concentration, temperature, high tensile stress state and dynamic strain all must likely be established and maintained in order for crack growth (if any) to occur. The difficultly in establishing all of these conditions simultaneously renders SCC unlikely. However, an unresolved issue is the need to consider special oxidized species such as peroxide from gamma radiolysis on SCC. 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, and would also enable secondary effects such as both dissolution and hydrogen-induced vacancy injection. Classical hydrogen embrittlement is not considered to be of concern. However, the implications of hydrogen enhanced vacancy formation should be considered. 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 vacancy injection enhanced by either anodic dissolution or hydrogen absorption and its indirect role in supporting creep deformation at enhanced rates over expected "dry" thermally activated conditions should also be considered. Any enhancements in creep rate should either be factored into existing environment independent creep models or the technical basis for their dismissal should be developed.

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Coverage of SKB reports

Report sections considered in this review are listed in the table below.

Table A1:1

Reviewed report	Reviewed sections	Comments
SKB TR-11-01 Vol. I	4.8.2, 5.2.1, 5.4, 5.5.2, 5.5.3, 5.6.1, Tab 7-7, 8.3.2, 8.3.4, Tab 8-1	
SKB TR-11-01 Vol. II	10.2.5, 10.3.7, 10.3.13, 10.3.16	
SKB TR-11-01 Vol. III	12.6	
SKB TR-10-45	4.1, Appendix 4, pg. 96	
SKB TR-10-46	1.7-1.10, 3.5, 4.1, 4.5	
SKB TR-10-52	3.2, 3.3, 4, 5.3.5, 6.1, Fig. 6-74	
SKB TR-04	Entire	
SKB TR-10-66	Entire	
SKB TR-67	Entire	
SSM2010/4230	Entire	
SSM 2011-3399	Entire	
SSM 2010:17	Entire	
SKB TR-02-25	Entire	
SSM 10-11:09	Selected Sections	
SSM 10-11:34	Entire	
Working Report Posiva 2003-45	Entire	Bojinov, Makela

Appendix 2

Suggested needs for complementary information from SKB

The following information is requested from SKB:

1. References from the literature or SKB experiments that indicate unambiguously that H_2 liquid phase mass transport limits anoxic corrosion rates.
2. Further explanation for the current position that at a pH >4 and $Cl^- <$ 2M, copper will not corrode spontaneously as mentioned in TR-10-67, section 5.2 and TR-02-25 on p. 13-15 (SKB 2002; SKB 2010f) .
3. Uniform corrosion rate information which confirms stoichiometric dissolution of Cu^+ balanced by the mass transport of HS^- and the formation of Cu_2S in the presence of Cl^- or in the presence of Cl^- after HS^- dosing.
4. Evidence that Cu_2S does not spall or grows at parabolic rates.
5. Pit propagation rate modelling and results in Cu-HS^- systems that produced ~ cm pit depths alluded to in TR-10-67 but not reported on in detail.
6. Modelling of mixed potential or corrosion potentials under oxic and anoxic conditions as a function of environmental chemistry with and without HS^-.
7. Recent reports and references by Hanninen concerning corrosion-induced vacancy injection and vacancy enhanced deformation, creep or stress corrosion.
8. A three dimensional model of mass transfer to support understanding of the corrosion of copper by sulphide from pyrite dissolution in the buffer.
9. Further information on the magnitude of corrosion effects on cold worked material.
10. Discussion of the sensitivity of corrosion processes to temperature and whether the approach taken in the safety assessment is cautious with respect to temperature effects.
11. Discussion of the issue of clogging of a hole in the copper canister from iron corrosion products and any experiments being undertaken that could support its understanding, because it could support arguments regarding the cautious treatment of the effects of canister corrosion in the safety assessment.
12. Discussion of the potential for fission products to affect copper corrosion if released from fuel assemblies in the canister.

Appendix 3

Suggested review topics for SSM

The following issues should be addressed during the main review phase:

1. There is the need to address needs and gaps relating to the thermodynamics associated with each uniform Cu(I) formation mechanism. This includes the CuOH, $Cu\text{-}Cl^-$, and $Cu\text{-}HS^-$ mechanisms. H_2O reduction leading to Cu^+, $CuCl_2^-$ or $CuCl_3^{2-}$ in low or nil HS^-/high Cl^- environments has been considered in several reports such as TR-10-67 on pages p. 52, p. 62 (Hermansson and Eriksson 1999; SKB 2010f). However, the current position that at a pH >4 and $Cl^- < 2M$, copper will not corrode spontaneously as mentioned in TR-10-67, section 5.2 and TR-02-25 on p. 13-15 (SKB 2002; SKB 2010f) needs to be better justified.
2. The corrosion rate expressions for the CuOH, $Cu\text{-}Cl^-$, and $Cu\text{-}HS^-$ mechanisms are all considered to be limited by slow mass transport controlled process either towards or from the Cu interface. Key assumptions include the following slow transport processes: Cu-OH; H_2 liquid phase transport, Cu-Cl; $CuCl_2^-$ transport, and Cu-HS; HS^- transport. However, there are a few unresolved issued with regard to these assumptions regarding the viability of alternative fast transport paths such as gas phase transport when the bentonite is not fully saturated.
3. There is need to expand corrosion kinetic descriptions to more realistic waters such as those containing mixtures of species such as both HS^- and Cl^-. Hence, the logical next step is development of hybrid models considering corrosion in copper-sulfide-chloride-(sulfate) system by combined “HS^-” and “water reduction” under anoxic conditions.
4. The overall approach used to assess whether pitting is possible involves a threshold potential treatment where pit initiation is considered to be either “on” or “off” depending on how close the threshold potential, E_b is to the possible relevant reversible electrode potential reactions or mixed potentials that govern the potential of the copper surfaces (SKB 2002; SKB 2010f). Sufficient difference in voltage between these two potentials is taken as an indicator that pit initiation is unlikely (SKB 2002; SKB 2010f). Currently, there is no consistent probabilistic approach to determine what voltage difference between these two potentials is necessary to reduce the probability of pitting corrosion to a negligible level such that initiation may be ignored.
5. The overall approach summarized above can be applied to both the oxic and anoxic periods. Further concerns regarding the oxic period include (i) the need to include the possible effects of mixtures of chemical species present in the repository environment on E_b in lieu of the current treatment which considers mainly single aggressive species one by one in isolation of one another, (ii) the need to consider the role(s) and impact of possible deposits that do not function as a

physical crevice but rather function as ion exchange membranes enabling concentration of detrimental environments, (iii) the need to further consider nuclear processes such as gamma radiolysis of water and any related effects such as elevation in E_{corr} by the associated radicals and molecules thus developed, (iv) the need to develop a mixed potential model that predicts E_{corr} and some kind of empirical model for E_b that can incorporate the chemical concentrations present, understands what model parameters are statistically distributed, and can anticipate statistical distributions of key potential values. After this is accomplished, the probabilistic risk of pitting corrosion could be properly assessed.

6. The overall pitting approach can be applied to both the oxic and anoxic periods. Concerns regarding the anoxic period include the possibility of HS^- induced localized corrosion during the long anoxic period under conditions dominated by formation of a Cu_2S film. An extremely limited amount of data exists regarding both E_b and E_{corr} during this period. Furthermore, there is little understanding of what governs E_{corr} during this period. Not only is the mechanism of pitting poorly understood but there is a lack of understanding of whether there is a statistical distribution of E_b. Given the current state of understanding, the probabilistic risk of pitting by HS^- cannot be assessed and should be further explored.
7. The present treatment of pitting corrosion also relies on the use of extreme value statistics or an uncertain application of pit factors (PF) to rationalize that local corrosion will only occur to a limited extent (e.g., 5:1 pit factor) compared to general corrosion. There is little basis for such assertions. Moreover, as discussed above, uniform corrosion is treated in a non-conservative manner and this weakness is then propagated into the local corrosion scenario if a PF is applied based on the uniform corrosion rate. In cases where the risk of pitting assessed consistently by some sort of probabilistic analysis is not found to be very low, it may be prudent to rethink what pitting factors might actually exist in mixed environments instead of borrowing pit factors from other studies. Alternatively, it would be useful to develop a rational technical basis for pit stifling and/or repassivation. Otherwise, the technical basis to rationalize that pit depths would not be a safety issue is not strong.
8. There is also the possible need for probabilistic treatment should expected conditions be near the known required conditions for each SCC mechanism. This information can be revealed by detailed comparisons such as in TR-10-04 and TR-10-67 (SKB 2010e; SKB 2010f).
9. Whether SCC is rendered more favourable under oxidizing conditions created by gamma radiolysis should be checked.
10. SCC under anoxic conditions by a combination of HS^- induced SCC and the vacancy injection - embrittlement mechanism should be reviewed in light of emerging data.
11. Effects of vacancy injection and hydrogen induced vacancy formation (corrosion-induced vacancy formation) on thermally activated creep should also be reviewed in light of emerging data.

12. The prospects for solid metal embrittlement by an unknown Pb accumulation mechanism should also be reviewed.
13. A more detailed review of the model of copper corrosion by sulphide attack should be undertaken to understand the derivation and reliability of the transport resistance approach and the derived geometric factors.

2012:21

The Swedish Radiation Safety Authority has a comprehensive responsibility to ensure that society is safe from the effects of radiation. The Authority works to achieve radiation safety in a number of areas: nuclear power, medical care as well as commercial products and services. The Authority also works to achieve protection from natural radiation and to increase the level of radiation safety internationally.

The Swedish Radiation Safety Authority works proactively and preventively to protect people and the environment from the harmful effects of radiation, now and in the future. The Authority issues regulations and supervises compliance, while also supporting research, providing training and information, and issuing advice. Often, activities involving radiation require licences issued by the Authority. The Swedish Radiation Safety Authority maintains emergency preparedness around the clock with the aim of limiting the aftermath of radiation accidents and the unintentional spreading of radioactive substances. The Authority participates in international co-operation in order to promote radiation safety and finances projects aiming to raise the level of radiation safety in certain Eastern European countries.

The Authority reports to the Ministry of the Environment and has around 270 employees with competencies in the fields of engineering, natural and behavioural sciences, law, economics and communications. We have received quality, environmental and working environment certification.

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