# Natural Analogues and their Use in Supporting the Prediction of the Long-Term Corrosion Behaviour of Copper-coated UFC

NWMO TR-2021-19

November 2021

**Fraser King**

Integrity Corrosion Consulting Ltd

NUCLEAR WASTE MANAGEMENT ORGANIZATION
SOCIÉTÉ DE GESTION DES DÉCHETS NUCLÉAIRES

**Nuclear Waste Management Organization**
22 St. Clair Avenue East, 6th Floor
Toronto, Ontario
M4T 2S3
Canada

Tel:  416-934-9814
Web: www.nwmo.ca

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# ABSTRACT

**Title:** **Natural Analogues and their Use in Building Confidence in Supporting the Long-term Corrosion Behaviour of Copper-coated UFC**
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## Abstract

Natural analogues are useful supporting evidence for the prediction of the long-term corrosion behaviour of used fuel containers (UFC). Evidence from analogues can be used for a number of purposes, including to support the development of conceptual models for long-term performance, the validation of mechanistically based corrosion models, the provision of corrosion damage data (typically either corrosion rates or measurements of localized corrosion) over long exposure periods, or generally to build confidence in long-term predictions.

Because neither copper nor carbon steel are noble materials, the continued existence of archaeological artefacts and of native copper deposits relies on one of two basic principles. First, the metal object may be thermodynamically stable in the host environment such that the unoxidized metal is in chemical equilibrium with the dissolved and gaseous corrosion products. Second, the artefact or native deposit may be kinetically stable, so that the corrosion rate is so low that the object survives over historical or geological timescales, respectively. Kinetic stability may be the result of the formation of a protective corrosion product layer or because of the limited rate of transport of corrosive species towards, or of dissolved or gaseous corrosion products away from, the corroding surface. Here, an overview will be provided of the evidence from the most important analogues for copper and carbon steel, with a specific emphasis on whether they represent examples of either thermodynamic or kinetic stability and how the analogue can be used to support the prediction of the long-term performance of copper-coated UFC. Brief summaries of the most-relevant analogue studies are given in an appendix supporting the main text.

The use of analogues for supporting the prediction of the long-term corrosion performance of the UFC in the safety case is discussed. Analogue evidence that directly supports the treatment of different corrosion processes considered to lead to penetration of the copper corrosion barrier in the safety assessment is reviewed, as well as evidence to support the exclusion of other corrosion processes from consideration.

A number of areas in which future analogue studies could be useful are described, as well as a number that are considered to be less-worthwhile. Future analogue studies should be focussed on supporting the development and validation of conceptual models, rather than for the purposes of confidence building alone.

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# 1. INTRODUCTION

A key challenge in long-term management of used nuclear fuel is the justification of predictions of the performance of the system over periods of thousands, tens of thousands, and hundreds of thousands of years. This challenge applies not only to the prediction of the overall dose consequences but also to the long-term performance of individual system components, such as the used fuel container (UFC). There are various methods for building confidence in long-term predictions (King 2014), including: (i) demonstrating a mechanistic understanding of the processes involved, (ii) conducting large-scale *in situ* tests, (iii) using complementary modelling approaches for the prediction, and (iv) using evidence from natural analogues. In the case of the UFC, natural analogues exist in the form of native metal deposits and of various anthropogenic artefacts, both archaeological and more-recent in nature (Alexander et al. 2015; Apted 1992; Brandberg et al. 1993; Fayek and Brown 2015; Milodowski et al. 2015; Miller et al. 1994; Posiva 2012a,b). The study of analogues as a means of building confidence in long-term lifetime predictions is particularly relevant for the copper-coated steel UFC design as these are the only two alloy classes for which native deposits exist.

Evidence from analogues can be used to support long-term predictions in a number of ways, including:

- Provision of data for UFC lifetime prediction; for example, in the form of the long-term anaerobic corrosion rate of steel (Crossland 2005, Neff et al. 2006, Yoshikawa et al. 2008) or pit depths on copper alloys (Bresle et al. 1983, Denison and Romanoff 1950). As in the case of large-scale *in situ* experiments, analogues can be used to extend the timescale of exposure that is otherwise possible from laboratory studies.
- Development and validation of conceptual models for specific corrosion processes or for the long-term performance of the UFC as a whole. For example, extensive use has been made of analogues in the French program in order to develop a conceptual model for the development of corrosion product layers on steel (Dillmann et al. 2014, Neff et al. 2010). Similarly, King and Kolář (1996) have used copper concentration profiles in seabed sediments in contact with a submerged bronze cannon in an attempt to validate a reactive-transport model for the corrosion of copper UFC.
- Building confidence in the long-term performance of the UFC based on the persistence of copper and ferrous alloys when exposed to natural environments; in the case of native deposits over geological timescales (Crisman and Jacobs 1982; Hellmuth 1991a,b). The persuasiveness of evidence from analogues for both the layman and expert audiences (Schwartz 1996, 2008) should not be underestimated. Indeed, the use of evidence from analogues is a regulatory expectation (CNSC 2006).

However, it is also important to be aware of the limitations of the use of analogues. Inevitably, metallurgy was not as advanced in the past as it is today (Apted 1992), and the ancient metallurgist was focussed more on other properties of the alloy than the purity and chemical composition (Bresle et al. 1983). This is particularly so for analogues of the UFC liner since the majority of analogues are of iron rather than steel, but it also applies to archaeological copper alloy artefacts. The exposure environment is invariably different from that in a deep geological repository (DGR), although certain aspects (such as the salinity of the aqueous phase, or the redox conditions) may be representative. The reliance on evidence from museum samples introduces an inherent bias since these institutions will naturally collect the most-well preserved specimens (Miller et al. 1994). These differences have led some to conclude that the best use of analogues is the development and validation of system or sub-system conceptual models, rather than as a source of input data (corrosion rates, pit depths, etc.) (Apted 1992, Miller et al. 1994).

The term natural analogue is used in the broadest sense in this review. It includes both geological analogues in the form of native metal deposits and anthropological analogues in the form of archaeological artefacts and more-recent copper and steel objects. The advantage of including “modern day” analogues (such as copper potable water pipes and copper and steel specimens from long-term burial studies) is that the alloy properties are closer to those proposed for the UFC.

It is interesting to put the different types of analogue into context of the environmental conditions within the DGR. Figure 1 compares the temperature and pressure within unsaturated (i.e., Yucca Mountain) and saturated DGR designs and those associated with the formation of native Fe and Cu deposits. Also shown are the environmental conditions for transformation of the buffer material. While the conditions for the formation of native deposits are more extreme than those in the DGR, the conditions under which they and the various anthropological artefacts persist for extended periods of time are not. From a corrosion point of view, the redox conditions, pH, and salinity are highly relevant.

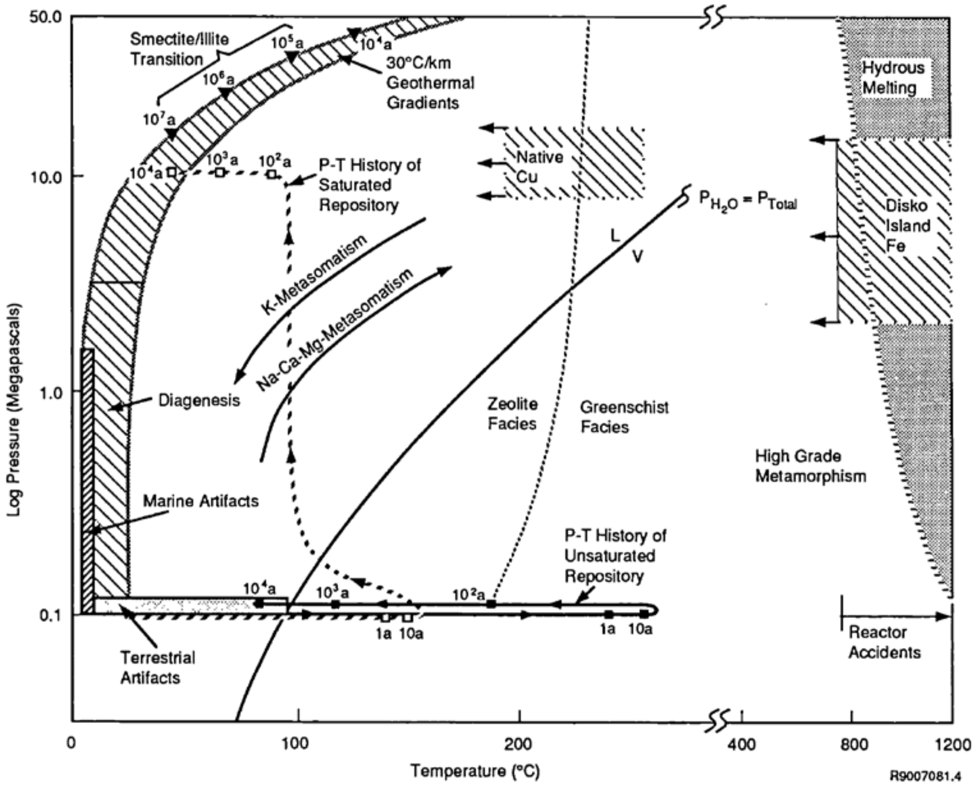

**Figure 1: Comparison of the temperature and pressure conditions for unsaturated and saturated repository designs and those for different geological processes for the formation and transformation of different engineered barriers (Apted 1992). The environmental conditions for marine and terrestrial artefacts are also shown. Reproduced with permission of © Elsevier.**

Another way to put the use of analogues into context is to compare the future timescales of interest with those from the past. Figure 2 contrasts the timescale of the evolution of the DGR environment and of the expected minimum UFC lifetime with the ages of some of the geological and archaeological analogues described in this report. Geological analogues tend to be older than the required UFC lifetimes, while archaeological analogues are more recent.

The fact that copper and iron persist after long-term exposure to corrosive environments is, of course, the main reason why such analogues are so useful in building confidence in the UFC lifetime predictions. This continued existence owes itself to either thermodynamic stability or kinetic stability. Thermodynamic stability can be the result of the redox potential and pH of the environment lying within the stability field of the metal or of the accumulation of corrosion products (dissolved metal ions and/or $H_2$) such that the system is in equilibrium. Kinetic stability can be the result of a passive film, mass-transport limitation of either products or reactants, or (unusually in the case of analogues) inhibition of the corrosion process. In order to make full use of an analogue, it is important to understand whether the persistence of the metal is due to thermodynamic or kinetic stability. Both concepts are used in the prediction of the long-term behaviour of the UFC.

There have been a number of reviews of the use of analogues in general (Alexander et al. 2015, Apted 1992, Brandberg et al. 1993, Fayek and Brown 2015, IAEA 2005, McKee and Lush 2004, Milodowski et al. 2015, Miller et al. 1994, Posiva 2012b, Reijonen et al. 2015), as well as specifically related to the corrosion behaviour of UFC (Crossland 2005; Dillmann et al. 2014; Féron et al. 2009; Hellmuth 1991a,b; Johnson and Francis 1980; Neff et al. 2006, 2010; Sridhar and Cragnolino 2002). This report is not intended as an exhaustive review of all analogue studies that have been conducted in the area of canister corrosion, although a compilation of 1-page summaries of 100+ such studies is included as an appendix to the main text. Instead, the intent of this report is to discuss in more detail some of the more important analogue studies for both copper and steel, with an emphasis of how the information that can be gleaned from these studies can be used to support the prediction of UFC lifetimes.

Chapters 2 and 3 of this report provide an overview of the different natural analogue studies that have been published for copper and iron, respectively. Evidence from native metal deposits and anthropogenic analogues are considered in each case. In Chapter 4, the use of this information in the safety assessment (i.e., the numerical calculation of UFC lifetimes, dose consequences, etc.) and the safety case (i.e., the qualitative description of the expected long-term performance) is discussed. This discussion focusses on the methodologies used to predict canister lifetimes and the extent to which these methods are supported by evidence from analogues. The role of analogues in various international nuclear waste management programs is also considered. Finally, possible additional analogue studies are considered in Chapter 5. In addition to identifying specific analogue studies, this section also includes a discussion of the general areas of investigation in which analogues could provide useful supporting information. As noted above, the main text is supported by an appendix consisting of 1-page summaries of 100+ analogue studies. Each summary contains bibliographic information, the original abstract or summary, and comments from the current author.

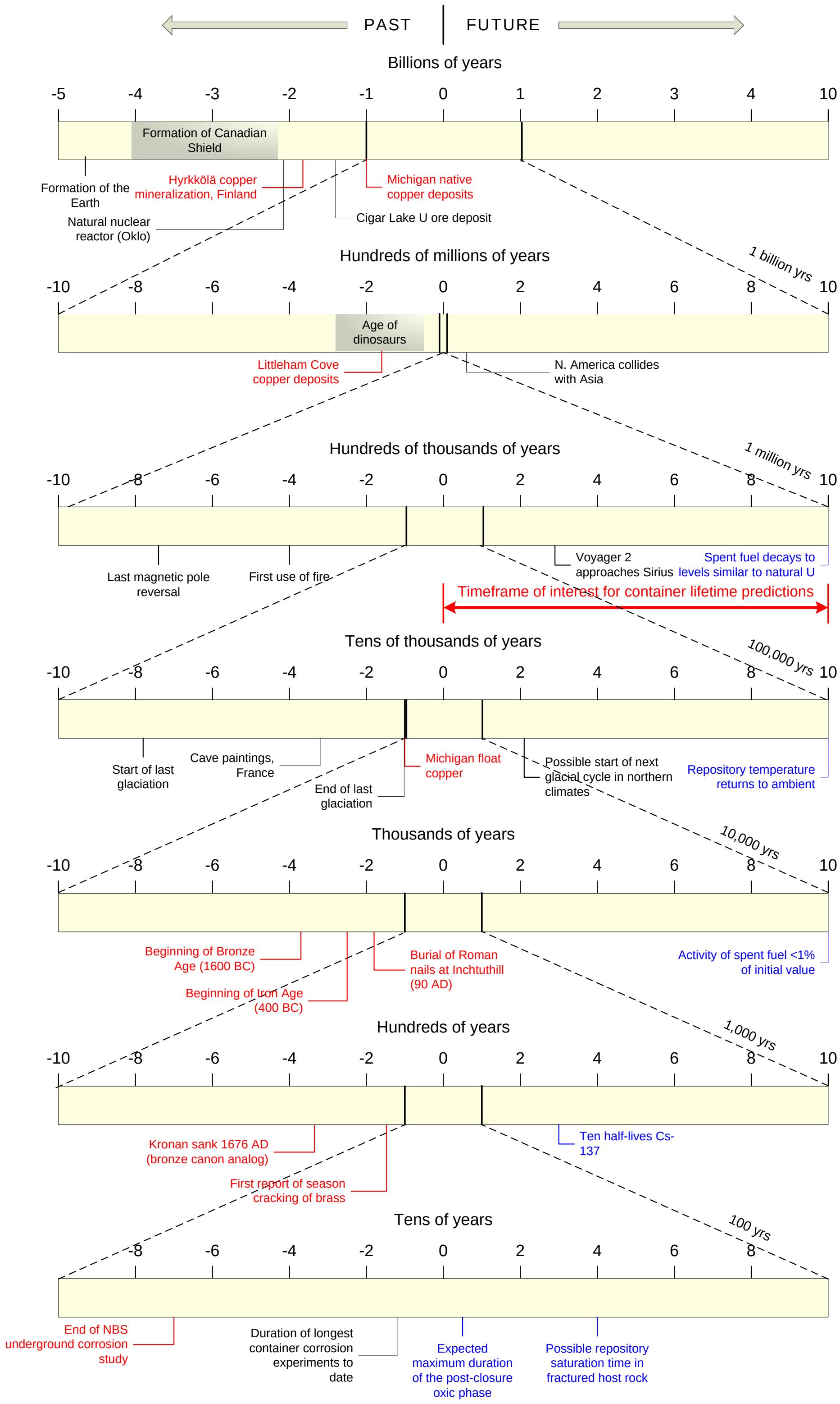

**Figure 2: Comparison of the Timescale of the Future Evolution of the DGR with Past Archaeological and Geological Events (after McMurry et al. 2003). The approximate dates of some of the analogues discussed in this report are indicated.**

# 2. COPPER ANALOGUES

## 2.1 NATIVE COPPER DEPOSITS

Copper, along with gold, silver, the platinum group of metals, and iron are the only metals to occur in their native state in significant quantities. Metallic copper is quite widespread globally and can be found in many different locations. The interest in native copper deposits as analogues is mostly from the viewpoint of the environmental conditions under which they continue to persist, although there is also some interest in their mode of formation, as discussed below. The majority of native copper has formed from hydrothermal fluids (i.e., due to the reduction of oxidized copper from hot aqueous solutions), although magmatic (precipitation from high-temperature molten systems) and supergene deposits (*in situ* secondary oxidation of a primary sulfide mineralization) are also known (BGS 2007). However, native copper is relatively rare, with approximately 90% of the copper in the earth's crust present in the form of various sulfide minerals.

### 2.1.1 Michigan Copper Deposits

Perhaps the most extensive native copper deposits are (were) those located in northern Michigan close to the shores of present-day Lake Superior. These deposits are believed to have formed when copper was leached into solution and transported in high-temperature, low to moderate pH, moderate redox potential (Eh), and high [$Cl^-$] hydrothermal fluids. Metallic copper was deposited when these fluids encountered cooler, more alkaline, and more dilute waters resulting from basalt-water interactions (Crisman and Jacobs 1982). It is estimated that the precipitation of copper occurred at a temperature in the range 150 $^oC$ to 300 $^oC$ (cf. Figure 1). The estimated age of the deposits is at least 1 billion years bp (before present). The native copper deposits of the Keweenaw Peninsula were mined commercially for much of the 19th and 20th centuries, with an estimated yield of 11 billion pounds ($5 \times 10^6$ tonnes) (Bornhorst and Barron 2011).

Crisman and Jacobs (1982) considered the factors that resulted in the persistence of the native copper. In near-surface mines, exposed copper is oxidized to $Cu_2O$, but remains unaltered in fractures. By reference to the Pourbaix (E-pH) diagram for the Cu-S-$H_2O$ system, Crisman and Jacobs attributed this absence of alteration of copper in the fractures to locally reducing water in the fractures as a result of water-rock interactions with reduced phases in the basalt. In addition, near-surface waters have a moderate pH and low total dissolved solids (TDS) content (of the order of 0.1 g/L). Deep groundwaters, however, are saline, with TDS up to 300 g/L and [$Cl^-$] up to 5 mol/L (Crisman and Jacobs 1982). Except for superficial alteration, native copper in deep mines is still largely unaltered, a fact that Crisman and Jacobs attributed to the low permeabilities of the deep basalts (i.e., mass-transport limitation) and "passivation of corrosion processes by the alteration products of the copper". Quite what this passivating species might be was not defined by Crisman and Jacobs (1982), but copper does form protective CuCl layers in chloride environments (Kear et al. 2004, King and Kolář 2000). An important characteristic of the Keweenaw deposit, in general, is the low S activity which precludes the formation of copper sulfide phases, although some chalcocite is found.

In addition to the native copper of the Keweenaw Peninsula, there are also sulfide-dominated copper deposits in the region, for example, in the Porcupine Mountains district (Bornhorst and Barron 2011). While the chalcocite at Keweenaw is believed to be a transformation product of the primary copper deposit, native copper at the Porcupine Mountains location is believed to be an oxidation product of the primary copper mineralization. Butler and Burbank (1929) suggest the following (supergene) process

$$Cu_2S + 3Fe_2O_3 + 5H_2SO_4 = 2Cu + 6FeSO_4 + 5H_2O \tag{1}$$

in which the reductive dissolution of hematite is coupled to the oxidation of S(-II) to S(VI). At the same time, Cu(I) is reduced to Cu(0). Supergene copper formation is discussed in more detail in Section 2.1.4.

The potential relevance of copper/$Cu_2S$ assemblages in further analogue studies is discussed in Section 5.1.1.

In addition to being a useful analogue study in its own right, the Michigan copper deposits were also a source of copper for a number of centuries, resulting in various copper artefacts that may be of interest (Anselmi 2004). The copper isotopic signature of these artefacts can be used to trace their origin to the different mineral deposits (Mathur et al. 2014), as can the elemental composition (Mauk and Hancock 1998).

### 2.1.2 Hyrkkölä Native Copper Mineralization, Finland

The Hyrkkölä native copper deposits are located in crystalline rock in southwest Finland (Marcos 1996, 1997, 2002; Marcos and Ahonen 1999; Marcos et al. 1999). Investigations were carried out in two stages; an initial examination of core samples from five drill holes (Marcos 1996, 1997) and a follow-up study in which core samples were obtained from two additional holes, along with ground water sampling (Marcos and Ahonen 1999, Marcos et al. 1999). One of the unique features of the site that makes it a potentially useful analogue study is the subsequent partial sulphidation of the original native copper deposits.

The original copper mineralization is believed to have occurred between 1.8 and 1.7 billion years ago at which point metallic copper was formed, most likely by reduction of dissolved copper in hydrothermal fluids. At some later stage, the host rock fractured, exposing the contained native copper to lower temperature hydrothermal fluids (<100$^{o}$C). The subsequent contact with ground water has resulted in the formation of various copper-containing assemblages:

- Copper/copper sulfide (in open fractures)
- Copper sulfides/copper iron sulfides (open fractures)
- Copper/$Cu_2O$ (open fractures)
- Copper/$Cu_2O$ (in closed fractures, presumably with previous access to hydrothermal fluids at some stage)
- Native copper (open fractures)
- Native copper (closed fractures)

As noted above, the existence of partially sulphidised native copper is of particular interest as it might provide some information about the rate of the reaction, as well as the properties of the copper sulfide alteration product. Two specific copper-copper sulfide assemblages are referred to by Marcos (1996) and Marcos and Ahonen (1999): a section of core referred to as sample number 40 ($S_{40}$) from drillhole 304 and a sample found at a depth of 68.30 m in drillhole Hy325 (sample Hy325/68.30). Figure 3 shows a number of images of the copper sulfide deposits in sample $S_{40}$ (Marcos 1996, 1997). The polished cross sections show a collection of thin copper flakes (<1.5 mm in width), with regions of copper sulfide (Figure 3(a), (c)). The enlarged image

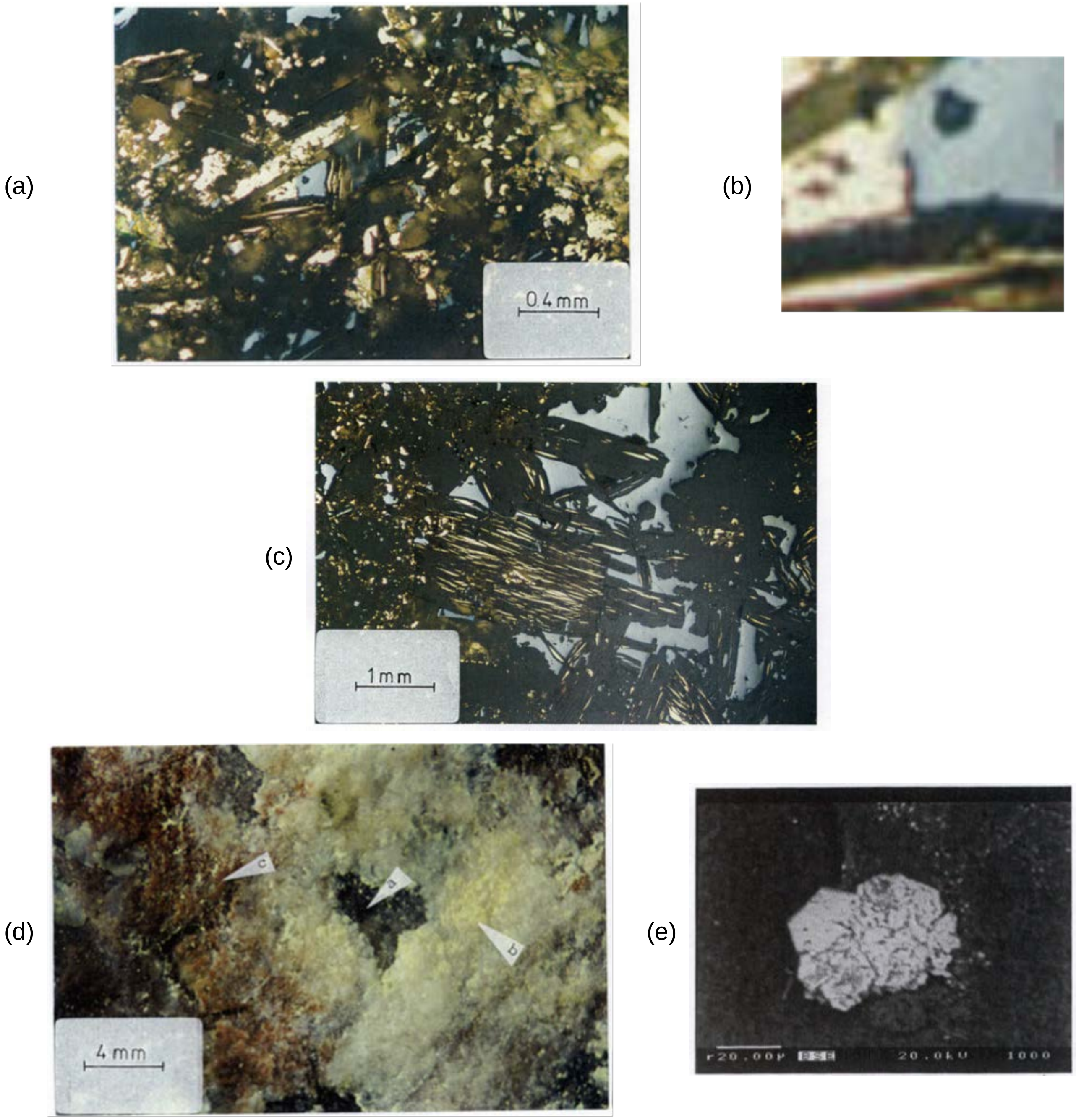

**Figure 3: Various images of native copper-copper sulfide assemblages from core sample $S_{40}$ from the Hyrkkölä analogue site (Marcos 1996). (a), (b), and (c) polished cross sections showing native copper in bright pink-yellow and copper sulfide in blue. (b) is an enlarged image of the interface between copper and copper sulfide from the assemblage shown in the center of (a). (d) and (e) are images from the fracture surface in sample $S_{40}$. In (d), the three marked features are a) djurleite, b) gummite (an amorphous mixture of uranium oxides, silicates, and hydrates, and c) ferric hydroxide. (e) is a back-scattered electron image of copper sulfide. Reproduced with permission of © Posiva Oy.**

(Figure 3(b)) shows what appears to be an interface between the native copper and copper sulfide, although the resolution is not high enough to indicate the structure of the corrosion product layer. Copper sulfide deposits were also found on the surface of a fracture in the sample (Figure 3(d) and (e)), which would have been in direct contact with the hydrothermal fluid. The fracture surface also shows evidence of U(VI) (gummite) and Fe(III) suggesting relatively oxidizing conditions, in contrast to the relatively reducing conditions under which the copper sulfide would presumably have been formed. Figure 4 shows a cross-section through a similar mineral assemblage from sample Hy325/68.30.

Microscopy with polarised light was used to identify the copper sulfide phase in sample $S_{40}$ as chalcocite ($Cu_2S$) (as opposed to covellite CuS). Electron microprobe analysis was used to further refine the stoichiometry, with the Cu:S ratio most closely matching that of djurleite ($Cu_{1.934}S$). Subsequent XRD analysis also identified the presence of monoclinic chalcocite (low chalcite, $Cu_{1.99-2}S$). Marcos and Ahonen (1999) identified the presence of digenite and djurleite phases in sample Hy325/68.30 (Figure 4). Another interesting observation was the presence of metallic silver at the point of contact between the native copper and copper sulfide for the sample shown in Figure 4. Silver sulfide has a lower solubility product than copper sulfide (CRC 2019) and might be expected to be the more-thermodynamically stable phase. Table 1 summarizes the compositions, crystal structures, and the temperature ranges over which various copper sulfides are stable (after Marcos and Ahonen 1999).

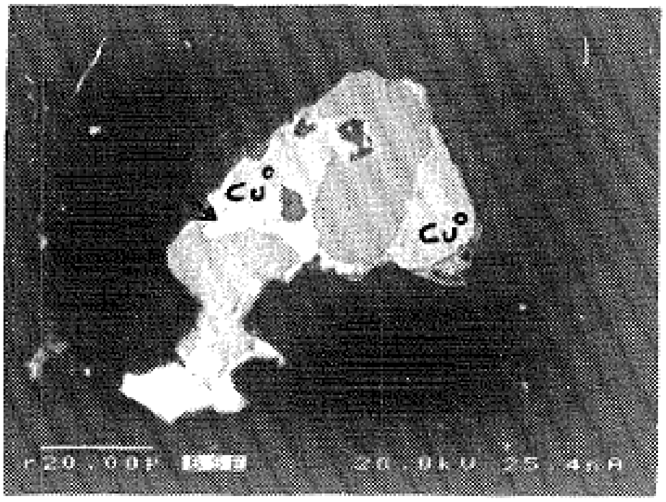

**Figure 4: Back-scattered electron image of native copper-copper sulfide assemblage from Hyrkkölä sample Hy325/68.30 (Marcos and Ahonen 1999). Metallic copper in light grey and copper sulfide in darker grey. Reproduced with permission of © Posiva Oy.**

**Table 1: Composition, Structure, and Temperature Stability Ranges of Various Copper Sulfides (after Marcos and Ahonen 1999).**

| Mineral | Composition | Crystal Structure | Temperature Stability Range |
|---|---|---|---|
| Chalcocite (low) | $Cu_{1.99-2}S$ | Monoclinic | T < 103 °C |
| Chalcocite (high) | $Cu_{1.98-2}S$ | Hexagonal | $T_{min}$ ~103 °C<br>$T_{max}$ ~435 °C |
| Djurleite | $Cu_{1.93-1.96}S$ | Monoclinic | T < 93 °C |
| Digenite (low) | $Cu_{1.75-1.8}S$ | Cubic | Metastable |
| Digenite (high) | $Cu_{1.834}S$<br>$Cu_{1.765}S$ | Cubic | T <93 °C<br>T <75 °C |
| Anilite | $Cu_{1.75}S$ | Orthorhombic | T <72 °C |
| Covellite | CuS | | |

Because of the absence of other sources of sulfide (e.g., pyrite mineral phases), Marcos (1996) and Marcos and Ahonen (1999) concluded that sulphidation was the result of contact of the native copper with a sulfide-containing aqueous phase. Based on the presence of calcite on the fracture surface of sample $S_{40}$, the pH of the aqueous phase was assumed to be pH 7.8. At a temperature of 25°C, djurleite would be stable at this pH at a minimum sulfide concentration of $10^{-5}$ mol/L (0.3 mg/L). If the alteration had occurred at a temperature of 5 °C, the minimum sulfide concentration could be as low as $10^{-6}$ mol/L (0.03 mg/L).

In addition to the copper sulfide phases, native copper-cuprite ($Cu_2O$) assemblages were also found in the core samples. In the five initial cores, $Cu/Cu_2O$ was found in a closed fracture (Figure 5(a)), from which it was assumed that the copper had corroded due to contact with a limited volume of oxidising hydrothermal fluid, but had then become isolated in the closed fracture (Marcos 1996). In the follow-up study, in addition to native copper present in low-porosity rock, $Cu/Cu_2O$ assemblages were also found in open fractures in contact with ground water (Figure 5(b), Marcos and Ahonen 1999). The $Cu_2O$ oxide rim around the copper particles (up to 1 mm in diameter) in these latter samples was of the order of 10-100 $\mu$m

In order to be able to relate the formation and persistence of the different mineral phases to the local environmental conditions, Marcos and Ahonen (1999) took ground water samples at five locations corresponding to different open fractures that displayed mineral assemblages (depths of 43-104 m). Surprisingly, all ground waters were oxidising with measured Eh values in the range 200-600 $mV_{SHE}$[1]. In addition, four of the five waters were marginally acidic (pH 6-6-6.8), with the fifth being slightly alkaline (pH 8.2). The waters were generally dilute bicarbonate-rich fresh waters, with ~$10^{-4}$ mol/L $Cl^-$ and $SO_4^{2-}$ and ~$10^{-3}$ mol/L $HCO_3^-$.

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[1] SHE refers to the standard hydrogen electrode potential scale

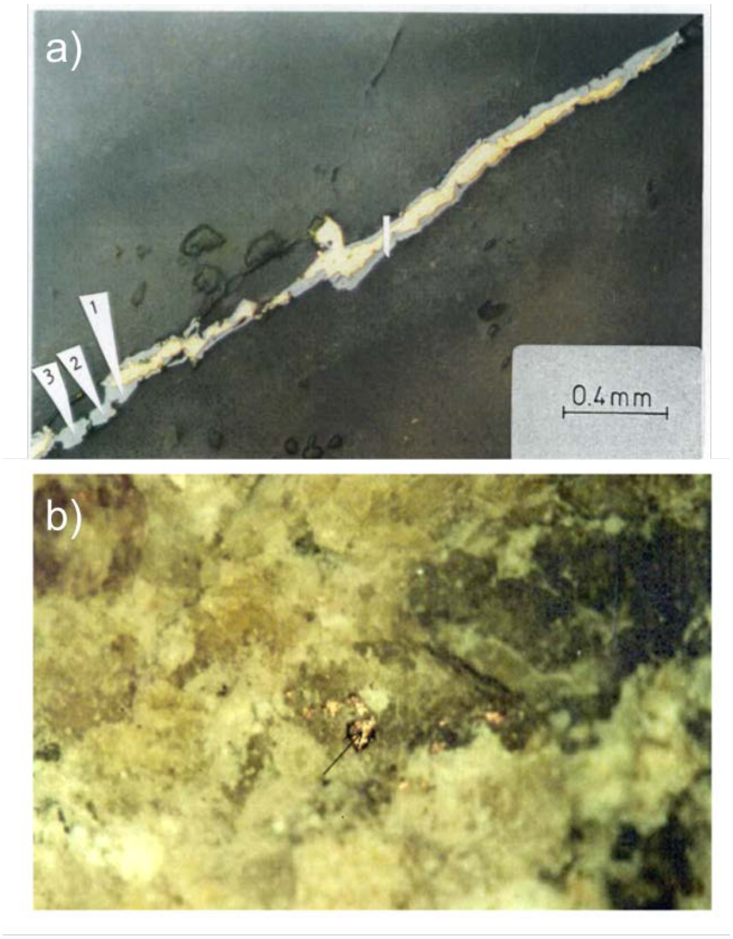

**Figure 5: Images of native copper with cuprite ($Cu_2O$) alteration products. (a) Polished section from Hyrkkölä sample $S_{30}$ showing copper in a closed fracture with cuprite border in light blue (Marcos 1996). (b) Fracture surface of sample Hy324/98.75, width of image 24 mm (Marcos 2002). Reproduced with permission of © Posiva Oy and N. Marcos.**

These ground water conditions are inconsistent with the formation of copper sulfides and clearly are not representative of the hydrothermal fluids responsible for the alteration of the native copper. It is also difficult to reconcile the relatively limited alteration of Cu to $Cu_2O$ in open fractures in contact with oxidising ground water, unless the oxide film is strongly passivating. However, the low pH of the majority of ground water samples makes it unlikely that copper would be passive in these conditions (Qin et al. 2017).

The presence of U-containing phases on the fracture surfaces allowed the age of some of the samples to be estimated using uranium series disequilibrium techniques (Marcos and Ahonen 1999, Marcos et al. 1999). These studies indicated that the sulphidation phase may have ended more than 200,000 years ago, making the persistence of copper sulfides for such a long time in oxidising ground water quite unexpected.

### 2.1.3 Copper Plates, Littleham Cove, UK

Native copper occurs as thin plates up to 160 mm in diameter in the consolidated Permian Littleham Mudstone formation at Littleham Cove, U.K. (Milodowski et al. 2000, 2001, 2002, 2003). The occurrence of metallic copper in the formation is relatively rare, but the finds have been studied in some detail as a natural analogue for long canister lifetimes in the SKB program, partly due to the abundance of clay within the formation. Although the clay is not a montmorillonite-containing material like the bentonite to be used in the DGR, it is an effective long-lived analogue for the sealing system. Because the plates exhibit deformation damage, the native copper is believed to pre-date the compaction of the sediments, which occurred some 176 million years ago. There has been significant alteration of the copper, but 30-80% of the original thickness of 1-2 mm remains uncorroded despite exposure to saturated conditions for an extended period of time.

Milodowski et al. (2002) have summarized the various stages of alteration as follows:

1. "Corrosion of copper and formation of coarse copper oxide (cuprite $Cu_2O$) as the *main* alteration of the copper metal.
2. Deformation and fracturing and extension of the copper sheets.
3. Copper and/or nickel arsenide overgrowths with minor replacement of copper metal, accompanied by minor copper-sulfides (principally chalcocite, $Cu_2S$).
4. Precipitation of a later phase of cobalt-rich nickel and/or copper arsenide.
5. Further overgrowths and some possible replacement of earlier formed minerals by earthy cuprite and copper arsenates.
6. Replacement of early cuprite by copper-oxide-sulfate $Cu_4SO_4\,(OH)_6.H_2O$ (observed in one sample only).
7. Near surface dissolution (due to surface weathering effects at outcrop) of copper metal and copper oxides, accompanied by the precipitation of secondary malachite, azurite, copper arsenates and complex Cu-chlorides."

The earliest alteration of the copper to $Cu_2O$ occurred prior to compaction of the sediments and the deformation of the plates. This was followed, by minor alteration to copper sulfide and arsenide phases during the long-term exposure to the saturated compacted sediments. More recently on a geological timescale, a period of oxidative alteration has occurred following uplift of the rock, outcropping, and weathering and has continued until the present time. The long-term persistence prior to uplift of the sediments is attributed to the low permeability of the compacted mudstone (Milodowski et al. 2002). The persistence of the copper appears, therefore, to be a consequence of kinetic limitations rather than thermodynamic stability. Interestingly, evidence for concentration profiles away from the copper surface and extending into the matrix of the host rock by a few tens of micrometres has been found, although it is unclear whether this "halo" of copper is left over from the time when the copper plates first formed or whether it is due to subsequent alteration and the transport of corrosion products away from the corroding interface.

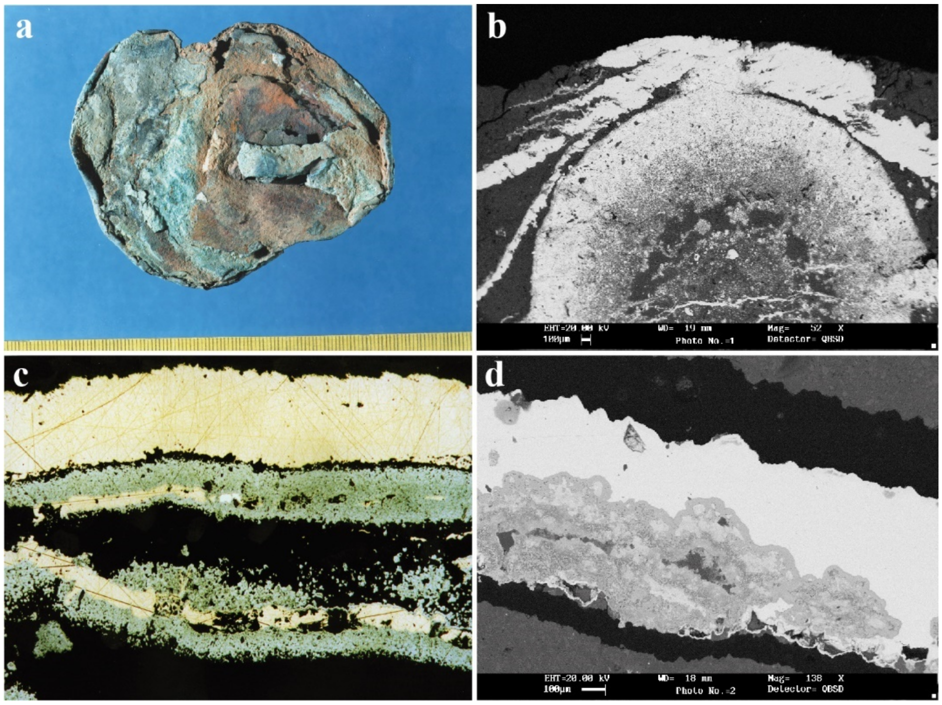

**Figure 6: Various optical and electron images of copper plate from the Littleham Cove natural analogue site (Milodowski et al. 2001). Reproduced with permission of © SKB.**

### 2.1.4 Other Native Copper Deposits

Supergene native copper deposits form when deep-lying primary sulfide ores are oxidized, either by infiltrating oxidizing waters or as a result of uplift bringing the primary ore closer to the surface. The most common primary copper mineral is chalcopyrite ($CuFeS_2$), accounting for approximately half of all copper production (BGS 2007). Figure 7 and Figure 8 illustrate the process of supergene enrichment of chalcopyrite, highlighting the vertical sequence of mineral phases that is commonly observed with such deposits. The interesting aspect of these formations is that this sequence is entirely consistent with thermodynamic predictions and, indeed, are represented by a vertical section through the Cu-Fe-S-$H_2O$ Pourbaix diagram at neutral to moderately alkaline pH (Figure 9).

Native copper is also found in oceanic basement rocks (Dekov et al. 2013). The proposed mechanism involves the infiltration of cool, oxic sea water into the crust at mid-ocean ridges (MOR), where it oxidizes primary copper ores as it travels downwards through the basement rock and is heated by the earth's centre (Figure 10). The copper-containing hydrothermal fluid then vents at discharge zones where the S activity is low and metallic copper is precipitated. Dekov et al. (2013) proposed that the precipitation of metallic copper involves the reaction:

$$4CuCl_2^- + 2H_2O \rightarrow 4Cu + O_2 + 8Cl^- \tag{2}$$

This is an interesting hypothesis as this reaction represents the exact opposite of that for the aerobic corrosion of copper UFC in contact with $O_2$-containing $Cl^-$ environments (King and Kolář 2000).

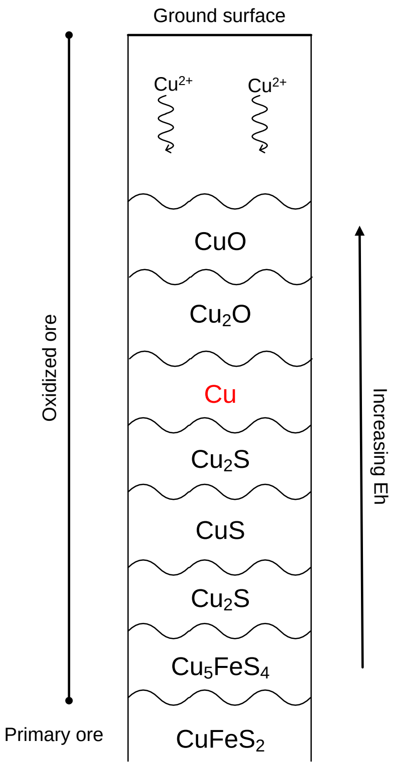

**Figure 7: Simplified vertical section representing the supergene enrichment of the primary mineral chalcopyrite ($CuFeS_2$) (after Amcoff and Holényi 1992).**

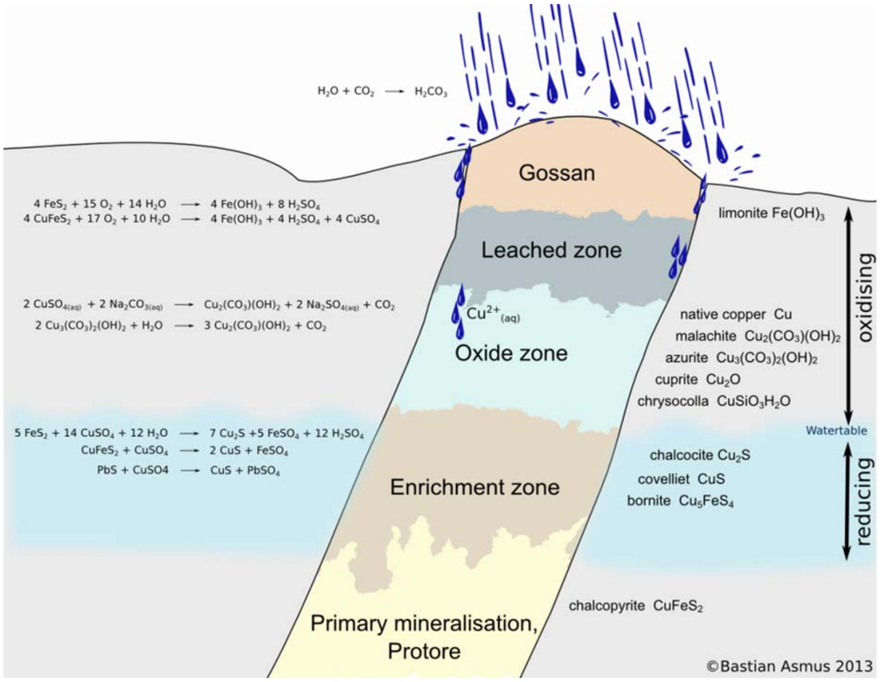

**Figure 8: Schematic illustration of supergene enrichment of a primary chalcopyrite ore deposit (B. Asmus, https://en.archaeometallurgie.de/gossan-iron-cap/, downloaded July 22, 2020).**

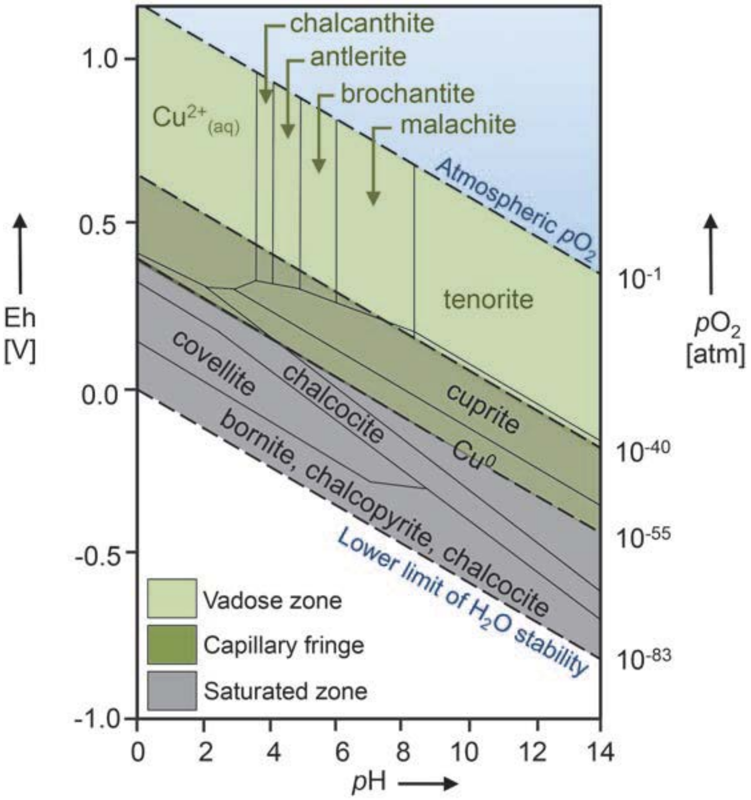

**Figure 9: Potential-pH (Pourbaix) diagram for the Cu-Fe-S-$H_2O$ system showing the various stable mineral phases (Reich and Vasconcelos 2015). Chalcopyrite, bornite, chalcocite, covellite, cuprite, and tenorite have the chemical formulae $CuFeS_2$, $Cu_5FeS_4$, $Cu_2S$, CuS, $Cu_2O$, and CuO, as shown in the sequence in Figure 7. Reproduced with permission of © Mineralogical Society of America, modified after Sillitoe (2005).**

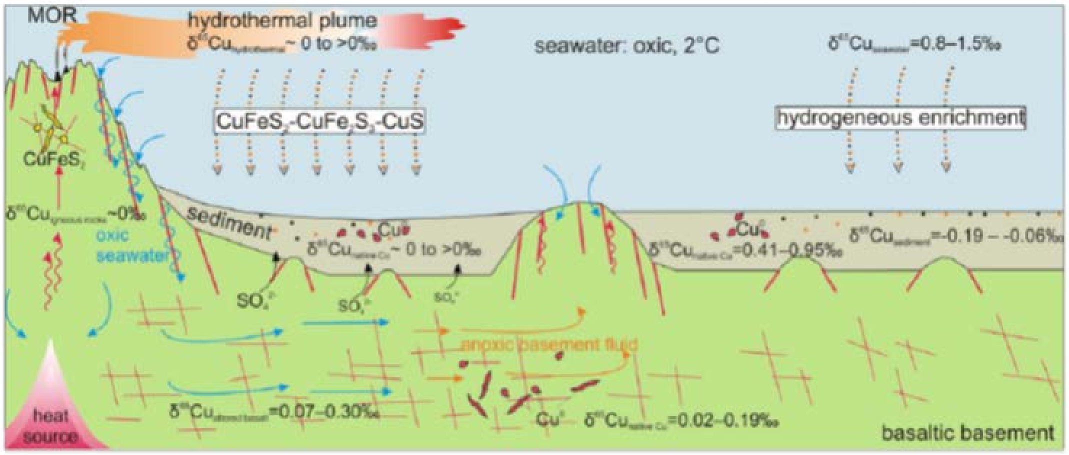

**Figure 10: Proposed mechanism for the formation of native copper in oceanic basement rocks (Dekov et al. 2013). Reproduced with permission of © Elsevier.**

## 2.2 ANTHROPOGENIC COPPER

Anthropogenic copper analogues are of two main types; archaeological artefacts and more-modern man-made objects. The distinction is not particularly important, except that the alloy composition of the more-contemporary analogues is generally more relevant than those of the archaeological artefacts.

### 2.2.1 Bronze Age Artefacts

Perhaps the oldest anthropogenic analogues are those dating from the Bronze Age, beginning approximately 1600 BC (Bresle et al. 1983). Bronze Age artefacts are useful analogues primarily because of their age. The term bronze is used to describe many alloys of copper, generally including tin ranging from 4-15 wt.% mixed with other elements, including lead, nickel, arsenic, and sometimes silver; the term bronze is sometimes also applied to copper:zinc alloys that are more correctly referred to as brasses. Unfortunately, however, the alloy composition and the environmental conditions to which they were exposed are invariably different from those of interest. Although corrosion rates have been derived from the study of artefacts (Bresle et al. 1983, Chen et al. 2004, Demchenko et al. 2004, Tsai 2017), these are of limited use as the lifetime prediction for copper UFC is based on mass-balance and mass-transport arguments rather than on the extrapolation of an empirical corrosion rate. Use has been made, however, of measurements of localized corrosion from the study of Bresle et al. (1983). These data were used to refine the estimate of the pitting factor used in the early SKB program (Swedish Corrosion Institute 1983, Werme et al. 1992) and in an estimate of the maximum pit depth based on extreme value analysis (King and Kolář 2000, King and LeNeveu 1992).

The main use of Bronze Age analogues, however, is confidence building in the predicted long lifetimes of copper UFC.

### 2.2.2 Kronan Bronze Cannon

The case of a bronze cannon submerged in seabed sediments was first used as an analogue by Hallberg et al. (1988) and later re-analyzed by King (1995). The cannon had been submerged muzzle down for a period of 309 a during which the bronze matrix and oxide inclusions had undergone corrosion and dissolution in the oxidizing saline environment (Figure 11). Sediment core samples were taken perpendicular to the axis of the cannon and were analyzed for the copper and iron contents. Apart from the permanently aerobic nature of the sediments, other aspects of the alloy and exposure environment were not dissimilar from those expected in a DGR. For example, the bronze has a particularly high Cu content of 96.3 wt.% and the sediments consisted of a mixture of illite, montmorillonite, and kaolinite clays. In addition, the salinity of the seawater is not dissimilar to that found at repository depth in crystalline rock formations in Canada and Sweden, although the temperature of 2-11 $^{o}$C (King 1988) is cooler than that expected in the repository. Hallberg et al. (1988) developed a conceptual model to describe the formation of various corrosion products and redox reactions involving CuO oxide inclusions, and organic matter and Fe(II) in the seawater. Extrapolation of the observed corrosion resulted in an estimate of <10 mm corrosion in 100,000 a.

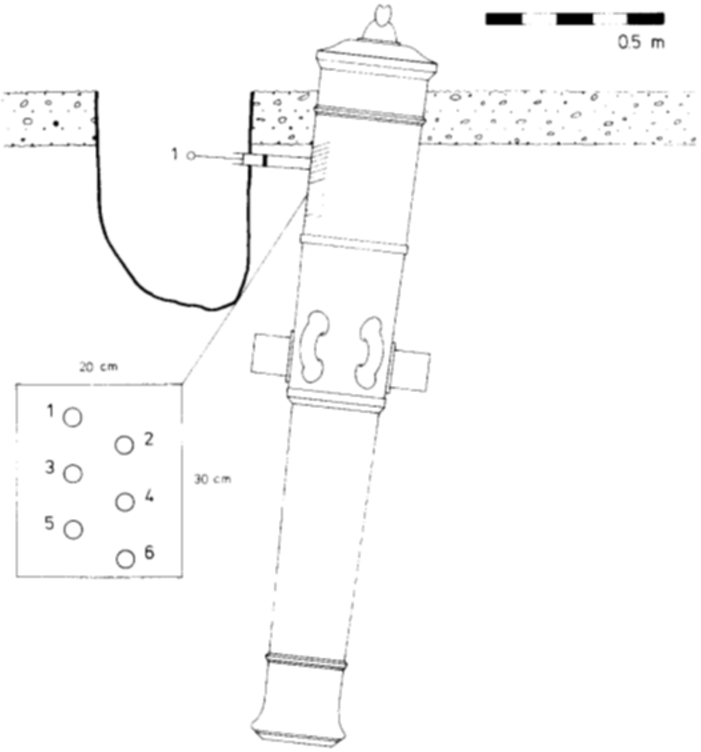

**Figure 11: Schematic of the bronze cannon from the Kronan submerged in sea sediments and an illustration of the six core samples taken perpendicular to the cannon surface (Hallberg et al. 1988). Reproduced with permission of © Elsevier.**

King (1995) re-analyzed the original data and, in particular, the observed copper profiles in the clay sediments. It was suggested that the extent of diffusion of copper away from the surface of the cannon was consistent with that observed in corrosion experiments in which copper coupons were place in contact with groundwater-saturated compacted buffer material. Effective diffusivities derived from the Kronan Cu profiles were consistent with values derived from the experimental studies when extrapolated to the lower temperature conditions of the cannon. Subsequently, the cannon Cu concentration profiles were used in an attempt to validate the Copper Corrosion Model (King and Kolář 1996), the underlying mechanism of which was presented as an alternative to that proposed by Hallberg et al. (1998) to describe the observed corrosion behaviour of the cannon.

### 2.2.3 Ferryland

The Ferryland archaeological site on the east coast of Newfoundland is the most thoroughly investigated analogue site related to the corrosion of UFC in Canada (McMurry et al. 2001). The site dates back to the European Avalon community of the early 1600’s and has been investigated by the archaeological unit of Memorial University (MUN) since 1992. Ontario Power Generation was granted access to the site and a total of 62 copper, iron, and soil samples were provided for further laboratory examination, in addition to various on-site environmental measurements (McMurry et al. 2001).

Being a near-surface coastal location, the soil conditions were found to be generally oxidising and moderately acidic. The different soil horizons were found to contain up to 30 wt.% organic material and $Cl^-$ contents of up to 1500 μg/g. The copper samples provided by MUN consisted of kettle fragments, a can lid, nails, rivets, and other fasteners and were generally made of brass, in some cases with significant Pb content (added to the alloy to improve machineability). The iron samples consisted of nails, hardware, and miscellaneous iron fragments. More complete (and archaeologically valuable) artefacts were also recovered from the site but were retained by MUN.

Various corrosion measurements were made on the samples. Based on the oxide thickness, the corrosion rate of the brass samples was estimated to be in the range 0.07 μm/a to 0.5 μm/a. Copper was found to have entered the surrounding soil, with concentrations as high 50,000 μg/g in the soil inside a brass thimble. The corrosion rate based on the integrated amount of Cu in the soil was in the range 0.01 μm/a to 0.02 μm/a. Pit depths were measured on 18 copper alloy samples, with a maximum depth on any of the samples of 451 μm. The pit depth data were fitted to an extreme value distribution in an attempt to extend the analysis of King and LeNeveu (1992) by adding a data point for an exposure period of ~300 a to supplement the earlier data points at ~3000 a (based on the Bronze Age artefact data of Bresle et al. 1983) and 2-14 a (based on the underground corrosion study of Denison and Romanoff 1950). Possible evidence of stress corrosion cracking (SCC) was found on the fracture surface of a folded brass sheet which fractured upon handling. Cleavage-like features were observed on the fracture surface, although McMurry et al. (2001) were uncertain whether these were the result of cracking or of intergranular corrosion which was also observed on other samples from the site. The iron artefacts were heavily corroded and no attempt was made to estimate the corrosion rate. No evidence was found for galvanic corrosion between a brass and iron sample found in close proximity and which were thought possibly to have originally been in intimate contact.

As part of the field studies, the pH and redox potential of the soil were measured close to where various copper-alloy artefacts were discovered. Figure 12 shows these data superimposed on the Pourbaix diagram for the Cu-$H_2O$ system at 25°C. It is interesting to note that all of the measured values fall below the $Cu_2O$/CuO equilibrium line and that some lie within the stability field of metallic copper, although McMurry et al. (2001) did not suggest that any of the artefacts were thermodynamically stable. These field Eh (potential) and pH measurements, of course, correspond to conditions under which Zn will corrode, and it is possible that some of the artefacts would have been subject to dezincification, especially those with Zn contents greater than 15 wt.% (Sarver et al. 2010).

### 2.2.4 Contemporary Copper Analogues

Although contemporary copper analogues have shorter exposure periods than archaeological analogues, the alloy compositions tend to be closer to that proposed for the container than the ancient alloys. In addition, the greater number of more-recent objects allows greater selectivity in their application. Three examples are given here, although there are numerous others that could be used.

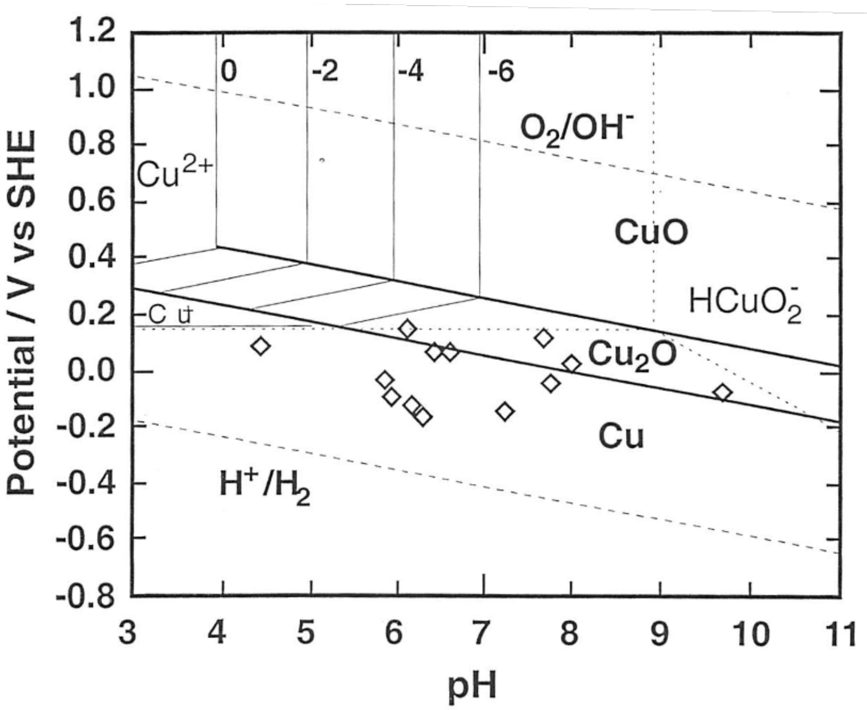

**Figure 12: Potential-pH diagram for the Cu-$H_2O$ system at 25°C with soil pH and redox potential measurements at locations of various copper artefacts from the Ferryland site (McMurry et al. 2001).**

### 2.2.4.1 Season Cracking of Brass Cartridge Cases

The season cracking of brass is included here not because it is a close analogy for the expected corrosion behaviour of copper UFC but because it is one of the rare examples of an analogue for environmentally assisted cracking (EAC). Season cracking of brass is an example of the SCC of cold-worked brass by ammonia under moist humid atmospheric conditions and is perhaps the first documented case of EAC (Shipilov 2008). The problem was first encountered by British troops in India in the second half of the 19th century who found that brass cartridge cases split where they had been deformed (Figure 13). Cracking seemed to be most prevalent during the wet monsoon season when conditions were humid and with munitions stored in stables. Ammonia from the horses urine was eventually discovered to be the SCC agent and cold work and high hoop stresses where the cartridge case was crimped produced a particularly susceptible material and introduced a source of tensile stress. These conditions resulted in axial cracking of the cartridge case in the direction perpendicular to the maximum tensile stress (Figure 13). The problem was solved by annealing the cartridge case after crimping in order to relieve the residual stress.

**Figure 13: Various images of the season cracking of brass cartridge case (http://firearmshistory.blogspot.com/2015/04/what-is-season-cracking.html)**

### 2.2.4.2 Pitting of Copper Potable Water Pipes

Pitting of copper potable water pipes is a well-known, although relatively rare, phenomenon (Tuck et al. 2010). Pitting is generally associated with specific water chemistries, leading to the classification of Types I, II, and III pitting, although residual carbon films remaining on the inner pipe surface from fabrication are thought to play a role in Type I pitting. The phenomenon occurs under aerated conditions, with the presence of $O_2$ necessary for the initiation and propagation of pits, although Cu(II) may be the actual species undergoing cathodic reduction (Lucey 1967). Although some have questioned the concept of a “pitting water” (Ellis 2000), it is generally accepted that pitting is the result of the breakdown of a passive $Cu_2O$ film by aggressive ions such as $Cl^-$ and $SO_4^{2-}$ (Cong et al. 2009, Lytle and Schock 2008).

Despite the possible roles of residues from the fabrication process, the pitting of copper water pipes is a relatively good analogy for the localized corrosion of copper-coated UFC during the initial aerobic transient phase if the near-field is saturated. Copper water pipes are fabricated from relatively pure copper (>99.9 wt.%) and are typically made from a phosphorus-deoxidized grade with high residual phosphorus (UNS C12200). There are examples of copper pitting in hot potable waters, although the largest database is for ambient temperatures. Because of these similarities to certain aspects of the UFC and near-field environment, King and Kolář (2000) used Lucey's (1967) pitting mechanism as the basis for a conceptual model for the localized corrosion of copper under repository conditions involving the non-permanent separation of anodic and cathodic sites.

#### 2.2.4.3 NBS Long-term Burial Tests

During the period 1932-1948 the U.S. National Bureau of Standards undertook an extensive experimental study of the corrosion of engineering alloys in a range of soil types (Denison and Romanoff 1950, Romanoff 1989). The alloys exposed included various iron and steel alloys, as well as different oxygen-free copper alloys, brasses, copper-silicon, and copper-nickel alloys. A total of 125 soil types of varying moisture content, pore-water chemistry, redox conditions, and resistivity were selected, although not all alloy types were exposed to all soils. Samples were extracted at five different intervals corresponding to between 2 a and 14.3 a exposure and characterized in terms of the extent of general corrosion and of pitting. In total, more than 36,500 samples of different alloys were exposed in what remains to this day the largest study of its kind (Romanoff 1989).

Some of the usual criticisms about the relevance of alloy types and disposal environment of archaeological artefacts also apply to the NBS long-term burial tests. The near-surface environmental conditions are undoubtedly dissimilar to those expected in the near-field of the DGR, although some aspects of some soils may be relevant to certain aspects of the repository evolution (for example, high-clay soils, or aerobic-unsaturated soils, or saturated-anoxic soils). Similarly, not all of the alloys tested are relevant, although five of the copper alloys used had Cu contents of >95 wt.% and included two oxygen-free grades (tough pitch copper UNS C12500 and phosphorus deoxidized copper UNS C12200). However, there are some advantages to the dataset, including the accurate reporting of pit depths and the range of exposure times, which permits time-dependent trends to be investigated.

Notwithstanding the limitations of the dataset, King and LeNeveu (1992) used the pit depth data in their extreme-value analysis of pitting of copper containers (see also King and Kolář 2000). The same data were used by SKB to refine their estimate of the pitting factor used to account for the extent of localized corrosion in earlier safety assessments and lifetime predictions (Swedish Corrosion Institute 1983, Werme et al. 1992), and a subset of these data was used for the empirical pitting expression in the probabilistic pitting model of Briggs et al. (2021). The latter model predicts a maximum pitting period of 6.9 years and a maximum pit depth (for 1 million realizations) of 1.2 mm. Using the extreme-value analysis methodology of King and LeNeveu (1992) and assuming the same period of pit growth, the pit depth for a cumulative probability of 0.999999 (equivalent to the deepest pit in 1 million realizations of the probabilistic model) is 0.49 mm for a copper-coated UFC with a surface area of 4.54 $m^2$. Thus, the maximum pit depths predicted using two different methods, but using the same dataset of measurements from analogue studies, are similar.

## 3. STEEL ANALOGUES

As for copper, there are both geological and anthropogenic analogues for the UFC steel substrate, although again the relevance of the alloy composition and of the exposure environment is often questionable. The vast majority of analogues, and certainly all of those of geological or archaeological provenance, are iron rather than steel.

### 3.1 NATIVE IRON DEPOSITS

Although less well-known than native copper deposits, metallic iron deposits do occur in nature. In addition to the remnants of meteorites (Johnson and Francis 1980), the two native iron deposits that have been investigated as natural analogues are the iron carbide blocks of Disko Island, Greenland (Bird et al. 1981, Klöck et al. 1986) and the Bühl native iron deposit in Germany (Hellmuth 1991a,b). The Disko iron blocks, weighing up to 22 tons, are actually an assemblage of iron, iron carbide, and various silicate, sulfide, and oxide inclusions. The iron is thought to have formed by reduction of basaltic magma by carbon from shale and coal deposits; hence the presence of iron carbide (Klöck et al. 1986). The iron blocks then underwent some alteration when exposed to the near-surface environment during past glaciation events, with much of the $\alpha$-Fe having been altered to wustite ($Fe_{1-x}O$) and magnetite (Bird et al. 1981). Hellmuth (1991b) estimated the alteration timescale to be of the order of $10^{-3}$-$10^{-4}$ a. The Bühl iron is in a basalt matrix and has been exposed to $O_2$-containing ground water for a period in excess of 1 million years.

Hellmuth (1991b) investigated the mechanisms for the preservation of native iron under otherwise corrosive conditions. It was concluded that the Bühl iron was protected from corrosion by the low-permeability basalt matrix, as well as by consumption of $O_2$ by reaction with FeO in the matrix. Based on a simple reactive-transport model, Hellmuth (1991b) predicted that an oxidized redox front would only penetrate into the basalt matrix by 2.3 mm in 1 million years, consistent with the persistence of the Bühl native iron. Hellmuth (1991a) also suggested that native Fe could be thermodynamically stable in olivine-rich ultrabasic rocks (low in $SiO_2$ content) due to serpentization, in which the olivine ($(Mg,Fe)_2SiO_4$) is converted to serpentine ($Mg_3Si_2O_5(OH)_4$) (Lamadrid et al. 2017)

$$2Mg_2SiO_4 + 3H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 \qquad (3)$$

The minor Fe(II) constituent of the olivine is released as $Fe^{2+}$, which then undergoes a Schikorr-type reaction resulting in the formation of magnetite and $H_2$

$$3Fe^{2+} + 4H_2O \rightarrow Fe_3O_4 + H_2 + 6H^+ \qquad (4)$$

The produced $H_2$ is considered to create reducing conditions in which metallic Fe is thermodynamically stable (Hellmuth 1991a).

The thermodynamics of the Fe-$H_2O$ system is discussed in more detail in Section 4.2.

The usefulness of information from the study of meteorites is tempered by the fact that Fe-rich meteorites typically contain 5-60 wt.% Ni, along with minor amounts of Co, P, and Ag (Johnson and Francis 1980).

## 3.2 ANTHROPOGENIC IRON AND STEEL ANALOGUES

### 3.2.1 Roman Nails, Inchtuthil, UK

The Iron Age dates from approximately 2600 years ago (Figure 2) and there are many examples of iron objects and artefacts that still exist after extended exposure to near-surface corrosive environments. An early example and one often cited in various nuclear waste management programs as an analogue of steel containers is the hoard of Roman-era nails from the Inchtuthill site in the U.K. dating from 87 A.D. (Mapelli et al. 2008, Milodowski et al. 2015). Almost one million nails were discovered in a pit (Figure 14) where they were thought to have been stashed as the Romans abandoned the site. Many of the nails were remarkably well preserved, with those in the centre of the hoard having been protected from incoming $O_2$-containing groundwater by the formation of a low-permeability halo of corrosion products formed when the nails around the edges of the pit corroded.

Corrosion rates can be derived from the thickness of corrosion products on the nails, although the major benefit of the analogue is to build confidence in the concept that iron-based structures (i.e., containers) can survive for periods of two thousand years in corrosive environments.

**Figure 14: Iron nail from the centre of the pit of Roman nails excavated from the Inchtuthil site (Miller at al. 1994). The nail is approximately 35 cm in length. Reproduced with permission of © Elsevier.**

### 3.2.2 Delhi Iron Pillar

The Delhi iron pillar is a well-known attraction in Delhi, India that has withstood 1500 a exposure to atmospheric corrosion conditions (Balasubramaniam 2000, Balasubramaniam and Dillmann 2003, Dillmann et al. 2002). The absence of corrosion is a consequence of the formation of a P-containing corrosion product that formed as a result of the high P content of the iron (estimated variously to be between 0.1 and 0.5 wt.%). Thus, the metallurgy of the iron pillar is unlike that of alloys proposed as container materials in various countries. However, there could be some value in the analogue for the French program in which an extended period of unsaturated conditions is expected during the period when the possibility of retrieval of the waste is mandated.

### 3.2.3 Characterization of Corrosion Products

As discussed in Section 4.4.2, the study of analogues has been a central feature of Andra's R&D program (Dillmann et al. 2014, Féron et al. 2009, Neff et al. 2010). Many of the studies have focussed on the development of a conceptual model for the structure and properties of corrosion product layers in soils, concrete, and under atmospheric conditions. The model is similar under all three conditions, and comprises a series of layers consisting of the uncorroded metal, corrosion product, and transformed medium (in the case of soils and concrete) consisting of a mixture of corrosion products and the original matrix (soil or concrete) (Figure 15). In addition to the overall structure of the corrosion product layer, studies have been conducted to determine:

- The distribution of electronic properties of the corrosion product using copper tracing (Saheb et al 2011a).
- Micromechanical properties of the corrosion product (Dehoux et al. 2012).
- Porosity of the corrosion product using mercury intrusion porosimetry (Pons et al. 2005, Vega et al. 2007) (Figure 16).
- The use of $^{18}O$ to determine the corrosion rate and the location of the anodic and cathodic reactions (Burger et al. 2011b; Vega et al. 2005a,b, 2007).
- The use of $D_2O$ to determine the corrosion rate and the location of the anodic and cathodic reactions (Saheb et al. 2012).
- The use of EIS to determine the nature of the rate-determining process for the corrosion of steel artefacts under near-surface burial conditions (Pons et al. 2005).

The integration of this information into the overall Andra corrosion program is discussed in Section 4.4.2.

### 3.2.4 Corrosion Rates

A major product of the various studies of iron archaeological artefacts is a large database of estimated corrosion rates over a broad range of "exposure" times (Figure 17). In the French program, the historical corrosion rates are used to build confidence in the overall prediction of container lifetimes, whereas in the Japanese program there is a more-direct use of analogue corrosion rates to extend the timescale of laboratory experiments to longer "exposure" times (Figure 18). Crossland (2005) has analyzed corrosion from archaeological and more-recent iron and steel samples and found reasonable correlations as a function of time for both aerobic and anaerobic conditions in soils and seawater (Figure 19).

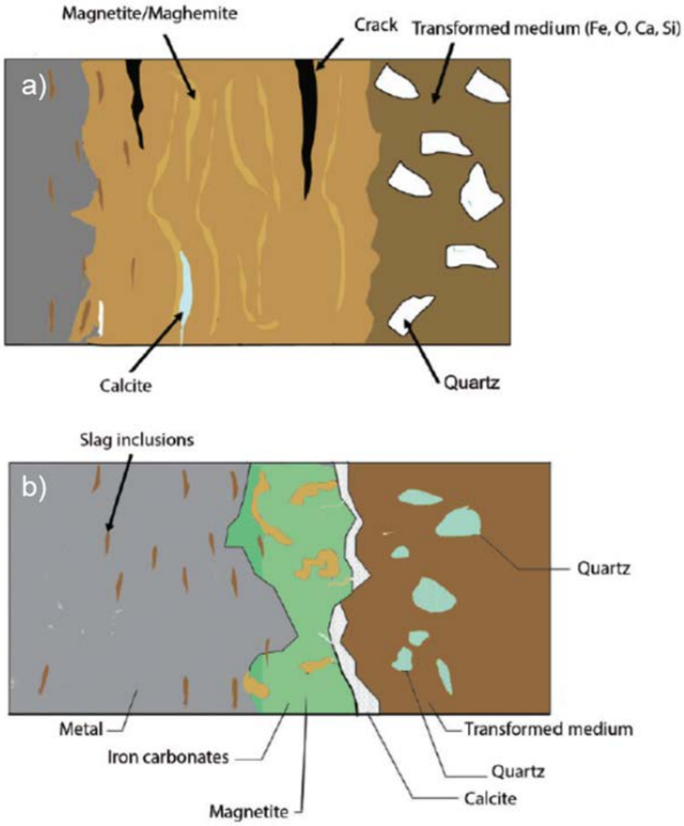

**Figure 15: An example of the conceptual model for the structure of corrosion product layers derived from the study of analogues in the French program (Dillmann et al. 2014). Reproduced with permission of © Taylor and Francis.**

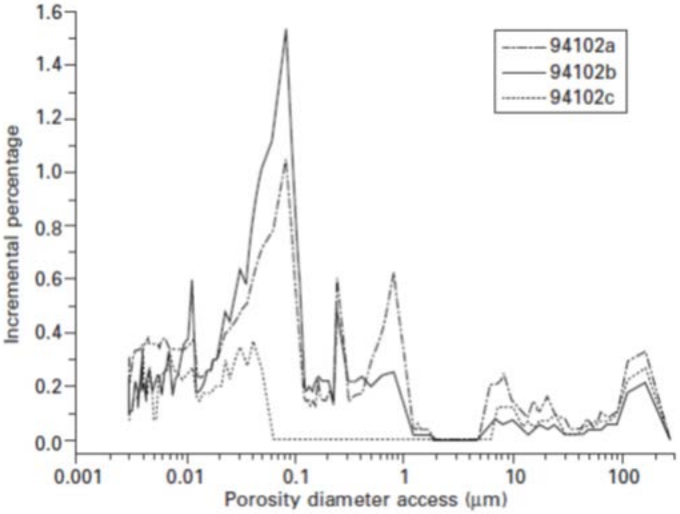

**Figure 16: Distribution of pore-size diameters in corrosion product layer on an iron rod from the 400-year old Glinet site in France (Vega et al. 2007).**

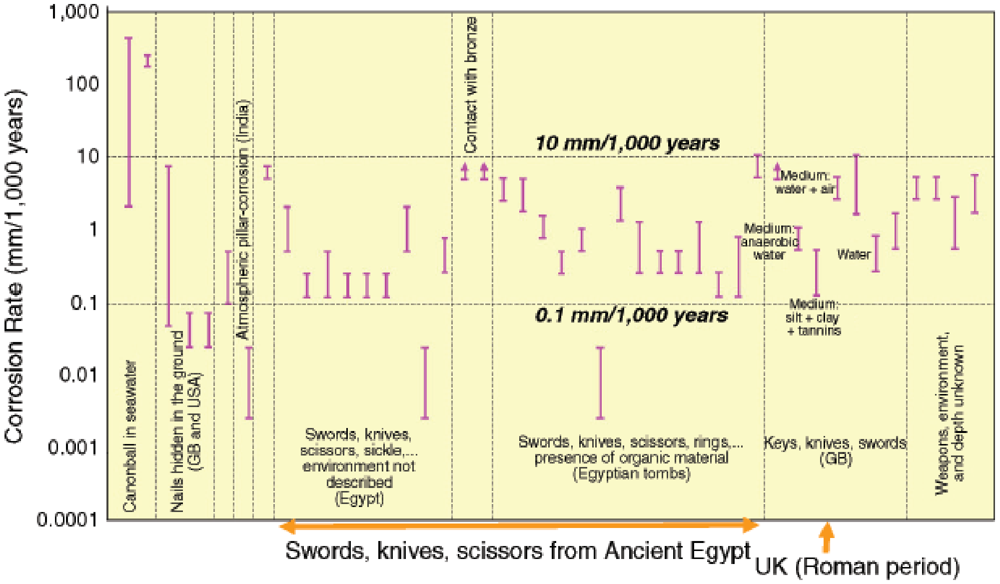

**Figure 17: Compilation of estimated corrosion rates of buried iron archaeological artefacts (Féron et al. 2009). Reproduced with permission of © AMPP.**

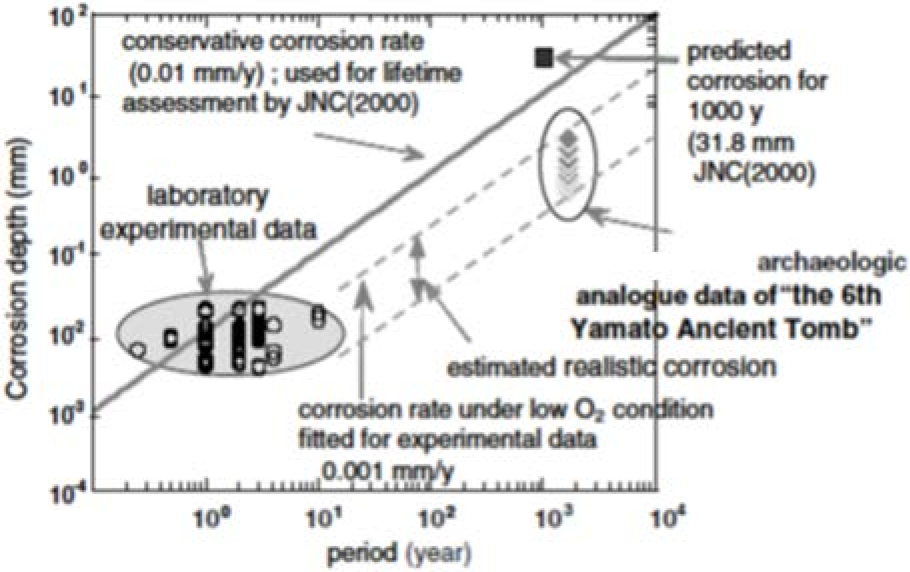

**Figure 18: Comparison of the time dependence of the depth of corrosion of laboratory samples and archaeological artefacts (Yoshikawa et al. 2008). Reproduced with permission of © Elsevier.**

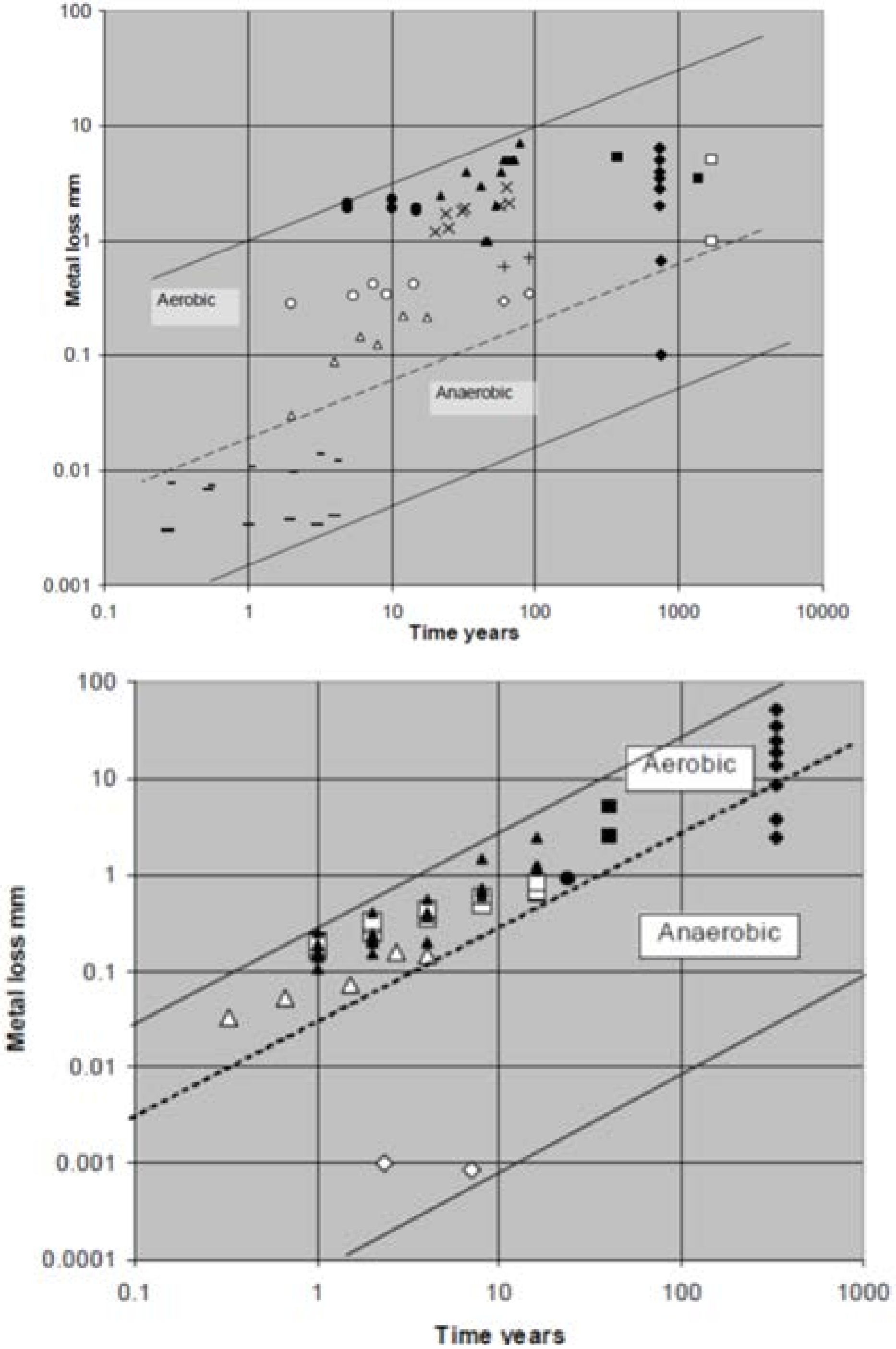

**Figure 19: Compilation of time-dependents depths of corrosion of iron and steel objects in soil (upper) and seawater (lower) under aerobic and anaerobic conditions (Crossland 2005). The lines were used by the original author to denote the best fit and maximum and minimum bounds to the data. The sources of the data can be found in the original reference.**

The corrosion depths shown in Figure 19 come from studies involving a range of alloy types and soil and seawater environments, all of which may or may not be directly relevant to the corrosion behaviour of carbon steel in the DGR. However, the similarity of these analogue corrosion rates with long-term rates measured in the laboratory using modern alloys in well-controlled environments (Diomidis 2014) makes it tempting to place some reliance on the historical data.

It is not just the extent of uniform corrosion that can be obtained from analogue studies. In both the French and Japanese programs use is made of pit measurements from analogues to extend the relationship between the pitting factor (the ratio of the maximum to the mean penetration) as a function of the mean depth of corrosion (Figure 20).

Overall, therefore, there is a far greater direct use of empirical corrosion damage measurements on steel and iron analogues than is the case for copper.

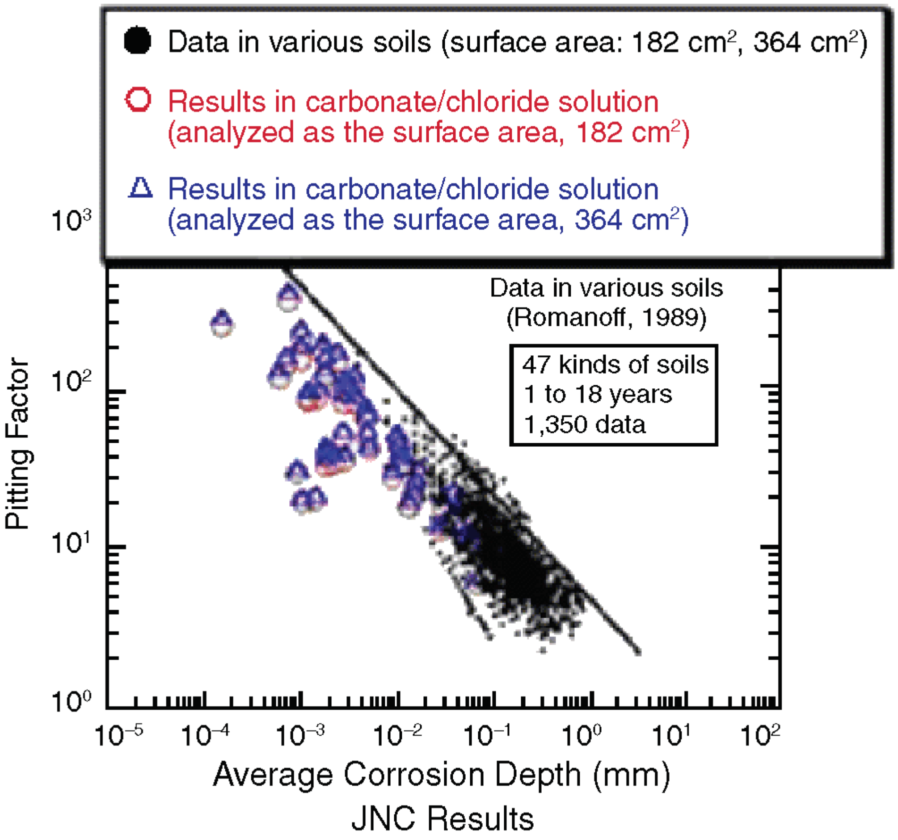

**Figure 20: Pitting factor of carbon steels and iron as a function of average depth of corrosion compiled from various laboratory and analogue sources (Féron et al. 2009). Reproduced with permission of © AMPP.**

# 4. USE OF ANALOGUES TO SUPPORT LONG-TERM CORROSION PREDICTION

## 4.1 TREATMENT OF CORROSION PROCESSES IN THE SAFETY CASE

In order to understand how analogues can be used to support predictions of the long-term performance of UFC it is important to understand how various corrosion processes are treated in the safety case. It is customary to predict the UFC lifetime based solely on the time required to penetrate the copper corrosion barrier, although credit can also be taken for the time to penetrate the steel liner of the copper-coated UFC design (Kremer 2017). Basing UFC lifetimes only on the corrosion performance is acceptable for dual wall copper-steel/iron canister designs (either the KBS-3 or copper-coated designs) because the two barriers serve different functions (copper for corrosion resistance and steel/iron for structural stability) and because there is no significant time-dependent reduction in mechanical properties of the steel/iron structural member due to corrosion. This situation is in contrast to the case of a single-wall steel container design, where the one material provides both corrosion and mechanical resistance and there is a significant impact of corrosion on the mechanical properties of the steel due to the absorption of hydrogen under anaerobic conditions (King et al. 2014a).

When considering the corrosion behaviour of the copper barrier, it is usual to divide the different processes into those that are considered possible under repository condition and those that are not (Kwong 2011; NWMO 2017; Posiva 2012a; SKB 2010a,b). For those processes considered possible, it is then necessary to define a corrosion allowance or a corrosion rate in order to determine the extent of corrosion as a function of time. The corrosion processes included in the lifetime prediction, and the manner in which they are treated in the safety assessment, are similar in the Canadian (Keech et al. 2020), Swedish (SKB 2010b), and Finnish (Posiva 2012a) programs, and include:

- Uniform corrosion due to the initially trapped $O_2$ – corrosion allowance based on a conservative mass-balance approach.
- Localized corrosion under aerobic conditions – treated using a fixed surface roughening allowance.
- External radiolytic corrosion – corrosion allowance based on extrapolation of empirical data or modelling.
- Atmospheric corrosion prior to emplacement (SKB, Posiva) – corrosion allowance based on empirical atmospheric corrosion rate and estimated duration of exposure.
- Localized corrosion under anaerobic conditions (SKB, Posiva) – corrosion allowance based on limited penetration under transport-limited conditions.
- Uniform corrosion under anaerobic conditions – based on rate of supply of sulfide to the UFC surface.

Of the various copper corrosion processes considered unlikely to occur under repository conditions, the most important are:

- Stress corrosion cracking – excluded based on the argument that the pre-requisite conditions of a susceptible material condition, sufficient tensile stress, and required SCC agent will not be present simultaneously.
- Microbially influenced corrosion and biofilm formation on the UFC surface – excluded based on the suppression of microbial activity by the highly compacted bentonite surrounding the UFC.
- Anoxic corrosion in the absence of sulfide – excluded based on the absence of evidence to support the claim of corrosion of copper in $O_2$-free water (Hedin et al. 2018, Senior et

al. 2019) or because of the limited extent of corrosion due to the presence of high [$Cl^-$] (Lilja et al. 2020).

A number of different approaches or assumptions are used, therefore, to support the estimation of the UFC lifetime in the safety case. For example, estimation of the extent of uniform corrosion under anaerobic conditions is based on the assumption that the rate is controlled by the supply of sulfide to the container surface. In turn, this implies that the $Cu_2S$ corrosion product is non-passive, as otherwise the rate would be controlled by the film properties rather than by the properties of the surrounding buffer material. Other corrosion allowances are based on the extrapolation of empirical data, such as the allowances for external radiolytic corrosion, and for localized corrosion under both aerobic and anaerobic conditions.

Other assumptions are used to justify the exclusion of certain corrosion processes. For example, the properties of the compacted buffer are judged to limit microbial activity, for which there is some evidence from analogue studies (Posiva 2012b). The claim that copper does not corrode in $O_2$-free water is based on the argument that the UFC is thermodynamically stable in the repository environment. In the case of corrosion in anoxic high-[$Cl^-$] conditions, a number of approaches can be used, including the extrapolation of empirical corrosion rates (Senior et al. 2019) or the combined assumption of thermodynamic equilibrium at the canister surface with the rate of corrosion determined by the slow transport of corrosion products ($H_2$ or $CuCl_n^{1-n}$) (Lilja et al. 2020).

Thus, a combination of approaches based on the extrapolation of empirical data or the concepts of thermodynamic or kinetic (mass-transport) stability are used to justify the UFC lifetime predictions. The possible future analogue studies discussed in Chapter 5 are assessed based on whether they provide support for the manner in which these various corrosion processes are treated in the safety case.

## 4.2 THERMODYNAMIC VERSUS KINETIC STABILITY

The continued existence of uncorroded metal in natural environments is a consequence of either thermodynamic or kinetic stability. While it would seem likely that native metal deposits can only have persisted over geological timescales because they are thermodynamically stable, it is not apparent from the analogue literature whether this is indeed the case. The conditions under which both copper and iron may be considered to be either thermodynamically or kinetically stable are considered below.

### 4.2.1 Thermodynamic Stability

The issue of thermodynamic stability is conveniently discussed with the use of potential-pH (Pourbaix) diagrams (Figure 21). Pourbaix (1974) defined regions of immunity, corrosion, and passivation based on the boundaries between the stability region of the metal and either dissolved species or solid corrosion products (Figure 22). The boundary between corrosion and “immunity” was defined as corresponding to a dissolved metal ion activity of $10^{-6}$ mol/L and between immunity and passivation based on the relative stability of the two solid phases. Based on this definition, Cu is immune to corrosion in $O_2$-free water (i.e., it is thermodynamically stable) because the zone of immunity extends into the region of stability of $H_2O$ traditionally indicated by the lines (a) and (b) on Pourbaix diagrams. Based on the same criteria carbon steel (as represented by Fe) is not thermodynamically stable on $O_2$-free water (Figure 22(B)).

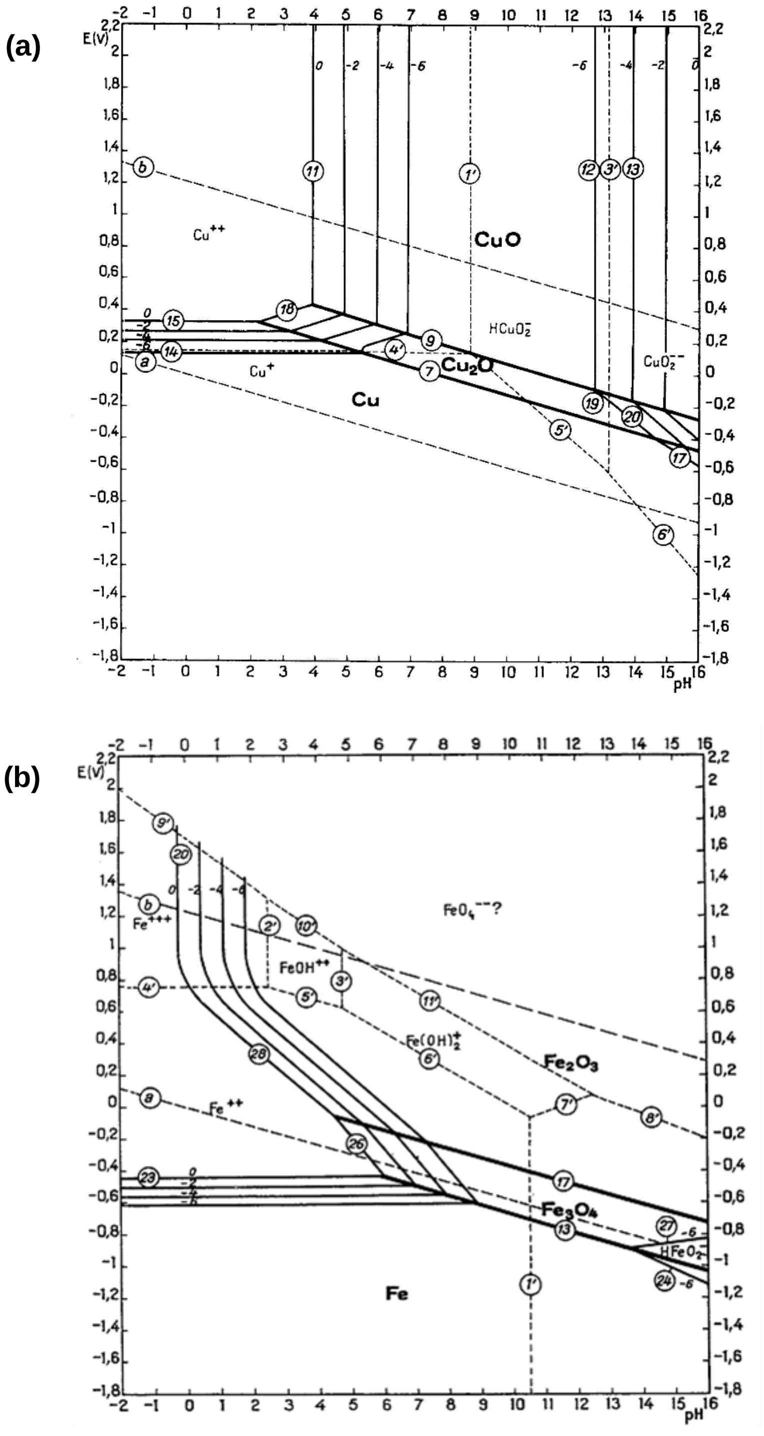

Figure 21: Pourbaix diagrams for (a) Cu-$H_2O$ and (b) Fe-$H_2O$ systems at 25°C (Pourbaix 1974). Reproduced with permission of © AMPP.

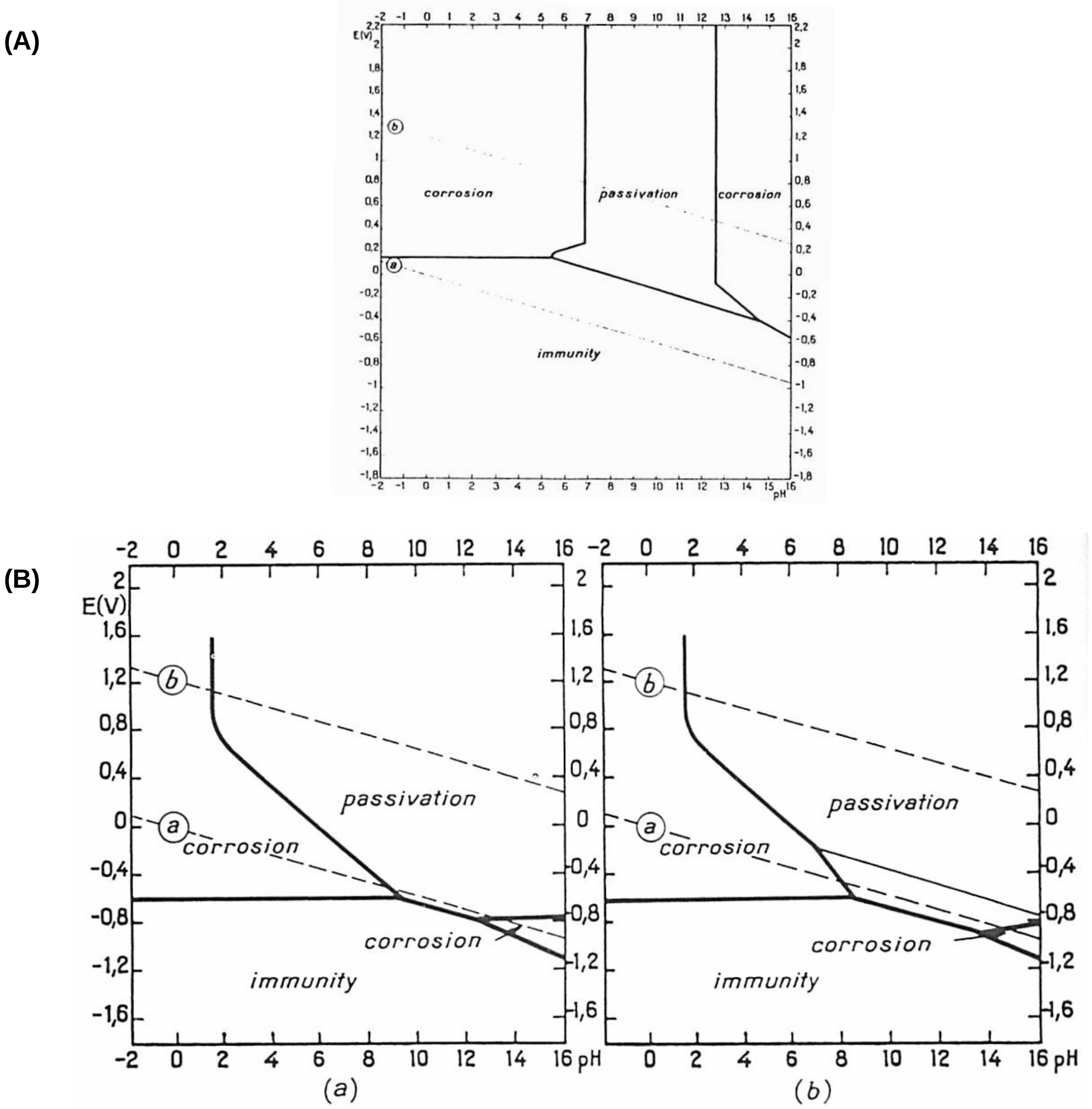

**Figure 22: Zones of immunity, passivation, and corrosion based on Figure 21 for (A) copper and (B) iron on the assumption of passivation by (left) $Fe_2O_3$ or (right) $Fe_2O_3/Fe_3O_4$ films. Reproduced with permission of © AMPP.**

However, Pourbaix's definitions of immunity, corrosion, and passivation were designed for practical purposes for structures with intended service lives of decades. In the case of geological timescales or the expected service lifetime of a UFC, it is necessary to re-assess the criteria for immunity. In particular, the location of the line (a) on the Pourbaix diagram is dependent on the assumed $H_2$ partial pressure

$$H^+ + e^- = \frac{1}{2} H_2 \qquad (5)$$

$$E_{eq} = E^0 + \frac{RT}{F} \ln \left\{ \frac{[H^+]}{p_{H_2}^{1/2}} \right\} \qquad (6)$$

where $E_{eq}$ and $E^0$ are the equilibrium and standard potentials for Reaction (5), respectively, F, R, and T are the Faraday and gas constants, and the absolute temperature, respectively, and the concentration of protons $[H^+]$ and partial pressure of $H_2$ ($p_{H2}$) are more correctly represented by the activity and fugacity. Thus, according to Equation (6), line (a) shifts to more-negative potential with increasing $p_{H2}$, and vice versa.

As is well understood from the debate about the corrosion of copper in $O_2$-free water, copper is <u>not</u> thermodynamically stable under these conditions (Hedin et al. 2018), contrary to the conclusion based on Pourbaix's practical definition of immunity. The equilibrium $H_2$ pressure for the reaction

$$2Cu + H_2O = Cu_2O(cr) + H_2(g) \qquad (7)$$

is 2.3 × $10^{-16}$ atm. at 25°C, based on $\Delta G_f^0$ values of -147.90 kJ/mol (Puigdomenech and Taxén 2000) and -237.140 kJ/mol (OECD NEA 2001) for $Cu_2O$ and $H_2O$, respectively. Thus, if the $H_2$ pressure is sufficiently low, the line (a) would move up and the zone of immunity would disappear on the Pourbaix diagram. However, given the extremely low equilibrium $H_2$ pressure, copper is to all intents and purposes immune to corrosion in pure water.

The situation is different for Fe. Consider the reactions:

$$Fe + 2H_2O = Fe(OH)_2(cr) + H_2(g) \qquad (8)$$

and

$$3Fe + 4H_2O = Fe_3O_4(cr) + 4H_2(g) \qquad (9)$$

for which the equilibrium $H_2$ pressures are 13.8 MPa and 84.7 MPa, respectively (based on $\Delta G_f^0$ values of -486.5 kJ/mol and -1015.4 kJ/mol for $Fe(OH)_2$ and $Fe_3O_4$, respectively, Wagman et al. 1982). These $H_2$ pressures, especially that for the formation of magnetite, would likely exceed the strength of the host rock and are impossible to achieve either in the laboratory or in a DGR setting.

Even though copper is effectively immune to corrosion in $O_2$-free $H_2O$, the presence of ligands for Cu(I), such as $Cl^-$ and $HS^-$, could induce corrosion in anoxic environments. Chloride is a relatively weak complexing agent for copper(I) but does promote the anoxic corrosion of copper at sufficiently low pH and high $[Cl^-]$:

$$Cu + nCl^- + H^+ \rightleftharpoons CuCl_n^{1-n} + \tfrac{1}{2}H_2 \qquad (10)$$

Figure 23 shows the equilibrium concentrations of dissolved corrosion products as a function of $Cl^-$ concentration (Lilja et al. 2020). A dissolved $H_2$ concentration of $10^{-7}$ mol/kg is equivalent to a partial pressure of 1.3 × $10^{-4}$ atm, or approximately 12 orders of magnitude higher than that for reaction (7). However, the equilibrium dissolved Cu(I) concentration is <$10^{-6}$ mol/kg even for 5 mol/kg $Cl^-$ and is insignificant in terms of corrosion (Lilja et al. 2020). This is consistent with the analyses of Crisman and Jacobs (1982) regarding the stability of the Michigan native copper deposits in the presence of saline deep mine waters.

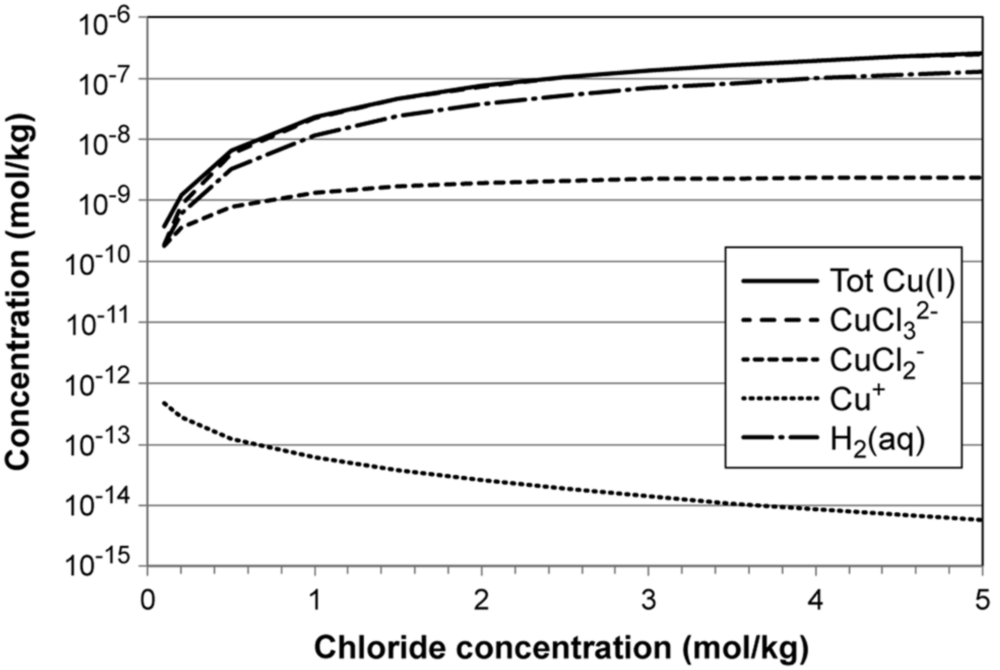

**Figure 23: Predicted equilibrium concentrations of dissolved species for the corrosion of copper in anoxic chloride solution as a function of chloride concentration at 25°C (Lilja et al. 2020). Reproduced with permission of © authors under Creative Commons License.**

Sulfide is a much stronger complexing agent for Cu(I) and copper corrodes readily in the presence of $HS^-$ to form $Cu_2S$

$$2Cu + HS^- + H_2O \rightarrow Cu_2S + H_2 + OH^- \qquad (11)$$

The equilibrium $H_2$ pressure for reaction (11) is 760 MPa at 25°C and pH 8 and a sulfide activity of $10^{-5}$ mol/L (based on $\Delta G_f^0$ values of -84.11 kJ/mol, 12.243 kJ/mol, and -157.33 kJ/mol for $Cu_2S$, $HS^-$, and $OH^-$, respectively, Puigdomenech and Taxén 2000).

Figure 24 shows the Pourbaix diagram for the Cu-S-$H_2O$ system considering only sulfide and sulfate as the stable dissolved sulphur species. The interesting feature of this diagram is that there are two regions of stability of copper metal: one at very low potentials and the other between the regions of stability of $Cu_2S$ and $Cu_2O$. The existence of this latter region is a consequence of the thermodynamic stabilities of sulfide and sulfate, with the oxidized species predicted to be the more thermodynamically stable at potentials lower then the Cu/$Cu_2O$ equilibrium line. As can be seen from the figure, this second region of stability of copper metal occurs at potentials more oxidizing than the $H_2O/H_2$ equilibrium line. Even if the formation of thiosulfate is assumed (thiosulfate also oxidizes copper to $Cu_2O$, Macdonald and Sharifi-Asl 2011), a region of copper metal stability is still predicted to exist between the $Cu_2S$ and $Cu_2O$ regions. What is interesting about this E-pH diagram is that a section upwards through the various stable solid species at pH 8-10 is analogous to that observed in geological supergene copper deposits (Figure 7). Thus, observations in nature are consistent with the predictions based on thermodynamics.

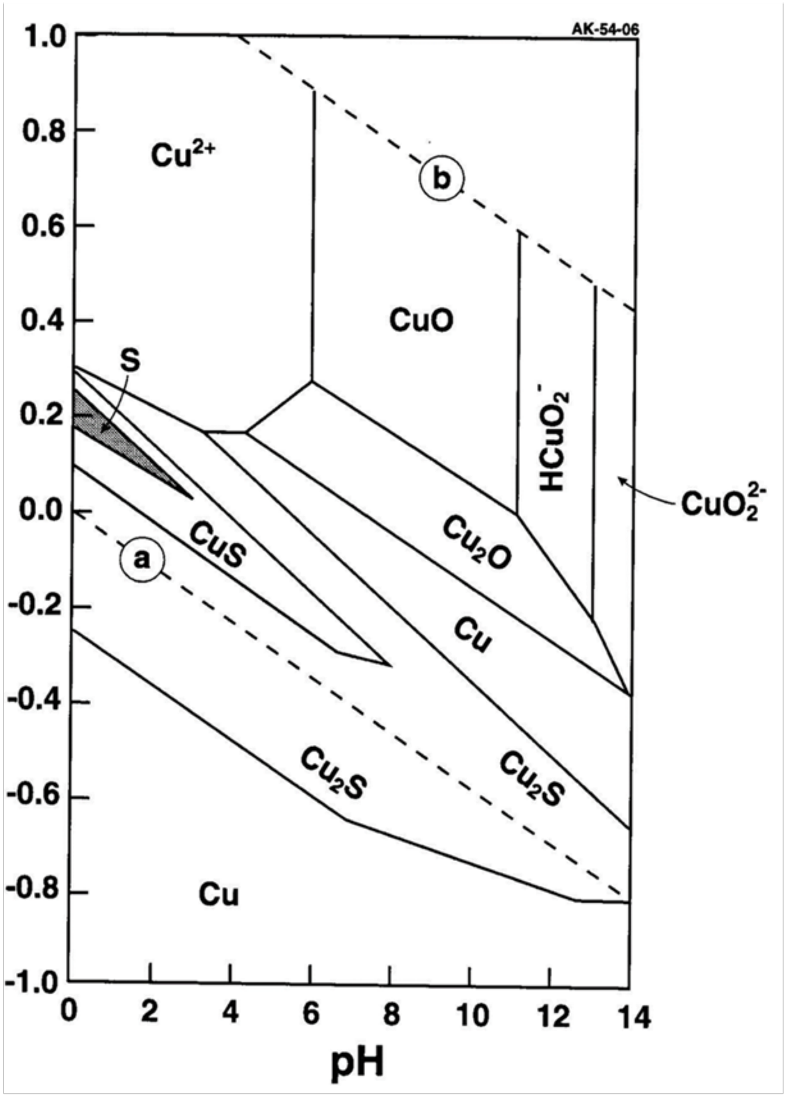

**Figure 24: Pourbaix diagram for the Cu-S-$H_2O$ system at 25 °C (King 1996, Woods et al. 1987). Activity of dissolved copper $10^{-6}$ mol/L, activity of dissolved S species (sulfide and sulfate) $10^{-2}$ mol/L. The shaded area labelled "S" shows the stability region of elemental sulphur. Reproduced with permission of © Atomic Energy of Canada Limited.**

In summary, therefore, it would appear that there is every reason to believe that native copper, and by inference the uncorroded copper-coated UFC, could be thermodynamically stable in the DGR. In the absence of S species, this thermodynamic stability would be the result of the accumulation of sufficient corrosion products ($H_2$ and/or dissolved Cu(I)) species) for the system to attain equilibrium. This does not necessarily mean that corrosion will not occur, but any corrosion would be limited by the rate at which these corrosion products can be transported away from the UFC surface, which implies a degree of kinetic stability (see Section 4.2.2.1). Thermodynamic stability under anaerobic conditions in the presence of S species is unlikely unless the S activity is exceedingly small. For a $H_2$ partial pressure of 10 MPa (which might be achieved at the canister surface in a saturated repository in the presence of compacted buffer material), the sulfide activity would need to be less than approximately $10^{-7}$ mol/L in order to achieve equilibrium. It is conceivable that for transport-limited corrosion of copper UFC due to remotely produced sulfide, such a low interfacial [$HS^-$] might be achieved (King et al. 2017). In that case, thermodynamic stability might be possible even in the presence of sulfide. In the case of Fe, however, it is unlikely that thermodynamic stability could be achieved due to the accumulation of $H_2$ since the equilibrium partial pressure far exceeds the breakthrough pressure of gas through compacted buffer material and, in some cases, the strength of the host rock. Thermodynamic stability of Fe under geological or repository conditions is only likely, therefore, if the Fe is galvanically coupled to a more-active material, such as Al or Zn.

What this analysis does show, however, is that observations from various copper deposits are consistent with the predictions from thermodynamic analysis. In turn, this implies that thermodynamics can be used to predict the long-term corrosion behaviour of copper-coated UFC in the repository.

### 4.2.2 Kinetic Stability

If native metallic deposits or anthropogenic artefacts are not thermodynamically stable, then their continued existence relies on kinetic stability. Various methods are used industrially to ensure corrosion protection by limiting the kinetics of dissolution, including the use of inhibitors, coatings, and cathodic protection. Here, two further methods of ensuring kinetic stability are discussed in terms of their relevance to natural analogues.

#### 4.2.2.1 Mass-transport Considerations

The rate of corrosion of a native metal deposit, archaeological artefact, or the UFC may be limited by the rate of transport of reactants towards, or of corrosion products, away from the corroding surface. Transport of remotely produced sulfide to the UFC surface is considered to be the rate-controlling step for the anaerobic corrosion of copper in the DGR (Briggs et al. 2017, King et al. 2017).

The concept of a mass-transport limited corrosion (alteration) process has been invoked to explain the persistence of both copper and iron native deposits. For example, Crisman and Jacobs (1982) suggested slow mass transport processes could account for some aspects of the Keweenaw copper deposits, as did Milodowski et al. (2002) in reference to the Littleham Cove copper. More interestingly, Hellmuth (1991b) suggested that the low permeability of the basalt matrix rocks contributed to the preservation of the Bühl native iron deposits. None of these authors identified what the nature of the rate controlling process was or, indeed, what species was considered to be limiting. This is particularly interesting in the case of the Bühl iron deposit as the calculations above suggest that the system is unlikely to have been at equilibrium because of the requirement for a high $H_2$ partial pressure. It is possible that the transport of $H_2O$ through the basalt to the iron was rate limiting.

Mass transport control can not only result from the low diffusivity/permeability of the host medium, but also because of a low concentration of corroding species. For example, the rate of sulphidation of copper could be transport limited because of a low rate of remote sulfide production, rather than the rate of $HS^-$ transport to the corroding surface. No such mechanism has been proposed in the analogue literature reviewed here.

#### 4.2.2.2 Passivation and Protective Corrosion Products

Another significant kinetic limitation that could account for the long-term survival of metallic objects is that the surface becomes protected by a passive film. Corrosion rates of contemporary Ni-Cr-Mo-, Zr-, and Ti-based alloys are of the order of nm/yr (Diomidis 2014) and some analogues may exhibit similarly protective passive films. The most obvious analogue examples of a passive material are the architectural features embedded in concrete from cathedrals and other structures studied in the French program (Chitty et al. 2005a,b, 2007; L'Hostis et al. 2008). In fact, these artefacts may not have been as passive today as they were when originally installed as the concrete matrix would have undergone carbonation over the centuries, resulting in a decrease in pore-water pH and a loss of passivity (Burger et al. 2011b). Other examples where passivity has been invoked to explain the persistence of analogues include the Keweenaw copper deposits (Crisman and Jacobs 1982), although it is unclear what the nature of the passive film was, and the Roman nails of Inchtuthil which were protected by the formation of protective film due to aerobic corrosion of the nails around the periphery of the pit in which they were found (Mapelli et al. 2008, Milodowski et al. 2015).

In other cases, the corrosion product film that develops on artefacts is not considered to be passive, but instead is classified as being porous (Figure 16). This is the case for the DPL (dense product layer) and TM (transformed media) layers in the conceptual model for the corrosion of iron objects in soil developed in the French program (Figure 15). In this case, the corrosion product layers may slow the rate of corrosion by acting as a mass-transport barrier rather than being a truly passive film.

In fact, for copper, it is argued in the safety case that passivation of the UFC surface is unlikely under either aerobic or anaerobic conditions. The “active” or “nonpassive” nature of the surface film is an important concept in the justification of long container lifetimes because non-passive surfaces cannot be subject to localized film breakdown and the pitting that may result, whereas passive surfaces may be subjected to localized corrosion. As Canadian DGR conditions are likely to produce “active” surface films (Briggs et al. 2020), copper analogues that owe their persistence to the formation of a passive film cannot be generally considered good analogues for the state of the UFC surface in the repository. In this regard, the nature of the $Cu_2S$ film formed on native Cu in water-bearing fractures of the Hyrrkölä analogue is of interest (Figure 3). The extent of alteration (sulphidation) appears to be of the order of 10’s-100’s $\mu$m but may have occurred over periods of 100,000’s or millions of years (U-series disequilibrium studies suggest the alteration may have ceased as much as 200,000 years ago, Marcos and Ahonen 1999, Marcos et al. 1999). The question then is whether the apparently limited alteration is due to a very slow rate of mass transport or the formation of a passive $Cu_2S$ film?

## 4.3 ANALOGUES IN SUPPORT OF UFC LIFETIME PREDICTIONS METHODOLOGY

In this section, the available analogue evidence in support of the methodology used to predict UFC lifetimes described in Section 4.1 is briefly discussed. The focus here is on the methodology used for copper-coated UFC in the Canadian program, although there is clear overlap with similar methodologies used in support of the KBS-3 style canister proposed for use in Sweden and Finland.

Suggestions for further analogue studies that could provide useful support for different aspects of the lifetime prediction are described in Chapter 5.

### 4.3.1 Copper Corrosion Barrier

The description of the different corrosion processes for the copper corrosion barrier described below is based on the treatment summarized by Keech et al. (2020).

| | |
|---|---|
| *Corrosion from radiation-related processes* | There are no existing analogue studies with which to quantify the extent of radiolytic corrosion of the copper corrosion barrier or of the possibility of radiation damage. Current estimates of radiolytic corrosion are based on empirical corrosion rates and/or bulk radiolysis modelling and the assumption of fast interfacial kinetics. |
| *Non-uniform oxic corrosion* | The corrosion allowance of 100 μm used currently is based on surface roughness measurements on laboratory specimens following exposure to simulated near-field environmental conditions. No equivalent measurements have been made on analogues, although there is no reason why such measurements could not be made (see Section 5.1.2). The available analogue evidence for aerobic localized corrosion is in the form of pit depths (Bresle et al. 1983, Denison and Romanoff 1950), which have been variously used to estimate a pitting factor or a maximum pit depth based on extreme-value statistics (King and LeNeveu 1992, King and Kolář 2000), or, most recently, a probabilistic pitting model (Briggs et al. 2020). |
| *Unconverted oxic corrosion* | This corrosion allowance accounts for copper that corrodes under oxic conditions but which does not precipitate as an oxide film on the UFC, and includes dissolved copper in the bentonite pore water, precipitated basic Cu(II) salts, and Cu(II) adsorbed on the bentonite. The extent of corrosion is traditionally estimated based on either a conservative mass-balance calculation or the results of reactive-transport modelling which accounts for other processes that consume part of the initially trapped $O_2$. Because of the difficulty of defining the flux and inventory of $O_2$ in natural systems, there is no known analogue of the mass-balance approach. The Copper Corrosion Model (CCM), which is an example of a reactive transport model that accounts for various near-field $O_2$-consumption processes, has been validated against observations from the Kronan bronze cannon analogue (King and Kolář 1996). |
| *Oxide corrosion converted to sulfide-containing product* | The conversion of $Cu_2O$ to $Cu_2S$ by sulfide has been studied in the laboratory, but has not been considered in detail using analogues. Both native $Cu/Cu_2O$ and $Cu/Cu_2S$ assemblages have been found in separate fractures at the Hyrrkölä site (Section 2.1.2), but there is no evidence for the conversion of $Cu_2O$ to $Cu_2S$ (Marcos and Ahonen 1999, Marcos et al. 1999). There is evidence for alteration of $Cu_2O$ to $Cu_2S$ in the Littleham Cove native copper deposits (Section 2.1.3), but the chalcocite was described as a minor phase (Milodowski et al. 2002). The reverse process, the conversion of $Cu_2S$ to $Cu_2O$ under oxidizing conditions is a fundamental process in the formation of supergene native copper deposits (Figure 7-Figure 9, Section 2.1.4). |
| *Additional sulfide corrosion* | The additional sulfide corrosion allowance accounts for remotely produced sulfide that diffuses to the UFC surface. There are several components to this calculation, including definition of the source term |

| | |
|---|---|
| | (i.e., the sulfide concentration and the location at which it is produced), the permeability of the surrounding medium and whether transport is diffusive and/or advective in nature, and the impact of others sinks for sulfide. Marcos (1996) and Narcos and Ahonen (1999) estimated a minimum sulfide concentration of $10^{-6}$ mol/L to $10^{-5}$ mol/L at the Hyrrkölä site (depending on the assumed temperature) based on the conditions for the thermodynamic stability of the observed djurleite phase and a pH 7.8 (Section 2.1.2). No indication of the mass-transport conditions was provided. As discussed in Section 5.1.4, iron sulfide is thought to be a significant sink for sulfide diffusing to the UFC surface and the relative stabilities of mackinawite (FeS), greigite ($Fe_3S_4$), and pyrite ($FeS_2$) have been studied in relation to observations of corrosion products of Fe in water-logged sites (Rémazeilles et al. 2019a,b). |

In addition to corrosion processes that are expected to occur, there are a number of processes that are considered not to be possible under repository conditions and for which there might also be supporting analogue evidence.

| | |
|---|---|
| *SCC* | It is difficult to use analogue evidence to support the exclusion of SCC. Copper analogues are inevitably an imperfect representation of the disposal system, both because the material composition and microstructure are different from those of the copper coating and also because the environment to which the analogue was exposed cannot simulate the range of conditions during the long-term evolution of the DGR. These shortcomings apply to any corrosion process, but are particularly important for environmentally assisted cracking mechanisms which tend to be highly specific to the material properties, the presence of specific chemical species, and the need for sufficient tensile stress. In addition to these considerations, it can be difficult to prove a negative proposition, i.e., the absence of SCC, based on analogue evidence; just because an archaeological artefact does not exhibit stress corrosion cracks, how can we be certain that all of the pre-requisite factors were present? Evidence for SCC of brass artefacts has been reported, such as the evidence for a brittle fracture surface on a sample from Ferryland (Section 2.2.3) and the season cracking of cartridge cases (Section 2.2.4.1). However, although these observations show that copper alloys are susceptible to SCC, they do not show that copper-coated UFC are not. |
| *Near-field MIC and biofilm formation* | Near-field microbial activity is excluded from consideration based on multiple lines of evidence that suggest that one or more of the low water activity, high swelling pressure, and/or lack of physical space in compacted bentonite suppresses activity. If there is no microbial activity in the bulk of the buffer then, by inference, it is assumed that there is no possibility of biofilm formation on the UFC surface. There is consistent evidence from analogue studies that microbial activity is prevented in porous media with pore throat sizes $\leq 0.2\ \mu m$, based on measurements in Opalinus Clay (Stroes-Gascoyne et al. 2007), shale-sandstone formations (Fredrickson et al. 1997), Boom Clay |

(Boivin-Jahns et al. 1996), and bentonite from tunnels in the Tsukinuno mine (Fukunaga et al. 2005). The limiting factor in these studies was specifically the lack of physical space and the microbes that were present remained viable and could be cultured given appropriate nutrients, water, and space. There is also a lot of analogue evidence for the effect of low water availability in suppressing microbial activity (e.g., Kieft et al. 1997). The important point is that these factors limit microbial activity. There is much analogue evidence to show that microbes can withstand extreme conditions of desiccation, pressure, lack of space, elevated temperature, radiation fields, etc., but the argument here is not that they do not survive but that they are not active.

*Corrosion in $O_2$-free $H_2O$*

It is difficult to prove that copper does not corrode in $O_2$-free pure water based on evidence from analogues. Even though the existence of metallic copper in contact with an aqueous phase is consistent with the stability of copper, that stability may be the result of a passive $Cu_2O$ film which may limit the rate of corrosion but does not stop it entirely. Given that the equilibrium $H_2$ partial pressure and dissolved Cu(I) concentrations are infinitesimally small (of the order of $2 \times 10^{-9}$ atm and $3 \times 10^{-12}$ mol/L, respectively, Hedin et al. 2018), it is physically impossible to purify the initial environment in order to observe corrosion under well-controlled laboratory conditions, let alone in the context of a natural analogue.

*Corrosion in anoxic high-[$Cl^-$] pore water*

The persistence of copper in contact with $O_2$-free brines was considered as one of the mechanisms to account for the long-term stability of the Keweenaw native copper deposit (Crisman and Jacobs 1982). For the UFC, the argument can either be made that the rate of corrosion in anoxic brines is low, even on geological timescales, or that the system reaches equilibrium and that corrosion continues at the rate at which corrosion products (either $H_2$ or dissolved Cu(I)) is transported away from the UFC surface (Keech et al. 2020, Lilja et al. 2020). In the first instance, analogue evidence is required for the kinetics of the forward reaction. In the second approach, analogue evidence for the establishment of equilibrium is required, as well as of the rate of transport of corrosion products. Crisman and Jacobs (1982) considered the thermodynamic equilibrium in brines, but did not address the mass-transport of corrosion products.

### 4.3.2 Carbon Steel Vessel

Kremer (2017) considered the corrosion consequences for the carbon steel vessel of an initial through-coating defect in the copper corrosion barrier. The assessment was based on an empirical corrosion rate model that accounted for the dependence of the rate on temperature, redox conditions, and the degree of saturation. The corrosion rates predicted for the carbon steel vessel ranged from 10 μm/a under warm, aerobic conditions to 0.1 μm/a under cool, anoxic conditions. Other corrosion processes that might affect the steel vessel are galvanic corrosion under aerobic conditions and hydrogen-induced cracking in anoxic environments.

| | |
|---|---|
| *Uniform corrosion rate of carbon steel* | As discussed in Section 3.2.4, there is a large database of empirical corrosion rates derived from various analogue studies. The range of corrosion rates used by Kremer (2017) are well-supported by the rates shown in Figure 17-Figure 19. |
| *Galvanic corrosion of steel in contact with copper under aerobic conditions* | No specific analogue study has been found that specifically addresses galvanic corrosion of steel or iron in copper with copper alloys under aerobic conditions. |
| *Hydrogen-induced cracking of steel* | As in the case of the SCC of the copper corrosion barrier, it is difficult to conceive of a suitable analogue for the HIC of the steel vessel. Not only is the susceptibility to HIC material-specific, but the environment to which the steel vessel will be exposed (limited amount of entrained water, high radiation fields, elevated temperature) is quite unlike that for the majority of natural analogues. However, as discussed in Section 5.1.12, there may be some value in reviewing the conditions under which pipeline steels have, and have not, been found to be susceptible to various forms of H-related degradation. |

### 4.3.3 Structural Integrity and Joint Mechanical-Corrosion Degradation Processes

The structural integrity of the UFC is outside of the scope of the current report. However, the availability of analogues to support two particular aspects of the mechanical performance of the copper-coated UFC design are briefly considered below.

| | |
|---|---|
| *Structural stability under compressive isostatic loads* | The best analogy for the high hydrostatic load to which the UFC will be exposed is the structural performance of submarines and deep-sea bathyspheres. |
| *Delamination of the copper coating due to formation of expansive steel corrosion products* | In contrast to the absence of studies on galvanic corrosion under aerobic conditions, there are analogue studies of the consequences of galvanic coupling between iron and copper alloys in the absence of $O_2$ (Smart and Adams 2006; Smart et al. 2003, 2004). No evidence was found for the formation of expansive iron corrosion products or of any resulting deformation. |

## 4.4 USE OF CONTAINER ANALOGUES IN INTERNATIONAL WMO PROGRAMS

All international waste management organizations (WMOs) make use of analogues to some degree, whether it be in the development and validation of conceptual models, the provision of data, or for building confidence in long-term predictions. This section provides a brief summary of how analogues have been used by various WMOs.

### 4.4.1 Canada

Analogues have been used extensively in the Canadian program to validate conceptual models, to provide input data for models for localized corrosion, and for general confidence building purposes.

Analogues are used in the safety case to build confidence in the long-term predictions. The postclosure safety assessment reports for the last two NWMO safety cases (NWMO 2013,

2017) each contain a section on analogues in which analogues for used nuclear fuel, the engineered barriers (UFC, bentonite, and sealing materials), and the geosphere are presented and discussed in the overall context of the safety case. Native copper analogues are used to support the longevity of the copper corrosion barrier and anthropogenic and native iron deposits are used in support of the long-term performance of the carbon steel vessel (NWMO 2017).

Data from various anthropogenic copper analogues has been used in past studies to estimate maximum pit depths on copper containers (King and Kolář 2000, King and LeNeveu 1992). Pit-depth data from Bronze Age artifacts (Bresle et al. 1983) and the NBS burial studies (Denison and Romanoff 1950, Romanoff 1989) were analyzed using extreme-value statistics by fitting the maximum pit depth from a number of samples to a Gumbel-type double exponential distribution. The Gumbel distribution is characterized by two parameters, the shape parameter and the location parameter. The time dependence of the maximum pit depth was estimated by using the time dependence of the location parameter derived from separate sets of data corresponding to different exposure times. (The shape parameter was found to be invariant with time). The extrapolated location parameter was then used to estimate the depth of the deepest pit on any of the UFC in the repository after 1 million years, based on the conservative assumption that aerobic conditions persisted indefinitely.

Analogue data have also been used to validate the CCM reactive-transport model (King and Kolář 1996). An attempt was made to reproduce the copper concentration profiles observed in the clay sediments in contact with the submerged bronze cannon from the Kronan (Hallberg et al. 1988) using the CCM. The agreement was reasonable, although the model predictions underestimate the extent to which the copper had diffused, possibly because of uncertainty over the temperature dependence of the diffusion coefficient for $Cu^{2+}$ (King and Kolář 1996). The model has been developed further since that time and another attempt to replicate the observed findings might be more successful.

### 4.4.2 France

The study of analogues is a key feature of the Andra program, which is reflected in the large number of studies published in the literature (see Appendix A). An integrated approach is being taken, in which information from analogues and the results of laboratory and large-scale *in situ* experiments is used to develop and validate predictive models (Figure 25). The main purpose of the analogue studies is to develop conceptual models for the corrosion of steel in soils, under atmospheric conditions, and in the presence of concrete. These conceptual models are based on extensive analyses of the structure and properties of the corrosion product layers and surrounding medium from various analogue sites in France. In addition to information about the structure and composition of the corrosion layers, other information, such as the film porosity and the location of anodic and cathodic reactions, has also been obtained.

This information in then used in numerical simulation and modelling (Figure 25). Mohamed-Said et al. (2017) describe a 1-D, finite-element, reactive-transport model to simulate the growth of a thick $FeCO_3$ corrosion product layer. The model is similar in structure to similar models developed in the oil and gas industry and also for carbon steel UFC in the Canadian program (King et al. 2014b). In particular, Mohamed-Said et al. (2017) considered the effect of different models for the formation of the porous $FeCO_3$ film on the predicted corrosion rate.

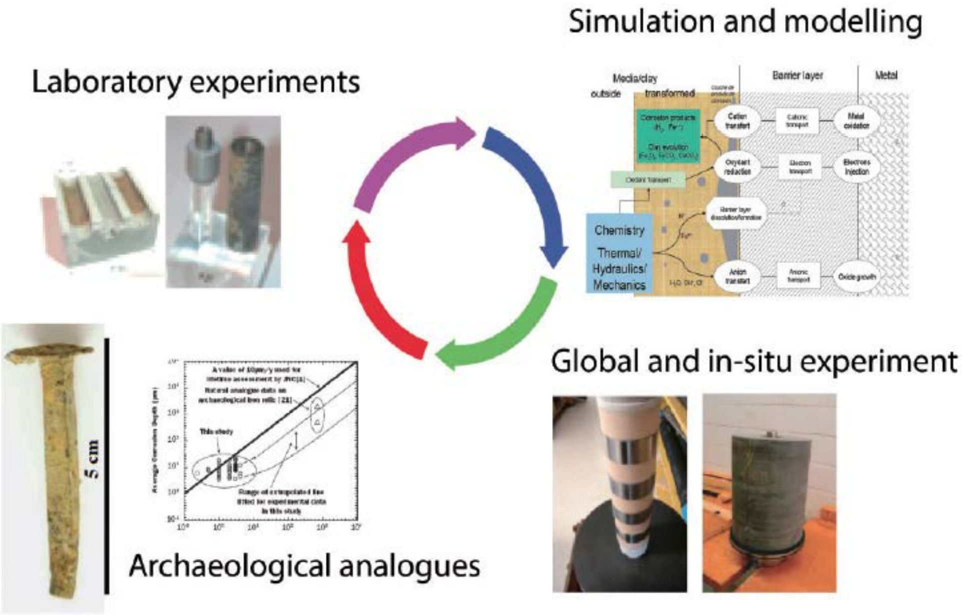

**Figure 25: Overall approach to the justification of container lifetime predictions in the Andra program (Dillmann et al. 2014). Reproduced with permission of © Taylor and Francis.**

### 4.4.3 Japan

In addition to general confidence building, analogue information is used in the Japanese program to assist in the extrapolation of laboratory corrosion rates to longer timescales (JNC 2005; Mitsui et al. 2012; Yoshikawa 2008, 2009). Figure 26 shows a comparison of corrosion depths measured during long-term laboratory experiments up to 4-year duration, and analogue studies from underground pipes (up to 100 years exposure), and from archaeological artefacts (up to 1500 years exposure). These latter measurements correspond to a similar exposure period as the 1000-year prediction for the container, also shown in Figure 26. The similarity of the corrosion depths from the analogues and that predicted for the container is designed to provide support for the long-term prediction.

### 4.4.4 Finland

Analogues are used in the general context of confidence building for different aspects of the performance of the various natural and engineered barriers system in the Finnish program. The suite of safety case documents produced for the construction licence application included a stand-alone document on “complementary considerations” (Posiva 2012b), which was essentially a review of analogue evidence in support of the safety assessment. Anecdotally, the 2012 Complementary Considerations report was the single most downloaded report of the various safety case documents.

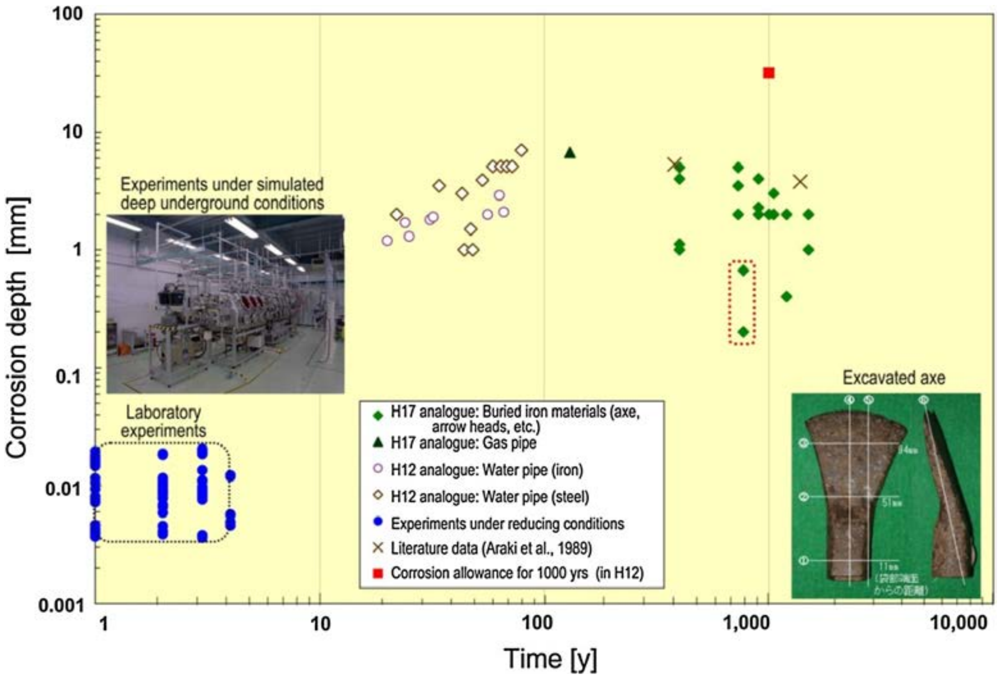

**Figure 26: Comparison of corrosion rates derived from laboratory and analogue studies and the 1000-year corrosion allowance for carbon steel containers in the Japanese program (JNC 2005).**

### 4.4.5 Sweden

Very much like the Finnish program, SKB uses analogues to build confidence in the models and predictions for the various natural and engineered barriers. The more-recent focus of the SKB corrosion program has been on the development of data and models based on laboratory studies, although historically a number of analogue studies have been performed, including the study of Bronze Age artefacts (Bresle et al. 1983), the Kronan bronze cannon (Hallberg et al. 1988) and the Littleham Cove native copper deposits (Milodowski et al. 2000, 2001, 2002, 2003).

### 4.4.6 Switzerland

Historically, the Swiss program had a strong analogue component (Miller et al. 1994) although, more recently, the emphasis on the use of analogues for long-term prediction of the behaviour of the container has been secondary to the use of laboratory corrosion rates.

### 4.4.7 Other Countries

Other national programs that have used analogue studies to support prediction of the long-term corrosion performance of the container include those from Taiwan (Tsai 2017), China (Chen A. et al. 2004, 2015 and Chen Z. et al. 2004, 2005), Ukraine (Demchenko et al. 2004, Manichev et al. 2005), Argentina (Palacios et al. 2005), the U.K. (Milodowski et al. 2015), and the U.S. (Crisman and Jacobs 1982, Johnson and Francis 1980, Sridhar and Cragnolino 2002).

# 5. POTENTIAL FUTURE ANALOGUE STUDIES

The focus of this chapter is on identifying potential future analogue studies that can help support the long-term prediction of the corrosion (and mechanical) behaviour of the UFC. There is little value to be gained from what might euphemistically be referred to as “stamp collecting”, i.e., unfocussed analogue studies with no clearly defined aim. Rather than describing specific analogue studies, the discussion is structured in terms of different topics associated with the underlying understanding or prediction of the long-term performance of the UFC and for which the study of analogues may or may not prove useful. The first section describes areas in which the use of analogues would be useful, regardless of whether specific studies or analogues can be identified. The relative importance of each of these topics, based on the opinion of the current author, is also given. In the second section, topics that may be of equal importance but for which the use of analogues is unlikely to be as helpful in supporting the safety case are considered. The intent of this second list is to identify possible future analogue studies which, in the current authors opinion, are less worthwhile pursuing. This does not mean that topics in this section are not important, it may simply be that evidence from analogues would not be highly supportive. In each case, the rationale for the study and the reasons why the use of analogues would, or would not, be useful are discussed.

As above, the definition of an analogue is used in the broadest sense and includes contemporary anthropogenic analogues.

As discussed in the Introduction, there are various uses of the information obtained from analogue studies. The focus in this chapter is on information that specifically contributes to the development or validation of conceptual models or the provision of data. In a sense, all analogue studies help to “build confidence” in the UFC lifetime prediction, but that attribute alone is not considered here in whether a particular study is deemed to be useful or not. However, it is recognized that some analogue studies, such as the study of local native copper artefacts, are useful specifically for the reason that they help build confidence in the overall program.

Table 2 summarizes the future analogue studies that are considered to be useful, while Table 3 summarizes those which, in the opinion of the current author, are less worthwhile.

## 5.1 USEFUL ANALOGUE STUDIES

### 5.1.1 Properties of $Cu_2S$ Corrosion Product

The properties of $Cu_2S$ films formed on copper is currently a matter of debate in the corrosion literature and centres on whether the films should be regarded as porous and non-protective (Martino et al. 2019a,b) or passive and susceptible to localized film breakdown and pitting (Huttunen-Saarivirta et al. 2018, 2019). It is apparent that $Cu_2S$ film properties are highly dependent on the rate at which they are grown, i.e., on the sulfide flux, and that films grown under repository conditions will undoubtedly be porous (Salonen et al. 2020).

**Table 2: Summary of Useful Future Analogue Studies.**

| Section | Topic | Rationale | Analogue Identification/ Availability | Importance |
|---|---|---|---|---|
| 5.1.1 | Properties of $Cu_2S$ corrosion product | Evidence to support position that $Cu_2S$ films formed under repository conditions are porous, rather than being passive and susceptible to localized film breakdown. | Native copper deposits (Keweenaw, Hyrkkölä) and possibly anthropogenic examples | High |
| 5.1.2 | Localized corrosion under anaerobic conditions | Evidence for pitting and/or micro-galvanic coupling | Same samples as above | High |
| 5.1.3 | Thermodynamic versus kinetic stability | Identification of reason for long-term stability should be part of all analogue studies | Various | Medium |
| 5.1.4 | Stability of precipitated iron sulfide | Evidence that precipitated iron sulfides act as an irreversible sink for sulfide | Need terrestrial analogue to complement existing evidence from waterlogged shipwrecks | High |
| 5.1.5 | Effect of impurity levels on corrosion of copper | Cold spray copper has relatively high O content, electrodeposited copper can contain amounts of P, S, and/or H depending upon the process | Uncertain | High |
| 5.1.6 | Localized corrosion under aerobic conditions | Evidence for surface roughening versus pitting, under both saturated and unsaturated conditions | Sheltered surfaces exposed to atmospheric conditions, samples exposed to saturated soils for various exposure periods | High |
| 5.1.7 | Rate parameters for mechanistic models | Provide rate constants to replace current guestimates in CCM | Mineral samples (atacamite), modelling of contaminant plumes | Medium |
| 5.1.8 | Radiolytic corrosion of copper | Included as corrosion allowance in lifetime prediction | Decommissioned reactor components, native copper in proximity to U deposits | Medium |
| 5.1.9 | Mechanism of suppression of microbial activity by bentonite | Is low water activity, high swelling pressure, or lack of space the key determining factor, or a combination of all three? | Ideally obtain evidence for microbial activity as a function of clay density | Medium |
| 5.1.10 | Mechanical performance of UFC | Support for structural stability for maximum external load of 45 MPa | Validation of structural models against deep-sea submersible design and failure analysis data | Medium |
| 5.1.11 | Joint corrosion-mechanical effects | Evidence to support absence of corrosion product formation and/or penetration along Cu/steel interface | Galvanically coupled copper/iron artefacts from aerobic environment | Medium |

Continued …

**Table 2: Summary of Useful Future Analogue Studies (concluded).**

| Section | Topic | Rationale | Analogue Identification/ Availability | Importance |
|---|---|---|---|---|
| 5.1.12 | HIC of carbon steel | Possible time-dependent degradation of mechanical properties of structural component of UFC | Review field experience of oil and gas and $H_2$ transport pipelines | Medium |
| 5.1.13 | Fate of initially trapped $O_2$ | Determines duration of oxic phase, as well as extent of general and localized corrosion. Current uncertainty regarding processes responsible for $O_2$ consumption under DGR conditions | Validation of $O_2$-consumption models against mill tailings and landfill analogues. | High |
| 5.1.14 | Conversion $Cu_2O$ to $Cu_2S$ | Included in UFC lifetime corrosion allowances | Possible native copper deposit, anthropogenic samples | High |

**Table 3: Summary of Less-worthwhile Analogue Studies**

| Section | Topic | Rationale | Analogue Identification/ Availability | Importance |
|---|---|---|---|---|
| 5.2.1 | SCC of copper | Process is highly specific to material, stress, environment. Difficult to prove a negative proposition using analogue. | - | Low |
| 5.2.2 | Radiation damage of copper and steel | Extremely unlikely for UFC fluence. | Irradiated test reactor components, reactor pressure vessel steel | Low |
| 5.2.3 | Corrosion rate of copper and steel | Not useful for copper, lots of existing data for iron/steel | - | Low |
| 5.2.4 | HIC of carbon steel | Process is highly specific to material, environment. Difficult to prove a negative proposition using analogue. | - | Low |

**Figure 27: Image of a vein of native copper (light) and chalcocite (dark) from the Baltic mine (Butler and Burbank 1929). The exact locations of the copper and chalcocite veins were not identified in the original publication. Credit: U.S. Geological Society.**

Nevertheless, it would be useful to demonstrate the porous nature of the $Cu_2S$ through the characterization of such films on analogues where the underlying copper metal has undergone a certain degree of sulphidation. Ideally, such studies would not only characterize the properties of the film but also provide some indication of the corresponding sulfide flux. As well as properties such as the porosity, structure, and adherence of the $Cu_2S$ films, it might be possible to decorate the site of the cathodic reaction by exposure of the sample to an aqueous $Cu^{2+}$ solution (Saheb et al. 2011a).

One obvious source of suitable samples is from the various native copper deposits described in Section 2.1. Figure 27 shows an image of a sample from the Baltic mine in the Keweenaw region. Chalcocite is described as being widespread throughout the region but not abundant in any one location, although veins of solid chalcocite several inches in width are found in the Baltic lode (Butler and Burbank 1929). One issue to bear in mind is whether the $Cu_2S$ is an alteration product of the original native copper or whether Cu has formed from the oxidation of $Cu_2S$ (as in supergene formations). The main interest here is in samples where the primary native copper has been subsequently exposed to sulfide to form the $Cu_2S$. Copper sulfide is found as an alteration product on native copper in certain fractures from the Hyrkkölä site in Finland (Marcos and Ahonen 1999). In particular, samples $S_{40}$ (Figure 3) and Hy325/68.30 (Figure 4), currently held at the Finnish Geological Survey, exhibit $Cu/Cu_2S$ interfaces that might be of interest. Finally, there is a suggestion of Cu alteration to $Cu_2S$ in some of the samples from Littleham Cove (Section 2.1.3), but this seems to be an exception rather than a common observation (Milodowski et al. 2002).

In terms of anthropogenic samples, Jacobs and Edwards (2000) have described the formation of porous sulfide scales on the inside of copper potable water pipes in the laboratory (Figure 28), but presumably there are also field examples that exhibit similar behaviour.

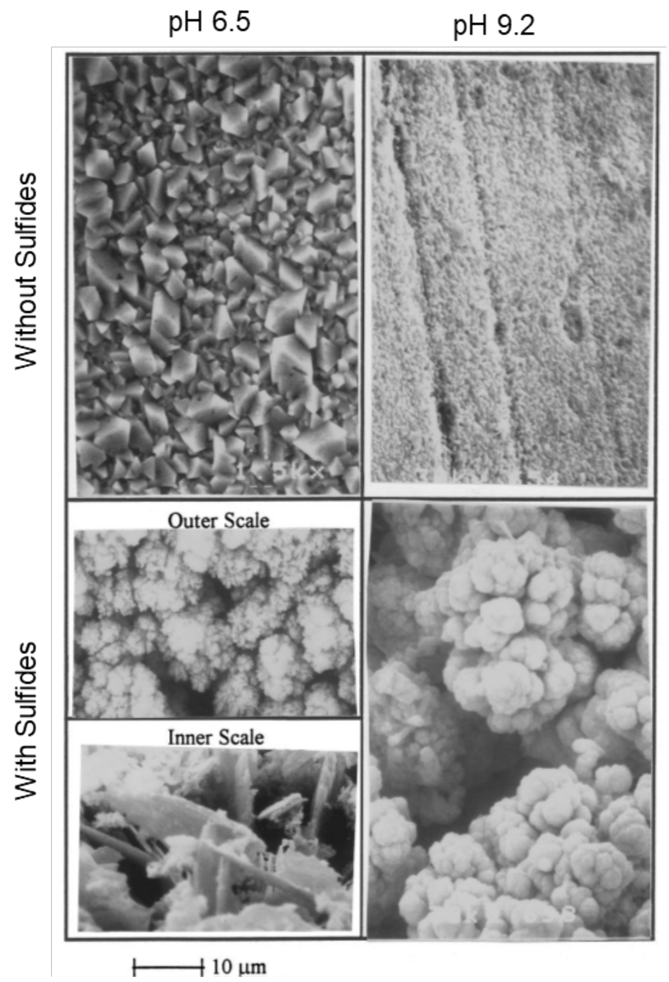

**Figure 28: SEM of corrosion product films on the inside of copper piping with and without exposure to sulfide in the circulating water (Jacobs and Edwards 2000). Reproduced with permission of © Elsevier.**

### 5.1.2 Localized Corrosion Under Anaerobic Conditions

In the calculation of the various copper corrosion allowances, corrosion due to sulfide under anaerobic conditions is assumed to be entirely uniform (Keech et al. 2020). However, there is the ongoing debate about the properties of the $Cu_2S$ film (see above), one consequence of which is the suggestion that pitting is possible in the presence of $Cl^-$ if the film is passive (Mao et al. 2014). Furthermore, Chen et al. (2017) have described a localized phenomenon in the presence of sulfide that they attribute to micro-galvanic coupling of spatially separated anodic and cathodic sites under porous $Cu_2S$ films, and which SKB has accounted for in recent canister lifetime predictions (SKB 2019).

Examination of the film-metal interface on copper-$Cu_2S$ assemblages would be a useful analogue to determine whether localized corrosion occurs under anaerobic conditions and, if it does, how to quantify it for the purposes of determining the necessary corrosion allowance. The samples identified in Section 5.1.1 would also be suitable for examining the localized corrosion behaviour.

### 5.1.3 Demonstration of Thermodynamic Versus Kinetic Stability

Both kinetic and thermodynamic arguments are used in support of the prediction of various copper corrosion processes that may, or may not, occur on the UFC under repository conditions. Determining whether the continued existence of an analogue is the result of kinetic or thermodynamic limitations should be a component of all analogue studies, but particularly of the study of native copper deposits. The type of evidence that is required includes estimates of the redox potential and pH of the environment and, ideally, of the corrosion potential ($E_{CORR}$) of the object *in situ*. It would be difficult to measure the $E_{CORR}$ *in situ* without damaging the artifact as a good metal contact is required. Measurement of the redox potential, which represents the maximum value of $E_{CORR}$ is, however, feasible. In the case of thermodynamic stability, the concentrations of reactants and corrosion products should also be determined. If kinetic stability is suspected, then the properties of passive films or the mass-transport characteristics of the disposal environment should be determined. The overall aim should be to reasonably predict the observed corrosion or alteration rate based on a conceptual kinetic or thermodynamic model using as input parameters the values of pH, potential, permeability, etc. determined from the analogue study.

### 5.1.4 Stability of Precipitated Iron Sulfide Phases

In recent reactive-transport modelling conducted as part of the SKB-Posiva funded Integrated Sulfide Project (ISP), the precipitation of iron sulfide was found to be a significant sink for remotely produced sulfide (Idiart et al. 2019, King and Kolář 2019, Pękala et al. 2019). Depending upon the availability of dissolved Fe(II) between the source of the sulfide (assumed to be microbial activity in the excavation-damaged zone surrounding the deposition holes and disposal tunnels) and the UFC surface, up to 99% of the sulfide produced was predicted to precipitate as mackinawite (FeS) prior to reaching the container surface.

Thus, the precipitation of FeS is predicted to be an important sink for remotely produced sulfide and to significantly decrease the extent of container corrosion. However, the solubility product of $Cu_2S$ is lower than that of FeS (CRC 2019). In the model of Pękala et al. (2019), mackinawite precipitation was treated as reversible and, in low-[$HS^-$] conditions, sulfide was released by FeS dissolution and was transported to the UFC where it resulted in corrosion.

Rémazeilles et al. (2009; 2017; 2019a,b) have presented evidence that in water-logged wooden components from shipwrecks, the FeS that is originally formed from the corrosion of iron nails is transformed progressively to greigite ($Fe_3S_4$) and eventually to pyrite ($FeS_2$). Greigite and, especially, pyrite are more thermodynamically stable forms of iron sulfide with lower solubilities than FeS (King 2013). Rémazeilles et al. (2017; 2019a,b) attributed this transformation, which occurred over periods of centuries, in part due to the presence of organic material from the decaying wood from the shipwrecks.

The extent of FeS precipitation depends on the availability of a relatively soluble Fe(II) phase in the bentonite. Siderite ($FeCO_3$) is a common accessory mineral in some, but not all, bentonites and acts as a source of Fe(II) for FeS precipitation (Idiart et al. 2019, King and Kolář 2019, Pękala et al. 2019). Given the apparent importance of this process in limiting the transport of remotely produced sulfide to the UFC surface, it would be useful to find analogue evidence for the $FeS \rightarrow Fe_3S_4 \rightarrow FeS_2$ transformation in clay systems in the absence of organic matter from decaying water-logged wood. The stability of various iron sulphide phases has also been considered by Behazin et al. (2021).

No specific analogue sites or samples have been identified at present.

### 5.1.5 Effect of Impurity Levels on the Corrosion of Copper

The copper coating on the UFC will be applied using a combination of electrodeposition and cold spray techniques (Guerreiro et al. 2020, Keech et al. 2020). Oxygen is the main impurity of concern for cold spray copper, although other metal impurities in the feedstock have been identified (Guerreiro et al. 2020). Electrodeposition of copper will also introduce impurities from the plating solution, including hydrogen and either phosphorus (from orthophosphate baths) or sulphur (from acidic sulfate plating solutions). Material properties, including acceptable impurity and alloying contents, have been defined for the wrought oxygen-free copper with added phosphorus (OFP Cu) to be used for the KBS-3 canister (SKB 2010a), but there remains a question regarding the effect of impurities (especially O, H, S, and P) on the corrosion behaviour of electrodeposited and cold spray copper (Keech et al. 2020).

It is not uncommon for the impurity content of analogues to be reported, but the analyses tend to be limited to metals (e.g., Ag, Pb, Sn, Zn, Fe, Ni, As, Bi, Na) rather than the non-metallic elements of interest here (Bresle et al. 1983, Mauk and Hancock 1998).

While it would likely be feasible to measure the non-metallic impurity levels in future analogue studies, a question remains as to whether the use of analogues is the best means to determine the effects of these impurities on the corrosion behaviour of the copper coating. Because of the wide variability of exposure environments associated with analogues, it is unlikely that a difference in corrosion behaviour due to different impurity levels will be apparent unless that difference in behaviour is large. At the same time, if there is a significant effect of these impurities on the corrosion behaviour, then it would be more apparent, and probably better investigated, based on laboratory experiments.

As part of a new collaborative project funded by NSERC and NWMO, Western University initiated a task to locate, observe, and acquire natural Cu specimens and perform characterization and corrosion testing. The current plan is to have two excursions to conduct field work. The first will be a trip to the Keweenawan Peninsula of Northern Michigan to investigate natural Cu deposits at the surface, and the second will be to examine occurrences of natural Cu in bedrock north of Sault Ste. Marie and undertake Indigenous community engagement in the Sault Ste Marie region. Researchers at Western University also have conditional permission to access commercial drill core sheds in the Sault Ste Marie region to seek and retrieve specimens from Cu deposits found at depths of ~900 m. The goal is to target Cu deposits both at the surface and the depth. Selection of specimens will also be guided by the findings of the Michigan International Copper Analogue (MICA) Project, a collaboration of the Geological Survey of Finland, BGE (Germany), NWMO, SKB, Nagra, and RWM (Radioactive Waste Management, UK), that will run in parallel to this project and will identify natural Cu materials that have been altered by specific geological processes.

### 5.1.6 Localized Corrosion Under Aerobic Conditions

Because the corrosion barrier for the copper-coated UFC design is relatively thin (especially compared with the KBS-3 canister), it is important to identify any possibility of localized corrosion. Historically, use has been made of analogues to quantify the extent of pitting on KBS-3 style canisters (King and LeNeveu 1992, Werme et al. 1992). These early studies tended to be conservative and did not properly take into account the limited amount of oxidant in the DGR (either the initially trapped $O_2$ or the resulting Cu(II) species). In addition, it became accepted that any localized corrosion of copper under repository conditions would take the form of surface roughening rather than pitting (King et al. 2013). For that reason, aerobic localized corrosion is usually treated in the safety assessment using a surface roughening allowance of the order of 100 μm (Keech et al. 2020). However, that allowance is based on a limited set of laboratory measurements and there is little understanding about how the surface roughness develops over time. Furthermore, recent studies have shown that passivation of copper in bentonite pore water is possible under repository conditions, especially if the pore-water is alkaline and of low salinity (Briggs et al. 2020, Qin et al. 2017).

Because archaeological artefacts are often located in near-surface aerobic environments, the study of such analogues may provide useful information for supporting the treatment of aerobic localized corrosion in the safety assessment. Among the types of information that would be useful are:

- Evidence for the time dependence of the development of surface roughening under conditions in which the copper analogue surface is not passive. Evidence for the non-permanent spatial separation of anodic and cathodic sites, such as the presence of stifled pits, would be especially useful.
- Determination of the conditions under which the copper surface is passivated and subject to localized corrosion. This study would require the measurement (or estimation) of the near-surface pH and pore-solution composition (of $Cl^-$, $SO_4^{2-}$, and $HCO_3^-$), temperature, and the redox and/or corrosion potentials.
- Maximum pit depth data for copper objects exposed to saturated environments for a period of a few hundred years. These data would then provide an additional data point in the time-dependent extrapolation of the location parameter of the Gumbel extreme-value distribution (see Section 4.4.1). This study is considered of relatively low priority because the time-dependent extrapolation of the extreme-value pit-depth distributions is no longer used in the safety case.
- Examination of the characteristics and depth-distribution of copper exposed to atmospheric conditions. In addition to information regarding the depth and spatial distributions of pits, evidence may also be available regarding different stifling mechanisms.

In all of these studies, however, it is important to quantify as far as possible the availability of $O_2$. Ideally, the availability of $O_2$ would be expressed as an $O_2$ inventory per unit surface area of the artefact. Alternatively, the flux of $O_2$ might be estimated from the permeability of the environment (soil) and a reasonable understanding of the boundary conditions for $O_2$ transport.

No specific analogue sites or samples have been identified at present. For samples exposed to atmospheric conditions, the surfaces should preferably have been exposed to indoor or, at least, sheltered conditions, rather than to the periodic washing characteristic of surfaces exposed to the elements (e.g., copper roofs or architectural objects). A marine or coastal location would also be preferable, both because of the presence of salt-containing aerosols and also because of the relatively high humidity.

Because of the importance of quantifying the extent of localized corrosion for the copper-coated UFC, this topic is considered to be of high priority, therefore, additional work (Section 5.1.5) is underway to validate the results of laboratory testing and add more confidence to long term prediction with regard to localized corrosion of copper

### 5.1.7 Estimation of Rate Parameters for Mechanistic Models

In some cases, analogues may be useful sources of input data for predictive models, including the CCM. In addition to data from laboratory studies, natural systems may serve as an additional source of data.

A current uncertainty in CCM modelling (King and Briggs 2020) is the kinetics of $Cu^{2+}$ adsorption and desorption on bentonite in compacted systems. There are many studies of the kinetics of $Cu^{2+}$ adsorption/desorption in loose clay systems, but the resulting rate constants do not replicate the observed time-dependence of the corrosion potential ($E_{CORR}$) when modelled using the CCM. (The adsorption/desorption of $Cu^2$ have a significant effect on $E_{CORR}$ because they determine the concentration of pore-water $Cu^{2+}$ which can then be cathodically reduced on the copper surface). There are various reasons why the kinetics in a compacted system may differ from those with loose clay, including a reduction in the number of available sorption sites and stearic hindrances in smaller pores in the compacted clay. It is difficult to study adsorption/desorption kinetics of compacted clay systems in the laboratory because of the uncertain impact of diffusion on the adsorption/desorption kinetics.

Compacted bentonite is used industrially to control the transport of toxic elements, including $Cu^{2+}$. There may be field data on the development of concentration plumes away from sources of dissolved Cu that could be simulated using a modified version of the CCM in order to infer values for the sorption characteristics.

Another uncertain parameter in the CCM is the rate constant for the dissolution of atacamite ($CuCl_2{\cdot}3Cu(OH)_2$), which is formed as a precipitated corrosion product on copper in contact with compacted buffer material (King and Kolář 2000). The mechanism of dissolution is also uncertain. King and Strandlund (unpublished data) studied the dissolution of atacamite using a rotating ring-disc electrode in acidic $Cl^-$ solution. The disc electrode was cored from a mineral sample of atacamite (Figure 29). The potential of the gold ring electrode was controlled to determine whether copper dissolved as Cu(I), suggesting a reductive-dissolution mechanism, or as Cu(II), consistent with a chemical dissolution process. The study was very preliminary and no conclusive evidence for the dissolution mechanism or of the associated rate constant was derived. However, this is an example illustrating the possible use of a mineral analogue sample to obtain input data for predictive models.

**Figure 29: Remnants of a mineral sample used to fabricate an atacamite disc electrode for dissolution studies.**

### 5.1.8 Radiolytic Corrosion of Copper and Steel

Although the external γ-radiation field is higher for the copper-coated UFC design than for thicker-walled canister designs, the absorbed dose rate for the reference 30-year-cooled fuel is estimated to be approximately 1 Gy/hr at the time of emplacement. Such a dose rate is modest in comparison to those found to accelerate the rate of corrosion (Shoesmith and King 1999), although an allowance of several 10's μm is made for external radiolytic corrosion in the UFC lifetime prediction (Keech et al. 2020).

Although the extent of radiolytic corrosion is expected to be small, it is an obvious topic of query by reviewers and it is an appropriate subject for study. In terms of samples, irradiated reactor components that were in contact with an aqueous phase and for which the irradiation history is known would make suitable samples. Turnbull et al. recently reported the results from examinations of irradiated Cu surfaces that were harvested from a shutdown nuclear research reactor (Turnbull et al. 2021). These Cu samples had been exposed to about 40 years of gamma and neutron radiation (at ~0.015 Gy/h) under uncontrolled humid air conditions at a temperature of approximately 40 °C. For comparison, this dose rate is equivalent to that expected at the Cu surface of the UFC after around 200 years in a DGR. Surface analysis and metallographic examinations including etched cross section and micro-hardness measurements concluded that long-term gamma and neutron irradiation of Cu, of the dose rates and cumulative dose described above, did not affect the integrity of the Cu samples.

### 5.1.9 Controlling Mechanisms for Microbial Activity in Bentonite

The possibility of near-field microbial activity and of biofilm formation on the UFC surface are dismissed in the safety case because of the properties of compacted bentonite in suppressing microbial activity. The controlling mechanisms are thought to be one or more of the following: low water activity, high swelling pressure, or lack of physical space. As discussed in Section 4.3.1, there are already a number of analogue studies that support the contention that all of these factors do indeed limit microbial activity. However, given the importance of microbially produced sulfide and of the current uncertainty in assessing corrosion under a biofilm, additional analogue studies in this area are appropriate.

From an engineering perspective, microbial activity is considered to be suppressed above a threshold clay dry density, variously considered to be between $\geq 1.4$ Mg/m$^3$ (Bengtsson et al. 2017) and $\geq 1.6$ Mg/m$^3$ (Wolfaardt and Korber 2012). In addition to further studies of the individual possible controlling processes, an analogue study to confirm the engineering guidance of a threshold dry density for microbial activity would be useful.

No specific analogue sites or samples have been identified at present.

### 5.1.10 Mechanical Performance of the UFC

The focus of this report has been on the long-term corrosion behaviour of the UFC, but failure of the container due to mechanical overload is also an important consideration from the viewpoint of safety. The UFC is designed to withstand the expected maximum external load of 45 MPa, comprising the buffer swelling pressure, hydrostatic pressure at repository depth, and an additional hydrostatic load due to an assumed 3000-m-thick glacier at the DGR site (Giallonardo et al. 2017).

Given the design and shape of the UFC, the most obvious analogue for the mechanical response to high external compressive loads is the design and performance of submarines and other deep-sea submersibles. Failure analyses on submarines and other steel structures exposed to high hydrostatic pressures may also provide information on potential failure processes. Because of differences in design and service conditions between the analogues and UFC, the greatest value from such studies may come from the validation of structural analysis codes used for submersible design and failure analysis if these codes are also used for design and analysis of the UFC.

### 5.1.11 Evidence for Joint Corrosion-Mechanical Effects

As briefly discussed in Section 4.1, the dual-layer copper-steel/iron container design is relatively devoid of joint corrosion-mechanical effects. The case of SCC of the copper corrosion barrier is described in Section 5.2.1 and of hydrogen-induced cracking (HIC) of the steel vessel in Section 5.1.12.

One possible joint corrosion-mechanical effect that could be studied using analogues is the impact of galvanic coupling between the copper and steel under aerobic conditions as might occur if there is an initial through-coating defect in the copper. Smart and Adams (2006) and Smart et al. (2003, 2004) have used analogues to investigate the possible formation of expansive corrosion products under anaerobic conditions, but significant galvanic coupling is most likely in the presence of $O_2$. The evidence from corrosion experiments is that, rather than precipitate within the defect, steel corrosion products remain soluble and only precipitate on the external copper surface (Standish et al. 2016). Thus, the formation of expansive corrosion products that might disbond the copper coating appears unlikely, but this conclusion could be usefully confirmed through the use of analogues. Rather than the study of preserved archaeological artefacts as performed by Smart and co-workers, the ideal analogue for this study would still retain the corrosion products so that the spatial relationship between the location of steel dissolution and of precipitation of corrosion products can be understood.

### 5.1.12 Hydrogen-Induced Degradation of Steel

The HIC of the carbon steel vessel features here in both the list of useful analogues and the list of less-worthwhile studies (Section 5.2.4). Prior to through-wall penetration of the copper coating, the only source of hydrogen for HIC of the steel vessel is the small amount of water that might be carried over in improperly dried fuel bundles. The possibility of HIC is considered to be small, both because the amount of $H_2O$ (and, hence, H) is expected to be limited and because the vessel will be fabricated from a relatively low strength alloy of limited susceptibility (Hatton 2015).

Despite the expected low probability of HIC, it might be useful to review field experience of the use of carbon steels in corrosive environments in order to define the envelop of conditions under which HIC is observed. Such a study would build on the analysis used by JNC (2000) to justify the exclusion of HIC as a failure mode for carbon steel UFC (Figure 30). The aim of the study would be to show that the conditions in the DGR, both in terms of the strength of material and the availability of H, fall well outside those that have been found to lead to different forms of H degradation. The latter information would largely come from experience in the oil and gas industry, but could also be supplemented by issues associated with the storage and transportation of $H_2$ gas. The review should be focussed on practical experience (analogues), but could be supplemented by evidence from laboratory studies.

### 5.1.13 Fate of the Initially Trapped Oxygen

The fate of the initially trapped $O_2$ in the DGR, i.e., the fraction consumed by UFC corrosion, microbial activity, oxidation of mineral phases, and/or other processes, is an important consideration in determining the extent and nature of corrosion during the aerobic phase. Evidence is available from large-scale *in situ* tests and from reactive-transport models, but there is still uncertainty about the processes responsible for $O_2$ consumption and the fraction of the initial inventory that will support corrosion.

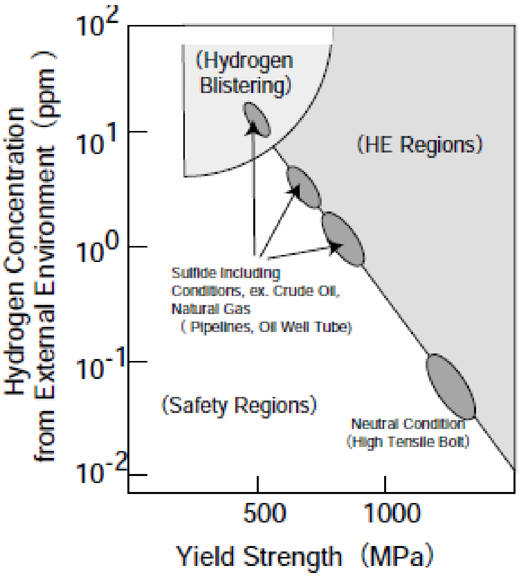

**Figure 30: Relationship between absorbed hydrogen concentration, material yield strength and the conditions for various forms of hydrogen-related damage of steels (JNC 2000).**

It is unlikely that we could identify a direct analogue for the competitive consumption of $O_2$ by the specific processes of interest in the DGR. Perhaps a more suitable approach would be to validate the reactive-transport model against analogues from other natural systems in which the redox conditions evolve with time. Two obvious examples are acid mine drainage from mill tailings (Salmon and Malmström 2004) and the evolution of the redox conditions in landfills (Islam et al. 2001). The cause of acid mine drainage is the oxidation of pyrite by atmospheric $O_2$, which is one of the processes thought to be responsible for consumption of $O_2$ in the DGR (Giroud et al. 2018). Modelling of gas evolution in landfill sites is typically focussed on the formation of methane, which is a process further down the microbial redox chain than those associated with $O_2$ consumption. Nevertheless, landfills start off as aerobic and there may well be useful analogues available in the literature that include time-dependent gas compositions.

### 5.1.14 Conversion of $Cu_2O$ to $Cu_2S$

In the current estimate of the depth of corrosion of the copper barrier, an allowance is made for the conversion of $Cu_2O$ formed during the aerobic phase to $Cu_2S$ when sulfide reaches the UFC (Keech et al. 2020). Conversion of $Cu_2O$ to $Cu_2S$ has been demonstrated in the laboratory (Hollmark et al. 2012, Kristiansen et al. 2015, Smith et al. 2007), and it may be useful to confirm the process through the use of an analogue.

Both $Cu/Cu_2O$ and $Cu/Cu_2S$ assemblages are found at the Michigan (Section 2.1.1) and Hyrkkölä (Section 2.1.2) native copper sites, but apparently not as a $Cu/Cu_2O/Cu_2S$ assemblage. There are indications that Cu progressively transformed to $Cu_2O$ and then $Cu_2S$ at the Littleham Cove site (Section 2.1.3), although the sulfide phase is not widely found. Other possible analogues include copper piping exposed to sulfide-containing waters, such as those discussed in Section 5.1.1.

## 5.2 LESS-WORTHWHILE ANALOGUE STUDIES

As noted above, the topics listed in this section are not necessarily less important than those discussed in the previous section, but are considered to be less amenable to study with the use of analogues. There are a number of reasons why these topics may not make suitable analogue studies, including:

- The importance of alloy properties and the unlikelihood of being able to relate the properties of analogues to those of the materials of construction of the UFC, particularly in the case of electrodeposited or cold spray copper.
- The importance of environmental conditions on the process and the unlikelihood of being able to characterize the relevant conditions in the case of the analogue.
- The resulting information is not useful for supporting the safety case or the UFC lifetime prediction.

### 5.2.1 SCC of Copper

Stress corrosion is the result of a complex interaction between material, tensile stress, and a suitable corrosive environment. Small differences in environmental conditions, such as the ratio of the concentrations of SCC agent (ammonia, nitrite or acetate ions) to the concentration of inhibiting $Cl^-$ ions or the interfacial pH and potential, will impact the probability of cracking. Similarly, the absence of sufficient tensile stress or a degree of cold work to increase the susceptibility of otherwise ductile copper will prevent SCC. Thus, of any corrosion process, the susceptibility of a material to environmentally assisted cracking is highly dependent on the correct combination of material, environment, and mechanical loading. Because these prerequisite conditions are not expected to occur together in the DGR, the SCC of copper is excluded from consideration in the safety assessment (NWMO 2017, King and Newman 2010).

Quite apart from the relevance of the material and environmental conditions, however, the greatest drawback with analogues for SCC is that it is difficult to prove a negative proposition using an analogue.

### 5.2.2 Radiation Damage of Copper and Steel

Occasionally, questions arise as to whether the neutron fluence and integrated gamma dose experienced by the canister is sufficient to cause radiation damage that could impact the mechanical or corrosion performance of the UFC. Various reactor components subject to high neutron fluences do exhibit radiation damage and a degradation in material properties, for example, the radiation embrittlement of reactor pressure vessel steels (English and Hyde 2007).

Most recently, SKB re-visited this question in their response to the Swedish government to the request for supplementary information about the copper canister (SKB 2019). Additional calculations were performed on the amount of radiation damage (in terms of the number of displacement per atom, dpa) resulting from both gamma and neutron irradiation of the canister. These calculations confirmed the conclusions of earlier studies (Asano and Aritomi 2010, King et al. 2012) that the effects are negligible, with total damage of the order of $10^{-7}$ dpa and $10^{-9}$ dpa for neutron and gamma irradiation, respectively. The insignificant impact of gamma irradiation was confirmed experimentally by Padovani et al. (2019) who were unable to detect any measurable difference in various material properties of OFP Cu irradiated to a total absorbed dose of 100 kGy, which approximates the total lifetime absorbed dose for a KBS-3 canister.

Although suitable analogue samples may be available from decommissioned research reactors, the study of the possibility of radiation damage is considered to be of low priority because of the overwhelming theoretical and experimental evidence that the extent of irradiation of the UFC components is many orders of magnitude below that found to cause radiation damage.

### 5.2.3 Rate of Uniform Corrosion of Copper and Steel

Estimated corrosion rates are a common outcome of analogue studies of copper and iron archaeological artefacts. However, further study primarily for the purposes of estimating corrosion rates is not considered worthwhile unless an opportunity were to arise within a siting region. In the case of copper analogues, the estimation of the corrosion rate is not useful because the lifetime of the UFC is calculated on the basis of mass-balance and/or mass-transport arguments, not on the basis of the corrosion rate. In the case of carbon steel, there is a significant existing database of estimated corrosion rates from analogues spanning exposure periods from several tens to several thousands of years (Section 3.2.4). It does not seem worthwhile to expend additional effort to expand this existing database, especially since the steel vessel is not the primary corrosion barrier in the copper-coated steel UFC design.

### 5.2.4 Hydrogen-Induced Degradation of Steel

As discussed above (Section 5.1.12), hydrogen-induced degradation of steel is included in both the lists of useful and less-worthwhile future analogue studies. As a counter to the benefits of such a study described previously, it is important to remember that the susceptibility of a structure to HIC is dependent on factors such as the microstructure, hardness, local yield strength, and the level of residual stress. Weld regions can be particularly susceptible to HIC, the properties of which would never be replicated by an analogue.

## 6. CONCLUSIONS

Natural analogues in the form of native metals and anthropogenic artefacts can be useful for supporting predictions of the long-term performance of a copper-coated UFC. In addition to general confidence building with a range of expert and non-expert stakeholders, analogues are also useful for the development and validation of conceptual models for various corrosion processes. In some circumstances, analogues can also provide input data for direct use in UFC lifetime predictions.

The study of natural analogues is particularly useful for the copper-coated container design because native metal deposits and man-made objects are available for both the copper corrosion barrier and the steel structural vessel. Examples of each type of analogue have been described for both materials, along with an attempt to determine whether the persistence of the analogue is the result of thermodynamic or kinetic stability.

It is important to place the study of natural analogues into the context of the manner in which the long-term corrosion performance of the container is treated in the safety assessment (i.e., in terms of the calculation of the UFC lifetime) and in the broader safety case. The availability of analogues to support the treatment of corrosion processes that are, and are not, considered to lead to UFC corrosion has been considered.

Consideration has also been given to possible future analogue studies in support of the prediction of the long-term corrosion performance of the UFC. Any future study should be focussed on providing specific information in support of some aspect of the methodology for predicting the long-term corrosion behaviour of the container. This is not to say that the characterization of analogues with the general aim of confidence building is not valuable, but more value is to be obtained if there is a specific focus to the study.

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# APPENDIX A: 1-PAGE SUMMARIES OF ANALOGUE STUDIES

This appendix comprises a collection of 1-page summaries of various analogue studies available in the literature. The collection is not designed to be exhaustive, but does contain many of the more important studies, as well as a representative sample of studies from the different international nuclear waste management programs.

Each 1-page summary contains the following information:

- a unique reference number,
- bibliographic information, including title, authors, source, and year of publication,
- an indication of the engineered barrier of interest (copper, steel, or bentonite buffer),
- an indication of the potential use of the analogue, in terms of either supporting the development or validation of conceptual models, the provision of data, or general confidence building,
- a set of keywords,
- the abstract, summary, or conclusions from the original publication, and
- brief comments from the current author.

*Ref. no.:* 001

*Title:*

Copper deposits of the western Upper Peninsula of Michigan

*Authors:*

Bornhorst, T.J. and R.J. Barron

| *Source:* | *Year:* |
|---|---|
| Geological Society of America Field Guide 24, p. 83-99. | 2011 |

*Relevant engineered barrier:*

Copper

*Relevant use or application of the study:*

Possible source of samples for future studies, properties of $Cu_2S$ films

*Keywords:*

Native copper, Keweenaw, chalcocite, copper sulphide

*Original abstract/summary/conclusions*

The western Upper Peninsula of Michigan is well known for hosting significant concentrations of copper in copper-dominated deposits. Most of the copper is hosted by rocks of the Mesoproterozoic Midcontinent Rift. Copper deposits in the western Upper Peninsula can be subdivided into two overlapping world-class copper mining districts. The Keweenaw Peninsula native copper district produced 11 billion lbs of copper and a lesser unknown but significant quantity of silver. Native copper deposits in this district are stratiform and hosted by tops of rift-filling subaerial basaltic lava flows and interflow coarse clastic sedimentary rocks. These deposits are interpreted to be the result of mineralizing hydrothermal fluids derived from rift-filling basaltic volcanic rocks that migrated upwards, driven by late Grenvillian compression of the rift some 40–50 million years following cessation of active rifting. The Porcupine Mountains sediment-hosted copper district produced or potentially will produce 5.5 billion lbs of copper and 54 million ounces of silver. These stratiform/stratabound deposits are hosted in rift-related black to gray shale and siltstone and dominated by chalcocite rather than native copper. Chalcocite is interpreted to be the result of introduction of copper-bearing fluids during diagenesis and lithification of host sediments. At the now-closed White Pine Mine, the chalcocite mineralizing event was followed by a second stage of native copper deposition that demonstrates a spatial and temporal overlap of these two world-class mining districts. While these two districts have been dormant since 1996, favorable results from recent exploration at Copperwood suggest a revival of the mining of copper-dominated deposits in the western Upper Peninsula of Michigan.

*Current author review comments:*

Discusses the existence of chalcocite ($Cu_2S$) at two specific locations (Keweenaw Peninsula and Porcupine Mountains). At Keweenaw Peninsula, native copper predominates although there is some chalcocite. It is suggested that the chalcocite was deposited after the native copper. At the Porcupine Mountains location, the predominance is reversed, with native copper present in smaller amounts. It is suggested that the chalcocite formed prior to the native copper mineralizing (at White Pine).

This suggests that $Cu/Cu_2S$ samples are more likely to be available form the Keweenaw Peninsula formation than from the Porcupine Mountain region.

*Ref. no.:* 002

*Title:*
Challenges of using copper isotope ratios to trace the origin of native copper artifacts: an example from the Keweenaw Peninsula

*Authors:*
Mathur, R., M. Wilson, and M.L. Parra

| *Source:* | *Year:* |
|---|---|
| Annals of Carnegie Museum, <u>82</u>, 241-245. | 2014 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Aging of native copper samples, estimation of corrosion product thickness

*Keywords:*
Native copper, Keweenaw, isotope ratio

*Original abstract/summary/conclusions*

In an effort to understand how and if Cu isotopes can be used to trace native copper artifacts to their mineral deposits of origin, this study presents Cu isotope measurements from weathered native Cu artifacts and ores known to be derived from the Precambrian native copper deposits of Michigan. The five weathered artifacts have Cu isotope compositions ranging from $\delta^{65}$Cu= +0.54 to -1.15‰. Weathered glacial till native copper nuggets range from $\delta^{65}$Cu= -0.12 to +0.54‰, non-weathered ores have $\delta^{65}$Cu= +0.33 ± 0.2‰ (n= 42 from the literature and this study), a completely oxidized copper rind derived of large glacial boulder of native copper has -0.04‰. The oxidized rinds along with the weathered artifacts possess isotopically lighter signatures in comparison to the non-weathered ores and interiors of weathered copper nuggets.

The copper isotope data indicate the interiors of oxidized nuggets correlate with the non-weathered ores. Copper from the artifacts was sampled as micro drill bits (0.001-0.0009 g) and larger cut pieces of the artifacts (>0.5 g). Only the larger sample artifacts have the same copper isotope composition as the non-weathered ores, and not the oxidized rinds, and non-weathered interiors of copper nuggets. Therefore, when considering the unreacted interior of the native copper artifacts, the copper isotopic composition matches that of the known copper ore source. In contrast, weathering clearly depletes $^{65}$Cu on the surfaces of artifacts and micro-sampling of the outer rims does not yield similar isotope results between sources and artifacts.

*Current author review comments:*

The copper samples from the Keweenaw Peninsula (and presumably from other locations in the Michigan deposit) have characteristic isotopic signatures for the un-weathered (i.e., un-corroded) cores and for the weathered (i.e., corroded) surface layers. It is not exactly clear how this could be used in support of the UFC corrosion studies, but it is an interesting observation that is worth noting.

*Ref. no.:* 003

*Title:*
Native copper deposits of the Portage Lake Volcanics, Michigan: Their implications with respect to canister stability for nuclear waste isolation in the Columbia Rover basalts beneath the Hanford Site, Washington

*Authors:*
Crisman, D.P. and G.K. Jacobs

| *Source:* | *Year:* |
|---|---|
| Rockwell International Report for the U.S. Department of Energy, RHO-BW-ST-26 P. | 1982 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Support for geochemical stability of copper

*Keywords:*
Keweenaw, native copper, geochemical stability, million years

*Original abstract/summary/conclusions*

Copper deposits in the Portage Lake Volcanics of northern Michigan have been evaluated as a natural analogue for canister material to be emplaced in a nuclear waste repository located in the basalts beneath the Hanford Site near Richland, Washington. The native copper, which precipitated from high temperature (200°C to 300°C) hydrothermal solutions between 500 and 800 million yr ago, has remained relatively unaltered in the Portage Lake basalt-groundwater system. The results of this study illustrate the stability of copper in solutions of moderate pH, low to moderate Eh, and low total dissolved solids. Chemical trends and geochemical modeling of the near-surface waters suggest that similarities (moderate pH, low Eh, low total dissolved solids) exist between the groundwater-basalt system of the Keweenaw Peninsula and the groundwater-basalt system at the Hanford site. These similarities and the stability of copper in the Keweenaw basalts imply that copper alloys are adequate materials for nuclear waste canisters emplaced in a repository located in basalt.

*Current author review comments:*

Geochemical study of the sub-surface conditions in the Keweenaw Peninsula and an attempt to define the environmental conditions under which copper exhibits long-term stability (>>1 million years). The co-existence of native copper and hematite was used to infer a sub-surface Eh in the range +100 mV to -250 mV. This relatively wide Eh range encompasses the values expected in the DGR as the environment shifts from initially aerobic to long-term anoxic. The estimated pH of 7.8-8.8 would also be similar to that expected in the buffer pore water. However, the waters are generally thought to be fresh, and may have been more-dilute than those expected in the DGR. Crisman and Jacobs do acknowledge, however, that even in mines with saline ground water, the extent of alteration is relatively minor.

Considered to be a useful resource in supporting the long-term stability of native copper in low Eh, near-neutral pH environments.

|  |  |
|---|---|
| *Ref. no.:* 004 | |
| *Title:*<br>The history of the United States cent revealed through copper isotope fractionation | |
| *Authors:*<br>Mathur, R., S. Titley, G. Hart, M. Wilson, M. Davignon, and C. Zlatos | |
| *Source:*<br>J. Archaeological Sci., 36, 430-433 | *Year:*<br>2009 |
| *Relevant engineered barrier:*<br>Copper | |
| *Relevant use or application of the study:*<br>Unclear, but would support studies of native copper in general | |
| *Keywords:*<br>Michigan, native copper, isotope | |

*Original abstract/summary/conclusions*

Copper isotope fractionation in United States cents traces changes in the source of copper and identifies historical events. Application of copper isotopes as a geochemical tracer requires consistent isotopic signatures of the ores and refined metals. Overlapping isotopic signatures of crushed ores, chalcocite and refined metal extracted from Morenci, Arizona indicate modern mining processes that produce distinguishable single ore deposit geochemical signatures. The coincidence of copper isotope ratios in metals and ore deposits also exists within the United States cents analyzed here. Specifically, historical records confirm two different sources for copper in cents from 1800 through 1867. The copper isotope composition of the 1828, 1830, 1836, 1838 and 1843 cents coincides with the Cornwall ores of England, and cents post 1850 (1859, 1862) correspond with the Michigan ores of the United States. Three of the thirty-six post 1867 cents measured possess fractionated copper isotope ratios and indicate the change in source of copper for the United States cent.

*Current author review comments:*

A second study indicating the unique copper isotope ratio of different sources of copper. Again, it is not clear exactly how this could be used, but it is interesting to note that the isotope signature of the refined copper reflects that of the copper source, regardless of whether the source was native copper or a copper sulphide mineral.

*Ref. no.:* 005

*Title:*
Trace element geochemistry of native copper from the White Pine Mine, Michigan (USA): Implications for sourcing artefacts.

*Authors:*
Mauk, J.L. and R.G.V. Hancock

*Source:*
Archaeometry, 40, 97-107.

*Year:*
1998

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Effect of copper purity

*Keywords:*
Cold spray, (im)purity, trace elements, native copper, Michigan

*Original abstract/summary/conclusions:*

Eighty-five samples of native copper from the White Pine mine in upper Michigan were analysed by neutron activation to document geochemical variability within a single location. Silver, sodium, antimony and scandium contents vary by two orders **of** magnitude, whereas arsenic values vary by three orders of magnitude. This variability reinforces the need for provenance studies of artefacts to examine sufficient samples to test for heterogeneity within the source area. The White Pine suite contains some of the most impure native copper that has been analysed to date. Arsenic and silver values of these impure samples overlap with those of European coppers, but consideration of several elements can still distinguish native copper from European copper.

*Current author review comments:*
Provides information on the range of impurity elements in native copper samples from one location of the Michigan deposits. The effect of impurity level is of importance in specifying the cold spray technique although oxygen, the element of most concern, was not assessed.

The neutron activation analyses were performed using the Slowpoke reactor at the U of T.

*Ref. no.:* 006

*Title:*
The copper deposits of Michigan

*Authors:*
Butler, B.S. and W.S. Burbank

*Source:*
U.S. Geological Survey, Professional Paper 144.

*Year:*
1929

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Background information on Michigan deposits, identification of possible future samples

*Keywords:*
Keweenaw, native copper, copper sulphide

*Original abstract/summary/conclusions:*

The difficulty and high cost of obtaining geologic data in this generally drift-covered district has made it desirable to collect and to put on record all such data that are available. Field observation have therefore been presented in the text and on the maps and sections in greater detail than has been customary in reports of this character. The attempt has been made also to show on the maps all known developments in the district, with the hope that this would promote the most effective planning of future developments. The facts of the occurrence of copper have been set forth as they have been ascertained, and a general discussion of the origins of the ores is given. The attempt has been made to keep fact and speculation distinct, and it is hoped that the reader will draw his own conclusions from the facts rather than unqualifiedly accept those here presented. In the section on the application of geology to mining are described methods in the search for ore deposits that seem to give most promise of success.

*Current author review comments:*

An extensive 275-page review of the geological and early mining history of the Michigan copper deposits. It provides a wealth of background information on the region.

There are also some indications regarding the possible existence of $Cu/Cu_2S$ samples that might be useful in future studies of copper sulphide film properties. On page 55, it states “Where copper is associated with chalcocite in fissures either mineral may be the earlier, or the two may be contemporaneous. In the lodes the sulphide-bearing fissures are at least in part later than the copper of the lodes.” It is also proposed, however, that metallic copper could have formed from the oxidation of $Cu_2S$ coupled to the reduction dissolution of hematite, especially under acidic conditions:

$$Cu_2S + 3Fe_2O_3 + 5H_2SO_4 = 2Cu + 6FeSO_4 + 5H_2O$$

Thus, in selecting samples in which Cu and $Cu_2S$ co-exist, it will be necessary to determine whether the Cu has transformed to $Cu_2S$, or vice versa.

| | |
|---|---|
| *Ref. no.:* 007 | |
| *Title:*<br>Petrogenesis of Uivfaq iron, Disko Island, Greenland | |
| *Authors:*<br>Bird, J.M., C.A. Goodrich, and M.S. Weathers | |
| *Source:*<br>J. Geophys. Res., 86, 11,787-11,805. | *Year:*<br>1981 |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Evidence for long-term stability of iron | |
| *Keywords:*<br>Native iron, iron carbide | |

*Original abstract/summary/conclusions*

Massive blocks of native iron and iron carbide, weighing up to 22 tons, have been found at Uivfaq, Disko Island, western Greenland. The iron blocks are associated with Tertiary basalts that erupted during rifting between Greenland and Baffin Island, early in the opening of the Davis Strait. The 'iron' is an assemblage of iron and iron carbide (cohenite) and various silicate, sulphide, and oxide inclusions containing highly reduced and iron-rich phases, including fayalite, wustite, troilite, ulvospinel, ilmenite, ferriferous pigeonite, and FeO-rich glass. The chemistry and petrography of the inclusions are used to derive a paragenetic history for the Uivfaq iron assemblage. Petrographic study of a massive Uivfaq iron block shows that the block formed through accumulation of partly molten spherules of iron and cohenite, ~0.5 to 1.0 mm in diameter. Basaltic liquid was trapped by the accumulating metal spherules and reacted with the metal to form various highly reduced and iron-enriched immiscible liquids. These liquids solidified as inclusions in the iron mass. Various models are considered for the origin of the iron-cohenite spherules; at present, a carbon-reduction mechanism is preferred. The association of graphite-rich plagioclase-spinel xenoliths( thought to be derived from sediments) with the iron masses suggests a genetic relation between the two. We suggest that graphite was assimilated by mantle-derived basaltic magma. The carbon reduced iron oxide components of the basalt at a depth of 3 km or less and formed small immiscible droplets of high-carbon iron-carbon liquid. These droplets were erupted with the magma. The droplets settled and accumulated near or at the base of a flow or sill to form massive iron blocks.

*Current author review comments:*

It is not clear how useful this study is as evidence for the longevity of native iron. It is stated that much of the alpha iron has actually been altered to wustite or magnetite, so Fe was not stable as such. In addition, there is no information about the environmental conditions that resulted in this alteration.

*Ref. no.:* 008

*Title:*
A catalogue of analogues for radioactive waste management.

*Authors:*
Milodowski, A.E., W.R. Alexander, J.M. West, R.P. Shaw, F.M. McEvoy, J.M. Scheidegger, and L.P. Field.

| *Source:* | *Year:* |
|---|---|
| British Geological Survey Commissioned Report, CR/15/106. | 2015 |

*Relevant engineered barrier:*
Copper, steel, buffer

*Relevant use or application of the study:*

*Keywords.:*
Review

*Original abstract/summary/conclusions*
Natural, archaeological and older industrial systems can provide an important source of supplementary evidence that can be used in support of a safety case for a geological disposal facility (GDF) for radioactive wastes. These systems may not exactly mimic a GDF. However, they provide insights and information on the long-term processes, and physical and chemical behaviour, affecting many aspects of the engineered and geological barrier, over the very long timescales relevant to the post-closure timeframe for a geological disposal facility. Analogues can be helpful in demonstrating understanding of aspects of GDF performance and provide evidence that certain materials can persist for long periods. However, they do not provide conclusive proof that these materials will maintain their required functions for the required periods in the environments of a particular GDF, as the conditions under which the analogue material has persisted may not match those expected to occur or evolve in a GDF.

This catalogue of analogues presents examples from the natural environment (including archaeological sites and older industrial sites) that illustrate aspects of the performance of potential GDF systems over long time scales, and which can be used to support a safety case. Specifically, it presents a series of summary descriptions as stand-alone data sheets for each analogue system, with references to additional sources of information where more detailed accounts can be found. The analogues are grouped according to the main GDF safety barrier functions which they demonstrate applicability. The catalogue does not aim to provide a comprehensive list of all known analogues; it presents a spread of examples that relate to the main safety barrier functions of a GDF.

The catalogue is presented at a level that is appropriate for an audience involved in the waste management process who are not necessarily specialists in analogue systems. It is also suitable for the general scientific audience and may prove a useful background resource for undergraduates.

*Current author review comments:*
Of the 36 analogue studies catalogued, only two canister-related analogues; namely, the Littleham Cove native copper deposits and the Roman nails from the Inchtuthil site, UK.

*Ref. no.:* 009

*Title:*
Trace elements in natural metallic iron from Disko Island, Greenland.

*Authors:*
Klöck, W., H. Palme, and H.J. Tobschall

| | |
|---|---|
| *Source:*<br>Contrib. Mineral. Petrol., 93, 273-282. | *Year:*<br>1986 |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Native iron

*Keywords:*
Disko Island

*Original abstract/summary/conclusions*

The largest occurrence of natural metallic iron on Earth is on the island of Disko, Greenland. Metallic iron is found there in a variety of different types, from small metal particles in basalts to large meter-sized blocks. We have studied three different types of metallic iron: small metal spherules (< 300 μm) in basaltic magma; larger metal grains (300 μm-3 mm), often composed of aggregates of smaller particles, in similar host rocks; and massive iron lumps (up to several tons). Analytical data for 13 siderophile elements in samples from these three types are presented. All metals analysed have a distinctly crustal pattern of siderophile elements. High Co/Ni, Re/Ir or W/Ir ratios clearly demonstrate that a meteoritic origin for the metallic iron must be excluded. Since the Co/Ni and Re/Ir ratios are approximately chondritic in the upper mantle of the Earth, a mantle origin for the Disko metals can also be ruled out. This supports earlier petrological and geological evidence that the metallic iron was formed through reduction of basaltic magma by carbon derived from Tertiary shales and coals. Significant differences in absolute and relative abundances of siderophile elements occur among the three kinds of metals. The strongly siderophile elements (e.g. Ir, Re, Ni) increase in concentration from the small metal spherules through the larger grains to the massive iron lumps. The contents of less strongly siderophile elements (P, W, Ga) decrease in the same sequence. Evidence is presented that the small metal spherules are formed by in situ reduction. Larger iron metal grains and massive iron lumps are composed of small spherules, accumulated by gravitational settling in a magma reservoir. These metal cumulates have extracted highly siderophile elements from a larger volume of basaltic melt.

*Current author review comments:*

Another study focused on the genesis of the metallic iron, rather than its subsequent weathering, which would be more useful as an analogue study.

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| *Ref. no.:* 010 | |
| *Title:*<br>Natural Analogue Studies in the Geological Disposal of Radioactive Wastes | |
| *Authors:*<br>Miller, W., R. Alexander, N. Chapman, I. McKinley, and J. Smellie. | |
| *Source:*<br>Studies in Environmental Science 57 (Elsevier, Amsterdam). | *Year:*<br>1994 |
| *Relevant engineered barrier:*<br>Copper, steel, buffer | |
| *Relevant use or application of the study:* | |
| *Keywords:*<br>Review | |
| *Current author review comments:*<br>Comprehensive review of relatively early analogue studies (pre-early 1990's). Includes discussion of the use of analogues and their application to different disposal concepts (primarily the KBS-3 and Nagra concepts), the selection of analogue studies, analogues for different repository materials and radionuclide release and transport. An appendix includes brief summaries of fourteen different analogue studies/sites. | |

| | |
|---|---|
| *Ref. no.:* 011 | |
| *Title:*<br>Durability of metals from archaeological objects, metal meteorites, and native metals | |
| *Authors:*<br>Johnson, A.B., Jr. and B. Francis | |
| *Source:*<br>Batelle Pacific Northwest Laboratory report for U.S. Department of Energy, PNL-3198. | *Year:*<br>1980 |
| *Relevant engineered barrier:*<br>Copper, steel | |
| *Relevant use or application of the study:*<br>Lifetime prediction, empirical data | |
| *Keywords:*<br>Corrosion rate | |

*Original abstract/summary/conclusions*

Metal durability is an important consideration in the multi-barrier nuclear waste storage concept. Several metals have shown impressive durability over centuries and millenia in several environments. This study summarizes the ancient metals, the environments, and factors which appear to have contributed to metal longevity. The ancient metals include archaeological objects, metal meteorites, and native metals.

The seven metals of antiquity are gold, silver, copper, lead, iron, tin, and mercury. Archaeological and radiochemical dating suggest that human use of metals began in the period 6000 to 7000 BC. Thousands of metallic artifacts exist, some still in good repair after several millenia. They have been found in caves, tombs, graves, shipwrecks, and various other environments above and below ground. Gold is clearly the most durable, but many objects fashioned from silver, copper, bronze, iron, lead, and tin have survived for several thousand years. Dry environments, such as tombs, appear to be optimum for metal preservation, but some metals have survived in shipwrecks for over a thousand years.

The metal meteorites are iron-base alloys with 5 to 60 wt% nickel and minor amounts of cobalt, phosphorous, and sulfur. Approximately 530 metal meteorites have been identified. Over half show minimal weathering. Some meteoritic masses with ages estimated to be 5,000 to 20,000 years have weathered very little. Other masses from the same meteorites are in advanced stages of weathering. Those which survived best fell in dry locales, were not buried in the ground, were largely free of aggressive species such as chlorides, and may have been protected by oxides formed by high-temperature reactions with the earth's atmosphere. First hand examination of corrosion on several meteorites is discussed.

Native metals are natural metallic ores. Gold, silver, copper, and mercury occur as native metals in commercial quantities. Other metals occur but in relatively small amounts. On a tonnage basis, copper has been the most significant native metal. Approximately five million tonnes were mined from native copper deposits in Michigan.

Copper masses from the Michigan deposits were transported by the Pleistocene glaciers. We have examined two masses of this so-called "float" copper. Areas on the copper surfaces which appear to represent glacial abrasion show minimal corrosion. The last glaciers receded about 8,000 years ago, so the abrasion is at least that old.

The foregoing examples of impressive multi-century metal durability provide a useful baseline for extrapolations and offer valuable insights to optimum storage environments. However, they differ from nuclear waste canister environments: the temperatures are lower and radiation has been absent.

*Check if additional Comments made* ☒

*Original abstract/summary/conclusions (continued):*
In liquidous environments, effects of these two factors are difficult to assess and extrapolate. In an engineered dry environment, the temperature/radiation effects appear much more amenable to assessment and appear less likely to be problematic.

Dry cooling tower technology has demonstrated that in pollution-free moist environments, metals fare better at temperatures above than below the dewpoint. Thus, in moderate temperature regimes, elevated temperatures may be useful rather than detrimental for exposures of metal to air.

In liquid environments, relatively complex radiolysis reactions can occur, particularly where multiple species are present. A dry environment largely obviates radiolysis effects.

The major conclusions of this study are:

- that several metals have shown impressive multi-century and multi-millenia durability in natural environments
- that dry or mildly moist environments have been optimum for metal preservation
- that dry or mildly moist environments appear most amenable to data extrapolation and to preservation of nuclear waste containers.

*Current author review comments:*
This was perhaps the first study to consider the use of natural and archaeological metal samples for long-term prediction of the corrosion behaviour of nuclear waste container materials. It is still a valuable resource.

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| *Ref. no.:* 012 |
| *Title:*<br>The oldest steel in the world? |
| *Authors:*<br>Alexander, W.R. |

| | |
|---|---|
| *Source:*<br>Presentation at NAWG-15, 23-25th March 2017, available at https://www.natural-analogues.com/ | *Year:*<br>2017 |

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| *Relevant engineered barrier:*<br>Steel |
| *Relevant use or application of the study:* |
| *Keywords:*<br>Steel, metallurgy, smelting |

*Current author review comments:*

NAWG presentation describing a potential analogue for the corrosion of steel, as opposed to iron. Iron Age settlement in Scotland dating back between 2200-2800 years ago, with a range of steel artifacts (jewellery, metal bars, tools, weapons, fittings). Alloys are high-C (close to 2 wt.%?), P-containing (0.7-0.9 %) alloys, with evidence for heat treatment and quenching. Range of aerobic and anaerobic exposure conditions.

The suggestion is that there is some benefit to studying steel, as opposed to iron artifacts. However, for modern alloys, there is little difference between the corrosion rate of C–steel and cast iron.

It is not clear what additional information could come from this proposed analogue.

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|---|---|
| *Ref. no.:* 013 | |
| *Title:*<br>Archaeology analogues for geological disposal of spent nuclear fuels (SNFs) – current status and future outlook in Taiwan. | |
| *Authors:*<br>Tsai, T.–L. | |
| *Source:*<br>Presentation at NAWG-15, 23-25th March 2017, available at [https://www.natural-analogues.com/](https://www.natural-analogues.com/) | *Year:*<br>2017 |
| *Relevant engineered barrier:*<br>Copper | |
| *Relevant use or application of the study:* | |
| *Keywords:* | |
| *Current author review comments:*<br>NAWG presentation on the examination of copper and iron alloy artifacts from Taiwan. The objects were buried at a depth of 3-4 m in a coastal region at Hanben, Taiwan. The estimated age is 1100-1800 years. Soil and meteorological information available. Variety of analytical techniques to examine corrosion products, including tomography.<br>Objects included an iron hook, bronze bell, and a bronze adornment. Micro-CT provided an estimate of the thickness of the corrosion product layer, from which corrosion rates were derived for both Fe and bronze. | |

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| *Ref. no.:* 014 |
| *Title:*<br>Copper analogues – status and future outlook |
| *Authors:*<br>Ahonen, L., T. Bornhorst, T. Ruskeeniemi, and H. Reijonen |

| | |
|---|---|
| *Source:*<br>Presentation at NAWG-15, 23-25th March 2017, available at [https://www.natural-analogues.com/](https://www.natural-analogues.com/) | *Year:*<br>2017 |

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|---|
| *Relevant engineered barrier:*<br>Copper |
| *Relevant use or application of the study:* |
| *Keywords.:*<br>Michigan, native copper, Keweenaw Peninsula |

*Current author review comments:*

Description of a possible future analogue study based on the native copper deposits in Michigan.

Three possible types of copper samples identified:
- native copper still in place
- transported copper (float copper)
- excavated copper (e.g., chisel chips)

Possible areas of study;
- geochemical characterization of waters from various depths
- Long-term exposure to anoxic brines
    - native copper exposed to anoxic brines for 1 billion years (presumably to establish conditions of stability)
    - conditions under which copper has been deposited from brines (inverse of corrosion conditions?)
- Long-term exposure to anoxic brine followed by incursion of anoxic-oxic groundwater
    - Study of shallow mine sites
    - Lake copper
    - Gravel copper
    - Float copper
- Oxidation of metallic copper prior to anoxic brine incursion(?)
    - Chisel chips
    - Lake copper
- Long-term exposure to anoxic brine followed by incursion of anoxic-oxic groundwater followed by re-exposure to anoxic brines
    - Precambrian weathering
    - Shallow mine
- Overall stability of metallic copper
    - All samples

*Check if additional Comments made* ☒

*Comments (continued):*

Proposing that these studies will contribute to :

- Corrosion in different environments
- Protective properties of corrosion products
- Effects of material flaws (access of fluids in porous float copper)

But there seems to be a disconnect between what is proposed and how we think of or treat the corrosion behaviour of canisters in the repository. For example, we argue that copper corrosion products are not protective, because they otherwise increase the probability of localised film breakdown.

One possible area of interest is in the thermodynamic stability of copper in anoxic brines. This might build on the Crisman and Jacobs study. For instance, can we derive activity coefficients in concentrated solution from some of these data?

*Ref. no.:* 015

*Title:*
Influence of microstructure on the corrosion of archaeological iron observed using 3D synchrotron micro-tomography.

*Authors:*
Simon, H.J., G. Cibin, C. Reinhard, Y. Liu, E. Schofield, and I.C. Freestone.

*Source:*
Corros. Sci. 159, 108132

*Year:*
2019

*Relevant engineered barrier:*
Cast iron, steel

*Relevant use or application of the study:*
Analytical technique

*Keywords.:*
Micro-tomography, grey cast iron, white cast iron graphite flakes

*Original abstract/summary/conclusions*
A combination of X-ray analytical techniques has been used to study the microstructure and corrosion of a 450-year-old cast-iron cannonball fragment from the Mary Rose shipwreck. Using a 3D approach, it has been shown that akaganeite, β-FeO(OH, Cl), starts to appear ~1.5mm below the outer surface of the object, occurring selectively around non-contiguous graphite flakes in the microstructure, with no corrosion in graphite-free regions. This spatial analysis has given a new look inside a 450-year-old system, to see how metallographic features interact with local chemical environments to give complex corrosion products, centuries in the making.

*Current author review comments:*
An interesting study of ancient metallurgy and materials, and a caution about the dangers of conservancy gone awry. The subject matter (a cast iron cannon ball) is not particularly relevant to the NWMO C-steel substrate and no relevant corrosion information is contained in the paper.

However, this is an interesting application of 3D synchrotron micro-tomography with a pixel resolution of 7.9 μm, that might find some application using the Canadian Light Source.

*Ref. no.:* 016

*Title:*
Natural analogues for the predictive reliability of the engineered barrier system for high-level waste.

*Authors:*
Apted, M.J.

*Source:*
In Proc. Fourth Natural Analogue Working Group Meeting and Poços de Caldas Project Final Workshop, B. Côme and N.A. Chapman (eds.), European Commission Report, EUR 13014 EN, pp. 73-93.

*Year:*
1991

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Thermodynamic stability

*Keywords.:*
Keweenaw, native copper

*Original text (partial):*

“Copper is one of the few elements, and certainly the least expensive, that occurs in its native state under geological conditions relevant to repository isolation. The most prominent natural analogue is the massive native-copper deposits on the Keweenaw Peninsula, Michigan, U.S.A. (Crisman and Jacobs 1982). These deposits occur in the Precambrian (-500 million years old) Portage Lake Volcanics, a series of basaltic lava flows interbedded with conglomerates (Figure 2). Some copper occurs as veins cutting these rocks, but principally either in the lava flows filling amygdules, or in the conglomerates filling interstices. The copper was initially distributed as a trace component in silicate minerals of underlying formations; later, hydrothermal waters caused propylitic alteration (zeolite facies) of the rocks, mobilized the copper under acidic conditions, and deposited it as metallic copper upon contact with the reducing, sulfur-poor basaltic lavas and conglomerate beds. *In situ* occurrences show negligible signs of post-emplacement alteration or mobilization.

This natural analogue for copper can be inverted. Massive metallic copper does not occur as a primary phase in fresh basalt, even under reducing conditions at which it is calculated to be stable. Instead it occurs initially as a trace component in silicate and sulfide phases. This is a consequence of copper's low abundance and the tendency toward free-energy minimization (via formation of solid solutions) within natural systems. Formation of massive metallic copper nodules and veins results from release and migration under low-grade propylitic alteration of the host basalt. Viewed in this way, the same Keweenaw deposits support the contention that copper can be extremely reactive and mobile under certain geological conditions (Jacobs 1984). The utility of such an analogue, therefore, is not the 500 million year persistence of metallic copper, *per se.* Rather, it validates that the reactivity and mobility of copper in natural systems (and by analogy, repository systems) can be predicted using geochemical principles and thermodynamic data.”

*Check if additional Comments made* ☒

*Current author review comments:*

An interesting interpretation of the genesis and alteration of the native copper deposits in Michigan from a geochemists viewpoint. Instead of using them as an example of long-term (“thermodynamic”) stability, Apted argues that they are equally indicative of the reactivity and mobility of copper.

Instead, he argues that their value lies in the confirmation of the application of geochemical principles to such natural systems.

Also published as J. Geochem. Explor. 46, 1992, 35-62 (see #021)

*Ref. no.:* 017

*Title:*
Natural analogue study on native iron.

*Authors:*
Hellmuth, K.–H.

*Source:*
In Proc. Fifth CEC Natural Analogue Working Group Meeting and Alligator Rivers Analogue Project (ARAP) Final Workshop, H. von Maravic and J. Smellie (eds.), European Commission Report, EUR 15176 EN, pp. 333-342.

*Year:*
1994

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*

*Keywords.:*

*Original abstract/summary/conclusions*

Native iron formed at high, magmatic temperatures is rare because of the special conditions of formation. Millions of tons have survived millions of years mostly at shallow depths within the rock matrix due to mass transport limitations and/or pore water conditions favouring passivation of the metal. For a comprehensive understanding of the preservation of native iron further investigation of the nature and role of the corrosion products is needed.

Native iron formed at lower, hydrothermal to ambient temperatures during the serpentinization of ultrabasic rocks is more abundant than commonly believed. In this case preservation is due to thermodynamic stability under highly reducing groundwater conditions generated during serpentinization. High-FeO olivine used as backfill could assure favourable groundwater conditions in nuclear waste repositories.

*Current author review comments:*
An interesting early discussion of the use of native Fe as analogues for C-steel. The paper suggests that, the reducing environment required for deposition of the Fe in the first place (high temperature, $H_2$ overpressure, could persist.

The main take-home message from this paper is that native metal deposits fall into two categories:

Kinetically stable – mass-transport limitations, passivation
Thermodynamic limitation – thermodynamically stable

Thermodynamic stability is easier to see in the case of Cu, as opposed to Fe, although since all(?) Cu and Fe deposits were formed by reduction of oxidized species, there must have been sufficiently reducing conditions at some stage for the metals to form in the first place.

| | |
|---|---|
| *Ref. no.:* 018 | |
| *Title:*<br>Natural analogues for canister performance. | |
| *Authors:*<br>Vira, J. | |
| *Source:*<br>In Proc. Sixth EC Natural Analogue Working Group Meeting, H. von Maravic and J. Smellie (eds.), European Commission Report, EUR 16761 EN, pp. 163-342. | *Year:*<br>1996 |
| *Relevant engineered barrier:*<br>Copper, steel | |
| *Relevant use or application of the study:* | |
| *Keywords.:*<br>NAWG | |

*Original abstract/summary/conclusions*

Corrosion behaviour of waste canisters seems to be one of the few areas where natural analogues have been directly applied in performance analysis. Studies of archaeological objects and native existence of canister materials have been used to support models and estimates. None of the studied cases are truly representative of the conditions in the planned repositories, but they do confirm that important processes are understood. In general, the uncertainties as to canister performance seem to be small in relation to uncertainties in the safety analysis of final disposal as a whole, but noting the emphasis placed on the canister in some planned disposal systems, additional evidence would probably not be overlooked, in particular, if it came from conditions sufficiently similar to those at disposal.

*Current author review comments:*

Brief summary of early (mainly SKB and Nagra) inclusion of canister corrosion analogue studies in safety assessment.

*Ref. no.:* 019

*Title:*
A corrosion study of the ferrous medieval reinforcement of the Amiens cathedral. Phase characterisation and localisation by various microprobes techniques.

*Authors:*
Monnier, J., D. Neff, S. Réguer, P. Dillmann, L. Bellot-Gurlet, E. Leroy, E. Foy, L. Legrand, and I. Guillot.

*Source:*
Corros. Sci. 52, 695-710.

*Year:*
2010

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*

*Keywords.:*
Atmospheric corrosion, corrosion products, Fe(III) phases

*Original abstract/summary/conclusions*
In this study, long term corrosion mechanisms are approached through the characterisation of corrosion products formed on ancient artefacts over 500 years. Thirty-one artefacts were sampled in the Amiens cathedral. The thick corrosion product layers have been characterised at a microscopic scale by coupling complementary microbeam analytical techniques (SEM-EDS, Raman microspectroscopy, X-ray microdiffraction and microfluorescence, X-ray absorption microspectroscopy under synchrotron radiation). The main phase of the corrosion layer is goethite but lepidocrocite and akaganeite are also present locally in the corrosion layer. In addition, the presence of low crystallinity phases (feroxyhyte and/or ferrihydrite) is showed. These phases are electrochemically reactive, thus they could play a key role in the corrosion mechanisms.

*Current author review comments:*
Qualitative study of corrosion product composition and structure on 31 artifacts exposed to atmospheric conditions with ages up to 500 years. Of the 31 samples, 6 exhibited ferrite-pearlite microstructure stated to be consistent with carbon steel, and the other 25 were primarily ferrite with different amounts of P. These “are classically found in pre-Bessemer ferrous alloys”.

*Ref. no.:* 020

*Title:*
Natural analogues: studies of geological processes relevant to radioactive waste disposal in deep geological repositories.

*Authors:*
Alexander, W.R., H.M. Reijonen, and I.G. McKinley.

| *Source:*<br>Swiss J. Geosci. 108, 75-100. | *Year:*<br>2015 |
|---|---|

*Relevant engineered barrier:*
UFC, copper, steel

*Relevant use or application of the study:*
Confidence building

*Keywords.:*
Littleham Cove

*Original abstract/summary/conclusions*

The geological disposal of radioactive wastes is generally accepted to be the most practicable approach to handling the waste inventory built up from over 70 years accumulation of power production, research–medical–industrial and military wastes. Here, a brief overview of the approach to geological disposal is presented along with some information on repository design and the assessment of repository postclosure safety. One of the significant challenges for repository safety assessment is how to extrapolate the likely long-term (i.e. ten thousand to a million years) behaviour of the repository from the necessarily short term data from analytical laboratories and underground rock laboratories currently available. One approach, common to all fields of the geosciences, but also in such diverse fields as philosophy, biology, linguistics, law etc., is to utilise the analogue argumentation methodology. For the specific case of radioactive waste management, the term 'natural analogue' has taken on a particular meaning associated with providing supporting arguments for a repository safety assessment. This approach is discussed herewith a brief overview of how the study of natural (and, in particular, geological) systems can provide supporting information on the likely long-term evolution of a deep geological waste repository. The overall approach is discussed and some relevant examples are presented, including the use of uranium ore bodies to assess waste form stability, the investigation of native metals to define the longevity of waste containers and how natural clays can provide information on the stability of waste tunnel backfill material.

*Current author review comments:*

Overview and summary of analogue studies for all aspects of deep geological disposal, including canister corrosion. Focusses on two specific areas for corrosion: (i) the use of analogue corrosion rates to support C-steel lifetime prediction and (ii) the use of Littleham Cove copper deposits as an example to support potential contention of long lifetimes. Interestingly, in respect of Littleham Cove, authors suggest:

*"However, uncertainties remain and these include:*
*• The porosity and permeability of the mudstone host rocks has not been examined but the permeability is likely to be greater than would be the case for an engineered bentonite buffer in a repository (i.e. more corrosion would be expected at Littleham Cove)*
*• Similarly, the porewaters in the Littleham Mudstone Formation may have been significantly different to those anticipated in a radioactive waste repository."*

If Littleham Cove has a higher rate of mass transfer than compacted bentonite, then it would indeed be an impressive example of "kinetically-stable" native copper.

*Ref. no.:* 021

*Title:*
Natural analogues for predicting the reliability of the engineered barrier system for high-level waste.

*Authors:*
Apted, M.J.

| *Source:* | *Year:* |
|---|---|
| J. Geochem. Explor. 46, 35-62. | 1992 |

*Relevant engineered barrier:*
Copper, steel

*Relevant use or application of the study:*
Lifetime prediction

*Keywords.:*
Welds

*Original abstract/summary/conclusions*

The application of natural analogues in predicting the long-term reliability of engineered barrier materials is reviewed. Excellent natural and archaeological analogues exist for predicting the stability conditions for several metals as container materials. Analogues for corrosion-resistant and corrosion allowance materials are problematical, they are non-existent for the former and restricted to modes of failure (i.e., uniform corrosion) for the latter materials that are irrelevant to their expected failure at weldments, for which there are no suitable analogues. Abundant natural analogues indicate that at temperatures below 100°C, smectitic clay will remain unaltered for more than $10^6$ years. Natural analogues also confirm the expected dissolution behavior and alteration sequence for metastable alteration products of nuclear waste forms under repository conditions. Numerous natural analogues also confirm the applicability of thermodynamic equilibrium and mass-transfer models in predicting the migration of radionuclides through the near field.

The role of natural analogues in guiding experimental work and evaluating the adequacy of experimental apparatus is often overlooked and should be extended in this direction. In particular, "acceleration" of short-term laboratory tests to collect data under repository-relevant conditions that are representative of much longer durations should be based on correlations developed from natural systems. Analogues composed of two or more components of the engineered barrier system (EBS) should be sought to evaluate the potential for synergistic reactions. Coprecipitation of trace-element concentrations of radioelements under low-temperature conditions is a complex, yet vital, issue that should be resolved by natural analogue studies in conjunction with laboratory tests

*Current author review comments:*

Insightful critique of the usefulness of analogues for container corrosion. Native metal deposits may be of most use although, in the case of copper, they are commonly not analogues of thermodynamic stability but more the general applicability of geochemical thermodynamic and kinetic models and, in the case, of Fe, they are of limited use because of the dissimilarity of the alloy. Archeological analogues are even less useful as (i) the metallurgy is wrong, (ii) the disposal environment is inappropriate, and (iii) they only really address uniform and localised corrosion which may be the important processes for certain alloys, but not for corrosion-resistant container materials (for which welds may be particularly susceptible and, for which, there are no analogues).

Journal publication based on NAWG conference presentation (see #016).

*Ref. no.:* 022

*Title:*
On the corrosion resistance of the Delhi iron pillar.

*Authors:*
Balasubramaniam, R.

*Source:*
Corros. Sci. 42, 2103-2129

*Year:*
2000

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Not useful for Canadian program

*Keywords:*
Atmospheric corrosion, wet-dry cycles, phosphorus

*Original abstract/summary/conclusions*

The nature of the protective passive layer on the corrosion resistant Delhi iron pillar (DIP) has been addressed based on a detailed characterization of its rust. Rust characterization clearly established that the major constituents of the scale were crystalline iron hydrogen phosphate hydrate ($FePO_4 \cdot H_3PO_4 \cdot 4H_2O$), α–, γ–, δ–FeOOH and magnetite. The iron oxide/oxyhydroxides were present in the amorphous form. The role of slag particles in the matrix of the DIP iron in enhancing the passive film formation is briefly addressed initially. The process of protective rust formation on DIP iron is outlined based on the rust analysis. Initially, the corrosion rate of iron is high due to the presence of slag particles. This results in enhancement of surface P content. In the presence of P, the formation of a protective amorphous compact layer of δ-FeOOH, next to the metal surface, is catalyzed and this confers the initial corrosion resistance. The critical factor contributing to the superior corrosion resistance of the DIP, however, is the formation of iron hydrogen phosphate hydrate, as a thin layer next to the metal-metaloxide interface. The formation of the crystalline modification of this phosphate from the amorphous form is aided by alternate wetting and drying cycles (i.e. the environmental factor). The rate of corrosion is further lowered due to the low porosity content of the crystalline phosphate phase. The passive film formation on the DIP has been contrasted with the rusting of normal and weathering steels.

*Current author review comments:*

Oft cited, but relatively un-useful, analogue for longevity of C–steel containers. The absence of corrosion is a consequence the formation of a P-containing corrosion product that formed as a result of the high P content (estimated variously to be between 0.1 and 0.5 wt.%). This may be a suitable analogue for the Andra program with an extended unsaturated phase, but is not helpful for the Canadian program.

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|---|---|
| *Ref. no.:* 023 | |
| *Title:*<br>Copper tracing to determine the micrometric electronic properties of a thick ferrous corrosion layer formed in an anoxic medium. | |
| *Authors:*<br>Saheb, M., D. Neff, C. Bataillon, E. Foy, and Ph. Dillmann. | |
| *Source:*<br>Corros. Sci. 53, 2201-2207. | *Year:*<br>2011a |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Properties of corrosion product layers | |
| *Keywords:*<br>Distribution anodic and cathodic sites, corrosion product, porosity | |

*Original abstract/summary/conclusions*

In anoxic carbonated environments, the corrosion layer formed on iron is composed of magnetite and ferrous carbonates with different distributions, influencing the electronic properties of the whole layer. This study aims at determining at a micrometric scale the electronic properties of such corrosion layers, with a reaction tracing based on the use of the $Cu^{2+}/Cu(0)$ redox couple. Experiments reveal that the electrons formed at the metallic interface are available everywhere in the pores of a thick corrosion layer. This result is of importance to elucidate the corrosion mechanisms because it implies a decoupling of the anodic and the cathodic reactions.

*Current author review comments:*

Elegant experimental method to explore the spatial distribution of conductivity and, potentially, of anodic and cathodic processes.

*Ref. no.:* 024

*Title:*
Micromechanical study of corrosion product layers. Part I: Experimental characterization.

*Authors:*
Dehoux, A., F. Bouchelaghem, Y. Berthaud, D. Neff, and V. L'Hostis.

| *Source:*<br>Corros. Sci., 54, 52-59. | *Year:*<br>2012 |
|---|---|

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Joint mechanical corrosion analysis of galvanic coupling

*Keywords:*
Stress-strain curves, Young's modulus, micro-indentation

*Original abstract/summary/conclusions*
A micromechanical characterization had been performed on ancient artefacts corrosion products. The proposed experimental approach allies scanning electron microscopy observations, micro-indentation tests which allow the characterization of the local stiffness of elementary constituents, and finally Raman micro-spectroscopy tests which give access to the local crystallised phases of the samples. The experimental campaign contains a large series of tests, which give us the opportunity to interpret the dispersion of local stiffness measurements.

*Current author review comments:*
Another elegant approach to measuring properties of corrosion product layers, in this case the mechanical properties. It is not clear how this could be applied in the Canadian program as we have no mechanism that depends on the material properties of corrosion products, except possibly for the delamination of the copper coating due to the formation of C–steel corrosion products. In that case, however, it is the technique rather than the age of the sample which is relevant.

*Ref. no.:* 025

*Title:*
Analogues for the corrosion-induced expansion of iron in HLW containers.

*Authors:*
Smart, N.R., R. Adams, and L. Werme.

*Source:*
Mat. Res. Symp. Proc. 807, 879-884.

*Year:*
2004

*Relevant engineered barrier:*
Copper, steel

*Relevant use or application of the study:*
Galvanic corrosion

*Keywords:*
Pinhole, expansive corrosion products

*Original abstract/summary/conclusions*

In Sweden, spent nuclear fuel will be encapsulated in sealed cylindrical canisters, consisting of a cast iron insert and a copper outer container. The canisters will be placed in a deep geologic repository and surrounded by bentonite. If a breach of the outer copper container were to occur the cast iron insert would undergo anaerobic corrosion, forming a magnetite film whose volume would be greater than that of the base metal. In principle there is a possibility that accumulation of iron corrosion product could cause expansion of the copper canister. Anaerobic corrosion rates are very slow, so in the work described in this paper reference was made to analogous archaeological materials that had been corroding for long periods in natural anoxic aqueous environments. This paper describes a number of archaeological artefacts containing iron and copper corroding in constrained geometries in anoxic natural waters. No evidence has been obtained which would suggest that severe damage is likely to occur to waste canisters as a result of expansive corrosion of cast iron under repository conditions.

*Current author review comments:*
Could be useful for treating possible delamination of copper coating due to galvanic corrosion at pinhole in coating.

However, because of the short-term nature of this process, it is quite amenable to laboratory study under more-relevant and better-controlled conditions. Therefore, the value of the analogue is not so much to provide mechanistic insight that is otherwise unavailable, but more to build confidence.

*Ref. no.:* 026

*Title:*
Corrosion of iron archaeological artefacts in soil: Estimation of the average corrosion rates involving analytical techniques and thermodynamic calculations.

*Authors:*
Neff, D., P. Dillmann, M. Descostes, and G. Beranger.

*Source:*
Corros. Sci. 48, 2947-2970.

*Year:*
2006

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Estimation lifetime steel inner shell

*Keywords:*
Corrosion rate, iron, corrosion product layer

*Original abstract/summary/conclusions*
Archaeological artefacts have been analysed in order to determine the average corrosion rate of low carbon steel after long burial periods. The method adopted consists of two steps. The first one is based on the thickness measurement of the corrosion products, which after density correction and sample age consideration, provides a corrosion rate. As the obtained value is a minimum, another step is required to evaluate a maximal limit. This is calculated by simulating the dissolution of the phases identified in the corrosion products, considering the burial conditions. Results show that it is possible to establish a reliable maximal limit for corrosion forms containing goethite and magnetite in oxidising conditions. The estimated average corrosion rates do not exceed 4 μm/year.

*Current author review comments:*
Contribution to the database of iron corrosion rates in soils under relatively oxidizing conditions. Of limited usefulness for NWMO.

*Ref. no.:* 027

*Title:*
Long-term corrosion of iron and copper.

*Authors:*
Crossland, I.

*Source:*
In Proc. 10th Int. Conf. Environ. Remediation Radioactive Waste Management, ICEM'05, September 4-8, 2005, Glasgow, Scotland (American Society Mechanical Engineers, New York, NY), paper ICEM05-1272.

*Year:*
2005

*Relevant engineered barrier:*
Copper, steel

*Relevant use or application of the study:*
Lifetime estimate steel shell, confidence building

*Keywords:*
Corrosion rate, iron, copper, aerobic, anaerobic, soils, water

*Original abstract/summary/conclusions*

Analysis of long-term corrosion data for iron and copper shows that parabolic kinetics provide an adequate description of the corrosion behaviour in soil over thousands of years. When iron corrodes in free water however, the corrosion rate is approximately constant with time. The implications of these observations are discussed.

*Current author review comments:*

Useful compilation of analogue corrosion rate data for both iron and copper alloys, in soils and in water, and under aerobic and anaerobic conditions. The iron data are directly useful for supporting long-term predictions of the lifetime of the steel shell, whereas the copper data are useful for confidence building.

*Ref. no.:* 028

*Title:*
The corrosion of more than 176 million year old native copper plates from a deposit in mudstone in South Devon; United Kingdom.

*Authors:*
Milodowski, A.E., M.T. Sykes, L. Werme, and V.M. Oversby.

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|---|---|
| *Source:*<br>In Proc. CORROSION/2003, NACE International (Houston, TX), paper no. 03681. | *Year:*<br>2003 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Longevity of native copper, confidence building

*Keywords:*
Native copper, Littleham Cove

*Original abstract/summary/conclusions*
Copper is the selected material for the corrosion barrier in the canister for encapsulation of spent nuclear fuel from the Swedish power reactors. These canisters will be buried in a deep geological repository in granitic rock at a depth of 400 to 700 m. At these depths, the groundwater will be reducing and copper will be immune to corrosion in the absence of dissolved sulphides. Under these conditions the spent fuel canisters are expected to meet with a very high margin SKB's design goal of 100 000 years. Extrapolations of short-term experimental data to such long times will always have some degree of uncertainty. Therefore, natural analogues are sometimes used to bridge the gap between laboratory time scales and the very long times for which a repository is designed. In the present paper, we present an analysis of the corrosion of native copper plates that have survived in a water-saturated clay environment for more than 176 million years. Although the native copper is affected by corrosion, the study shows that a significant proportion (30-80 % of the original thickness) of the copper sheets is preserved in the saturated compacted clay environment of the Littleham Mudstone. Apart from the recent weathering effects due to exposure at outcrop, petrographical studies demonstrate that most of the observed corrosion and alteration of the native copper is geologically old (i.e. predating the main sediment compaction) and also occurred before the end of the Lower Jurassic. This demonstrates that the native copper can remain stable in a saturated and compacted clay environment for geological timescales well in excess of the timescales considered for performance assessment of a deep geologic repository for spent nuclear fuel.

*Check if additional Comments made* ☒

*Current author review comments:*
Characterisation of five native copper plate samples. Suggestion that indications of “compactional deformation” indicate that sheets were deposited prior to compaction of the mudstones, i.e., at a time when the sediments were of lower density and higher porosity. Plates are of high copper content (>99%). There is a halo of $Cu_2O$ in the mudstone around the copper plates, but is is unknown whether this represents copper that was not reduced completely to Cu(0) at the time that the native copper was formed or, alternatively, whether it represents copper that has subsequently corroded and diffused away from the plates before precipitating as $Cu_2O$. Either way, this halo is only of the order of 20-200 mm in width. Speculation that Cu(0) was reduced from an oxidised aqueous solution by reduction associated with organic detritus.

Suggestion is that there was a period of corrosion after the plates were formed, but that the environment then returned to reducing conditions and the plates became stable. The implication is, therefore, that they are thermodynamically stable.

Interestingly, only one side of the platelets tends to be corroded. Furthermore, in stacks of platelets, it is always the same side of the platelet that is corroded. No obvious difference in the compacted sediment on either side of the plates could be discerned to explain this observation.

However, not clear whether this could also be an example of kinetic (mass transport) stability. Could the corrosion of the platelets have been suppressed by compaction of the deposits.

*Ref. no.:* 029

*Title:*
Species transport in the corrosion products of ferrous archaeological analogues: a contribution to the modelling of long-term iron corrosion mechanisms.

*Authors:*
Vega, E., P. Dillmann, P. Berger, and P. Fluzin.

*Source:*
In Corrosion of Metallic Heritage Artefacts, European Federation of Corrosion Green Book, Volume 48, chap. 6, pps. 92-108.

*Year:*
2007

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Model validation

*Keywords:*
Corrosion product, porosity, distribution anodes and cathodes

*Original abstract/summary/conclusions*

Different archaeological specimens coming from the site of Glinet (France) have been analysed to determine the corrosion system. As proposed in previous studies, this system can be described using specific terms: Metal (M), Dense Product Layer (DPL) and Transformed Medium (TM). The coupling of OM, EDS–SEM, µXRD and µRaman spectroscopy reveals two different corrosion systems: one contains siderite, the second only goethite and magnetite/maghemite mixes. On this second type of corrosion system, specific study of species transport using different kinds of markers was performed. Immersion of the corrosion system in a water solution saturated in $^{18}O$ confirms the hypothesis made in previous studies that both anodic and cathodic reactions were located at the metal/DPL interface. Then, to investigate whether the transport of dissolved oxygen in the DPL pores controls the corrosion kinetics, instantaneous corrosion rates were evaluated using different methods: (i) under the hypothesis of control by oxygen transport in the DPL pores, (ii) by evaluating the quantity of $^{18}O$ atoms that reacted during the immersion experiment, and (iii) by extrapolating the average corrosion rate deduced from the nature, thickness and age of the corrosion products. Comparison of the different values obtained seems to confirm the fact that the diffusion of dissolved oxygen controls the kinetics and it is not necessary to invoke a barrier layer to obtain relatively slow corrosion rates after 400 years (about 0.1–0.6 µm/year). Moreover, it seems that the corrosion kinetics cannot be modelled by a simple parabolic law, on the one hand because the first stage of the corrosion is more likely to follow a linear law and the duration of this first stage is not known, and on the other hand because the appearance of cracks in the DPL could provoke kinetic breaks that have to be taken into account in the model. Future work will focus on a finer estimation of apparent diffusion coefficient in the DPL, by using other experimental methods such as diffusion cells and other markers. Moreover, the modelling of the corrosion kinetics will be improved by taking into account the role of cracks.

*Current author review comments:*

The conclusion that both anodic and cathodic reactions occur at the metal/DPL interface is contrary to the conclusion of Saheb et al. (2011) (#023) for magnetite/carbonate corrosion product layers. It is not clear whether this just represents an evolution in thinking from 2007 to 2011, or whether the spatial distribution of anodes and cathodes is different for magnetite/maghemite (in this paper) than for magnetite/carbonate films (#023).

Mercury intrusion porosimetry measurements of corrosion product suggests total porosity of 25%, distributed between micropores and nanopores.

*Ref. no.:* 030

*Title:*
Inferences from a corrosion study of a bronze cannon, applied to high level nuclear waste disposal.

*Authors:*
Hallberg, R.O., P. Östlund, and T. Wadsten.

*Source:*
Appl. Geochem. 3, 273-280.

*Year:*
1988

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*

*Keywords.:*
Bronze cannon, Kronan

*Original abstract*
A bronze cannon was used as an analogue of corrosion processes for Cu. The cannon has been embedded in clay sediments in the Baltic Sea since 1676. Corrosion products are cuprite and malachite, mainly derived from transformation of tenorite inclusions of the bronze alloy. The bronze matrix exhibits little corrosion and a conservative estimate for the maximum corrosion of Cu is <10 mm in 100,000 a. Mechanisms for the chemical corrosion processes are suggested.

*Original conclusions*
The cannon which was recovered in 1985 has been embedded for more than 300 a in a clay which largely has the same properties as the clay considered for use in the final storage of Swedish nuclear fuels. The Cu concentration in the bronze alloy is abnormally high, 96.3 wt %, compared with a more normal 90 wt %, which makes it a more suitable object in studies of Cu corrosion. The main corrosion products of Cu are cuprite and malachite, where cuprite dominates. The transformation of tenorite to cuprite can be explained by redox processes where $Fe^{2+}$, organic matter and elemental Cu are the major electron donors.

*Current author review comments:*
This is an important analogue study for copper UFC, for a number of reasons:

1. It represents a Cu-rich component (96.3 wt.% Cu) in contact with illite-montmorillonite-kaolinite clay in a saturated saline environment, albeit under oxidizing conditions (Eh = +0.45 $V_{SHE}$, pH 7.0)
2. Although the original study was used to derive a corrosion rate, the re-analysis by King (#031) provided mechanistic support for what was to become the CCM.

*Ref. no.:* 031

*Title:*
A natural analogue for the long-term corrosion of copper nuclear waste containers – reanalysis of a study of a bronze cannon.

*Authors:*
King, F.

*Source:*
Appl. Geochem. 10, 477-487.

*Year:*
1995

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Model validation, conceptual model development

*Keywords:*
Kronan, clay sediments, diffusion, CCM

*Original abstract/summary/conclusions*

The study of natural analogues is often used to support long-term predictions of the safety of geological disposal of used nuclear fuel. The case of a bronze cannon, submerged in seawater-saturated clay sediments for a period of 310 a, is reassessed with reference to a corrosion mechanism developed for copper nuclear waste containers in a conceptual disposal vault in the Canadian Shield. Redox reactions between Cu, Fe and dissolved $O_2$ are believed to have played an important role in the corrosion of the bronze cannon and also form an essential part of the corrosion mechanism proposed for nuclear waste containers. Limited rates of mass transport through compacted clay are also important in determining the corrosion behaviour of both the cannon and containers.

*Current author review comments:*

Further analysis of the Kronan cannon, in this case used to provide support for the conceptual mechanism that underlies the Copper Corrosion Model (CCM).

*Ref. no.:* 032

*Title:*
Mechanistic modelling of the corrosion behaviour of copper nuclear fuel waste containers.

*Authors:*
King, F. and M. Kolář

| | |
|---|---|
| *Source:*<br>In Proc. 1996 Canadian Nuclear Society Meeting, Winnipeg. Also published as AECL Report AECL-11644, COG-96-327. | *Year:*<br>1996 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Model validation

*Keywords.:*
Copper corrosion model, Kronan, bronze cannon

*Original abstract/summary/conclusions*
A mechanistic model has been developed to predict the long-term corrosion behaviour of copper nuclear fuel waste containers in a Canadian disposal vault. The model is based on a detailed description of the electrochemical, chemical, adsorption and mass-transport processes involved in the uniform corrosion of copper, developed from the results of an extensive experimental program. Predictions from the model are compared with the results of some of these experiments and with observations from a bronze cannon submerged in seawater-saturated clay sediments. Quantitative comparisons are made between the observed and predicted corrosion potential, corrosion rate and copper concentration profiles adjacent to the corroding surface, as a way of validating the long-term model predictions.

*Current author review comments:*
Classic example of the use of analogues to validate long-term model predictions. This also represents one of the few attempts to validate the CCM against experimental (or analogue) data. The validation was most successful in terms of the observed and predicted [Cu] profiles through the sediments away from the surface of the cannon.

The comparison of the analogue to the model was probably more useful for validating the conceptual model (in particular the diffusive transport of Cu(II) away from the surface) than other aspects, such as the predicted corrosion rate.

*Ref. no.:* 033

*Title:*
Anthropogenic analogues for geological disposal of high level and long lived waste.

*Authors:*
IAEA (International Atomic Energy Agency)

| *Source:* | *Year:* |
|---|---|
| International Atomic Energy Agency, IAEA-TECDOC-1481. | 2005 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Argentina, China, Ukraine, corrosion rates

*Original summary (partial)*

The studies examined the thickness and nature of the alteration layer on the corroded metal objects and on glass fragments, and allowed to drew [sic] conclusions on mechanisms and rates of uniform corrosion. The principle findings of the studies can be summarised as follows:

— The Chinese bronze samples from archaeological sites in semi-tropical humid regions exhibited corrosion crusts of 320–800 µm compared to 50–260 µm measured for samples from sites in drier, temperate climate zone. A maximum corrosion rate of about 0.27 µm/a was estimated, which was close to the average values of Tylecote and Johnson/Francis [6–7] (see Figure 1).

— The Argentinean bronzes spanned a greater range of corrosion rates. The five artefacts for which rates could be estimated with high certainty (Group 1 in Figure 1) were within the range 0.08 to 0.17 µm/a. Those with high uncertainty (from the La Paya site — Group 2 in Figure 1) could have a maximum rate an order of magnitude higher (up to about 2.5 µm/a). The Group 1 values were within the range observed by Johnson and Francis [6]. No pitting corrosion was observed on any of the bronze samples.

— Corrosion rates for the 2100–2400 year old bronzes from the Ukraine were related to their Sn content (see Figure 1) and they are in a similar range to the other materials reported in this project, with maximum values somewhat greater than the Johnson and Francis control set. High Sn bronzes had the lowest corrosion rates, which were of an order of magnitude lower than the typical rate of an atmospheric corrosion of a modern tin bronze. However, they were subject to brittle mechanical failure. One artefact made of low Sn bronze that had been thermally and mechanically worked after casting had an equivalently low corrosion rate.

— Corrosion of bronzes mobilised Cu from the metal, forming a passivating corrosion crust. In the Chinese bronzes, this comprised an inner layer of red oxide overlain by an outer carbonate (malachite) layer, with associated minor oxide, carbonate and hydroxide phases of Sn, Cu and Pb. The two sites studied in the Ukraine had different soils, with those containing higher levels of organic matter, S and Cl and with a higher pH being the most aggressive with respect to corrosion.

— Pure copper artefacts from the Ukraine displayed an outer rim of cuprite, malachite, and covellite mineralization, incorporating Cl, C, Fe and Al from the surrounding soils. Simple cast samples had larger and less homogeneous grain sizes compared to thermally and mechanically worked – forged – castings and were prone to corrosion penetration along grain boundaries. Corrosion rates for worked copper are in the lower end of the overall range for bronzes (see Figure 1). A cast copper artefact had a higher
corrosion rate, near the upper end of the range given by Johnson and Francis.

*Check if additional Comments made* ☒

*Current author review comments:*
A summary report from an IAEA Coordinated Research Program (CRP) on man-made analogues for various engineered barriers. Report includes appendices detailing on three specific studies conducted in Argentina, China, and Ukraine as part of the CRP (see #034, 035, 036). In large part, the studies are based on characterization or the copper samples and estimation of corrosion damage (either corrosion rate or corrosion depth), rather than conceptual model development of model validation. Despite what is stated in the summary, it is not clear what mechanistic information was gleaned.

*Ref. no.:* 034

*Title:*
Studies on the behaviour of ancient man-made materials as analogues of materials used for the disposal of high-activity and long lived waste.

*Authors:*
Palacios, T.A., E.D. Cabanillas, C. Semino, and L.R. González.

*Source:*
In International Atomic Energy Agency, IAEA-TECDOC-1481, Appendix A

*Year:*
2005

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Characterisation, corrosion rate, Argentina, bronze

*Original abstract/summary/conclusions*

The disposal of high-activity and long lived waste (HLW) requires the study of ancient materials distinguished by their longevity in different environments in order to predict the long-term durability of the waste containers. The patina thickness of pre-Columbian and historical artefacts from Argentina was measured and their corrosion rates determined. The results can be used as an example of the durability of some man-made materials for designing HLW repositories.

*Current author review comments:*

Characterisation of corrosion products and estimation of corrosion rates for 10 bronze artifacts with ages from 176-1030 a and with Cu contents of 66-92 wt.%.

*Ref. no.:* 035

*Title:*
A study on the corrosion of unearthed bronze relics.

*Authors:*
Chen, Z., Y. Lin, G. Fan, Z. Wen, S. Sun, Y. Li, and Z, Zhang.

| | |
|---|---|
| *Source:*<br>*Source:*<br>In International Atomic Energy Agency, IAEA-TECDOC-1481, Appendix B. | *Year:*<br>2005 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Characterisation, corrosion rate, China, bronze

*Original abstract/summary/conclusions*
This paper presents compositional analyses and structure observations of bronze relict samples and environmental conditions of the sites where the samples were collected. These bronze samples were taken from the dry region of northern China and the humid region of southern China. Their ages were 1800, 3000 and 3300 years. Research results revealed that the bronze relics had been continuously corroded with time. The corrosion layer consisted of at least two sub-layers, such as oxide and carbonate. There was a mechanical corrosion sublayer found in few samples (a loose sub-layer). A $SnO_2$ sub-layer also occurred in a few samples. The thickness of bronze corrosion layers varied with the different climate environments in which the samples were taken. Their thickness was 50–260 μm and 320–800 μm in the dry and humid climate regions, respectively. With respect to natural corrosion resistance, bronze is recommendable as a material for HLW repository system canisters.

*Current author review comments:*
Characterisation of corrosion products and estimation of corrosion rates for 15 bronze artifacts with ages from 1800-3300 a and with Cu contents of 65-94 wt.%.

*Ref. no.:* 036

*Title:*
The stability of the ancient metal and glass from archaeological sites of the Northern Prichernomor’e (Ukraine) and their physical and chemical interactions with their burial environment.

*Authors:*
Manichev, V., L. Demchenko, B. Zlobenko, V. Kadoshnikov, and L. Spasova.

| *Source:* | *Year:* |
|---|---|
| In International Atomic Energy Agency, IAEA-TECDOC-1481, Appendix D. | 2005 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Characterisation, corrosion rate, Ukraine, bronze

*Original abstract/summary/conclusions*
A study has been carried out regarding degradation processes occurring on glass, copper and bronze artefacts excavated from the ancient settlement sites of Kamenka and Olbiya (the North Coast of the Black Sea). Its goal was to perform scoping evaluation of long-term resistance of some materials considered for the use as engineered barriers in a geological repository (waste form, container). The geochemical environment was characterised by analysis of accompanying soil. A variety of methods were employed to characterize the physical-chemical properties of the samples, including spectrography, X ray diffractometry, X ray spectrometry, infrared spectrometry, optical microscopy, scanning electron microscopy, chemical, mineralogical, spectral, radiocarbon dating, etc. and other analytic techniques. The study has shown that, under hydration conditions (weathering), a superficial layer of complicated structure was formed on the glass surface independent on glass composition; the thickness of this film varied from several tens to hundreds microns. The samples of ancient glass which contained organic substances showed the highest degree of alteration/degradation, but the reasons have not been revealed. It could be concluded that among the metallic ancient anthropogenic analogues of materials the most suitable were pure copper and low-tin bronzes (especially if subjected to mechanical-thermal treatment, such as cold and hot forging); however, their performance was significantly dependent on the geochemical conditions of the environment. Among the cast metals, the high-tin bronzes were the most corrosion-resistant, probably due to formation of thin protective film of oxidative phase on its surface.

*Current author review comments:*
Characterisation of corrosion products and estimation of corrosion rates for 3 copper and bronze artifacts with ages from 176-1030 a and with Cu contents of 76-99 wt.%

*Ref. no.:* 037

*Title:*
Interfacial layer on archaeological mild steel corroded in carbonated anoxic environments studied with coupled micro and nano probes.

*Authors:*
Leon, Y., M. Saheb, E. Drouet, D. Neff, E. Foy, E. Leroy, J.J. Dynes, and P. Dillmann.

*Source:*
Corros. Sci. 88, 23-35.

*Year:*
2014

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development

*Keywords.:*
Conceptual model, oxide layer, corrosion product, French program

*Original abstract/summary/conclusions*
The interfacial layer formed on archaeological artefacts corroded during 450 years in carbonated anoxic water was studied using FEG–SEM, Raman, STEM, STXM. This layers forms between the metallic substrate and an outer carbonate layer. Interfacial layer shows various thicknesses from about 100 nm to several μm. It is made of a mix of iron oxides (maghemite or magnetite). A formation mechanism is proposed and based on slight pH increase at the interface. $D_2O$ labelling experiments show that the penetration of water in the pore network seems to be significantly hindered at the interface by the presence of the oxide layers.

*Current author review comments:*
Detailed analysis of the structure of the corrosion product layer revealed a dense inner (barrier?) layer, with significantly lower porosity that outer carbonate layer. Speculate that rate control may be due to this layer, although it is not stated whether this is due to mass transport or electron transfer limitation.

*Ref. no.:* 038

*Title:*
Long-term behaviour of iron embedded in concrete: from the characterisation of archaeological analogues to the verification of the oxygen reduction as the limiting step for corrosion rate.

*Authors:*
Chitty, W.-J., B. Huet, P. Dillmann, V. L'Hostis, G. Beranger, and H. Idrissi.

| *Source:* | *Year:* |
|---|---|
| In Corrosion of Metallic Heritage Artefacts, European Federation of Corrosion Green Book, Volume 48, chap. 7, pps. 109-130. | 2007 |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development

*Keywords.:*
Concrete, modelling

*Original abstract/summary/conclusions*
This chapter is constructed in two complementary parts. The first (Section 7.2) deals with the characterisation of archaeological ferrous artefacts corroded in binders in order to better understand the corrosion system and to give some significant parameters (such as the apparent diffusion coefficient of oxygen in the water of the pores of the DPL) for phenomenological modelling of long-term iron corrosion. The second part (Section 7.3) presents the first stages of this modelling that will be developed in the French CEA in the next few years in the framework of the CIMETAL project.
Ferrous artefacts from 11 archaeological sites were studied in order to understand the corrosion system that can form in binders after long periods. The samples studied came from various areas and periods; hence material comparability with the steel considered for the nuclear waste management systems was checked. Binders are different in many ways (morphology, porosities, chemical composition, phases observed). But it was underlined that the system Metallic Substrate, Dense Product Layer, Transformed Medium and Binder is noted in all samples. These different media were characterised. In all the studied samples, the same phases were found in the DPL: mainly goethite containing magnetite and/or maghemite marblings. Other oxyhydroxides were noted on some samples (lepidocrocite and akaganeite). Because the matrix of the corrosion products is composed of a non-conductive oxy-hydroxide (goethite), the hypothesis can be made that both anodic and cathodic reactions are located at the metal/DPL interface. Thus, it is probable that the oxygen diffusion in the water of the pores of the corrosion products is the limiting step of the corrosion processes. This point has to be verified in future work. In addition to those characterisations, thickness measurements coupled to a local density correction allowed the evaluation of average corrosion rate. Moreover, it was shown that several elements (calcium, chlorine, iron, etc.) could migrate in the Binder, the Transformed Medium or the Dense Product Layer. Last but not least, using an iodine marker, an apparent diffusion coefficient for oxygen in the pore water was roughly evaluated. Despite several limitations linked on the one hand to the choice of iodine and on the other to the evaluation method, this parameter is of great importance for modelling and gives an idea of the transport phenomenon kinetics that can take place in the corrosion products of archaeological artefacts.
In the second part of the chapter, a mathematical model was proposed, assuming, as demonstrated by the archaeological analogues analyses, that the corrosion product layer is not conductive and using the apparent diffusion coefficient rate that was measured in the first part. The initial results presented here show that the corrosion rate depends strongly on whether or not the binder on the one hand, and the DPL on the other, is saturated with water. When only the DPL is saturated with water, the calculated corrosion rates are in good agreement with the average corrosion rates measured on archaeological artefacts. All these points will be refined in further studies.

*Check if additional Comments made* ☒

*Current author review comments:*
Part of the long-term development of a model for predicting the failure of steel reinforced concrete containers, including the effect of the formation of expansive corrosion products and cracking of the concrete.

The format follows very much the same lines as the characterisation of corrosion products on steel exposed to soils and atmospheric conditions, i.e., in terms of various layers, including a dense product layer (DPL), a transformed media layer (TM), and in this case a binder (B) layer comprising the concrete.

The porosity of the DPL is given as 5-25% for the four samples characterized.

As the subject matter involves reinforced concrete, of relatively little interest to NWMO.

*Ref. no.:* 039

*Title:*
Long-term anoxic corrosion of iron.

*Authors:*
Saheb, M., D. Neff, P. Dillmann, M. Descostes, and H. Matthiesen.

*Source:*
In Corrosion and Conservation of Cultural Heritage Metallic Artefacts, European Federation of Corrosion Green Book (Woodhead Publishing, Cambridge, UK), Volume 65, chap. 13, pps. 260-284.

*Year:*
2013

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Corrosion rate, conceptual model development

*Keywords:*
Separation of anodic and cathodic sites, French program

*Original abstract/summary/conclusions*
Understanding the long-term corrosion mechanisms of iron in an anoxic environment is essential in the field of the preservation of archaeological heritage artefacts and nuclear waste management. Corrosion mechanisms have been assessed by examining nails 400 years old from the archaeological site of Glinet. This chapter provides an overview of the characterisation of the entire corrosion system environment/samples through coupled multiscale analytical tools. The environment is anoxic, calco-carbonated and water-saturated. Three corrosion patterns composed of ferrous carbonates (siderite and chukanovite) and magnetite have been identified. Depending on the connection between the phases and their location, the electronic properties of the corrosion layers have been established. The electrochemical behaviour of the corrosion system shows that water reduction at the metallic interface is negligible. Furthermore, the electron consumption sites are mainly localised on the external part and the precipitation sites on the internal part of the corrosion layer. The corrosion rate is estimated to be less than 2 µm/year and a corrosion mechanism is proposed based on a decoupling of the anodic and cathodic sites and on the existence of a nanometric corrosion layer at the metallic interface.

*Current author review comments:*
Use both deuterium and copper tracing to identify location of cathodic reaction.

| | |
|---|---|
| *Ref. no.:* 040 | |
| *Title:*<br>Contribution of iron archaeological artefacts to the estimation of average corrosion rates and the long-term corrosion mechanisms of low-carbon steel buried in soil. | |
| *Authors:*<br>Neff, D., E. Vega, P. Dillmann, M. Descostes, L. Bellot-Gurlet, and G. Béranger. | |
| *Source:*<br><u>In</u> Corrosion of Metallic Heritage Artefacts, European Federation of Corrosion Green Book, Volume 48, chap. 4, pps. 41-76. | *Year:*<br>2007 |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Conceptual model development, corrosion rates | |
| *Keywords:*<br>Steels, corrosion products, DPL, transformed media | |

*Original abstract/summary/conclusions*

Fifty-four artefacts from five different archaeological sites were analysed in order to better understand the iron corrosion behaviour during very long periods. Samples were taken with the adhering soil in order to study the entire system composed of the metal, the corrosion products and the soil. Optical and electronic microscopic observations, combined with composition analyses by EDS coupled to SEM and EPMA, were performed to study the metallic substrates and the corrosion products. Moreover, two complementary techniques were used to investigate the local structure: µXRD under synchrotron radiation and micro Raman spectroscopy. A specific terminology, well adapted to describing corrosion on ancient artefacts, was proposed: metallic substrate (M), dense product layers (DPL), transformed medium (TM) and soil (S). It was determined that all artefacts were composed of hypoeutectoid steels except for two hypereutectoid steels and four cast iron samples from the Glinet site. Some also contain phosphorus in higher amounts than contemporary steels as well as numerous inclusions heterogeneously distributed. This heterogeneity of structure is responsible for the localised corrosion observed at the metal/corrosion product interface but does not seem to influence the generalised corrosion layer.

Corrosion products are composed mainly of a dark matrix of goethite embedding lighter veins of magnetite/maghemite, and in specific conditions (of reducing potential) siderite can be detected. This corrosion layout is independent of the local composition of the metallic matrix.

This study has revealed that species transport phenomena play an important role in the corrosion processes, i.e. the diffusion of oxygen and other species in the water of the DPL pores and cracks controls the corrosion process. Moreover, the local pH and redox potential in the corrosion scale can explain the variation of the corrosion forms obtained on samples from the same site.

During long periods of burial, corrosion systems constituted of metal, corrosion products and the environment are constantly evolving. With this in mind, a method of estimating the corrosion rate (CR) of archaeological artefacts has been set up. These CR are based on the estimation of the quantity of iron that comes from the artefacts into the corrosion products and the environment. This method of assessment proceeds in two steps, giving a minimal and a maximal CR:

1 Analytical techniques were utilised to measure the thickness of the corrosion product layers: by optical microscope for DPL and by establishing average elementary distribution profiles for TM.

2 The maximal limit was calculated by evaluating the likely iron amount that is generated by the dissolution of the corrosion layers.

*Check if additional Comments made* ☒

As a first conclusion, we have shown that it is possible to establish a reliable maximal CR limit for goethite and magnetite in oxidising conditions. In contrast, maximal limits are far higher than the minimal CR values for goethite and magnetite in reducing conditions and for siderite, whatever the conditions (pH, Eh, $P$CO2 ). The presence of siderite in some samples could be due to the specific burial environment: calcium in siderite, a large amount of iron in the soil, or competition between carbonate and oxygen that was not considered in the calculations. Solubility calculations need to be refined in order to get closer to the real conditions of burial: correlation of the complex compound concentrations, pH and potential with *in situ* measurements.
In conclusion, CR values measured on a corpus of 54 archaeological artefacts are under 4 µm/year. Compared with data in the literature for buried low-carbon steels, these CR values are low. Moreover, they tend to decrease with time, showing that the corrosion products themselves play a role in long-term corrosion mechanisms.

*Current author review comments:*

Useful summary paper of a lot of the French analogue work in soils, providing evidence for the structure of the various layers, their properties, rate-controlling processes, and estimated corrosion rates.

*Ref. no.:* 041

*Title:*
Long-term corrosion of 2,000-year-old ancient iron sword.

*Authors:*
Mitsui, S., A. Fujii, M. Higuchi, and K. Nishimura.

| *Source:* | *Year:* |
|---|---|
| Mater. Res. Soc. Symp. Proc. 1475, 545-550. | 2012 |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Corrosion rates

*Keywords:*
Empirical lifetime prediction, kinetic stability

*Original abstract/summary/conclusions*
An ancient iron sword (ca 2,000 year old) excavated from Ohtake-nishi archaeological site in Osaka Prefecture, is one of the oldest cast iron swords in Japan. Because of a good state of preservation, such as the sharply-defined "Shinogi" (the longitudinal ridge) on the surface, we studied relationship between the burial environment and corrosion behavior. As environmental conditions, we investigated groundwater chemistry and corrosion rate with iron probe monitor, etc. Regarding corrosion state, we analyzed corrosion depths with an X-ray computed tomography and corrosion products with a portable X-ray diffractometer equipped with X-ray fluorescence spectrometer. As results, we found that the redox potential and dissolved oxygen level as environmental conditions were very low, and that the corrosion rate ($7.5\times10^{-4}$ mm/y) evaluated from measured corrosion depths was smaller than the probe corrosion rate ($3.2–5.2\times10^{-2}$ mm/y) by two orders of magnitude. The results suggested that the corrosion layer of siderite formed on the iron sword surface inhibited corrosion reaction.

*Current author review comments:*
Detailed characterisation of 2000-year old sword. Japanese program tends to be very much focused on using corrosion rates from analogues to extend laboratory data and support empirical lifetime prediction.

Although here there is also some suggestion of interpretation in terms of kinetic stability due to a protective carbonate corrosion product film.

*Ref. no.:* 042

*Title:*
Native copper in Permian mudstones from south Devon: A natural analogue of copper canisters for high-level radioactive waste.

*Authors:*
Milodowski, A.E., M.T. Styles, L. Werme, and V.M. Oversby.

*Source:*
In Nuclear Waste Containment Materials. Papers related to the SKB waste disposal programme presented at the Materials Research Society Spring Meeting, April 19, 2001. Swedish Nuclear Fuel and Waste Management Co Technical Report, SKB TR-01-25.

*Year:*
2001

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Littleham Cove

*Original abstract/summary/conclusions*

Native copper (>99.9% Cu) sheets associated with complex uraniferous and vanadiferous concretions in Upper Permian mudstones from south Devon (United Kingdom) have been studied as a “natural analogue” for copper canisters designed to be used in the isolation of spent fuel and high-level radioactive wastes (HLW) for deep geological disposal. Detailed analysis demonstrates that the copper formed before the mudstones were compacted. The copper displays complex corrosion and alteration. The earliest alteration was to copper oxides, followed sequentially by the formation of copper arsenides, nickel arsenide and copper sulphide, and finally nickel arsenide accompanied by nickel-copper arsenide, copper arsenide and uranium silicates. Petrographic observations demonstrate that these alteration products also formed prior to compaction. Consideration of the published history for the region indicates that maximum compaction of the rocks will have occurred by at least the Lower Jurassic (i.e. over 176 Ma ago). Since that time the copper sheets have remained isolated by the compacted mudstones and were unaffected by further corrosion until uplift and exposure to present-day surface weathering.

*Current author review comments:*

Summary of SKB TR. No indication of whether the continuing existence of the plates is due to thermodynamic or kinetic stability.

*Ref. no.:* 043

*Title:*
Native Cu from the oceanic crust: Isotopic insights into native metal origin.

*Authors:*
Dekov, V.M., O. Rouxel, D. Asael, U. Hålenius, and F. Munnik.

| *Source:* | *Year:* |
|---|---|
| Chem. Geol. 359, 136-149. | 2013 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Conceptual model development, confidence building

*Keywords:*
Isotope, mechanism, native copper, sea water

*Original abstract/summary/conclusions*

Ocean drilling has revealed that, although a minor mineral phase, native Cu ubiquitously occurs in the oceanic crust. Cu isotope systematics for native Cu from a set of occurrences from volcanic basement and sediment cover of the oceanic crust drilled at several sites in the Pacific, Atlantic and Indian oceans constrains the sources of Cu and processes that produced $Cu^0$. We propose that both hydrothermally-released Cu and seawater were the sources of Cu at these sites. Phase stability diagrams suggest that $Cu^0$ precipitation is favored only under strictly anoxic, but not sulfidic conditions at circum-neutral pH even at low temperature. In the basaltic basement, dissolution of primary igneous and potentially hydrothermal Cu-sulfides leads to $Cu^0$ precipitation along veins. The restricted Cu-isotope variations ($\delta^{65}Cu$ = 0.02–0.19‰) similar to host volcanic rocks suggest that $Cu^0$ precipitation occurred under conditions where $Cu^+$-species were dominant, precluding Cu redox fractionation. In contrast, the Cu-isotope variations observed in the $Cu^0$ from sedimentary layers yield larger Cu-isotope fractionation ($\delta^{65}Cu$ = 0.41–0.95‰) suggesting that $Cu^0$ precipitation involved redox processes during the diagenesis, with potentially seawater as the primary Cu source. We interpret that native Cu precipitation in the basaltic basement is a result of low temperature (20°–65 °C) hydrothermal processes under anoxic, but not $H_2S$-rich conditions. Consistent with positive $\delta^{65}Cu$ signatures, the sediment cover receives major Cu contribution from hydrogenous (i.e., seawater) sources, although hydrothermal contribution from plume fallout cannot be entirely discarded. In this case, disseminated hydrogenous and/or hydrothermal Cu might be diagenetically remobilized and reprecipitated as $Cu^0$ in reducing microenvironment.

*Current author review comments:*
The mode of deposition of native copper is not of primary interest for this report, but this particular paper has a number of interesting aspects, including:

- Use of Cu isotopes
- Hydrothermal alterations under near-ambient conditions
- Proposed reverse of Cu corrosion processes

Different deposition modes proposed for native copper in basaltic basement rock (from copper-containing seawater that had intruded at a higher depth and is then ejected in vents) and in the seabed sediments (reduction from overlying sea water).

*Ref. no.:* 044

*Title:*
A 17th century bronze cannon as analogue for radioactive waste disposal.

*Authors:*
Hallberg, R.O., P. Östlund, and T. Wadsten.

*Source:*
In Natural Analogues in Radioactive Waste Disposal, B. Côme and N.A. Chapman (eds.), Commission European Communities report, EUR 11037 EN, pp. 135-139.

*Year:*
1987

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Conceptual model development, confidence building

*Keywords:*
Kronan

*Original abstract/summary/conclusions*

The cannon which was recovered in 1985 has been embedded for more than 300 years in a clay which largely has the same properties as the clay considered for use in the final storage of Swedish nuclear fuels.

The copper concentration in the bronze alloy is abnormally high, 96.3% instead of a more normal 90 %, which makes it a suitable object in studies of copper corrosion.

The main corrosion products of copper are cuprite and malachite where the cuprite dominates.

The formation of cuprite involves a transformation of tenorite and can be explained by redox processes where Cu(s), $Fe^{2+}$ and organic matter are the major electron donors.

*Current author review comments:*

Early report of the Kronan bronze cannon study.

*Ref. no.:* 045

*Title:*
Natural and anthropogenic analogues – insights for management of spent fuel.

*Authors:*
McKee, P. and D. Lush.

*Source:*
Nuclear Waste Management Organization Background Papers. 4. Science and Environment.

*Year:*
2004

*Relevant engineered barrier:*
Copper, steel, buffer

*Relevant use or application of the study:*
Confidence building

*Keywords.:*
Overview

*Original summary (partial)*

Because of the long management time frames involved in the management of spent reactor fuels and the lack of any “engineering” precedence for the behaviour of containment systems designed to last over many thousands of years the argument is sometimes raised that the behaviour of spent fuel management systems cannot be reliably predicted. One can, however, look to natural and anthropogenic (man made) analogues to provide insight into how spent fuel waste management systems and their component parts may behave over these long time periods. In the natural and archaeological environments, there are analogues for spent fuel as it comes from the reactor as well as for spent fuel after it has decayed to activity levels found in natural uranium minerals. There are also analogues for the materials that may be used in engineered containment systems, such as cement, iron, copper and the clays proposed to contain spent fuel on surface or seal a deep geological disposal site. Analogues are also present that can provide insights into how various radionuclides behave as they cycle through the natural environment.

This paper provides a short discussion of a number of natural and archaeological analogues that can assist in understanding many of the issues associated with the long-term management of spent fuel. Analogues in the sense that they are used in this discussion paper do not “prove” that any particular concept is safe, but they can provide insights and serve to “bound” issues that may be of concern in carrying out safety assessments. In a similar manner, the fact that spent fuel after a period of time has the same total radioactivity as the original uranium minerals from which it was made does not mean that a deep geological repository will behave exactly the same as a natural uranium ore body.

Despite their limitations, analogues are useful, in that they can provide valuable insights and can serve to “bound” certain issues and concepts to be addressed in the management of spent fuel. In this context, analogues have been studied as a part of the nuclear waste management programs in many countries around the world.

*Current author review comments:*

High-level introduction to the concept and use of analogues to support various aspects of nuclear waste disposal.

*Ref. no.:* 046

*Title:*
Natural and anthropogenic analogues for high-level nuclear waste disposal repositories: A review.

*Authors:*
Fayek, M. and J. Brown.

| | |
|---|---|
| *Source:*<br>Canadian Nuclear Safety Commission Report, RSP-310. | *Year:*<br>2015 |

*Relevant engineered barrier:*
Copper, steel, buffer

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Overview, CNSC

*Original abstract/summary/conclusions*

This report provides a review of natural and anthropogenic analogues for high-level nuclear waste disposal in a deep geological repository (DGR). We also occasionally highlight analogues that have been used for low and intermediate waste. Most studies define natural analogues as either naturally occurring or anthropogenic (manmade) systems. In this report, we distinguish between natural analogues and anthropogenic analogues because anthropogenic analogues generally provide non-technical (anecdotal) illustration of concepts and processes for the safety case, whereas natural analogues can provide technical and quantitative information. In addition, natural analogues can provide information over geological time- (millions of years) and spatial- (kilometers) scales whereas anthropogenic analogues provide information over a much more limited time-scale (hundreds or thousands of years). Regardless of the definition, analogue studies provide one of the multiple lines of evidence intended to increase confidence in the safe geologic disposal of high-level nuclear waste. They are deemed necessary because they complement the experiments that are carried out over a period of months or years. They also provide a way to validate numerical long term safety assessment models with information and data covering geological time- and spatial-scales.

The first part of this report describes the analogue concept. The second and third parts provide examples of natural and anthropogenic analogues for engineered barrier systems (EBS) and natural barriers (NB). Part four describes analogues for complex coupled transport processes and finally we provide general and specific recommendations for future research in part five of the report.

A key recommendation is that a concerted effort should be made to ensure that there is a transfer of data from the complex, natural analogue field studies to simplistic models which, by necessity, are used in safety assessments (SA). Field analogue studies should be planned to interface with laboratory experiments and, ultimately, with *in situ* field experiments, when the final repository site is selected. This will involve using natural analogue data in a quantitative way to support the DGR safety case.

*Current author review comments:*

Use of analogues from a regulatory perspective.

*Ref. no.:* 047

*Title:*
A review of the archaeological analogue approaches to predict the long-term corrosion behaviour of carbon steel overpack and reinforced concrete structures in the French disposal systems.

*Authors:*
Neff, D., M. Saheb, J. Monnier, S. Perrin, M. Descostes, V. L'Hostis, D. Crusset, A, Millard, and P. Dillmann.

*Source:*
J. Nucl. Mater. 402, 196-205.

*Year:*
2010

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development, corrosion rates

*Keywords:*
Review, French program, analytical techniques, isotopic labelling

*Original abstract/summary/conclusions*

This paper gives a review of several years of research on archaeological analogues in order to predict the long term behaviour of the steel canisters or the reinforced concrete structures involved in disposal or interim storage of nuclear wastes in France. This article aims at showing the specific methodology, the complementariness with different other approaches and the complete integration of the research on analogues in the frame of research programs on long term prediction. Archaeological sites on which field measurement can be performed were referenced and described. A significant number of artefacts collected from these sites was selected for study. Detailed chemical and microstructural characterisation of the artefacts were undertaken by a combination of microbeam analytical techniques (µRaman, µXRD, µRaman spectroscopy,...). Hypotheses on the corrosion mechanisms were then tested using specific isotopic markers during re-corroding experiments on analogues. Specific parameters were measured, allowing crucial steps in modelling long-term corrosion of steel.

*Current author review comments:*

Concise review of the many aspects of the French analogue program.

*Ref. no.:* 048

*Title:*
An analytical study of corrosion products formed on buried ferrous archaeological artefacts.

*Authors:*
Neff, D., P. Dillmann, and G. Béranger.

| *Source:* | *Year:* |
|---|---|
| In Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, D. Féron and D.D. Macdonald (eds.), European Federation of Corrosion Green Book, Number 36, Chap. 20, pps. 295-315. | 2003 |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development, corrosion rate

*Keywords:*
French program, 1st LTC

*Original abstract/summary/conclusions*
A statistical approach to long term corrosion behaviour of iron in soil has been initiated with a study of nine archaeological iron artefacts. By combining classical materials science analytical techniques (optical and scanning electron microscopy and electron microprobe) with microdiffraction under synchrotron radiation, the three components of the corroded iron in soil have been characterised: the metallic substrate (structure and composition), the corrosion products (identification of three main phases: goethite, magnetite and siderite) and the soil (specific compositions close to the original surface of the artefact). An estimate of the corrosion rate has been made from thickness measurements of the corrosion products.

*Current author review comments:*

One of the early publications from the French program ,establishing the general approach of surface analysis of corrosion products, definition of the M/DPL/TM(S) structure, and an estimation of corrosion rates.

*Ref. no.:* 049

*Title:*
Archaeological analogue studies for the prediction of long term corrosion of buried metals.

*Authors:*
David, D., C. Lemaitre, and D. Crusset.

*Source:*
In Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, D. Féron and D.D. Macdonald (eds.), European Federation of Corrosion Green Book, Number 36, Chap. 17, pps. 241-260.

*Year:*
2003

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
n/a

*Keywords:*
Overview, 1st LTC

*Original abstract/summary/conclusions*
The prediction of the behaviour of metallic materials exposed to soil corrosion depends on many parameters. Any consideration of the effect of time, over long periods, can result only from a comparison with real cases of corrosion. It is the material-soil association which is the determining factor. This paper reports studies performed using modern techniques of materials science. The studies concern not only the characterisation of solid phase components, especially corrosion products since it is also necessary to conduct electrochemical evaluation of corroded layer properties.

*Current author review comments:*

Very general introduction to a variety of topics, including: corrosion, electrochemistry, soils and their aggressiveness, surface analytical techniques, etc., all in association with their use in analogue studies. No specific information of use.

*Ref. no.:* 050

*Title:*
Corrosion resistance of the Delhi iron pillar – scale characterisation and passive film growth models.

*Authors:*
Balasubramaniam, R. and P. Dillmann.

*Source:*
In Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, D. Féron and D.D. Macdonald (eds.), European Federation of Corrosion Green Book, Number 36, Chap. 18, pps. 261-279.

*Year:*
2003

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Confidence building, conceptual model development

*Keywords:*
Delhi iron pillar, atmospheric corrosion, 1st LTC

*Original abstract/summary/conclusions*

The corrosion resistance of the Delhi pillar iron has been reviewed. The corrosion products on several ancient Indian irons have been characterised. The role of the entrapped slag particles in aiding passive film formation in ancient Indian iron has been analysed by mixed potential theory. The protective rust formation process has been elucidated and possible models proposed. After an initial period of high corrosion rate, the initial corrosion resistance is conferred by the formation of protective amorphous compact layer of $\delta$-FeOOH. The corrosion rate is further lowered by the formation of phosphates and their phase transformations.

*Current author review comments:*

The paper is largely concerned with characterisation of the Delhi iron pillar and other iron objects from India. However, it also includes application and the development of conceptual models for passive systems, with an eye towards application for long-term prediction.

*Ref. no.:* 051

*Title:*
Expansion due to anaerobic corrosion of steel and cast iron: experimental and natural analogue studies.

*Authors:*
Smart, N.R., A.P. Rance, P. Fennell, and L. Werme.

| | |
|---|---|
| *Source:*<br>In Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, D. Féron and D.D. Macdonald (eds.), European Federation of Corrosion Green Book, Number 36, Chap. 19, pps. 280-294. | *Year:*<br>2003 |

*Relevant engineered barrier:*
Steel, copper

*Relevant use or application of the study:*
Conceptual model development

*Keywords:*
1st LTC

*Original abstract/summary/conclusions*
An apparatus was constructed to measure the expansion caused by the anaerobic corrosion of steel and cast iron whilst under representative compressive loads. The detection of hydrogen and the identification of magnetite on the surface of the specimens demonstrated the occurrence of anaerobic corrosion, but no expansion was observed after over two years' exposure, suggesting that the corrosion product is too soft and deformable to cause jacking of the walls of canisters used for encapsulating spent nuclear fuel. The use of natural analogues to examine the potential for expansion caused by anaerobic corrosion in confined spaces over long time periods is discussed.

*Current author review comments:*

Largely an experimental study, but contains a brief discussion of archaeological and industrial (oxide jacking, spalling concrete cover over rebar) analogues that support concept of the formation of expansive corrosion products. However, subsequent studies, including of the Coopergate helmet (#025) showed that this was not an issue for the copper-cast iron KBS-3 canister design.

*Ref. no.:* 052

*Title:*
Rust characterisation of ancient iron artefacts exposed to indoor atmospheric corrosion.

*Authors:*
Dillmann, P., V. Vigneau, F. Mazaudier, C. Blanc, and S. Hoerlé.

| | |
|---|---|
| *Source:*<br>In Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, D. Féron and D.D. Macdonald (eds.), European Federation of Corrosion Green Book, Number 36, Chap. 21, pps. 316-333. | *Year:*<br>2003 |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Characterisation, atmospheric corrosion, 1st LTC

*Original abstract/summary/conclusions*
A corpus of eleven iron artefacts exposed several centuries to indoor atmospheric corrosion has been collected. The general morphology of the rust layers has been studied as well as the iron substrate. Second phase particles (slag inclusions) and minor elements (carbon, phosphorus) were detected. The compositions of the rust layers have been analysed by EPMA on cross sections. The distribution of endogenous and exogenous elements has been studied. An original analytical method (micro XRD under synchrotron radiation) was used to study the structure distribution on thin film transverse sections. Using this technique, the different constitutive crystallised phases in the rust layer have been localised. Goethite has been detected preferentially in inner layers, lepidocrocite in outer layers. The goethite to lepidocrocite content ratio in the rust layers, the so-called protective ability index $\alpha/\gamma$, has been calculated and compared to values found in literature.

*Current author review comments:*

Early study associated with atmospheric corrosion of iron samples. Interesting use of the goethite:lepidocrocite ratio as a measure of the protectiveness of the corrosion product layer, based on literature use. The $\alpha/\gamma$ ratio increases with the age of the specimen, it was speculated due to the increasing number of wet-dry cycles experienced by the samples.

*Ref. no.:* 053

*Title:*
Long term behaviour of iron in clay soils: A study of archaeological analogues.

*Authors:*
Pons, E., L. Uran, S. Joiret, A. Hugot Le Goff, C. Lemaitre, and D. David.

| | |
|---|---|
| *Source:*<br>In Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, D. Féron and D.D. Macdonald (eds.), European Federation of Corrosion Green Book, Number 36, Chap. 22, pps. 3345-345. | *Year:*<br>2003 |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Electrochemistry, 1st LTC

*Original abstract/summary/conclusions*
Iron objects from a battlefield of World War I were studied to obtain a better understanding of corrosion phenomena in clay soils. The identification of the corrosion products by Raman Spectroscopy highlighted iron oxides and oxy-hydroxides. The orange-brown external layer is composed of oxy-hydroxides, mixed with soil crystals, while the oxides are always associated with the internal layer. Electrochemical experiments (Voltammetry and Electrochemical Impedance Spectroscopy) in Evian mineral water (pure or with sodium chloride), confirmed the porosity of the external layer, and the protective role of the internal products. The influence of the burial environment on the corrosion rate was also established.

*Current author review comments:*

Largely a study characterizing corrosion products.

*Ref. no.:* 054

*Title:*
Characterization of protective rust on ancient Indian iron using microprobe analyses

*Authors:*
Dillmann, P., R. Balasubramaniam, and G. Beranger.

*Source:*
Corros. Sci. 44, 2231-2242.

*Year:*
2002

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Delhi iron pillar, atmospheric corrosion

*Original abstract/summary/conclusions*

Local compositional and structural information was obtained from an ancient 1500-year old Indian iron and its protective scale utilizing microprobe techniques (μXRD and μPIXE). Different locations in the iron matrix and in the entrapped slag inclusions were also analyzed for P contents. The P content of the metallic iron matrix was very heterogeneous. Lower P contents were observed in the regions near slag inclusions. The surface oxide scales was layered. Enrichment of P in the metal–scale interface and in the scale adjacent to the interface was determined. The P content in the scale decreased on moving away from the interface. Microdiffraction patterns obtained at different locations in the oxide scale indicated that at locations where the P content was high (i.e. nearer the interface), the oxide was amorphous while at locations where P was low, crystalline phases were identified. The presence of crystalline phosphates was also confirmed at some regions in the scale, where the P content was relatively very high. The probable reasons for the presence of the identified phases in the atmospheric corrosion product have been discussed.

*Current author review comments:*

Another analysis of ancient Indian iron. Study involved characterisation of corrosion product layers, with a focus on the role of P and slag inclusions.

*Ref. no.:* 055

*Title:*
Electrochemical study of steel artefacts from World War I: Contribution of A.C. impedance spectroscopy and chronoamperometry to describe the behaviour of the corrosion layers.

*Authors:*
Pons, E., C. Lemaitre, D. David, and D. Crusset.

*Source:*
In Corrosion of Metallic Heritage Artefacts, European Federation of Corrosion Green Book, Volume 48, chap. 5, pps. 77-91.

*Year:*
2007

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Corrosion product layers, porosity

*Original conclusions*

Carbon steels excavated from a battlefield of World War I exhibited two thick and heterogeneous corrosion layers, formed during the subsequent long period of burial in the soil. Considering that their further corrosion was limited by the properties of the internal layer, the modelling proposed in this chapter lets us draw two distinct conclusions:

- The first series of experiments, carried out by electrochemical impedance spectroscopy, confirmed that the internal layer was porous, as was previously attested for the external one. The impedance diagrams showed that the corrosion was controlled by transport phenomena of the species through this porous internal layer. In Evian water, which has poor conductivity, it was necessary to consider simultaneously two processes: a diffusion process in the liquid medium filling the pores and a solid-phase transport process in the electrode material.
- In the second series of experiments, chronoamperometry tests revealed that the internal corrosion layer was protective, in spite of its porosity. This layer plays a significant role in hindering the further evolution of corrosion, leading to a large fall in the corrosion rate.

*Current author review comments:*

Follow-on study from #053.

*Ref. no.:* 056

*Title:*
Archaeological analogues and corrosion prediction: from past to future. A review.

*Authors:*
Dillmann, P., D. Neff, and D. Féron.

*Source:*
Corros. Eng. Sci. Technol. 49, 567-576.

*Year:*
2014

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development, corrosion rates, confidence building

*Keywords:*
Review, French program, microbial activity, LTC 2013

*Original abstract/summary/conclusions*

A new approach including the use of archaeological analogues is needed to predict corrosion phenomena over extended time periods lasting centuries to several millennia. The corrosion rates observed on analogues generally range from 0.1 to 10 $\mu$m/year, depending on the medium. Isotopic markers (deuterium or oxygen-18) can be used on archaeological objects to determine and localise the anodic and/or cathodic mechanisms. Modelling and simulation take into account statistical aspects (modelling by cellular automata) and kinetics, including localised corrosion phenomena (pitting factor).

*Current author review comments:*

A nice summary of the overall French approach to integrating lab and full-scale experiments, modelling, and analogue studies to support predictions of long-term performance. One of the few studies to specifically mention microbial activity (in particular SRB), although the conclusion is that although they may be active (as evidenced by S-containing corrosion products, mackinawite FeS and greigite $Fe_3S_4$) they do not lead to accelerated corrosion rates. This paper was presented at the LTC meeting in Japan, and the current author specifically asked about analogues for microbial activity. The response was that there is no reason to believe that microbes are not present and active in these soil systems so, by inference, any effect of microbes is inherently included in the estimated corrosion rate.

*Ref. no.:* 057

*Title:*
New data on the Hyrkkölä U-Cu mineralization: The behaviour of native copper in a natural environment.

*Authors:*
Marcos, N. and L. Ahonen.

| | |
|---|---|
| *Source:*<br>Posiva Oy Technical Report, POSIVA 99-23. | *Year:*<br>1999 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Long-term stability, confidence building

*Keywords:*
Copper sulphide, native copper, Hyrkkölä, djurleite, digenite

*Original abstract/summary/conclusions*

The Hyrkkölä Cu-U mineralization (SW Finland) is studied as an analogue to the behaviour of copper canister in crystalline bedrock. Uranium-native copper and uranium-copper corrosion products interactions are also addressed in this study. The integration of uranium series disequilibrium (USD) studies gives an estimate of the time-scales of the corrosion processes.

The mineral assemblages native copper - copper sulfide, copper sulfides - copper iron sulfides, and native copper - copper oxide (cuprite) occur in open fractures at several depth intervals within granite pegmatites (GP). The surfaces of these open fractures have accumulations of uranophane crystals and other unidentified uranyl compounds. The secondary uranium minerals are mainly distributed around copper sulfide grains. Microscopic intergrowths of copper sulfides and uranyl compounds also have been observed. The surface of the fracture where native copper and cuprite occur is covered with uranium-rich smectite. The very low $^{234}U/^{238}U$ activity ratio (0.29 - 0.39) in the main uranium fraction in smectite indicates chemical stable conditions (e.g., oxidising) during at least a time period comparable to the half-life of the $^{234}U$ isotope ($T_{1/2} = 2.44 * 10^5$ a).

Groundwater samples were collected from intervals where copper minerals occur within open fractures. The Eh and pH conditions were measured during long-term pumping (2-4 weeks per sample). Eh was measured both in situ and an the surface using three electrodes (Pt, Au, C). The actual groundwater conditions are oxidising and would not allow the sulfidization of native copper. Sulfidization may be considered as an old phenomenon, older than the precipitation of uranyl phases in the samples. The end of sulfidization may be earlier than the precipitation and/or remobilisation of U(VI) phases in a time span from about $2 * 10^5$ years (precipitation of uranophane) to $2.44 * 10^5$ (remobilisation of U from smectite).

*Current author review comments:*

This report summarises the second stage of investigations involving the drilling of two more boreholes specifically aimed at locating additional native copper deposits. In addition uranium series disequilibrium (USD) studies were used to better data the altered copper assemblages. Groundwater samples were taken from the fracture zones associated with the copper deposits.

*Check if additional Comments made* ☒

*Comments (continued):*

In these second two cores, additional native and altered Cu assemblages were found associated with open fracture zones, as well as native copper in low-porosity rock that had seemingly not been in contact with an aqueous phase:

- Cu/copper sulphide (in fracture, contact with ground water)
- Copper sulphides/copper iron sulphides (in fracture, contact with ground water)*
- Cu/$Cu_2O$ (in fracture, contact with ground water)*
- Native copper (in fracture, contact with ground water)*
- Native copper (0.4-0.5% porosity rock, not in contact with aqueous phase)

The observations labelled with an asterisk were not found in the 1996 analysis of the original five drill cores.

Summary of observations/findings:

- Re-analysis of sample $S_{40}$ from 1996 study shows evidence for low chalcocite ($Cu_{1.99-2}S$) in addition to the djurleite found earlier
- New Cu/copper sulfide sample (HY325/68.30), comprising digenite ($Cu_{1.8-1.86}S$) and djurleite. Native Ag found “at the contact of native copper and copper sulfide grains”
- Cu/$Cu_2O$ sample (in contact with groundwater) comprised Cu particles up to 1 mm in diameter, with rims of $Cu_2O$ 10-100 $\mu$m in width.
- Groundwater sampled from fracture zones associated with various copper deposits is oxidizing (Eh 300-600 $mV_{SHE}$, 0.5-5 mg/L $O_2$). Typically $10^{-4}$ mol/L $Cl^-$, $10^{-4}$ mol/L $SO_4^{2-}$, $10^{-3}$ mol/L $HCO_3^-$, pH 6.6-6.8, with one value of pH 8.2.
- USD suggests sulfidation ended at least 200,000 yrs ago, but there is no indication of when it might have started
- U(IV) also present in oxidizing waters
- $\delta^{34}S$ studies suggest sulfur is of sedimentary origin (does this mean non-microbial?)

Comments on observations:

- The oxidizing nature of the ground water is inconsistent with the observation of copper sulfides in open fractures. It is also inconsistent with the persistence of native copper, unless (a) the process is fairly recent and still in progress or (b) the $Cu_2O$ is extremely passivating. But pH of groundwater is too acidic for passivation.
- Co-existence of Ag and Cu/$Cu_2S$ is interesting as the solubility product of $Ag_2S$ is much lower than that of $Cu_2S$ (especially of non-stoichiometric copper sulfides?).
- The sulfidation phase seems to be much older than previously suggested, and may have ended at least 200,000 yrs ago. There is no indication of how long sulfidation phase might have lasted.

*Ref. no.:* 058

*Title:*
The Hyrkkölä native copper mineralization as a natural analogue for copper canisters.

*Authors:*
Marcos, N.

| *Source:* | *Year:* |
|---|---|
| Posiva Oy Technical Report, POSIVA 96-15. | 1996 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Long-term stability, confidence building

*Keywords:*
Copper sulphide, native copper, Hyrkkölä, djurleite

*Original abstract/summary/conclusions*

The Hyrkkölä U-Cu mineralization is located in southwestern Finland, near the Palmottu analogue site. The age of the mineralization is estimated to be between 1.8 and 1.7 Ga. Petrological and mineralogical studies have demonstrated that this mineralization has many geological features that parallel those of the sites being considered for nuclear waste disposal in Finland. A particular feature is the existence of native copper and copper sulfides in open fractures in the near-surface zone. This allows us to study the native copper corrosion process in analogous conditions as expected to dominate in the nuclear fuel waste repository. The occurrence of uranyl compounds at these fractures permits also considerations about the sorption properties of the engineered barrier material (metallic copper) and its corrosion products.

From the study of mineral assemblages or paragenesis, it appears that the formation of copper sulfide (djurleite, $Cu_{1.934}S$) after native copper ($Cu^0$) under anoxic (reducing) conditions is enhanced by the availability of dissolved $HS^-$ in the groundwater circulating in open fractures in the near-surface zone. The minimum concentration of $HS^-$ in the ground water is estimated to be of the order of $10^{-5}$ M (~$10^{-4}$ g/L) and the minimum pH value not lower than about 7.8 as indicated by the presence of calcite crystals in the same fracture.

The present study is the first one that has been performed on findings of native copper in reducing, neutral to slightly alkaline ground waters. Thus, the data obtained is of most relevance in improving models of anoxic corrosion of copper canisters.

*Current author review comments:*

This is the first in a series of reports by Marcos and co-workers on the Hyrkkölä deposit. This is a promising analogue as it appears to involve the subsequent sulphidation of the original native copper and could provide information about the rate, rate-determining process, and of the nature of the $Cu/Cu_{2S}$ interface.

This first report describes the results of inspection of core samples from five drill holes previously obtained from the site. Native copper was found in sealed fractures (as $Cu/Cu_2O$ assemblages) and in open fractures (as $Cu/Cu_2S$ assemblages), at relatively shallow depths (in the latter case approximately 8 m). Although the mineralization is dated as being 1.7-1.8 Ga, the minimum age of the secondary alteration was stated to be 10,000 yrs, since fractures would have opened up since the last ice age, although not alteration would have occurred during the glaciation. However, this must be considered to be a guess at the age, at best.

*Check if additional Comments made* ☒

*Comments (continued):*

The conditions under which the sulphidation occurred was based on a sequence of arguments:

- The presence of calcite on the fracture implies a pH of approximately 7.8
- EPMA microprobe analysis identified the copper sulphide as djurleite $Cu_{1.934}S$
- E-pH diagrams of stable copper sulphides, including several non-stochiometric species, indicate djurleite is stable at pH 7.8 for $[HS^-] \geq 10^{-5}$ mol/L at $25^oC$ and $\geq 10^{-6}$ mol/L at $5^oC$

The $Cu/Cu_2O$ mineral assemblages were found in sealed fractures and it was presumed that they had formed from a remaining oxidizing hydrothermal fluid.

It is not clear whether the $Cu/Cu_2O$ and $Cu/Cu_2S$ assemblages represent analogues for kinetic of thermodynamic stability. There is no mention of unaltered Cu deposits. Presumably, the Cu in the $Cu/Cu_2O$ assemblages in the sealed fractures persists because of the limited volume of hydrothermal fluid and the absence of further access to any aqueous phase. This would seem to represent kinetic stability, although it is possible than in a closed system the concentration of $H_2$ and dissolved $Cu^+$ has achieved equilibrium. In fact, it might be quite likely given how little corrosion product if required to reach the equilibrium position, even if the fracture was not perfectly sealed.

Neither is it clear in the case of the $Cu/Cu_2S$ assemblages. These were found in open fractures, so in order to establish thermodynamic immunity the system must have been sufficiently closed to maintain a sufficient $H_2$ partial pressure. Kinetic stability could result from the limited supply of $HS^-$, but we have no idea of the flux, or the passive nature of the $Cu_{1.934}S$ film.

In some ways, the formation of $Cu_{1.934}S$ is inconsistent with lab studies, which indicate $Cu_2S$ and an $E_{CORR}$ close to the $Cu_2S/HS^-$ equilibrium potential, which is more negative than the $Cu_{1.934}S/HS^-$ equilibrium potential.

*Ref. no.:* 059

*Title:*
Research plan for field studies at the Hyrkkölä native copper mineralization, SW Finland.

*Authors:*
Ahonen, L., N. Marcos, M. Paananen, and S. Paulamäki.

*Source:*
Posiva Oy Working Report, WR 97-49e.

*Year:*
1997

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Long-term stability, confidence building

*Keywords:*
Hyrkkölä

*Original abstract/summary/conclusions*

The small uranium-mineralization of Hyrkkölä in Nummi-Pusula was found in systematic ore exploration studies of the Geological Survey of Finland in the beginning of 1980's. A special feature of this mineralization is the occurrence of native copper together with uranium in narrow pegmatite veins. During the ore exploration phase, five cored boreholes were drilled to the area, so that there is preliminary information on the location and mode of occurrence of metallic copper in the bedrock of the site. However, ground water chemistry and hydrogeological conditions are not yet known, because the old boreholes are blocked.

According to the research plan presented in this report, one or more new boreholes would be drilled to the site for further mineralogical examinations and for groundwater research.

The purpose of the proposed research is to study the behaviour of native copper in the bedrock as a natural analogue to the copper canisters placed into the bedrock. The study will comprise 1) comparison of the groundwater composition in Hyrkkölä with the groundwaters of the candidate sites for nuclear waste disposal; 2) study of the possible secondary, low-temperature alteration of metallic copper, especially if in contact with groundwater; 3) isotopic studies aiming at estimation of the age and timescale of the possible alteration reactions.

*Current author review comments:*

Research plan for the studies reported in #057 and #062.

*Check if additional Comments made* ☐

| | |
|---|---|
| *Ref. no.:* 060 | |
| *Title:*<br>Studies of Hyrkkölä native-copper occurrence during summer 1997. Interim report. | |
| *Authors:*<br>Ahonen, L. and N. Marcos. | |
| *Source:*<br>Posiva Oy Working Report, WR 97-50e. | *Year:*<br>1997 |
| *Relevant engineered barrier:*<br>Copper | |
| *Relevant use or application of the study:*<br>Long-term stability, confidence building | |
| *Keywords:*<br>Hyrkkölä | |

*Original abstract/summary/conclusions*

A special feature of the Hyrkkölä uranium-copper mineralization in Nummi-Pusula, SW Finland is the occurrence copper as native metal. The present work aims at studying the stability of metallic copper in natural bedrock-groundwater conditions.

Two new boreholes, each about one hundred meters long, were drilled to the study site, and new samples of metallic copper were found in the drillcores. After drilling, drillholes were video-recorded to locate open fractures. During the summer and autumn, interesting copper-bearing zones were sampled for groundwater using the SKB mobile field laboratory.

*Current author review comments:*

Interim report of the drilling and ground water sampling phases of the studies reported in #057 and #062.

*Check if additional Comments made* ☐

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|---|---|
| *Ref. no.:* 061 | |
| *Title:*<br>The Hyrkkölä native copper mineralization: A natural analogue for copper canisters. | |
| *Authors:*<br>Marcos, N. Perea. | |
| *Source:*<br>Mat. Res. Soc. Symp. Proc. <u>465</u>, 1153-1160. | *Year:*<br>1997 |
| *Relevant engineered barrier:*<br>Copper | |
| *Relevant use or application of the study:*<br>Long-term stability, confidence building | |
| *Keywords:*<br>Hyrkkölä | |

*Original abstract/summary/conclusions*

The Hyrkkölä U-Cu mineralization is located in south-western Finland, near the Palmottu analog site, in crystalline, metamorphic bedrock. The age of the mineralization is estimated to be between 1.8 and 1.7 Ga. The existence of native copper and copper sulfides in open fractures in the near-surface zone allows us to study the native copper corrosion process in conditions analogous to a nuclear fuel waste repository.

From the study of mineral assemblages or paragenesis, it appears that the formation of copper sulfide (djurleite, $Cu_{1.934}S$) after native copper ($Cu^0$) under anoxic (reducing) conditions is enhanced by the availability of dissolved hydrogen sulfide ($HS^-$) in the groundwater circulating in open fractures in the near-surface zone. The minimum concentration of $HS^-$ in the groundwater is estimated to be of the order of $10^{-5}$ M (~$10^{-4}$ g/l) and the minimum pH value not lower than about 7.8 as indicated by the presence of calcite crystals in the same fracture.

The present study is the first one performed on occurrences of native copper in reducing, neutral to slightly alkaline groundwaters. Thus, the data obtained is of most relevance in improving models of anoxic corrosion of copper canisters.

*Current author review comments:*

Conference paper based on #058.

*Check if additional Comments made* ☐

*Ref. no.:* 062

*Title:*
New data on the Hyrkkölä native copper mineralization: A natural analogue for the long-term corrosion of copper canisters.

*Authors:*
Marcos, N., L. Ahonen, R. Bros, P. Roos, J. Suski, and V. Oversby.

*Source:*
Mat. Res. Soc. Symp. Proc. 556, 825-832.

*Year:*
1999

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Long-term stability, confidence building

*Keywords:*
Hyrkkölä

*Original abstract/summary/conclusions*

The Hyrkkölä U-Cu mineralization located in south-western Finland is reassessed with reference to the corrosion mechanisms affecting the stability of native copper and the time-scales of corrosion processes. The mineral assemblage native copper - copper sulfide occurs in open fractures at several depth intervals within granite pegmatites (GP). The surfaces of these open fractures have accumulations of uranophane crystals and other unidentified uranyl compounds. The secondary uranium minerals are mainly distributed around copper sulfide grains. Microscopic intergrowths of copper sulfides and uranyl compounds also have been observed. Groundwater samples were collected from the vicinity of the Cu samples. The hydrogeochemical features of these samples indicate that the present conditions are oxidising. The minimum age of U(VI) transport and deposition is about 200 000 years. This age is indicated by $^{234}$U/$^{238}$U and $^{230}$Th/$^{234}$U activity ratios of uranophane. The age of the hexavalent uranium precipitation may be somewhat later than the last influxes and/or demobilisation of sulfur.

The mineral assemblage native copper - copper oxide (cuprite) occurs only at one depth interval within altered granite pegmatite. The fracture surface was coated by smectite. The content of uranium in smectite was 69 - 75 ppm U. The $^{234}$U/$^{238}$U and $^{230}$Th/$^{234}$U activity ratios of smectite showed that it has been exposed to recent groundwaters (e.g., during the last million years). The pH of the groundwater at this interval was near neutral (6.9). The copper grains present at this fracture surface were as large as 1 mm in diameter

*Current author review comments:*

Conference paper based on #057.

*Check if additional Comments made* ☐

*Ref. no.:* 063

*Title:*
Lessons from nature – the behaviour of technical and natural barriers in the geological disposal of spent nuclear fuel.

*Authors:*
Marcos, N.

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|---|---|
| *Source:*<br>Ph.D. thesis, Helsinki University of Technology | *Year:*<br>2002 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Long-term stability, confidence building

*Keywords:*
Hyrkkölä

*Original abstract/summary/conclusions*

This work deals with the study of the long-term performance of materials and elements involved in the near- and far-field of an underground nuclear waste repository. Materials and elements occurring in nature are similar, or at least analogous, to the materials and elements manufactured or processed by man. Also, natural processes may be similar to those envisaged as occurring in a nuclear waste repository. This similarity makes it possible to study the behaviour of those materials in nature and to compare it with the behaviour of the manufactured materials to be used in a repository. As many materials and elements have been in the natural environment for long time periods (thousands to million of years), the data obtained can be extrapolated to estimate the future evolution of similar components in a nuclear waste repository. Thinking by analogy is the process of comparison, with those materials, elements and environments used to perform the studies that allow the comparison to be regarded as natural analogues.

The Hyrkkölä U-Cu mineralisation (SW Finland) was studied as an analogue to the behaviour of copper canisters in crystalline bedrock. This analogue could also address the interaction between copper corrosion products and uranium. Copper sulphides are shown to retain up to 25% of uranium as U (IV) even if oxidizing conditions prevail. Furthermore, uranium was observed in smectite (main component of bentonite) associated with native copper and cuprite, which constitutes an analogue to the behaviour of the repository near-field materials in a natural oxidizing environment.

In addition to the Hyrkkölä analogue, the issue of irreversible sorption or uranium immobilization is also addressed, in the studies of the boulder rock near Hämeenlinna. The behaviour of U, Th, and rare earth elements (REE) as analogues to the long-lived actinides is also evaluated in groundwater and rock samples at Olkiluoto (SW Finland). U and Th were shown to be released more easily from clean fracture surfaces than from fracture surfaces covered with calcite or kaolinite.

From the studies presented here, it may be seen that the Hyrkkölä analogue has been applied so far in safety assessments, mainly to demonstrate the canister lifetime and to a lesser extent to confirm the interactions between copper corrosion products and uranium. Up to the present, the issues of irreversible sorption or immobilization and the analogy between REE and actinides have not been taken into account in safety assessments. The results of the studies presented here indicate strong prospects that these issues could be new and powerful tools indispensable to safety assessments. More research and understanding is required, however, to form them into operational tools for this application.

*Check if additional Comments made* ☐

*Ref. no.:* 064

*Title:*
A study of transport phenomena in the corrosion products of ferrous archaeological artefacts using $^{18}$O tracing and nuclear microprobe analysis.

*Authors:*
Vega, E., P. Berger, and P. Dillmann.

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|---|---|
| *Source:*<br>Nucl. Instr. Methods Phys. Res. B 240, 554-558. | *Year:*<br>2005a |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Mechanistic understanding

*Keywords:*
Oxygen reduction, cathodic reaction, corrosion product layer

*Original abstract/summary/conclusions*

Studies of ferrous archaeological artefacts corroded in soil are of great interest for the cultural heritage community and for the prediction of very long term corrosion behaviour of low alloy steels. One important hypothesis of recent studies is that corrosion mechanisms seem to be controlled by oxygen diffusion that is solved in the soil water and in the porosities of the corrosion products. Consequently, cathodic and anodic corrosion reactions should happen at the metal/oxide interface. In order to verify this assertion, several experiments were done using $^{18}$O tracers, to visualize where the corrosion reactions take place in the system. Samples collected on archaeological ferrous artefacts were put with their already formed corrosion products in water previously deoxygenised and equilibrated with $^{18}$O at a pressure of 1.2 atm. After various exposition periods, samples were removed and transverse sections were made. The distribution of the remaining $^{18}$O precipitated product in the ancient corrosion products was mapped by means of the $^{18}O(p, \alpha)^{15}N$ reaction. Indeed, this 18O presence seems to reveal the precipitation of new oxidation products and confirm the location of the cathodic reaction at the metal/oxide interface.

*Current author review comments:*

Nice mechanistic study to identify location of cathodic reaction. See also #029.

*Check if additional Comments made* ☐

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| *Ref. no.:* 065 |
| *Title:*<br>A brief historical retrospective of investigations of archaic to contact period copper-based metal artifacts in northeastern North America. |
| *Authors:*<br>Anselmi, L.M. |

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|---|---|
| *Source:*<br>Ontario Archaeology 77/78, 81-94. | *Year:*<br>2004 |

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| *Relevant engineered barrier:*<br>Copper |
| *Relevant use or application of the study:*<br>Confidence buidling |
| *Keywords:*<br>Native copper, indigenous groups, First Nations |

*Original abstract/summary/conclusions*

The use of native or pure copper and European-introduced copper-based metals in the production of ornamental and utilitarian forms by First Nations groups has long been recognized in Ontario and the broader northeastern North America region. This paper presents a brief review of some of the projects that have examined these artifacts and the use of metal materials beginning with Sir Daniel Wilson's investigations in the late 1800s of native copper used by Archaic groups and ending with recent research into the use of European-introduced copper-based metals by First Nations groups during the early and middle contact periods undertaken at the University of Toronto. In particular, this paper highlights Martha A. Latta's role in these latter studies, many of which have been completed by graduate students under her supervision.

*Current author review comments:*

Overview of use of copper by First Nations groups, including native copper. Provides background of local interest.

*Check if additional Comments made* ☐

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|---|---|
| *Ref. no.:* 066 | |
| *Title:*<br>Instrumental neutron activation analysis of copper and brass from the Auger site (BDGW-3), Simcoe County, Ontario | |
| *Authors:*<br>Anselmi, L.M., M.A. Latta, and R.G.V. Hancock. | |
| *Source:*<br>Northeast Anthropology 53, 47-59. | *Year:*<br>1997 |
| *Relevant engineered barrier:*<br>Copper | |
| *Relevant use or application of the study:*<br>Confidence building | |
| *Keywords:*<br>Impurities | |

*Original abstract/summary/conclusions*

Instrumental neutron activation analysis was used to determine the trace element composition of 166 archaeologically recovered brass and copper artifacts from the Auger site (BdGw-3), Simcoe County, Ontario. Once defined, these trace element concentrations were grouped into separate chemical "fingerprints" and the groupings were used to estimate the minimum number of trade kettles recovered from the site, to establish the distribution of these kettles across the Auger site, and to draw preliminary connections between the Auger site and other sites in Huronia.

*Current author review comments:*

No corrosion information, as such, but does characterize metal impurity content of archaeological artefacts. Likely to be most useful as an example of local knowledge, rather than to determine the effects of impurities on the corrosion of cold spray copper.

*Check if additional Comments made* ☐

*Ref. no.:* 067

*Title:*
Understanding the corrosion of steel promoted by sulfides through the study of archaeological waterlogged composite wood-iron assemblies.

*Authors:*
Rémazeilles, C., F. Lévêque, E. Conforto, and P. Refait.

*Source:*
Presentation at 7th Int. Workshop on Long-term Prediction of Corrosion damage in Nuclear Waste Systems (LTC 2019).

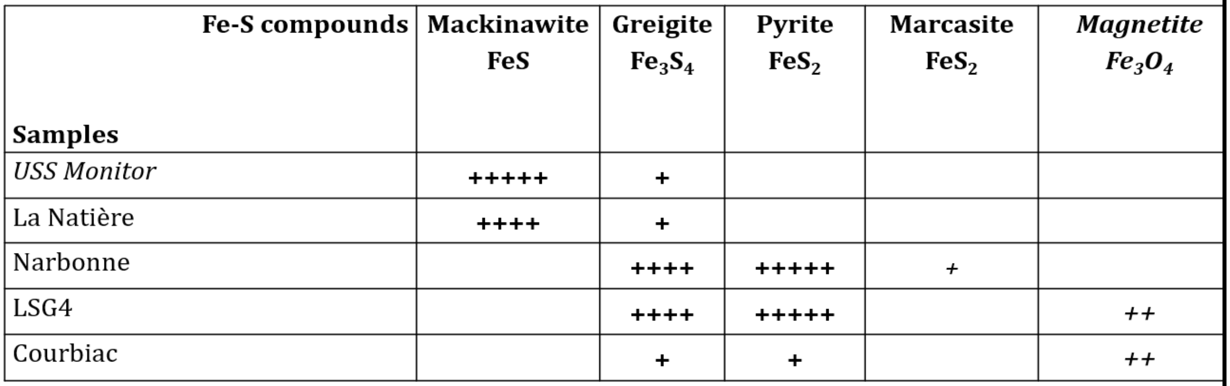
*Year:*
2019

*Relevant engineered barrier:*
Steel, bentonite

*Relevant use or application of the study:*
Safety assessment

*Keywords:*
Mackinawite, pyrite

*Original abstract/summary/conclusions*



| **Fe-S compounds**<br>**Samples** | **Mackinawite FeS** | **Greigite $Fe_3S_4$** | **Pyrite $FeS_2$** | **Marcasite $FeS_2$** | ***Magnetite $Fe_3O_4$*** |
|---|---|---|---|---|---|
| *USS Monitor* | +++++ | + | | | |
| La Natière | ++++ | + | | | |
| Narbonne | | ++++ | +++++ | + | |
| LSG4 | | ++++ | +++++ | | ++ |
| Courbiac | | + | + | | ++ |

With increasing age of the waterlogged wood, progression observed from mackinawite to pyrite, via the metastable greigite.

*Current author review comments:*

Useful analogue for the transformation of mackinawite to the more-stable pyrite in a natural system. Would ideally like a similar study in soil of clay to support the argument that sulphide is irreversibly sequestered by precipitation with Fe(II).

*Check if additional Comments made* ☐

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| *Ref. no.:* 068 |
| *Title:*<br>Mechanisms of long-term anaerobic corrosion of iron archaeological artefacts in seawater. |
| *Authors:*<br>Rémazeilles, C., D. Neff, F. Kergourlay, E. Foy, E. Conforto, E. Guiliminot, S. Reguer, Ph. Refait, and Ph. Dillmann. |

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|---|---|
| *Source:*<br>Corros. Sci. 51, 2932-2941. | *Year:*<br>2009 |

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| *Relevant engineered barrier:*<br>Steel |
| *Relevant use or application of the study:*<br>Confidence building |
| *Keywords:*<br>SRB, mackinawite |

*Original abstract/summary/conclusions*

An iron ingot immersed during 2000 years at 12 m depth in the sea has been examined with the help of a combination of microscale techniques. This methodology allowed us to show that the main phase precipitated during the immersion is an iron hydroxychloride ( $\beta$-$Fe_2(OH)_3Cl$) that is characteristic of corrosion in anoxic and chlorinated medium. Moreover locally on the external part of the corrosion products sulphur containing phases have been identified as mackinawite (FeS) in nanocrystalline or slightly oxidised state. The presence of this phase could be explained by the activity of sulphate-reducing bacteria. The presence of $\beta$-$Fe_2$(OH)3Cl could be interpreted via a thermodynamic modelling taking into account the environmental conditions.

*Current author review comments:*

Another paper on characterisation of corrosion products.

*Check if additional Comments made* ☐

*Ref. no.:* 069

*Title:*
Contribution of magnetic measurement methods to the analysis of iron sulfides in archaeological waterlogged wood-iron assemblies.

*Authors:*
Rémazeilles, C., F. Lévêque, E. Conforto, L. Meunier, and P. Refait.

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|---|---|
| *Source:*<br>Microchemical J. 148, 10-20. | *Year:*<br>2019 |

*Relevant engineered barrier:*
Steel, bentonite

*Relevant use or application of the study:*
Safety assessment, lifetime prediction

*Keywords:*
Mackinawite, greigite, pyrite

*Original abstract/summary/conclusions*

Pyrite and greigite were identified in the wood of two ancient shipwrecks using an original multi-technique analytical approach. Structural characterization methods such as environmental scanning electron microscopy, micro-Raman spectroscopy and X-ray diffraction were combined with magnetic measurement methods, such as magnetic susceptibility measurements and isothermal remanent magnetization acquisition curves. This is the first time that magnetic measurement methods are used in the field of cultural heritage to study wet organic archaeological materials. They proved to be particularly suitable to detect with a very high sensitivity ferromagnetic s.l. mineral phases inside waterlogged wooden samples, i.e. in the bulk. The occurrence of iron sulfides in archaeological shipwrecks extracted from waterlogged environments is usually attributed to microbiologically influenced corrosion of iron fasteners. This study demonstrates that the nature of the identified iron sulfides is consistent with a step-by-step in situ anoxic oxidation process of mackinawite.

*Current author review comments:*

Evidence for time-dependent transformation of mackinawite to pyrite via greigite.

*Check if additional Comments made* ☐

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|---|---|
| *Ref. no.:* 070 | |
| *Title:*<br>Safety case for the disposal of spent nuclear fuel at Olkiluoto – complementary considerations 2012 | |
| *Authors:*<br>Posiva | |
| *Source:*<br>Posiva Oy Technical Report, POSIVA 2012-11. | *Year:*<br>2012b |
| *Relevant engineered barrier:*<br>Copper, steel, bentonite, cement, spent fuel | |
| *Relevant use or application of the study:*<br>Safety case, confidence building, corrosion rates | |
| *Keywords:*<br>Review | |

*Original abstract/summary/conclusions*

*Complementary Considerations* sits within Posiva Oy's Safety Case "TURVA-2012" report portfolio and has the objective of enhancing confidence in the outcomes of the safety assessment for a spent nuclear fuel repository to be constructed at Olkiluoto, Finland.

The main emphasis in this report is on the evidence and understanding that can be gained from observations at the site, including its regional geological environment, and from natural and anthropogenic analogues for the repository, its components and the processes that affect safety. In particular, the report addresses diverse and less quantifiable types of evidence and arguments that are enclosed to enhance confidence in the outcome of the safety assessment. These complementary considerations have been described as evaluations, evidence and qualitative supporting arguments that lie outside the scope of the other reports of the quantitative safety assessment.

The experience with natural analogues for the long-term durability of the materials involved and the extent of processes provides high confidence in our understanding of the disposal system and its evolution. For each engineered barrier and key process, there is increasing analogue evidence to support the conceptual models and parameters.

Regarding the suitability of the Olkiluoto site to host a spent fuel repository, a number of factors have been identified that indicate the suitability of crystalline host rock in general, and that of the Olkiluoto site in particular.

The report also provides radiation background information for the use of complementary indicators, which aid in putting the results of the safety analysis presented in *Assessment of Radionuclide Release Scenarios for the Repository System* and *Biosphere Assessment* in a broader perspective to show that the radiation originating from a spent nuclear fuel repository remains in most cases much below natural background radiation or that caused by non-nuclear industries.

*Current author review comments:*

Posiva's review of analogue studies in support of TURVA-2012. Updated for TURVA-2020.

*Check if additional Comments made* ☐

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| *Ref. no.:* 071 | |
| *Title:*<br>Complementary considerations in the safety case for the deep repository at Olkiluoto, Finland: support from natural analogues. | |
| *Authors:*<br>Reijonen, H.M., W.R. Alexander, N. Marcos, and A. Lehtinen. | |
| *Source:*<br>Swiss J. Geosci. 108, 111-120. | *Year:*<br>2015 |
| *Relevant engineered barrier:*<br>Copper, steel, bentonite, spent fuel | |
| *Relevant use or application of the study:*<br>Safety case, confidence building | |
| *Keywords:*<br>Review | |

*Original abstract/summary/conclusions*

A report entitled ‘‘complementary considerations’’ has recently been published by Posiva, the organization implementing the spent fuel disposal programme in Finland. It is part of the documentation (called TURVA-2012 safety case) submitted in 2012 for the construction license for a deep geological repository at the Olkiluoto site in Finland. The complementary considerations report addresses diverse and less quantifiable types of evidence and arguments for long-term safety which enhance confidence in the outcome of the safety assessment, especially for times greater than a few thousand years. Natural analogues form the core of the ‘‘complementary considerations’’ with the focus very much on geological occurrences of materials and/or processes which mirror those in the repository. For example, native copper is found in fractures in the Fennoscandian Shield and an understanding of its persistence would be of use when assessing the likely lifetime of the copper canister which surrounds the spent fuel. Based on the outcome of this Olkiluoto site specific report, research topics have been identified in relation to processes affecting the performance and future behaviour of the engineered barrier system materials, especially in relation to corrosion of copper and iron (used in waste container outer shell and insert, respectively), alteration and deformation of the bentonite buffer (clay used in the voids between the waste container and bedrock) and interaction with cementitious materials (tunnel supports etc.) ‘‘complementary considerations’’ is not the sole user of natural analogue information within the safety case, but its main aim is to allow thorough discussion and provide background that can be referred to in other safety case documentation, such as process descriptions, assessment of repository performance etc.

*Current author review comments:*

Journal paper summary of #070, including discussion of canister analogues.

*Check if additional Comments made* ☐

*Ref. no.:* 072

*Title:*
Nails of the Roman legionary at Inchtuthil

*Authors:*
Mapelli, C., W. Nicodemi, R.F. Riva, M. Vedani, and E. Gariboldi.

*Source:*
La Metallurgia Italiana 101, 51-58.

*Year:*
2008

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Confidence building, corrosion rate

*Keywords:*
Aerobic

*Original abstract/summary/conclusions*

This study is focused on the nails found at Inchtuthil, Perthshire (UK) dated back to 87 A.D. The investigated nails were analyzed to characterize these objects. After the sectioning of the sample, an accurate optical microscopy examination has been performed in order to study the different structural constituents composing the microstructure. SEM-EDS analysis allowed to quantitatively characterize the chemical composition of non-metallic inclusions, while the SEM-EBSD examination revealed the crystallographic textures featuring the examined alloy. This information, coupled with the measurements of the micro-hardness suggests a new hypothesis on the plastic deformation process adopted for the realization of the observed nail.

*Current author review comments:*

Whilst the hoard of Roman nails from Inchtuthil is visually very impressive, as well as being impressive from the viewpoint that iron objects have persisted for such a long time under aerobic conditions, the value of the analogue is primarily in the sense of confidence building. Although it is possible to abstract a corrosion rate, the environmental conditions (near-surface, aerobic) are quite unlike those in a repository, so any resemblance of the rate with those used for long-term lifetime prediction is purely coincidental.

*Check if additional Comments made* ☐

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| *Ref. no.:* 073 |
| *Title:*<br>Long-term corrosion behaviour of low-carbon steel in anoxic environment: Characterisation of archaeological artefacts. |
| *Authors:*<br>Saheb, M., D. Neff, Ph. Dillmann, H. Matthiesen, and E. Foy. |

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|---|---|
| *Source:*<br>J. Nucl. Mater. 379, 118-123. | *Year:*<br>2008 |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development

*Keywords:*
French program, corrosion product characterization, LTC 2007

*Original abstract/summary/conclusions*

In the context of nuclear waste storage, archaeological artefacts can be used as analogues for long-term prediction of iron corrosion behaviour. As many studies are based on laboratory simulations, it is necessary to establish a link between short and long-term behaviour. In this study, corrosion product crystalline structures on archaeological artefacts buried in soils and iron coupons immersed in synthetic environments have been compared. The occurrence of carbonated iron (siderite $FeCO_3$ and iron hydroxycarbonate $Fe_2(OH)2CO_3$) has been observed on items from both environments using Raman microspectroscopy and X-ray micro-diffraction.

*Current author review comments:*

*Check if additional Comments made* ☐

*Ref. no.:* 074

*Title:*
Iron corrosion in an anoxic soil: Comparison between thermodynamic modelling and ferrous archaeological artefacts characterised along with the local in situ geochemical conditions.

*Authors:*
Saheb, M., M. Descostes, D. Neff, H. Matthiesen, A. Michelin, and P. Dillmann.

| | |
|---|---|
| *Source:*<br>Appl. Geochem. 25, 1937-1948. | *Year:*<br>2010 |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development

*Keywords:*
Thermodynamics

*Original abstract/summary/conclusions*

This article is part of an ongoing study on the long-term corrosion behaviour of ferrous archaeological artefacts. The aim of this study is to correlate the corrosion products formed on ancient artefacts in an anoxic medium to the environmental data using thermodynamic modelling. For this purpose, measurement campaigns have been conducted on the archaeological site of Glinet (16th century, High Normandy (Seine-Maritime), France) where the evolution of the pore water chemistry has been recorded for a period of one year. Three evolution steps have been distinguished after the oxidizing perturbation which was induced by the piezometers installation. The first step was related to an oxidizing environment in which pore water was in equilibrium with a Fe(III) precipitated phase: ferrihydrite (FeOOH·0.4H2O). The second step was considered as an intermediate step and Fe speciation had evolved; equilibrium was achieved between ferrihydrite and a Fe(II) carbonate phase: siderite ($Fe^{(II)}CO_3$). The last step of the evolution was related to a reducing stage where pore water was in equilibrium with magnetite ($Fe_3^{(II,III)}O_4$) and with chukanovite ($Fe_2^{(II)}(OH)_2CO_3$). As these phases were present in the corrosion layers formed on the archaeological samples, it is possible to conclude that the thermodynamic approach was helpful in developing a better understanding of the effect of geochemical conditions on the composition and mineralogy of the corrosion products formed on archaeological artefacts. This work could be used as a reference for further corrosion studies, especially on long-term corrosion processes applied to nuclear waste disposal.

*Current author review comments:*

The use of thermodynamics in this study was to demonstrate that the corrosion products observed are consistent with the predicted thermodynamically stable phases based on the (re-established) undisturbed ground water conditions.

*Check if additional Comments made* ☐

*Ref. no.:* 075

*Title:*
High-level waste disposal, ethics and thermodynamics

*Authors:*
Schwartz, M.O.

| | |
|---|---|
| *Source:*<br>Environ. Geol. 54, 1485-1488. | *Year:*<br>2008 |

*Relevant engineered barrier:*
Copper, bentonite

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Native copper, thermodynamics, KBS-3, DGR

*Original abstract/summary/conclusions*

Moral philosophy applied to nuclear waste disposal can be linked to paradigmatic science. Simple thermodynamic principles tell us something about rightness or wrongness of our action. Ethical judgement can be orientated towards the chemical compatibility between waste container and geological repository. A container-repository system as close as possible to thermodynamic equilibrium is ethically acceptable. It aims at unlimited stability, similar to the stability of natural metal deposits within the Earth’s crust. The practicability of the guideline can be demonstrated.

*Current author review comments:*

A presentation based on the authors personal philosophical position on the ethics of final disposal of nuclear waste. The author is clearly an advocate of the use of thermodynamics to demonstrate long-term stability, to the extent that he proposes the addition of metallic copper particles to the buffer to promote local equilibrium based on the redox couple $Cu + 2Cl^- = CuCl_2^- + e^-$ in the absence of sulphide, and the selection of a low-S bentonite (he prefers the Czech EKOBENT over MX-80 or Avonlea bentonites).

*Check if additional Comments made* ☐

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|---|---|
| *Ref. no.:* 076 | |
| *Title:*<br>Studies of natural analogues and geological systems. Their importance to performance assessment. | |
| *Authors:*<br>Brandberg, F., B. Grundfelt, L.O. Höglund, F. Karlsson, K. Skagius, and J. Smellie. | |
| *Source:*<br>Swedish Nuclear Fuel and Waste Management Co Technical Report, SKB TR 93-05. | *Year:*<br>1993 |
| *Relevant engineered barrier:*<br>Copper, bentonite, rock | |
| *Relevant use or application of the study:*<br>Confidence building | |
| *Keywords:*<br>Safety assessment, overview | |

*Original abstract/summary/conclusions*

This review has involved studies of natural analogues and natural geological systems leading to the identification and quantification of processes and features of importance to the performance and safety of repositories for radioactive waste. The features and processes selected for the study comprise general geochemical issues related to the performance of the near- and the far-field, the performance and durability of construction materials and the effects of glaciation. For each of these areas a number of potentially important processes for repository performance have been described, and evidence for their existence, as well as quantification of parameters of models describing the processes, have been sought from major natural analogue studies and site investigations. The review has aimed at covering a relatively broad range of issues at the expense of in-depth analysis. The quantitative data presented are in most cases compilations of data from the literature; in a few cases results of evaluations made within the current project are included.

The results of the study show that studies of natural analogues and natural geological systems have provided significant information regarding many issues of importance to repository performance. In several cases the evidence from natural analogues has demonstrated that processes assumed to take place in repositories actually occur in natural systems or under conditions similar to those predicted to prevail in a future repository. One example of such a process is coprecipitation of fission products and ferric oxyhydroxides as an analogue to corrosion products from a steel canister. In addition, the study of concentration gradients of uranium and other trace substances in the rock surrounding groundwater conduits confirm that matrix diffusion occurs in nature and that the diffusivities in the rock matrix measured in the laboratory are consistent with the observations in nature. Furthermore, observations within natural analogue studies of colloids associated with uranium, thorium and rare-earth elements indicate that colloids do not appear to transport significant amounts of these trace elements. This would suggest that either the sorption of the trace elements onto the colloids is reversible or the mobility of the colloids is low due to filtration effects or other phenomena.

Observations from natural systems and archaeological artefacts have been used to demonstrate the durability of the different materials comprising the near-field multibarrier system. Studies of copper and steel, bentonite and various types of cement and concrete strongly support the credibility of predicting long-term stability of these materials under repository conditions.

*Check if additional Comments made* ☒

*Comments (continued):*

Increasingly, natural analogue studies are providing the opportunity to test the thermodynamic solubility and speciation codes and associated data bases used in performance assessment. This has been carried out with some success. However, in situ speciation measurements are necessary to rectify the large uncertainties which still exist for some elements in the data bases.

In general, natural analogue studies are progressively making their impact felt on repository performance assessment, in particular studying processes which have been occurring over time scales compatible with those predicted for long-term radioactive waste disposal.

*Current author review comments:*

Overview of the use of analogues to support the safety assessment. Similar to Posiva’s Complementary Considerations report.

*Ref. no.:* 077

*Title:*
Mineral formation on metallic copper in a “future repository site environment”: Textural considerations based on natural analogs.

*Authors:*
Amcoff, Ö.

*Source:*
Swedish Nuclear Power Inspectorate, SKI Report 98:7.

*Year:*
1998

*Relevant engineered barrier:*
Copper, bentonite

*Relevant use or application of the study:*
Conceptual model development

*Keywords:*
Native copper, geology

*Original abstract/summary/conclusions*

Copper mineral formation in the Swedish "repository site environment" is discussed. Special attention is given to ore mineral textures (= the spatial relation among minerals), with examples given from nature.

<u>It is concluded</u>: By analogy with observations from natural occurences, an initial coating of Cu-oxide on the canister surface (because of entrapped air during construction) will probably not hinder a later sulphidation process. Early formation of Cu-sulphides on the canister surface may be accompanied by formation of CuFe-sulphides. The latter phase(s) may form through replacement of the Cu-sulphides or, alternatively, by means of reaction between dissolved copper and fine-grained iron sulphide (pyrite) in the surrounding bentonite. Should for some reason the bentonite barrier fail and the conditions become strongly oxidizing, we can expect crustifications and rhytmic growths of Cu(II)-phases, like malachite ($Cu_2(OH)_2CO_3$). A presence of $Fe^{2+}$ in the clay minerals making up the bentonite might prove to have an adverse effect on the canister stability, since, in this case, the bentonite might be expected to act as a sink for dissolved copper. The mode of mineral growth along the copper - bentonite interface remains an open question.

*Current author review comments:*

A very interesting background to the formation, persistence, and use of copper ore bodies as analogues for copper canisters, written from the perspective of a geologist. Otherwise obscure geological terms are simply described, making the report very accessible.

Interesting summary of the conditions under which native copper is stable; either under very reducing conditions, or under more oxidizing conditions where sulphide is oxidized resulting in very low sulphide activity. This corresponds with the “island” of Cu metal stability in the Cu-S-$H_2O$ E-pH diagram.

Also contains an implicit warning about overemphasizing the native Michigan deposits as analogues. These are unique from a geological viewpoint in that the S activity is so low. Therefore, this is not necessarily a useful analogue for the DGR if we believe that sulphide will be present.

*Check if additional Comments made* ☐

|  |  |
|---|---|
| *Ref. no.:* 078 | |
| *Title:*<br>Stability of metallic copper in the near surface environment. | |
| *Authors:*<br>Amcoff, Ö. and K. Holényi. | |
| *Source:*<br>Swedish National Board for Spent Nuclear Fuel, SKN Report 57. | *Year:*<br>1992 |
| *Relevant engineered barrier:*<br>Copper | |
| *Relevant use or application of the study:* | |
| *Keywords:*<br>Geology, geologist | |

*Original introductions*

The present study was initiated by the National Board for Spent Nuclear Fuel (SKN). It may be regarded as a review of the state of the art of copper stability - copper mobility in a low temperature-near surface environment. In the discussion, we have emphasized geological-geochemical milieus that have a direct bearing on the problem of final storage of spent nuclear fuel in copper canisters. The literature review has concentrated on copper in connection with: (a) low-temperature environments, and (b) stability-mobility, with particular emphasis on a chloride-rich, sulphur-rich milieu. The possible influence on the present processes of radiolysis and engineered barriers besides copper is not discussed in this report.

In order to facilitate the discussion, a number of examples on copper mineral stabilities and copper solubility etc. are given below, based on thermodynamic calculations. These calculations are simplified to a certain degree and the discussion is based on differences in orders of magnitude rather than on exact figures. The thermodynamic foundation for the calculations is given in an appendix. Conclusions and recommendations are outlined in general terms in a separate report.

The geological circumstances are explained at some length because we assume that the readers will be mainly non-geologists. All conclusions drawn are our own.

*Current author review comments:*

This is more of a review of copper corrosion information provided by SKB, than it is a specific application of natural analogues. However, the authors draw on a geological background to describe their picture of the stability of copper in near-surface environments. Covers some of the same topics as #077.

*Check if additional Comments made* ☐

*Ref. no.:* 079

*Title:*
Mineral formation on metallic copper in a “future repository site environment”.

*Authors:*
Amcoff, Ö. and K. Holényi.

| *Source:*<br>Swedish Nuclear Power Inspectorate, SKI Report 96:38. | *Year:*<br>1996 |
|---|---|

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Long-term stability, confidence building

*Keywords:*
Geology, non-passive $Cu_2S$ film, transport control

*Original abstract/summary/conclusions*

Formation of copper minerals in a "future repository site environment" is discussed. Since reducing conditions are expected much effort has been concentrated on Cu-sulphides and CuFe-sulphides. However, oxidizing conditions are also discussed. A list of copper minerals are included. It is concluded that mineral formation and mineral transitions on the copper canister surface will be governed by kinetics and metastabilities rather than by stability relations. The sulphides formed are less likely to form a passivating layer, and the rate of sulphide growth will probably be governed by the rate of transport of reacting species to the canister surface. A series of tests are recommended, in a milieu resembling the initial repository site conditions.

*Current author review comments:*

Interesting to note that, from a geologists point of view, the sulphide film is unlikely to be passivating. This conclusion seems to come from the knowledge that Cu ion transport in the film is rapid and the nature of the crystal growth (single crystal, dendritic). Also concluded that corrosion rate would be limited by the rate of supply of sulphide and that film growth would occur at the film/solution interface, both of which have been shown to be the case experimentally (King et al., Corros. Sci. Eng. Technol, 52:sup 1, 2017, 210-216; Chen et al. Mat. Res. Soc. Symp. Proc. 1475, 2012, doi: 10.1557/opl.2012.617).

*Check if additional Comments made* ☐

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|---|---|
| *Ref. no.:* 080 | |
| *Title:*<br>Study on corrosion of bronze relics – an example for anthropogenic analogue study on disposal system of high-level radioactive waste. | |
| *Authors:*<br>Chen, A., Y. Liu, G. Fang, Z. Wen, S. Sun, and Y. Li. | |
| *Source:*<br>Atomic Energy Sci. Technol. 38, 163-169 (in Chinese). | *Year:*<br>2004 |
| *Relevant engineered barrier:*<br>Copper | |
| *Relevant use or application of the study:*<br>Confidence building | |
| *Keywords:*<br>Bronze | |

*Original abstract/summary/conclusions*

The paper presents composition analyses and structure observation of bronze relic samples which were collected from Hubei , Jiangxi , Guangxi, Shaanxi , Beijing , environmental conditions of the sites where the samples were taken. Research results indicate that the bronze relics can be continuously corroded with time, the corrosion layer of bronze relics consists of at least two sub-layers, such as oxide and carbonate sub-layers. Sometimes, there is corrosion sub-layer mechanically such as loose sub-layer on a specific sample. And $SnO_2$ oxide sub-layer also occurs in a few samples. The thickness of bronze corrosion layers is varied with the different climate environments in which the samples studied were taken, and their thickness are 50～260 μm and 300～800 μm in the dried and humid climate region, respectively. As far as the natural corrosion-resistant is concerned, the bronze is available for material of canister of high-level waste (HLW) repository system.

*Current author review comments:*

Conclusion is unclear, but the authors may be suggesting that bronze is a suitable canister material.

*Check if additional Comments made* ☐

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|---|---|
| *Ref. no.:* 081 | |
| *Title:*<br>Study on the corrosion of Shang and Zhou dynasty bronze relics – a case study of artificial analogue of HLW disposal system canister. | |
| *Authors:*<br>Chen, A., Y. Liu, G. Fang, Z. Wen, S. Sun, Y. Li, Z. Zhang. | |
| *Source:*<br>Uranium Geol. 31, 121-127 (in Chinese). | *Year:*<br>2015 |
| *Relevant engineered barrier:*<br>Copper | |
| *Relevant use or application of the study:*<br>Confidence building | |
| *Keywords:* | |
| *Original abstract/summary/conclusions*<br>*Current author review comments:*<br>Seems to be virtually identical to #080, with only minor differences. | |

*Check if additional Comments made* ☐

|  |  |
|---|---|
| *Ref. no.:* 082 | |
| *Title:*<br>Role of previously formed corrosion product layers on sulfide-assisted corrosion of iron archaeological artefacts in soil. | |
| *Authors:*<br>Rémazeilles, C., D. Neff, J.A. Bourdoiseau, R. Sabot, M. Jeannin, and, Ph. Refait. | |
| *Source:*<br>Corros. Sci. 129, 169-178. | *Year:*<br>2017 |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Conceptual model development | |
| *Keywords:*<br>SRB, reactive iron carbonate layer | |

*Original abstract/summary/conclusions*

Iron archaeological nails (16th century) were used as representative of the mild steel structures envisaged for the storage of nuclear waste. The influence of sulfide species on the corrosion behavior of the nails was investigated via the thorough description of the modifications undergone by the corrosion products surrounding the metal after re-immersion in deaerated sulfide solution. The only observed modification was the formation of FeS at the corrosion product layer/soil interface. The corrosion product layer, mainly composed of $FeCO_3$, acts as protective barrier, the reactivity of $FeCO_3$ preventing sulfide species to reach the metal and influence the corrosion process.

*Current author review comments:*

Interfacial $FeCO_3$ layer prevents sulphide from reaching metal surface by dissolving as $Fe^{2+}$ and re-precipitating as mackinawite. Presumably FeS has a lower solubility product that $FeCO_3$.

*Check if additional Comments made* ☐

*Ref. no.:* 083

*Title:*
A natural analogue for copper waste canisters: The copper-uranium mineralized concretions in the Permian mudrocks of south Devon, United Kingdom

*Authors:*
Milodowski, A.E., M.T. Styles, and V.L. Hards.

*Source:*
Swedish Nuclear Fuel and Waste Management Co Technical Report, SKB TR-00-11.

*Year:*
2000

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Confidence building

*Keywords:*
Littleham Cove, native copper

*Original abstract/summary/conclusions*

This report presents the results of a small-scale pilot study of the mineralogy and alteration characteristics of unusual sheet-like native copper occurring together with uraniferous and vanadiferous concretions in mudstones and siltstones of the Permian Littleham Mudstone Formation, at Littleham Cove (near Budleigh Salterton), south Devon, England. The host mudstones and siltstones are smectitic and have been compacted through deep Mesozoic burial. The occurrence of native copper within these rocks represents a natural analogue for the long-term behaviour of copper canisters, sealed in a compacted clay (bentonite) backfill, that will be used for the deep geological disposal of high-level radioactive waste by the Svensk Kärnbränslehantering AB (SKB). The study was undertaken by the British Geological Survey (BGS) on behalf of SKB between November 1999 and June 2000. The study was based primarily on archived reference material collected by the BGS during regional geological and mineralogical surveys of the area in the 1970's and 1980's. However, a brief visit was made to Littleham Cove in January 2000 to try to examine the native copper in situ and to collect additional material. Unfortunately, recent landslips and mudflows obscured much of the outcrop, and only one new sample of native copper could be collected.

The native copper occurs as thin plates, up to 160 mm in diameter, which occur parallel to bedding in the Permian Littleham Mudstone Formation at Littleham Cove (near Budleigh Salterton) in south Devon. Each plate is made up of composite stacks of individual thin copper sheets each 1–2 mm thick. The copper is very pure (>99.4% Cu) but is accompanied by minor amounts of native silver (also pure - >99%) which occurs as small inclusions within the native copper. Detailed mineralogical and petrological studies of the native copper sheets, using optical petrography, backscattered scanning electron microscopy, X-ray diffraction analysis and electron probe microanalytical techniques, reveal a complex history of mineralisation and alteration that can be related to the burial and diagenetic history of the Permian strata.

The native copper mineralisation exhibits close temporal association with the formation of uraniferous and vanadiferous concretions (known as "fish-eyes") in the same rocks. Petrographical relationships indicate that both the copper and the "fish-eye" concretions formed during burial diagenesis but before the maximum compaction of the host mudstone and siltstone. The regional burial history Wessex Basin (Chadwick, 1985), indicates that the maximum compaction of the Permian strata would have been achieved by at least the end of the Lower Jurassic (possibly even in the Triassic). Therefore, the native copper mineralisation is older than 176 Ma.

*Check if additional Comments made* ☒

*Comments (continued):*

The native copper sheets display a complex sequence of alteration and subsequent mineral growth of minerals on their surfaces. The earliest alteration was to copper oxides – principally cuprite with minor tenorite, indicating a change to more oxidizing groundwater conditions. The dissolution of native silver and the growth of fringes of copper arsenides followed this. Nickel arsenides and chalcocite, associated with the precipitation of uranium silicates occurred in the later stages of alteration. This suggests a return to a more reducing porewater environment. Again, petrographical relationships indicate that this alteration and subsequent mineralisation is geologically old (i.e. Lower Jurassic or older).

Secondary malachite, intimately intergrown copper sulphate and copper oxides, copper chloride, copper-uranium arsenate and uranium vanadates have formed as late-stage alteration products of the native copper and earlier diagenetic cuprite, chalcocite, copper-nickel arsenide and uranium silicate alteration and mineralisation. This late-stage alteration is most probably attributable to near-surface weathering processes.

Although the native copper is affected by corrosion, the study has shown that a significant proportion (30–80% of the original thickness) of the copper sheets has been preserved in the saturated compacted clay environment of the Littleham Mudstone for many millions of years, at least since the end of the Lower Jurassic. Apart from the recent weathering effects due to exposure at outcrop, most of the observed corrosion and alteration of the native copper is geologically old and also occurred before the end of the Lower Jurassic. This demonstrates that the native copper can remain stable in a saturated and compacted clay environment for geological timescales (over 176 Ma) well in excess of the timescales considered for Performance Assessment. Since the copper sheets found in the Littleham Mudstone Formation are very thin (1–2 mm) and have survived over this long time, waste canisters – which will be made from much thicker copper – would be expected (by comparison) to show greater performance.

*Current author review comments:*

First report of the Littleham Cove native copper deposits. There is mention of chalcocite, but perhaps this is another example of that rare occurrence when the sulphide activity is low. On page 70, there is a suggestion of the previous existence of copper sulphide which have been subsequently oxidised to sulphate (sample e4). However, this suggestion is only based on the observation of S-containing spherules and the suggestion that such speherical features are common for metal sulphides. There is also a tenuous claim of the presence of sulphide based on the poor agreement in the EPMA mass-balance in table 5-4.

The earliest, and still the most dominant, copper alteration product is $Cu_2O$. This was subsequently altered to copper arsenides under more-reducing conditions (>176 Ma).

*Ref. no.:* 084

*Title:*
Alteration of uriniferous and native copper concretions in the Permian mudrocks of south Devon, United Kingdom. A natural analogue study of the corrosion of copper canisters and radiolysis effects in a repository for spent nuclear fuel.

*Authors:*
Milodowski, A.E., M.T. Styles, M.S.A. Horstwood, and S.J. Kemp.

| *Source:* | *Year:* |
|---|---|
| Swedish Nuclear Fuel and Waste Management Co Technical Report, SKB TR-02-09. | 2002 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Confidence building, long-term stability

*Keywords:*
Diffusion

*Original abstract/summary/conclusions*

This report presents the results of a study of the mineralogy and alteration characteristics of unusual concretions containing sheets of native copper, and uranium-vanadium mineralised concretions, in mudstones and siltstones of the Permian Littleham Mudstone Formation, at Littleham Cove (near Budleigh Salterton), south Devon, England. The study was undertaken by the British Geological Survey (BGS) on behalf of the Svensk Kärnbränslehantering AB (SKB), between August 2000 and June 2001. The main objectives of the study were:

- To investigate the corrosion characteristics of the native copper as a natural analogue for the long-term behaviour of copper canisters, sealed in a compacted clay (bentonite) backfill, that will be used for the deep geological disposal of spent fuel and high-level radioactive waste (HLW).
  This study developed from an earlier pilot study /Milodowski et al, 2000/, which demonstrated that the alteration of the native copper in the concretions from Littleham Cove was mineralogically and chemically complex. A more detailed investigation was undertaken to refine the geological relationships, confirm the identity of the alteration products, to establish the relationships between the alteration phases more precisely, and to constrain the age of mineralisation and alteration.
- To investigate the alteration and oxidation of minerals containing reduced species (e.g. ferrous iron) within the uranium-rich concretions as a natural analogue for the potential effects of oxidation induced by a-radiolysis of water in a HLW repository environment.

Native copper-bearing concretions in the Littleham Mudstone Formation are very rare. They occur, as thin lenticular disks developed largely along bedding lamina and thin low-angle fractures cutting the bedding laminae the upper part of the formation, about 10 m below the top of the formation. This part of the sequence comprises laterally discontinuous, fine-grained sheet-flood and channel sandstones and siltstones. Some of these sandstones, are more extensively-cemented by copper sulphides (mainly chalcocite), copper arsenides, cobalt-nickel arsenides, and uranium silicate. This mineralisation cements the intergranular porosity, replacing unstable detrital grains and early diagenetic carbonate cement (calcrete). Similar mineralisation occurs as alteration and overgrowth on the native copper sheets, and appears to be all part of the same mineralisation process. Traces of similar mineralisation were also found in steep fractures close to small faults near the base of the sequence. The thin permeable sandstones and siltstones, and fractures zones around small faults appear to have acted as the conduits for the movement of mineralising fluids through the mudstones.

*Check if additional Comments made* ☒

*Comments (continued):*

The native copper sheets all show a similar pattern of corrosion and alteration. However, the intensity of alteration is very variable, both from one sample to another and from one point on a sample to another. The alteration assemblage is also very complex and is closely related to the mineralisation observed in uraniferous and vanadiferous concretions ('fish-eye' nodules) found in greater abundance in the Littleham Mudstone Formation. With some modifications and additional information, this study largely confirms the observations reported in the pilot study by /Milodowski et al, 2000/.

The alteration of the copper is dominated by copper oxides. This the earliest alteration product observed and comprises principally cuprite ($Cu_2O$), with probable minor tenorite ($CuO$). The cuprite typically forms colloform layers on the copper surface, and localised lobate embayments or corrosion pits that 'eat' more deeply into the copper metal. Although, /Milodowski et al, 2000/ originally referred to the subsequently formed complex arsenide and sulphide mineralisation as alteration products, the more detailed investigation undertaken here demonstrates that these formed as additional overgrowths on the cuprite, rather than corrosion products of the copper. Several of alteration products appear to be hitherto unrecorded minerals.

The native copper, and subsequent cuprite, tenorite and subsequent complex arsenide and sulphide mineralisation formed during the early diagenesis of the rocks prior to maximum burial. The native copper remained relatively inert after the early diagenetic partial alteration to cuprite, until the sequence was uplifted and exposed to surface erosion and oxidative weathering in the present-day environment. This has resulted in the late-stage dissolution of copper metal and copper oxides, accompanied by the
precipitation of secondary malachite, azurite, copper arsenates and complex Cu-chlorides.

Microchemical observations reveal evidence for the enrichment of copper in the mudstone matrix immediately adjacent to the altered copper sheets. The copper concentration drops from around 100% in the cuprite rims of the sheets down to around 1 wt % over a distance of about 20 μm from the altered sheets. With increasing distances away from the sheets there is a more gradual decrease in copper concentration over distances of 100–200 μm to the local background level of the host rock – which may be as high as 2–3 wt % in some places but is generally of the order of 0.1 wt % $Cu_2O$. This is still a very high concentration of copper compared to that in for normal host rock that is not associated directly with copper mineralisation. The high copper concentration could be due to redistribution of copper from the corroded sheets. Alternatively, it could represent a diffusive 'halo' of copper enhancement around the original mineralised structure (bedding laminae or fracture) that formed at the same time as the copper sheets. In both cases, the observations indicate that diffusion occurred over distances of only a few hundreds of micrometres in the mudstone or siltstone matrix.

The uraniferous 'fish-eye' concretions contain high concentration of uranium within their cores. Most of the uranium is concentrated in the outer edges of the dark vanadium-rich core of the concretion and subsequent concentric bands of vanadium-enriched diffusion bands, and associated fin-like structures. Here, it is present largely as uranium silicate and subordinate uraninite (pitchblende), closely associated with copper, nickel and cobalt arsenides which form concentrated 'shells' of mineralisation at the interface between the vanadium-enriched concretion and the background matrix of the enclosing reduction spot. Chalcocite ($Cu_2S$) and small amounts of pyrite ($Fe_S2$) and clausthalite ($PbSe$) are also present. Despite, the close proximity of these reduced mineral species to the uranium mineral grains (they are often closely intergrown), the sulphide, arsenide and selenide minerals are all fresh, even where they are in direct contact with hydrated gel-like uranium silicate. There is no evidence for the oxidation of these minerals, except where they have been exposed to surface weathering on the beach outcrop.

*Check if additional Comments made* ☒

*Comments (continued):*

Mössbauer spectroscopy studies indicate that the iron present in the core of the concretion and the surrounding reduction spot is dominated by Fe[II]. In contrast, the iron in the background red mudstone is dominantly Fe[III], which is present largely as hematite and is responsible for the red pigmentation of the rocks. Mössbauer analysis of samples along three profiles from the radioactive core to background host rock found no change in Fe[II]:Fe[III] ratio, except at the sharp interface between the green reduction spot and the red-brown host rock. No evidence was found for oxidation of Fe[II] due to radiolysis effects associated with the uraniferous core of the concretion.

These concretions are early diagenetic, and for most of their history (>176 Ma) their mudstone host rock will have been well below the present water table, and remained water-saturated. Despite this long history of water saturation, there is no evidence, from either the mineralogical observations or Mössbauer spectroscopy studies, to indicate that radiolysis has been a significant process for inducing oxidation of Fe[II] or other reduced species in the water-saturated clay matrix of the Littleham Mudstone Formation.

It should be borne-in-mind, that the concentration of uranium (and hence radioactivity) is considerably lower in the concretions than that which would be expected from spent fuel waste. However, the concretions are geologically very old and this has presented an opportunity for any potential effects of radiolysis to accumulate for over 170 Ma. The absence of any discernable alteration attributable to radiolysis in these materials suggests that radiolysis may not have a great effect over the much shorter timescale (<2 Ma) considered in PA for radioactive waste disposal.

*Current author review comments:*

Good summary in Section 7.1 of occurrence and alteration of native copper. Also interesting to note Cu diffusion into the clay matrix; however, it is uncertain whether this is the result of corrosion of the native copy, or a remnant of the original diageneis.

Again though, sulphide is a minor actor here, indicative of a low sulphur activity at this site.

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| *Ref. no.:* 085 | |
| *Title:*<br>Natural analogues for expansion due to the anaerobic corrosion of ferrous materials. | |
| *Authors:*<br>Smart, N.R. and R. Adams. | |
| *Source:*<br>Swedish Nuclear Fuel and Waste Management Co Technical Report, SKB TR-06-44. | *Year:*<br>2006 |
| *Relevant engineered barrier:*<br>Copper, steel | |
| *Relevant use or application of the study:*<br>Confidence building, conceptual model development and validation | |
| *Keywords:*<br>Galvanic corrosion, mechanical stresses from expansive corrosion products | |

*Original abstract/summary/conclusions*

In Sweden, spent nuclear fuel will be encapsulated in sealed cylindrical canisters, consisting of a cast iron insert and a copper outer container. The canisters will be placed in a deep geologic repository and surrounded by bentonite. If a breach of the outer copper container were to occur the cast iron insert would undergo anaerobic corrosion, forming a magnetite film whose volume would be greater than that of the base metal. In principle there is a possibility that accumulation of iron corrosion product could cause expansion of the copper canister. Anaerobic corrosion rates are very slow, so in the work described in this report reference was made to analogous materials that had been corroding for long periods in natural anoxic aqueous environments. The report considers the types of naturally occurring environments that may give rise to anoxic environments similar to deep geological groundwater and where ferrous materials may be found. Literature information regarding the corrosion of iron archaeological artefacts is summarized and a number of specific archaeological artefacts containing iron and copper corroding in constrained geometries in anoxic natural waters are discussed in detail. No evidence was obtained from natural analogues which would suggest that severe damage is likely to occur to the SKB waste canister design as a result of expansive corrosion of cast iron under repository conditions.

*Current author review comments:*

Observations from the Coppergate helmet and an overview of museum samples available in the UK that might be interesting for future study. However, we need to note the caution of others that the use of museum samples can build in bias as these artefacts naturally tend to be the ones best presereved.

*Check if additional Comments made* ☐

*Ref. no.:* 086

*Title:*
Studies in pitting corrosion on archaeological bronzes. Copper.

*Authors:*
Bresle, Å., J. Saers, and B. Arrhenius.

| | |
|---|---|
| *Source:*<br>Swedish Nuclear Fuel Supply Company Report, SKBF-KBS-TR-83-05. | *Year:*<br>1983 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Confidence building, input data

*Keywords:*

*Original abstract/summary/conclusions*

Ever since the dawn of the science of archaeology, metal artifacts have played an important role as preserved evidence of a lost culture. It was also noted early that metal objects were subject to progressive degradation in the soil, and conservators at archaeological museums came to devote a great deal of effort to stopping the process of corrosion. It was hereby observed quite soon that once the objects had been taken up out of the soil and placed in the muesums' storerooms, a new degradation of the material took place.

Since the degradation of metal artifacts that took place in the museums took place right in front of the eyes of the museum staff, archaeological corrosion research came to be concentrated largely on this problem. The study reported here is therefore unique in a way, since it has nothing to do with the problem of preserving the archaeological bronzes in question but is instead concerned solely with measuring the pitting factor.

Special problems have been encountered in this measurement of pitting corrosion, since pitting corrosion can only be studied on relatively well-preserved bronzes, whereas in most cases general corrosion has completely ruined the original surface. The selected material is also skewed due to the fact that the studied material has already undergone one selection, so to speak, in that it has exhibited a corrosion resistance that has enabled it to survive at all. We can deduce from the many tombs that have been found empty of artifacts or where the only metal artifacts are of gold that only a very small portion of the original archaeological metal material has been preserved through the millennia. The fact that the time exponent is an important factor here is indicated by Saers' observation that the measured mean pit diameter on the studied bronzes increases with the age of the finds. The theory that a time factor directly influences the corrosion process can also offer new perspectives on the incidence of ancient archaeological finds.

But the present material also indicates that the time factor has had greater importance for the course of pitting corrosion than e.g. environmental conditions and alloying materials. This can probably be explained by the skewing of the material mentioned above. In other words, due to unstable alloys or a poor preservation environment, the object has not been preserved at all or has only been preserved in the form of fragments that are useless for the purposes of this study.

An interesting find is therefore, the low pitting factor in this bronze material, which represents numerous rather impure alloys, i.e. alloys with many trace elements. Metallurgy was not particularly advanced in the Bronze Age, and it is also probable that little effort was made to achieve pure alloys. The ancient metallurgist was much more interested in other properties than the purity of an alloy, such as the ease with which it

*Check if additional Comments made* ☒

*Comments (continued):*

could be melted. Composite alloys actually have advantages in these respects, advantages which the ancient bronzesmith knew how to exploit. But it might also be worth considering that these ununiform alloys may have offered a resistance to pitting corrosion of quite another kind than that exhibited by modern, well-defined pure alloys. Individual trace elements may have acted as corrosion inhibitors if they occurred in the right proportions, while the same trace elements may have contributed towards accelerated degradation at other concentrations.

The interesting results yielded by this study should therefore be supplemented with metallurgical analyses in order to more closely characterize the distribution of the trace elements and the crystalline structure of the alloys. This should also shed additional light on ancient metallurgy. Such knowledge might also permit modern practical applications, where the original alloys, possibly arrived at by chance, can provide indications for the formulation of copper alloys possessing high resistance to corrosion.

*Current author review comments:*

This study has been used extensively to provide pitting data, both in support of a lower pitting value for SKB and in the estimation of maximum pit depth for NWMO.

The study also includes data on impurities, but these are mainly (exclusively?) metal impurities, rather than O, P, S, and H of interest for the coating studies of NWMO.

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| *Ref. no.:* 087 | |
| *Title:*<br>Long-term corrosion resistance of metallic reinforcements in concrete – a study of corrosion mechanisms based on archaeological artefacts. | |
| *Authors:*<br>Chitty, W.-J., P. Dillmann, V. L'Hostis, and C. Lombard. | |
| *Source:*<br>Corros. Sci. 47, 1555-1581. | *Year:*<br>2005a |
| *Relevant engineered barrier:*<br>Steel, concrete | |
| *Relevant use or application of the study:*<br>Conceptual model development, corrosion rates | |
| *Keywords:*<br>Transformed media (TM), dense product layer (DPL), cement, concrete | |

*Original abstract/summary/conclusions*

This paper presents an analytical study on ferrous reinforcements embedded in binders found in ancient buildings aged from the Gallo-Roman period to the beginning of the 20th c. AD. The study of this kind of archaeological analogues is necessary to improve knowledge on the long-term corrosion behaviour of low carbon steels that could be used in concrete to build the substructure of nuclear wastes storage or reversible disposal facilities. The corrosion system can be described as a multi-layer pattern made of metal, a dense corrosion product layer, a transformed medium and a binder. The morphological, and physico-chemical properties like composition, structure and porosities of each part were studied with different analytical methods like optical and electronical microscopies, Energy Dispersive Spectrometry coupled with Scanning Electron Microscopy, Electron Probe MicroAnalysis, Mercury porosimetry, micro-Raman spectroscopy and micro-Diffraction under Synchrotron Radiation. Moreover, average corrosion rates were evaluated. These rates are relatively low compared to the same parameters measured on low alloyed contemporary steels and are comparable with corrosion rates noted for passivated systems.

*Current author review comments:*

Although not directly relevant to the DGR, this is another illustration of the extensive use and central role of analogues in the French program.

*Check if additional Comments made* ☐

|  |  |
|---|---|
| *Ref. no.:* 088 | |
| *Title:*<br>Corrosion behaviour of reinforced concrete: Laboratory experiments and archaeological analogues for long-term predictive modelling. | |
| *Authors:*<br>L'Hostis, V., F. Foct, and P. Dillmann. | |
| *Source:*<br>J. Nucl. Mater. <u>379</u>, 124-132. | *Year:*<br>2008 |
| *Relevant engineered barrier:*<br>Steel, concrete | |
| *Relevant use or application of the study:*<br>Validation of predictive model | |
| *Keywords:*<br>LTC 2007 | |

*Original abstract/summary/conclusions*

In the context of the nuclear waste storage, reinforced concrete will be used for various purposes such as cell structures and some types of containers (e.g. for intermediate level wastes). These structures are required to be safe and reliable in varying environments for long periods of time (up to several hundred years). This paper presents a specific approach that is developed in France at CEA and EDF for the prediction of long-term behaviour of such structures. It discusses the experimental and theoretical approaches which have been developed. It is based on interactive studies dedicated to short term experimentations (corrosion and mechanical behaviour of structures), characterization and specific tests on archaeological analogues, both used to develop mechanistic understanding and modelling of corrosion and mechanical behaviour of reinforced concrete. Advantages and limits of these different and complementary aspects are presented and discussed. Moreover the prediction results of a specific mechanistic model have been confronted to real structures exposed to atmospheric conditions for many years.

*Current author review comments:*

Not generally an analogue paper, but they do validate a predictive corrosion model against a 55-year-old concrete water tower. Nice illustration of the integration of laboratory experiments, predictive modelling, and analogues that is central to the French program.

The paper is also of interest because of the attempt to model the time-dependent cracking of the concrete cover due to the formation of expansive rebar corrosion products.

*Check if additional Comments made* ☐

*Ref. no.:* 089

*Title:*
Long term stability of iron for more than 1500 years indicated by archaeological samples from the Yamato 6th tumulus.

*Authors:*
Yoshikawa, H., E. Gunji, and M. Tokuda.

*Source:*
J. Nucl. Mater. 379, 112-117.

*Year:*
2008

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Confidence building, corrosion rates

*Keywords:*
Japanese program, long-term stability, LTC 2007

*Original abstract/summary/conclusions*

One of the candidate materials for overpack in the Japanese engineered barrier system for high-level radioactive waste (HLW) is iron and therefore its long-term stability for at least 1000 years is very important for safety analysis of the repository system. Therefore, several of the iron artifacts excavated from the Yamato 6th tumulus (ancient tomb) in Nara prefecture were analyzed using X-ray computed tomography (CT) to determine corrosion depth. The samples analyzed, both of two large and 11 smaller iron artifacts are called ‘Tetsutei’. The thickness of each rust layer was measured from a cross-section image of the sample and the difference in material density between rust and iron was shown by the image density by the X-ray CT. In the case of pitting corrosion in the sample, the depth of the pits was measured directly and estimated as total corrosion depth with general corrosion layer. The corrosion depths are 0.5–2.1 mm. These data indicate conservative predictions for the extrapolations based on experimental studies. Such corrosion data from archaeological samples are useful in analogue studies of high-level radioactive waste disposal as evidence of long-term stability of a waste container.

*Current author review comments:*

Example of the use of analogues to extrapolate lab-based corrosion rates in the Japanese program. Since the focus is generally on a 1000-year containment period, the use of analogues can be very powerful for confidence building.

*Check if additional Comments made* ☐

*Ref. no.:* 090

*Title:*
Native copper deposits and the disposal of high-level waste.

*Authors:*
Schwartz, M.O.

*Source:*
Int. Geol. Rev. 38, 33-44.

*Year:*
1996

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Long-term stability

*Keywords:*
Basalt, granite

*Original abstract/summary/conclusions*

Highly radioactive, heat-producing waste contains radionuclides and generates daughter products that have half-lives as long as millions of years. This high-level waste must be sealed from the biosphere for a very long period in stable containers stored in deep geological repositories. Copper has been seriously considered as a container material in several waste-disposal projects. Native copper deposits may serve as natural analogues for a chemically stable container-repository system. These deposits formed in terrestrial basalt-conglomerate sequences at temperatures of approximately 100 to 200°C. The hydrothermal systems possessed oxygen fugacities below the stability limit of cuprite and at least 3 log units above the magnetite-hematite buffer at 100°C, and at least 1 log unit above this buffer at 200°C. This corresponds to an oxygen fugacity range of ≤10 log units. The fluids were characterized by low total sulfur activities in subaerially extruded Cu-rich basalts interbedded with terrestrial conglomerates, which have undergone pervasive hydrothermal alteration.

*Current author review comments:*

Argues that basalt is a better geological host to ensure copper stability than granite, because the later: has a lower $O_2$ fugacity (and, therefore, cannot sit in the upper stable Cu region in the Cu-S-$H_2O$ E-pH diagram, as do copper supergene deposits), high total S activity, and the lower Cu content of the rock make sit more unlikely that you would reach Cu/$Cl^-$ equilibrium.

This is an interesting perspective on the effect of high ground water [$Cl^-$]. Whereas we tend to think in terms of the container as the source of copper, Schwartz argues that the host rock should be considered as the source. With high Cu content in the rock, it is more likely that the groundwater will be at equilibrium with respect to dissolved Cu(I)-$Cl^-$ complexes and that there will be no driving force for dissolution. This is the basis for the idea of adding copper particles to the buffer in #075.

*Check if additional Comments made* ☐

*Ref. no.:* 091

*Title:*
Corrosion of iron archaeological artefacts in soil: characterisation of the corrosion system.

*Authors:*
Neff, D., P. Dillmann, L. Bellot-Gurlet, and G. Beranger.

| | |
|---|---|
| *Source:*<br>Corros. Sci. 47, 515-535. | *Year:*<br>2005 |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development

*Keywords:*

*Original abstract/summary/conclusions*

This paper presents a study made on 40 iron archaeological artefacts buried in soil during several centuries. Samples were taken with the adhering soil and cross-sections were made. The used characterisation techniques are optical and electronic microscopies, EDS coupled to SEM, EPMA, micro-XRD under synchrotron radiation, micro-Raman spectrometry. A specific vocabulary is proposed to describe the corrosion product layout. The most identified corrosion layout is made of several ten micrometers zones of magnetite and/or maghemite embedded in a goethite matrix. A corrosion mechanism is proposed in order to explain this profile. When the soil water contains more chlorine or carbonates, some specific corrosion product appear as akageneite, oxychlorides and siderite.

*Current author review comments:*

This is one of the earliest papers to start to define the structure of the corrosion product layer.

*Check if additional Comments made* ☐

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| *Ref. no.:* 092 | |
| *Title:*<br>Study on unearthed bronzes relics of Xizhou dynasty, China. | |
| *Authors:*<br>Chen, Z., Z. Wen, g. Fan, and Y. Liu. | |
| *Source:*<br>Mat. Res. Soc. Symp. Proc. 807, doi.org/10.1557/PROC-807-867. | *Year:*<br>2004 |
| *Relevant engineered barrier:*<br>Copper | |
| *Relevant use or application of the study:*<br>Confidence building | |
| *Keywords:* | |

*Original abstract/summary/conclusions*

Engineered barrier for HLW repository is composed of the waste form, the canister and the buffer/backfill material. Assessment of the applicability of metal as candidate materials of canister for HLW has been conducted in some countries. Many bronze relics from the XiZhou Dynasty, China, dated from more than 3,000 years ago, have been preserved perfectly. The study on the corrosion of the bronze relics could contribute to the material selection and design of canisters for HLW. The corrosion products of ancient bronzes consist of copper carbonate hydrate, lead carbonate, copper oxides etc. The corrosion mechanism of the substrate was mainly characterized by electrochemical corrosion, whereas the corrosion mechanism of surface layers was characterized by direct chemical corrosion and electrochemical corrosion.

*Current author review comments:*

Similar to #080, #081.

*Check if additional Comments made* ☐

*Ref. no.:* 093

*Title:*
A study of the hydrothermal stability of copper for use as a container material for nuclear waste.

*Authors:*
Lazaar, P.I., G.C. Ulmer, and D.E. Grandstaff.

*Source:*
Mat. Res. Soc. Symp. Proc. 112, 805-813.

*Year:*
1988

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Long-term stability

*Keywords:*
Basalt, hydrothermal

*Original abstract/summary/conclusions*

The hydrothermal stability of copper has been studied to assess its suitability as a container material for disposal of nuclear waste in the proposed repository site at Hanford, Wa. The experiments (Cohassett basalt, synthetic Grande Ronde #4 groundwater, and copper powder with a water:rock:Cu-powder mass ratio of 20:1:1) were conducted at 300 $^{o}$C, 30 MPa, using Dickson rocking autoclaves for periods up to 3000 hours. Redox was calculated from dissolved $H_2$ measured by gas chromatograph and He-ionization detector.

After ca. 100 hours the solution Cu concentration stabilized at 2-3 ppm, near Cu saturation, and did not vary significantly during the remainder of the experiment. The *in situ* solution pH was slightly alkaline. The copper powder showed little evidence of etching. The Cu concentration did not reflect oxide-coating spallation effects such as those described by Johnston et al.[15]. Within 48 hours, the log $fO_2$ values decreased rapidly toward the magnetite-hematite phase boundary (-31 at 300$^{o}$C)**;** this is well within the stability field of native copper. SEM and EDX analysis of the reaction products revealed a copper-iron sulfide. One experiment used copper powder containing ca. 5% cuprite. Oxygen released by the cuprite overwhelmed the buffering capacity of the basalt. The resulting log $fO_2$ values stabilized near the copper-cuprite phase boundary (-23.1 at 300$^{o}$C) with the solution remaining within the copper stability field. Copper purity is important as oxygen contamination or oxidation of the copper containers may strongly affect the repository redox and mobility of radionuclides.

*Current author review comments:*

This is not an analogue study as such, but does illustrate the ability of basalt to redox buffer the system in the stability field of copper, provided there is less oxygen in the system than the redox-buffering capability of the amount of basalt (here a 1:1 basalt:copper mass ratio was used). However, the results suggest that conditions may be so reducing as to produce sulphide, which then reacts with the copper.

Useful laboratory background to Michigan analogue and Schwartz suggestions.

*Check if additional Comments made* ☐

*Ref. no.:* 094

*Title:*
Corrosion of archaeological artefacts from the Olviya site in Ukraine.

*Authors:*
Demchenko, L.V., B.P. Zlobenko, V.I. Manichev, V.V. Kadoshnikov, and L.V. Spasova.

| | |
|---|---|
| *Source:*<br>Mat. Res. Soc. Symp. Proc. 807, doi.org/10.1557/PROC-807-885. | *Year:*<br>2004 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Confidence building

*Keywords:*

*Original abstract/summary/conclusions*

Copper and bronze artefacts of Olviya archaeological collection dated the first century B.C. were the objects of this study. Susceptibility to soil corrosion of archaeological artefacts from pure copper and bronze was investigated. Detailed mineralogical and metallographic investigations were performed on specially prepared samples of metallic copper, such as cut and polished sections of a cylindrical body, etc. They reveal a complex picture of metal structure and mineralogical features that can be attributed to both original technological process of manufacturing and to alteration during the burial and weathering history. Corrosion products were researched and the thickness of the corrosion layer formed for the long period of time was determined. It is shown, that the corrosion rate of artefacts produced by casting depends on composition alloys and change of metal structure after the next mechanical-thermal processing. The soil corrosion rate of copper alloys also depends on the redox conditions in the soil of Olviya site.

*Current author review comments:*

Similar in scope to #036.

*Check if additional Comments made* ☐

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|---|---|
| *Ref. no.:* 095 | |
| *Title:*<br>A sampling method and data evaluation of archaeological samples to support long-term corrosion prediction. | |
| *Authors:*<br>Yoshikawa, H., S. Lee, and T. Matsui. | |
| *Source:*<br>Corrosion 65, 227-232. | *Year:*<br>2009 |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Corrosion rates | |
| *Keywords:* | |

*Original abstract/summary/conclusions*

Natural analogs for the long-term corrosion behavior of overpack materials, such as carbon steel data concerning the extent of corrosion from archaeological iron artifacts buried in soil, provide useful information as supporting evidence for the safety assessment of nuclear waste disposal. Although a lot of corrosion data are necessary to guarantee the validity of the long-term behavior, archaeological samples are invaluable but difficult to analyze. The purpose of this study was to investigate the corrosion behavior of an iron plow surrounded by soil excavated from Oda Castle in Japan. Usually, archaeological samples are excavated and removed carefully from the soil using a small brush and shovel; therefore, the environment around the sample, e.g., redox condition, changes during sampling. We non-destructively measured the thickness of rust of the iron sample in the soil itself using x-ray-computed tomography (x-ray CT) without contact with the atmosphere and analyzed various chemical components and microorganisms. The results show the corrosion environment of the sample was slightly oxidizing. The data were compared with other data from archaeological samples from 19 remains examined by Japan Atomic Energy Agency (JAEA, Ibaraki, Japan).

*Current author review comments:*

Another data point in the collection used in the Japanese program to support the use of short-term lab rates.

*Check if additional Comments made* ☐

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|---|---|
| *Ref. no.:* 096 | |
| *Title:*<br>Corrosion issues in the French high-level nuclear waste program. | |
| *Authors:*<br>Féron, D., D. Crusset, and J.-M. Gras. | |
| *Source:*<br>Corrosion 65, 213-223. | *Year:*<br>2009 |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Confidence building | |
| *Keywords:* | |

*Original abstract/summary/conclusions*

This paper gives an overview of the main corrosion issues related to the French program of the geological disposal of high-level nuclear wastes (HLNW). In addition to summarizing some specifics of the “dossier 2005 Argile” (clay underground repository concept, HLNW mainly composed of glass matrix, etc.), the French approach for the selection of the material (non-alloy steel) of HLNW overpacks is underlined with the combination of experimental work and semi-empirical modeling for estimation of service lifetimes, mechanistically based modeling for more robust and reliable prediction, and the use of archaeological artefacts to provide a database for testing and validating models.

*Current author review comments:*

Overview of the French program including an indication of how analogues fit into the overall strategy.

*Check if additional Comments made* ☐

*Ref. no.:* 097

*Title:*
Soil-corrosion studies, 1946 and 1948: Copper alloys, lead, and zinc.

*Authors:*
Denison, I.A. and M. Romanoff.

*Source:*
U.S. National Bureau of Standards Research Paper RP2077, 44, 259-289.

*Year:*
1950

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Data

*Keywords:*
Pitting

*Original abstract/summary/conclusions*

This report contains the results of measurements of the corrosion of copper, lead and zinc, and certain alloys of these metals after exposure to different soil conditions for a maximum of 14 years. The soils to which the materials were exposed range from well-aerated soils deficient in soluble salts to very poorly aerated soils containing high concentrations of water-soluble materials. The magnitude and progress of corrosion with respect to weight loss and pitting are interpreted in relation to the composition of the materials and the properties of the soils at the test sites. Comparative data are given for the corrosion of plain iron and steel, copper, lead , and zinc in typical soil environments.

*Current author review comments:*

Part of the large NBS underground corrosion test results. Albeit not a long-term study, nor a study involving archaeological samples, this study nevertheless presents a useful set of data that have found repeated use in various waste management programs.

*Check if additional Comments made* ☐

*Ref. no.:* 098

*Title:*
Underground Corrosion

*Authors:*
Romanoff, M.

*Source:*
National Bureau of Standards Circular 579, April 1957. Reprinted by NACE International (Houston, TX).

*Year:*
1989

*Relevant engineered barrier:*
Copper, steel

*Relevant use or application of the study:*
Data

*Keywords:*
Pitting

*Original abstract/summary/conclusions*

The Circular is a final report on the studies of underground corrosion conducted by the National Bureau of Standards from 1910 to 1955.

Up to 1922 the studies were confined to corrosion due to stray-current electrolysis and its mitigation. After it became apparent that serious corrosion occurred in soils under conditions that precluded stray-currents as an explanation, a field burial program was initiated in order to obtain information pertaining to the effect of soil properties on the corrosion of metals. More than 36,500 specimens, representing 333 various ferrous, nonferrous, and protective coating materials, were exposed in 128 test locations throughout the United States. During this time the electrical and electrochemical aspects of underground corrosion have been continuously studied in the laboratory. Results from both field and laboratory investigations are presented.

*Current author review comments:*

A record of the entire study including all material types.

*Check if additional Comments made* ☐

*Ref. no.:* 099

*Title:*
Corrosion of copper lightning conductor plates.

*Authors:*
Hallberg, R., A.-G. Engvall, and T. Wadsten.

| | |
|---|---|
| *Source:*<br>Br. Corros. J. 19, 85-88. | *Year:*<br>1984 |

*Relevant engineered barrier:*
Copper

*Relevant use or application of the study:*
Corrosion rates

*Keywords:*
Pitting, copper concentration profile

*Original abstract/summary/conclusions*

One method proposed for the long-term storage of nuclear waste is to place it in copper canisters buried deep underground. To give some information on the long term stability of copper in these circumstances, the corrosion of three copper plates, used as earth electrodes for lightning conductors, was studied in relation to the geochemical properties of the ambient soil. The plates had been buried for more than 50 years in three separate locations. Two of the plates were affected by pitting corrosion with a pitting factor of 5, while the third plate showed no pitting corrosion.

The experience from this investigation stresses the importance of careful sampling from a mechanical as well as a chemical point of view.

*Current author review comments:*

Interestingly, also provide some measure of the diffusion distance of copper into the adjacent soil.

*Check if additional Comments made* ☐

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|---|---|
| *Ref. no.:* 100 | |
| *Title:*<br>The existence of native iron – implications for nuclear waste management. Part I: Evidence from existing knowledge. | |
| *Authors:*<br>Hellmuth, K.-H. | |
| *Source:*<br>Finnish Centre for Radiation and Nuclear Safety Report, STUK-B-VALO67. | *Year:*<br>1991 |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Long-term stability | |
| *Keywords:*<br>Kinetic stability, mass-transport limitation, thermodynamic stability, serpentization | |

*Original abstract/summary/conclusions*

Occurrence of native iron in near-surface environments on the earth is a remarkable phenomenon, which has implications on issues of nuclear waste management, above all, long-term corrosion, matrix diffusion and water-rock interaction.

Existing knowledge on native iron is reviewed, laying stress on processes and parameters, which led to preservation of the iron during geological periods of lime. Types of occurrence, composition and properties of the iron, and mineral parageneses associated are described. Processes affecting the iron during the course of its evolution, passing through the stages of the melt, differentiation, crystallization, cooling, fracturing, hydrothermal fluid intrusion and low temperature weathering are discussed.

Because of their completely different nature, occurrences of iron formed at high, magmatic temperature in basalt are treated separately from those formed at lower hydrothermal to ambient temperatures during serpentinization of ultrabasic rocks. The former are rare not because of destruction by weathering, but because of the special conditions of formation. The latter are more abundant than commonly believed.

Native iron has survived for millions of years in the matrix of rocks. In basalt mass transport limitation in the matrix seems to be the major factor, which enabled preservation of the metal. In ultrabasic rock rich in FeO, iron is the result of massive intrusion of water. The serpentinization process leads to highly reducing conditions, where iron is thermodynamically stable.

Serpentinization leads to groundwater conditions favourable from the point of view of: waste container corrosion, waste matrix dissolution and radionuclide migration.

*Current author review comments:*

Considers native iron formed by two processes: high temperature magmatic activity (such as on Greenland) and serpentization (low temperature (<400°C) reaction of ultrabasic rocks with water). In the former case, the persistence of Fe is linked to mass-transport limitations, and in the latter to thermodynamic equilibrium between Fe, $Fe_3O_4$, $H_2O$, and $H_2$. But this does not seem possible since the equilibrium pH2 for Fe/$Fe_3O_4$ is 85 MPa.

*Check if additional Comments made* ☐

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|---|---|
| *Ref. no.:* 101 | |
| *Title:*<br>The existence of native iron – implications for nuclear waste management. Part II: Evidence from investigations of samples of native iron. | |
| *Authors:*<br>Hellmuth, K.-H. | |
| *Source:*<br>Finnish Centre for Radiation and Nuclear Safety Report, STUK-B-VALO68. | *Year:*<br>1991 |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Long-term stability | |
| *Keywords:* | |

*Original abstract/summary/conclusions*

The existence of native iron in near-surface environments is a remarkable phenomenon, which has implications on issues of long-term safety of nuclear waste repositories.

Samples of native iron, formed at high, magmatic temperatures in basalt, from the Bühl (FRG) and Disko, West Greenland were studied. The composition of natural iron is somewhat similar to technical iron and steel. Analyses of mineralogical and chemical composition of basalt alteration products and corrosion products of iron, studies on the porosity and diffusivity of the basalt matrix, electrochemical corrosion tests and theoretical calculations of the pore water in the basalt were conducted. The aim was to assess the processes and parameters leading to the life-times of native iron observed in nature.

The Bühl iron is enclosed in a basalt matrix, mostly intact, which itself has been exposed to oxygenized groundwaters for probably more than 1 Ma. Under these conditions corrosion of the iron has been limited by the sluggishness of diffusive mass transport. Furthermore, oxygen has, most probably, been depleted by reaction with FeO in the matrix. The resulting redox front has moved only a couple of centimetres per Ma. Pore water conditions in basalt (high pH, low Eh) are favouring passivation of the iron. Locally, even conditions near the stability field of iron might occur.

Native iron from outcrops on Disko island occurs in the form of interconnected inclusions, which also reach the exposed rock surface. The time scale of exposure to the weather is probably in the order of magnitude of $10^3$-$10^4$ a. The role of permafrost is difficult to assess. Corrosion has intruded only a few millimetres into the sample examined, except where hydrothermal influences led to pervasive alteration.

Based on evidence from occurrences of native iron in partly serpentinized ultrabasic rock, the use of high-FeO olivine as a redox-active backfill, working in a nature-analogue way, in nuclear waste repositories is proposed. Estimations show that the redox capacity of the backfill could assure favourable groundwater conditions (high pH, low Eh, low carbonate, low sulphide) in a repository in the long-term.

*Current author review comments:*

*Check if additional Comments made* ☐

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|---|---|
| *Ref. no.:* 102 | |
| *Title:*<br>Evaluation of analogs for the performance assessment of high-level waste container materials. | |
| *Authors:*<br>Sridhar, N. and G. Cragnolino. | |
| *Source:*<br>Center for Nuclear Waste Regulatory Analyses, CNWRA 2002-02. | *Year:*<br>2002 |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Conceptual model development, model validation | |
| *Keywords:*<br>Delhi iron pillar, industrial analogs, localized corrosion | |

*Original abstract/summary/conclusions*

There is considerable interest in the use of multiple lines of evidence in assessing the long-term performance of high-level radioactive waste containers. The U.S. Department of Energy (DOE) proposed the use of a nickel-base alloy for the outer container and stainless steel for the inner container of high-level waste packages. These alloys depend on a protective oxide film for their corrosion resistance and can suffer from localized corrosion under environmental conditions that lead to a breach of this protective film. Natural, archeological, and industrial analogs are explored in this report for their applicability to the assessment of container life in the DOE design as one of the multiple lines of evidence. Because the proposed alloys have existed only for tens of years and their corrosion behavior is highly dependent on the interplay between material microstructure and environmental conditions, the direct use of analogs in estimating the container life in a geologic repository, where both of these factors differ from those of the analogs, is not possible. Therefore, the focus in this report is on the use of metal analogs to increase the confidence in conceptual models of corrosion processes and in abstracted models used in performance assessment. The localized corrosion of iron meteorites, the Delhi Iron Pillar below ground, and excavated iron archeological objects is discussed. Since the alloys selected for container materials are of recent development, their industrial applications are examined for increasing the confidence in abstracted parameters, such as the repassivation and corrosion potentials, used in performance assessment codes.

*Current author review comments:*

Brief discussion of iron analogues, but main focus is stainless steel and Ni-Cr alloys, for which there are few long-term analogues.

*Check if additional Comments made* ☐

*Ref. no.:* 103

*Title:*
Study of archaeological artefacts to refine the model of iron long-term indoor atmospheric corrosion

*Authors:*
Monnier, J., L. Legrand, L. Bellot-Gurlet, E. Foy, S. Reguer, E. Rocca, P. Dillmann, D. Neff, F. Mirambet, S. Perrin, and I. Guillot.

| | |
|---|---|
| *Source:*<br>J. Nucl. Mater. 379, 105-111. | *Year:*<br>2008 |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development

*Keywords:*
LTC 2007

*Original abstract/summary/conclusions*

The study of long-term indoor atmospheric corrosion is involved in the field of the interim storage of nuclear wastes. Indeed study of archaeological artefacts is one of the only mean to gather information on very long periods. Concerning ancient items, due to the complexity of the system, it is necessary to couple many analytical techniques from the macro to the microscopic scale. This enables to propose a description of the Amiens cathedral chain rust layers, made of a matrix of goethite, with lepidocrocite and akaganeite locally present and marbling of a poor crystallized phase associated to ferrihydrite. Electrochemical measurements permit to study the reduction capacity of the rust layer and to draw reduction mechanisms of the so-called active phases, by in situ experiments coupled with X-ray diffraction and X-ray absorption spectroscopy.

*Current author review comments:*

Another example, this time under atmospheric conditions, of the use of analogues to support the conceptual model for the structure of the corrosion product layer.

*Check if additional Comments made* ☐

*Ref. no.:* 104

*Title:*
Fluctuation of redox conditions in radioactive waste disposal cell: characterisation of corrosion layers formed on archaeological analogues.

*Authors:*
Saheb, M., F. Marsal, H. Matthiesen, D. Neff, P. Dillmann, and D. Pellegrini.

*Source:*
Corros. Eng. Sci. Technol. 46, 199-204.

*Year:*
2011b

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development

*Keywords:*
LTC 2010, oxic-anoxic and anoxic-oxic transitions, thermodynamic prediction

*Original abstract/summary/conclusions*

Oxygen trapped during the operational phase in disposal cells of an underground radioactive waste repository is often considered to be quickly consumed, notably by corrosion of metallic materials or reducing microorganisms. This would lead to anoxic conditions in most of each disposal cell. In addition to this, a shift from anoxic to oxic conditions could not be excluded locally in disposal cells after their closure due to the ventilation in handling drifts that could contribute to the regeneration of oxygen at the head of each disposal cell. The impact of these transient phases on corrosion processes may affect the confinement properties of metallic components and should thus be assessed. To this end, ferrous archaeological analogues are studied. The present paper focuses on the characterisation of nails that have undergone such transient phases. First, a sample exposed for several hundred years to an aerated environment and then to an anoxic carbonated environment in laboratory for 3 years has been analysed. Corrosion layers after the oxic phase contain mostly oxihydroxides (such as goethite) and some layers perpendicular or parallel to the interface, which is in good agreement with an aerated corrosion. After 3 years under anoxic conditions, the main phase of the corrosion layer is siderite. Second, a sample exposed to an anoxic environment for several hundred years has been immersed in an aerated solution for 5 weeks. The main phases of the corrosion layer after the anoxic phase are iron carbonates and a goethite layer formed on the outer part of the corrosion layer after the immersion in an aerated solution. In both cases, the formation of new phases in the corrosion layer is in good agreement with predictions of thermodynamic modelling based on the respective environmental conditions.

*Current author review comments:*

Issue is similar to that of a leaking seal, although the concern seems to be fluctuating oxic-anoxic-oxic-anoxic conditions. Not sure what the benefit of using archaeological specimens as the starting material is, but the corrosion mechanism appears to be reversible given the similarity of the corrosion products regardless of the whether the transition is oxic-anoxic or anoxic-oxic.

*Check if additional Comments made* ☐

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| *Ref. no.:* 105 | |
| *Title:*<br>Corrosion behaviour of low alloy steels: from ancient past to far future. | |
| *Authors:*<br>Santarini, G. | |
| *Source:*<br>Proc. 2nd Int. Workshop Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, Nice, France, September 2004. Andra Science and Technology Series, pp. 97-105, available from www.andra.fr. | *Year:*<br>2005 |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Conceptual model development | |
| *Keywords:*<br>2nd LTC 2004 | |

*Original abstract/summary/conclusions*

With the envisaged concepts of long term storage and underground disposal of high level radioactive waste, corrosion science has to face a new challenge: to obtain reliable behaviour predictions over very long periods of time, up to thousands of years. For such durations, the development of mechanistically based models becomes an absolute necessity. In France, the first candidate materials considered for the containers of high level waste are low alloy steels because of their relatively low sensitivity to localized corrosion, when compared, for example, to passive materials: this characteristics makes their corrosion behaviour less difficult to predict.

In this mechanistic modelling, numerous physicochemical steps have to be taken into consideration, such as chemical and/ or electrochemical reactions, solid state diffusion of point defects, liquid state diffusion of chemical species in oxide pores, etc. However, since the complex links between all these steps highly depend on the nature and on the characteristics (porosity, conductivity, protectivity, etc.) of the corrosion products, the first stage before the model construction is to obtain experimental data on this phenomenology in the very near environment of the metal. At the opposite, once a model constructed, it is necessary to compare its predictions to field experience, and to verify that the mechanisms and phenomenology retained in the model remain unchanged over very long periods of time.

In the various stages of a progressive iterative model improvement, the examination of archaeological objects is liable to provide useful information. The considerable interest of such objects, in this context, comes from the long duration of the contact with a natural environment, a duration of the same order of magnitude as the one considered for high level waste storage. However, the differences between the ancient materials and the modern ones and also the poor knowledge about the initial conditions and about the variation of the environmental factors with time make this investigation very delicate. It is shown in this paper that, provided that sufficient care is taken, detailed analyses of archaeological artefacts, along with considerations relative to the morphology and the solubility of the corrosion products, are liable to give valuable indications about the possible mechanisms and about the long term corrosion kinetics.

*Current author review comments:*

One of the first expositions of the role of analogues in the French program.

*Check if additional Comments made* ☐

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| *Ref. no.:* 106 |
| *Title:*<br>Modelling carbon steels corrosion during a long period in soils: contribution of A.C. impedance spectroscopy. |
| *Authors:*<br>Pons, E., C. Lemaitre, D. Crusset, and D. David. |

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|---|---|
| *Source:*<br>Proc. 2nd Int. Workshop Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, Nice, France, September 2004. Andra Science and Technology Series, pp. 106-113, available from www.andra.fr. | *Year:*<br>2005 |

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| *Relevant engineered barrier:*<br>Steel |
| *Relevant use or application of the study:*<br>Conceptual model development |
| *Keywords:*<br>2nd LTC 2004, porosity, rate-determining step, barrier layer |

*Original abstract/summary/conclusions*

The corrosion of historical objects from World War I fields were studied by using two methods: characterization of the corrosion products by Raman laser spectroscopy, and behaviour of the corrosion layers by using electrochemical studies.

The first technique, previously used, had shown that two layers are present on these objects, containing both different oxides and oxy-hydroxides of iron. In the present part of the work, the A.C. impedance spectroscopy was used to show the differences between the two layers concerning the corrosion of these objects. In order to observe the different behaviours, the specimens were studied in three surface states: with the two layers, with the internal layer only, and without oxide.

The results have shown that the internal layer limits the corrosion kinetics. Then this layer was especially studied, particularly its porosity, by a comparison of the impedance results in two media with very different conductivity, and the evolution of these results with different immersion times.

The buried objects had the behaviour of a porous electrode, due to the presence of the internal layer. Thus, this behaviour can be modelled with the simplified De Levie theory, considering that each porosity is a semi-infinite hole. It appeared that the corrosion process at the oxidized interface corresponds to the transport in the electrolyte in the pores completed by a part of transport in the solid phase. These properties can be used to predict the long term corrosion behaviour of carbon steels in soils for long periods.

*Current author review comments:*

A good example of the use of analogues to establish the rate-controlling process for use in conceptual model development.

*Check if additional Comments made* ☐

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| *Ref. no.:* 107 |
| *Title:*<br>Long term corrosion of iron at the waterlogged site Nydam in Denmark: studies of environment, archaeological artefacts, and modern analogues. |
| *Authors:*<br>Matthiesen, H., L.R. Hilbert, D. Gregory, and B. Sørensen. |

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| *Source:*<br>Proc. 2nd Int. Workshop Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, Nice, France, September 2004. Andra Science and Technology Series, pp. 114-127, available from www.andra.fr. | *Year:*<br>2005 |

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| *Relevant engineered barrier:*<br>Steel |
| *Relevant use or application of the study:*<br>Confidence building |
| *Keywords:*<br>2nd LTC 2004, corrosion rates |

*Original abstract/summary/conclusions*

A study on long term corrosion of iron in waterlogged soil is ongoing at the archaeological site of Nydam in Denmark. In the period 200-500 AD, huge amounts of military equipment were sacrificed here, and several thousand iron artefacts have been excavated already. Since 1997, a monitoring program has been ongoing to evaluate the feasibility of preserving the remaining artefacts *in situ.* A three-pronged approach has been used in the studies:
1) monitoring of environmental parameters,
2) studies of the archaeological artefacts, and
3) use of modern iron samples placed in the soil.

This approach has been useful for understanding not only the current corrosion rate and threats against the artefacts but also the corrosion history, i.e. when were the deterioration patterns and corrosion products observed today actually formed. The corrosion rates for archaeological artefacts and modern analogues are compared and briefly discussed.

*Current author review comments:*

Not directly a nuclear waste management study, but came from a collaboration with French researchers.

*Check if additional Comments made* ☐

*Ref. no.:* 108

*Title:*
A study on species transport in the corroded products of ferrous archaeological analogues. A contribution to the modelling of iron long term corrosion mechanisms.

*Authors:*
Vega, E., P. Dillmann, and P. Fluzin.

*Source:*
Proc. 2nd Int. Workshop Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, Nice, France, September 2004. Andra Science and Technology Series, pp. 128-140, available from www.andra.fr.

*Year:*
2005b

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development

*Keywords:*
2nd LTC 2004, porosity, rate-determining step, location of anodic and cathodic reactions, corrosion rate

*Original abstract/summary/conclusions*

One of the main technological and environmental challenges for the next centuries is the safe storage of nuclear wastes. For this purpose, the behaviour during several centuries of every material constituting the barrier between wastes and environment must be predicted. In addition to modelling and laboratory simulations, the only mean to study corrosion systems formed during several centuries is to analyse archaeological ferrous artefacts buried in soil. Moreover, this kind of approach is of great interest for conservation purposes of archaeological artefacts.

Precedent studies on this kind of objects have shown that the corrosion system is formed by the Metallic core (M), a Dense corrosion Product Layer (DPL), a Transformed Medium (TM) constituted of a mix of corrosion products and soil compounds, and the Soil (S) itself. Moreover, analytical and electrochemical studies seem to show that the corrosion mechanisms are driven by the species transport in the dense product layer (DPL) and especially by oxygen migration in the DPL pores. Thus, it is necessary to precise the species transport properties in this part of the corrosion system.

This paper presents a study of species transport in the DPL of samples coming from 400 years old archaeological artefact from the site of Glinet (France). After a fine characterisation using µXRD under synchrotron radiation and µRaman spectroscopy, an artefact is chosen in order to proceed to specific experiments. To locate the cathodic reaction of oxygen reduction, the sample is immersed with his corrosion product in water saturated with $^{18}O$. The detection of $^{18}O$ by nuclear reaction using a microprobe reveals that both anodic and cathodic reactions are located at the M/DPL interface. In order to verify if the transport of dissolved oxygen in the water of the pores controls the kinetic of corrosion, the instantaneous corrosion rate is calculated following different ways. In a first way, the transport of dissolved oxygen is assumed to control the kinetic. Thus, to determine its apparent diffusion coefficient in the DPL, the sample is immersed in water saturated by NaI. After different immersion times, the acquisition of a Iodine profile on a transverse section of the DPL is possible and its modelling by a simple diffusion law conducts to obtain an apparent diffusion coefficient that is considered in first approximation at the same order of magnitude than the oxygen one, because Iodine and Oxygen have the same diffusion coefficient in water. An instantaneous corrosion rate can then be calculated using a Faraday law. The second way to determine a corrosion rate is to evaluate the $^{18}O$ atom quantity that has reacted

*Check if additional Comments made* ☒

*Comments (continued):*

during the immersion in $^{18}O$ saturated aqueous solution. Last, a third value of the instantaneous corrosion rate is given by the extrapolation of the average corrosion rate deduced from the thickness, the nature and the age of the corrosion product. The comparison of the different values seems to validate the hypothesis of a control by the dissolved oxygen transport in the pores of the DPL.

*Current author review comments:*

Nice paper describing the systematic analysis of archaeological and the derivation of mechanistic information.

*Ref. no.:* 109

*Title:*
On the characterisation of the corrosion layout of ferrous archaeological analogues in binders.

*Authors:*
Chitty, W.-J., P. Dillmann, V. L'Hostis, and G. Beranger.

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|---|---|
| *Source:*<br>Proc. 2nd Int. Workshop Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, Nice, France, September 2004. Andra Science and Technology Series, pp. 141-151, available from www.andra.fr. | *Year:*<br>2005b |

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development

*Keywords:*
2nd LTC 2004, concrete, corrosion rate, porosity

*Original abstract/summary/conclusions*

This paper deals with an analytical study on ferrous reinforcements embedded in hydraulic binders found in ancient buildings from the Middle Age period to the beginning of the 20th c. AD. The study of these kind of archaeological analogues is necessary to improve the knowledge on the long-term corrosion of low carbon steels that could be used in concrete to build the substructure of nuclear wastes reversible storage facilities. The corrosion system can be described as a multi-layer pattern made of the metal, a dense corrosion product layer, a transformed medium and a binder. All the morphological and physicochemical properties as composition, structure and porosities of these different parts were studied with different analytical methods as optical and electronical microscopy, EDS coupled to SEM, EPMA, mercury porosimetry, micro Raman spectroscopy and micro Diffraction under Synchrotron Radiation. Moreover, average corrosion rates were evaluated by two different methods. These rates are relatively low compared to the same parameters measured on low alloyed steels immersed in aqueous environments and are comparable with results obtained for passivated systems.

*Current author review comments:*

Another good description of the use of analogues in the French program to guide development of conceptual models, in this case for steel in concrete.

*Check if additional Comments made* ☐

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| *Ref. no.:* 110 | |
| *Title:*<br>Use of the gold markers method to predict the mechanism of iron atmospheric corrosion. | |
| *Authors:*<br>Burger, E., M. Fénart, S. Perrin, D. Neff, and P. Dillmann. | |
| *Source:*<br>Corros. Sci. 53, 2122-2130. | *Year:*<br>2011a |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Conceptual model development | |
| *Keywords:*<br>Atmospheric corrosion, pore blocking, cracking of corrosion product, wet-dry cycles | |

*Original abstract/summary/conclusions*

Iron corrosion under atmospheric conditions has been investigated by using the gold markers method. The corrosion experiments were performed in a climatic chamber with an accelerated treatment. The gold markers localization, carried out by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy, revealed that the rust layer growth was essentially due to an internal development. Moreover, microRaman mappings allowed prediction of the mechanism of rust layer evolution during the ageing treatment. Finally these results were compared to samples corroded for several 100 years in order to extrapolate our observations to long term corrosion.

*Current author review comments:*

Detailed study of development of the corrosion product layer during atmospheric wet-dry cycles. Comparison of composition of corrosion product after 820 wet-dry cycles with composition on sample from Amiens cathedral suggests similar mechanism.

*Check if additional Comments made* ☐

*Ref. no.:* 111

*Title:*
Electrochemical behavior of thick rust layers on steel artefact: Mechanism of corrosion inhibition.

*Authors:*
Rocca, E., H. Faiz, P. Dillmann, D. Neff, and F. Mirambet.

*Source:*
Electrochim. Acta 316, 219-227.

*Year:*
2019

*Relevant engineered barrier:*
Steel

*Relevant use or application of the study:*
Conceptual model development

*Keywords:*

*Original abstract/summary/conclusions*

The electrochemical behavior of aged corrosion layers (CL) on artefact was studied, in corrosive reference water without and with non-toxic corrosion inhibitors such as decanoate ions and flavonoids compounds, constituting the condensed tannins, such as catechin. Electrochemical impedance spectroscopy measurements on the metal/CL system and voltammetric studies of FeOOH phases on carbon paste electrode show that the corrosion inhibition mechanism is mainly based on the blocking of the dissolution of FeOOH-type phase and the decrease of the diffusion of ionic species in the pores network of CL. Indeed, the formation of iron decanoate, revealed by X-ray diffraction and microscopic observation, inhibits the electrochemical activity of FeOOH-type phases and blocks the electrochemical dissolution of FeOOH into $Fe^{2+}$ cations. On the other hand, the catechin compound modifies the surface of rust compounds into a blue-black compound, but this modification has a poor influence on the electrochemical activity of FeOOH-type compounds.

*Current author review comments:*

*Check if additional Comments made* ☐

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| *Ref. no.:* 112 | |
| *Title:*<br>Study of iron sulphides in long-term iron corrosion processes: Characterisation of archaeological artefacts. | |
| *Authors:*<br>Grousset, S., M. Bayle, A. Dauzeres, D. Crusset, V. Deydier, Y. Linard, P. Dillmann, F. Mercier-Bion, and D. Neff. | |
| *Source:*<br>Corros. Sci. 112, 264-275. | *Year:*<br>2016 |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Conceptual model development | |
| *Keywords:* | |

*Original abstract/summary/conclusions*

Iron sulphides are observed on long term anoxic corrosion profiles of iron artefacts. The archaeological nails studied came from two terrestrial sites (Glinet and Raadhuspladsen) and a subaquatic one (Arles-Rhône 3).

Greigite ($Fe_3S_4$) and/or mackinawite ($FeS_{1-x}$) are observed at the outer border of the corrosion product layer. The presence of mackinawite is discussed relatively to the establishment of stable anoxic burial conditions. The nails from the subaquatic site present pyrite globules in the transformed medium. The formation of pyrite ($FeS_2$) is attributed to the proximity of wood. The iron sulphides formation may also be explained by the presence of sulphate-reducing bacteria in the burial environment.

*Current author review comments:*

Suggestion that pyrite observed in the aquatic but not the soil environment because the presence of wood in the former provided a preferential surface condition for the nucleation of pyrite. This differs from the explanation given at LTC2019 which implied that it was the greater age of the shipwreck site that could account for the mackinawite-greigite-pyrite transformation.

*Check if additional Comments made* ☐

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| *Ref. no.:* 113 | |
| *Title:*<br>The long-term corrosion of mild steel in depassivated concrete: Localizing the oxygen reduction sites in corrosion products by isotropic tracer method. | |
| *Authors:*<br>Burger, E., J. Monnier, P. Berger, D. Neff, V. L'Hostis, S. Perrin, and P. Dillmann. | |
| *Source:*<br>J. Mater. Res. 26, 3107-3115. | *Year:*<br>2011b |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Conceptual model development | |
| *Keywords:*<br>Location of cathode, concrete, oxygen reduction, oxygen-18 | |

*Original abstract/summary/conclusions*

Over a long period (>10 years), the prediction of iron/mild steel corrosion in concrete requires the use of a mechanistic approach. For that purpose, a key point of the mechanisms involved is the localization of the oxygen reduction sites within the thick corrosion layers, which may greatly influence the nature of the rate-limiting step. In this context, iron rebars (originally covered with concrete) were sampled from a 50-year-old historical building and submitted to isotopic tracers methods ($^{18}O$) combined with structural Raman microspectroscopy analyses on transverse sections. By this method, the authors demonstrate that the oxygen reduction sites are strongly impacted by the presence of a conductive phase (magnetite) in contact with the metallic substrate.

*Current author review comments:*

*Check if additional Comments made* ☐

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| *Ref. no.:* 114 | |
| *Title:*<br>Investigation of iron long-term corrosion mechanisms in anoxic media using deuterium tracing. | |
| *Authors:*<br>Saheb, M., P. Berger, L. Rainbault, D. Neff, and P. Dillmann. | |
| *Source:*<br>J. Nucl. Mater. 423, 61-66. | *Year:*<br>2012 |
| *Relevant engineered barrier:*<br>Steel | |
| *Relevant use or application of the study:*<br>Conceptual model development, corrosion rate | |
| *Keywords:*<br>H embrittlement | |

*Original abstract/summary/conclusions*

In the context of the nuclear waste storage and the preservation of metallic artefacts, the long-term corrosion of iron is studied. In an anoxic medium, the cathodic process involves the reduction of water into gaseous hydrogen and hydrogen-containing species that can precipitate with iron(II). Consequently, to understand the corrosion mechanisms, isotopic deuterium tracing ($D_2O$) has been performed on archaeological artefacts to locate the precipitation zones in the corrosion layer. The presence of deuterium in the metallic matrix of the sample indicates that gaseous hydrogen has been formed and is a clue of the water reduction reaction. Moreover, the precipitation zones in the corrosion layer have been identified on its internal part. This is caused by the iron source location on this part of the corrosion layer. Deuterium concentration quantification made it possible to evaluate an instantaneous corrosion rate below 2 μm/year.

*Current author review comments:*

Another example of the use of $D_2O$ to elucidate mechanism.

*Check if additional Comments made* ☐

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| *Ref. no.:* 115 | |
| *Title:*<br>Metallic copper and iron artifacts in a corrosive depositional environment: the colony of Avalon archaeological analogue in Ferryland, Newfoundland. | |
| *Authors:*<br>McMurry, J., B.M. Ikeda, M.J. Quinn, S. Stroes-Gascoyne, C.J. Hamon, and P. Vilks | |
| *Source:*<br>Ontario Power Generation, Nuclear Waste Management Division, Report No: 06819-REP-01200-10070-R00. | *Year:*<br>2001 |
| *Relevant engineered barrier:*<br>Copper, steel | |
| *Relevant use or application of the study:*<br>Confidence building, pit depth data, corrosion rate | |
| *Keywords:*<br>SCC, copper concentration profile | |

*Original abstract/summary/conclusions*

At the Ferryland archaeological site on the east coast of Newfoundland, many iron artifacts dating back to the establishment of the Avalon colony in the 1600s have been recovered in close proximity to copper and bronze artifacts of the same age. The spatial relationship of the samples, their depositional environment, and their age provide an opportunity to study long-term redox processes between Cu and Fe in a clay-rich sediment exposed to saline water (sea spray and storm surges). With the cooperation of the Archaeology Unit of the Memorial University of Newfoundland, a small number of copper and iron artifacts were borrowed from the site archives for detailed examination and analysis, along with several excavated blocks of soil containing artifacts still in sedimentary matrix. The artifacts include a brass nail, a brass or copper thimble, a thick piece of hammered brass possibly from a kettle, a number of badly corroded iron nails, and various other copper items including straps, grommets, and rivets, and several thin sheets of metal. Additional artifacts were obtained from the field site while excavations were in progress, and fresh soil cores from the excavations were collected for microbial analysis.

The metal objects were characterized by various methods including chemical analysis, reflected-light microscopy, scanning electron microscopy, and X-ray diffraction to determine their composition and microstructure, fracture surfaces, pitting depths, and corrosion products. Corrosion products on the artifact surfaces vary in thickness and distribution but include the secondary minerals tenorite, cuprite, rosasite, stannite, and malachite, in addition to several tin and zinc oxides and copper chloride phases. The sediment blocks were examined by radiography to determine the location of metallic objects, with particular interest in objects that were likely to be made of copper. A sediment block containing a copper thimble was sectioned, and traverses of sediment away from the thimble were sampled for evidence of copper migration and for organic content. Cu concentrations were high in the sediments in the interior of the thimble, and there was evidence for Cu migration in the sediments immediately beneath the thimble but not laterally away from it. Interactions between metallic copper and iron were studied in a paired sample that consisted of a thin cone of metallic copper that was excavated within a few millimetres of a badly corroded iron nail with which it originally may have been in direct contact. Corrosion pit depth measurements were performed on 14 copper artifacts. Aseptically sampled sediment cores from two field locations have been analyzed to assess the potential impact of microbial activity on the corrosion of the artifacts. A large and heterogeneous microbial population was present in both samples, including aerobic and anaerobic heterotrophs, nitrate reducers, sulfate-reducing bacteria, and some iron-reducing bacteria. Laboratory and field measurements of soil pH and redox conditions indicated a slightly acidic, oxidizing depositional environment with locally variable and more reducing conditions.

*Check if additional Comments made* ☒

*Comments (continued):*

Various copper-bearing artifacts from the Ferryland site provided good examples of surface corrosion, pitting, and intergranular corrosion. Stress corrosion cracking (SCC) was indicated in some of the copper-bearing artifacts that were examined, and microbiological analyses of the sedimentary environment established that microbially influenced corrosion of artifacts also is a possibility at this location. A uniform corrosion rate was estimated from measurements of corrosion layer thickness on one artifact, and corrosion pitting data were obtained that demonstrated a good correlation between pit depth and the extreme value function for a copper corrosion model.

*Current author review comments:*

Interesting observation of possible SCC of folded brass sample, although authors were not certain that it was not a result of intergranular corrosion.