USED FUEL CONTAINER DESIGNS AND LIFETIME PREDICTION

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ABSTRACT

The Canadian method for long-term management of used nuclear fuel is Adaptive Phased Management, which consists of placing the fuel in a deep geological repository designed to contain and isolate the fuel for an extended period of time. This method involves encapsulating used-fuel bundles in durable containers and sealing the containers in the repository which would be built at a depth of about 500 m below ground. Several used-fuel container designs are being considered. Copper and carbon steel are candidate corrosion barrier materials for the used fuel containers. Over the past 20 years, many studies have been carried out to improve our understanding of the long-term behaviour of both materials in a deep geological repository in either a crystalline rock or a sedimentary rock environment. This paper presents an overview of recent work in used fuel container design and development in the Canadian program, including anticipated container performance and lifetime estimates based on our current knowledge of the relevant corrosion processes.

1. INTRODUCTION

The Nuclear Waste Management Organization (NWMO) is studying various corrosion barrier materials including copper and carbon steel for long-term containment and isolation of used nuclear fuel in a deep geological repository (DGR). The engineered barriers used to isolate the fuel in the deep geological repository include the used fuel containers (UFCs) and bentonite-based sealing materials placed between the UFC and the host rock. The surrounding bentonite provides a mechanical barrier, creates a favourable chemical environment and limits the transport rate of ionic species as well as the viability of bacteria. The conditions in the repository favour uniform corrosion over localized corrosion.

Both copper and carbon steel are corrosion allowance materials, which means that the corrosion rates need to be estimated and a corrosion allowance be included in the design of the container in order to achieve the required lifetime. Accordingly, the Canadian research program focuses on investigating the corrosion behaviour of copper and carbon steel in postulated repository environments. This paper reviews the work performed during the past 20 years on this subject as well as current predictions of container lifetimes.

2. COPPER USED FUEL CONTAINER

The current, reference copper UFC design is a double-vessel container comprising a 25 mm thick outer corrosion barrier of oxygen-free phosphorus doped (OFP) copper, a 100 mm thick inner steel load-bearing vessel, and interior baskets that hold the used fuel bundles in a specified geometry (Figure 1). The specification for OFP copper used by the Swedish nuclear waste program is as follows: < 5 ppm O, 50-70 ppm P, < 0.6 ppm H, and < 8 ppm S [1]. Phosphorus is added to the copper to improve the ductility of the material, which reduces the risk of creep rupture; the H and S contents are minimized for the same reason. The oxygen-free specification was originally based on the need to avoid porosity in the container lid closure electron-beam weld, although friction stir welding is also being considered for the final closure weld.

Extensive experimental and modeling work has been done on the corrosion of copper UFCs in Canada during the past 20 years. The experimental research has focused on uniform corrosion, stress corrosion cracking (SCC) and microbiologically influenced corrosion (MIC). Modeling has been used to evaluate uniform corrosion, pitting, SCC and MIC based on postulated environments through the various stages of repository evolution. Copper corrosion studies conducted in the Canadian program are summarized in a recent status report [2]. The Canadian studies concluded that a copper UFC in a repository will be subjected primarily to uniform corrosion. The degree of localized corrosion (pitting), MIC and SCC are expected to be less severe; they will slow down as the repository environment becomes anoxic and they can be controlled by means of good engineering design. The relevant corrosion mechanisms and recent calculations of corrosion allowance values are discussed below.

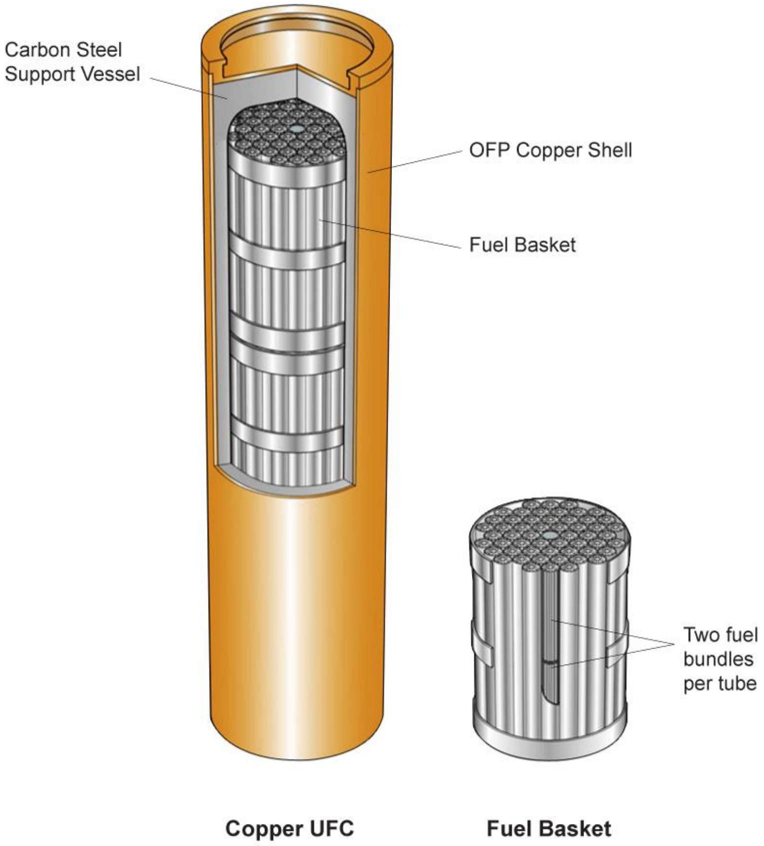

Figure 1. Copper Used Fuel Container Design Concept

2.1 Uniform Corrosion

Copper will corrode under atmospheric conditions. At relative humidities above ~ 60%, a thin water film will form on the copper surface, and metallic copper (Cu^0) can be oxidized to ionic forms, Cu^+, Cu^{2+}. This process can occur if copper donates electrons to a receptor in the surrounding environment, such as oxygen molecules (O_2), which in turn form oxide ions (O^{2-}), or hydrogen ions (H^+), which in turn form gaseous hydrogen (H_2).

$$2Cu^0 + \tfrac{1}{2}O_2 \Leftrightarrow Cu_2O \qquad (1)$$

The corrosion rate depends on the presence of atmospheric contaminants such as SO_2, NO_x and CO_2 [3]. The water film acts as an electrolyte supporting the electrochemical reactions and the impurities further enhance the corrosion process.

The repository slowly becomes anoxic. The oxide covered surface (Cu_2O / $CuCl_2{\cdot}3Cu(OH)_2$) does not support water reduction during the transition from aerobic and anaerobic conditions. This maintains the long-term separation of anodes and cathodes, supporting localized corrosion. Without oxygen, the corrosion process can be described as

$$2Cu^0 + H_2O \Leftrightarrow Cu_2O + \tfrac{1}{2}H_2 \qquad (2)$$

or

$$Cu^0 + H_2O \Leftrightarrow CuOH + \tfrac{1}{2}H_2 \qquad (3)$$

Known thermodynamic relationships indicate that the stability of the resulting copper oxide or hydroxide is uncertain [4] and therefore, reactions (2) and (3) are considered improbable in water. Under anaerobic conditions, copper corrosion needs impurities such as sulphide ions (HS^-) to sustain the process:

$$2Cu^0 + H^+ + HS^- \Leftrightarrow Cu_2S + H_2 \qquad (4)$$

The unlikelihood of reactions (2) and (3) has recently been challenged by two Swedish scientists. Gunnar Hultquist and Peter Szakálos from the Royal Institute of Technology. Their findings suggest that, contrary to thermodynamic predictions, water can act as an oxidant for copper with the formation of hydrogen via the formation of an unidentified, stable, surface intermediate species [5]. However, these findings have been contested and are the subject of ongoing study and analyses in Sweden and elsewhere.

The unique high salinity of groundwaters in Canadian sedimentary rock formations makes it necessary to conduct additional research to assess the stability of copper and the protective properties of its corrosion products in such environments. The corrosion behaviour of copper under the effect of salinity is often estimated based on thermodynamic equilibrium expressions. However, thermodynamic data (i.e. equilibrium constants, activity coefficients) for high concentration of chloride are limited. A work program to further evaluate the corrosion behaviour of copper in high salinity groundwater is under development.

Uniform corrosion on a copper container in a deep geological repository in sedimentary rock has been estimated to result in a maximum wall loss of 0.17 mm over a period of 10^6 years [6]. This estimate is higher than a previous corrosion modeling result which predicted only 0.011 mm [7]. The key differences between these two assessments are that the more recent calculation assumes a higher initial oxygen inventory in the repository and that (conservatively) does not take credit for oxygen consumption by microbial activity and reactions with Fe(II) minerals.

2.2 Localized Corrosion

Localized corrosion or pitting of copper UFCs has been investigated in several studies [8,9]. Results generally agreed that a copper UFC in a deep geological repository will not undergo classical pitting corrosion, but instead a surface roughening believed to be caused by temporary spatial separation of anodic and cathodic sites. With increasing relative humidity, the cathodic/anodic surface area ratio will decrease and localized attack will become more uniform. The extent of pitting corrosion on the copper container surface has been assessed using extreme-value analysis of literature pit-depth data, and the maximum pit depth was conservatively estimated to be 6 mm after 10^6 years. If localized corrosion on copper containers is assessed based on the argument that distinct pitting does not occur and that the surface roughening phenomenon is more realistic, especially with the elevated chloride concentration in sedimentary groundwater, a 0.1 mm pit depth is predicted [6].

2.3 Stress Corrosion Cracking (SCC)

Copper is known to be susceptible to stress corrosion cracking in environments containing ammonia, nitrite ions, acetate, or high concentrations of sulphide [9, 10]. Despite the fact that these SCC agents are not normally present in natural groundwater, they could be introduced by mining activities or from microbial activity. Many studies have been carried out in the Canadian nuclear waste research program to assess the SCC behaviour of copper in SCC agent-containing environments. The results consistently indicate that copper SCC susceptibility decreases with decreasing concentrations of the agents [11, 12, 13, 14]. The study results also suggest a threshold concentration level for each SCC agent below which SCC does not occur. Further observed in the studies is the inhibiting effect of chloride on copper SCC in the SCC agent-containing environments. The SCC susceptibility was also found to decrease with increasing chloride concentration.

Research results have suggested that in a deep geological repository SCC under aerobic conditions is unlikely since the pre-requisite conditions of corrosion potential, interfacial pH, and concentration of SCC agent do not exist simultaneously at the used fuel container surface [15]. According to mechanistic arguments, there is also no evidence to indicate that SCC of copper is possible under anaerobic conditions at the sulphide levels expected to prevail at the used fuel container surface [15]. Based on the nature of the repository environment, SCC does not appear to be a threat to the integrity of copper used fuel container. Based on the above arguments, SCC is excluded as a degradation process that may cause container failure in the lifetime assessment of a copper UFC in a deep geological repository.

Despite the low risk of SCC attack on copper, suitable engineering provisions can be applied to further minimize the probability of SCC. For instance, the level of airborne ammonia and nitrite during blasting operations can be kept to a level below the threshold concentration in order to preclude SCC; the residual stress following container shell and bottom manufacturing can be reduced by thermal stress-relief processes; and the residual stress on the final closure weld can be controlled/minimized by using suitable welding techniques.

2.4 Microbiologically Influenced Corrosion (MIC)

An extensive program has been carried out in Canada to determine whether microbes will be active in the near field, close to the container surface [16]. Results of this research have demonstrated that (i) a water activity below 0.96 effectively limits microbial culturability; (ii) swelling pressures above 2 MPa reduce bacteria survival; and (iii) the evolution of the repository environment creates conditions that can suppress microbial activity in the bentonite.

Microbial metabolic by-products may affect the SCC behaviour of copper since microbial activity can produce SCC agents such as ammonia, nitrite, and acetate ions [17, 18, 19]. King [20] has suggested that to assess the impact of MIC it is important to predict where and when microbial activity will occur. There is a large body of evidence indicating that in highly compacted bentonite microbial activity either does not occur [21] or proceeds at a very slow rate [22]. MIC rates based on sulphide transport rates yield an estimated 1 mm wall thickness loss after 10^6 years [23].

2.5 Corrosion Induced by Radiation

The corrosion behaviour of copper may be influenced by the gamma radiation field at the container surface. The main effect of γ-radiation on the corrosion of copper is through radiolysis of the moist air close to the container surface, which results in the production of oxidizing and reducing radicals and molecular species. In pure water, the oxidizing species are radicals like OH and molecular species like O_2, H_2O_2 and O_2-. The reducing species include H, e^- and H_2. In a closed system, a steady state will develop rapidly and the production of radiolytic species will stop.

Studies of the effects of γ-radiation on copper have been performed in Canada. Shoesmith and King [24] have conducted a thorough review of the effects of γ-radiation on the corrosion of high level waste canister materials, and AECL has carried out experimental research on copper corrosion in irradiated water [25]. Similar work has also been performed by Nagra in Switzerland [26] and in the Yucca Mountain Project in the U.S. for corrosion in moist air [27, 28]. There is no evidence for a detrimental effect of γ-radiation on the corrosion behaviour of copper. On the contrary, the available experimental information seems to indicate that for dose rates in the range of 10-100 $Gy.h^{-1}$ a more compact and protective surface film is formed, resulting in a lower corrosion rate.

3. CARBON STEEL USED FUEL CONTAINER

The carbon steel UFC, as shown in Figure 2, is being evaluated for a deep geological repository in sedimentary rock. The carbon steel UFC retains many design features of the inner steel vessel of the copper UFC. The essential difference between the two is that the top lid of the steel UFC is secured by a seal-weld, while the steel inner vessel lid is bolted.

Carbon steel presents a number of benefits, as well as some challenges, as a UFC material. For example, carbon steel corrodes uniformly in a predictable manner. As in the case of copper, localized corrosion, if it occurs, takes the form of surface roughening. However, carbon steel also generates hydrogen and corrosion products that may adversely affect the properties of the surrounding engineered barriers (bentonite). The corrosion behaviour of carbon steel under Canadian repository conditions in sedimentary rock is affected by the evolution of the near field environment (i.e. temperature, humidity and availability of oxygen) with time. A more detailed discussion on the effects of various corrosion mechanisms on the carbon steel container is presented below.

Figure 2. Carbon Steel Used Fuel Container Conceptual Design

3.1 Uniform Corrosion

In aerobic environments, the anodic dissolution of Fe is supported by the cathodic reduction of either O_2 or H_2O.

$$4Fe + 3O_2 + 2H_2O \Leftrightarrow 4FeO(OH) \tag{5}$$

For atmospheric uniform corrosion, there is a critical relative humidity (60-70% RH) for the formation of moisture on the metal surface, below which aqueous corrosion does not occur [3]. Carbon steel corrodes in both aerobic and anaerobic conditions. Under aerobic conditions, the corrosion rate is controlled by the rate of oxygen supply to the surface. The uniform corrosion rate on a steel UFC is therefore controlled by the diffusion rate of oxygen through the bentonite layer reaching the container surface. A review conducted by King and Stroes-Gascoyne [29] concluded that corrosion rates of steel under aerobic conditions are typically of the order of tens of $\mu m.a^{-1}$. In a later analysis [30], King applied conservative assumptions and estimated the wall penetration due to aerobic uniform corrosion to be in the range of 1-10 mm over a 10^4 year period.

As the environment becomes anoxic, the Fe(III) corrosion products are expected to convert to Fe(II) via Reaction (8)

$$2FeOOH + Fe + 2H_2O \Leftrightarrow 3Fe(OH)_2 \tag{6}$$

Under anaerobic conditions, iron hydroxide is formed and hydrogen is produced. Depending on temperature and pH, the ferrous hydroxide may transform into magnetite, leading to the evolution of additional hydrogen. The Schikkor reaction (Equation (8)) is favoured by increasing temperature because magnetite is thermodynamically more stable than ferrous hydroxide at higher temperatures.

$$Fe + 2H_2O \Leftrightarrow Fe(OH)_2 + 2H_2 \tag{7}$$

$$3Fe(OH)_2 \Leftrightarrow Fe_3O_4 + 2H_2O + H_2 \quad \text{(Schikkor reaction)} \tag{8}$$

Overall reaction:

$$3Fe + 4H_2O \Leftrightarrow Fe_3O_4 + 4H_2 \tag{9}$$

The corrosion rate at this stage is controlled by the rate of film growth, with magnetite (Fe_3O_4) films forming in aqueous solution and carbonate-containing Fe(II) films forming in compacted bentonite [31]. A recent study conducted at the University of Toronto reported corrosion rates in the range of 0.01 – 0.1 $\mu m.a^{-1}$ during the unsaturated, anaerobic phase [39]. Several studies have reported that carbon steel corrodes in bulk NaCl solutions at a rate of approximately 0.1 $\mu m.a^{-1}$. Based on existing data the estimated maximum wall loss of carbon steel during the repository anaerobic phase is 1 mm.

3.2 Localized Corrosion

Carbon steel may be susceptible to some degree of localized attack, especially in high-carbonate groundwaters [32]. Localized attack is more likely to occur under aerated wet conditions. Similarly to copper UFCs, the carbon steel UFCs are expected to experience surface roughening rather than distinct pitting. Localized attack is often initiated either by the reductive dissolution of Fe(III) corrosion products formed during the aerobic phase, non-uniform wetting of the container surface as the repository saturates, or by the breakdown of a passive film [31]. Preliminary modeling by King [30] using conservative assumptions estimated the carbon steel used fuel container may have a wall thickness loss of 8-24 mm due to localized corrosion.

3.3 Stress Corrosion Cracking

Substantial reasons exist to exclude the possibility of SCC occurring in carbon steel used fuel containers. These include [16]:

- The absence of a suitable environment (such as caustic, phosphate, nitrate, CO-CO_2, or high concentration of HCO_3^- / CO_3^{2-} environments);
- The absence of cyclic loading (which is required for SCC to occur in HCO_3^- / CO_3^{2-} environments); and
- The assumption of adequate post-weld stress relief (all environments)

Many international studies also presented credible arguments to support the above observations [32, 33]. In general, the susceptibility to SCC failure increases with increasing mechanical strength of the steel. The material selection for containers should therefore be restricted to the conventional steel grades which have greater corrosion resistance over a broader range of service conditions than higher strength steels.

3.4 Microbiologically Influenced Corrosion (MIC)

Bacteria metabolism affects the thermodynamics and kinectics of the electrochemical reactions that determine the corrosion rate of steel. With respect to bacteria activity in the expected repository conditions, many studies have presented evidence that the culturability and viability of microbes is compromised in compacted bentonite. In particular, the following observations have been concluded [16]:

1. A minimum dry density of 1.6 $Mg.m^{-3}$ is sufficient to prevent significant microbial activity in compacted bentonite;
2. A pore water salinity of ≥ 60 $g.L^{-1}$ is sufficient to prevent microbial activity in bentonite;
3. A water activity of less than 0.96 is sufficient to prevent significant microbial activity; and
4. Biofilm formation on the container surface can be inhibited through the use of highly compacted bentonite.

The above observations are supported by international consensus that microbial activity will not occur close to the container surface, thus precluding biofilm formation and limiting corrosion that may result from the diffusion of aggressive metabolic by-products [30]. Mass balance models using very conservative estimates of the possible MIC corrosion damage yielded similar results. Based on these analyses it was concluded that the metabolic activity of bacteria at the metal surface is limited by the rate of supply of organic nutrients and, therefore, the risk of MIC is small [34].

The current approach for assessing the extent of MIC on a carbon steel container is based on the premise that research results obtained from the studies on MIC of copper are applicable in the case of the steel UFC.

3.5 Hydrogen Generation and Transport

Hydrogen gas generated (Reaction (11)) may dissipate via different mechanisms. While some hydrogen will be absorbed by the steel, most of the hydrogen evolved will migrate through the bentonite buffer layer and through the geological barrier. How hydrogen will dissipate through the bentonite depends on the rate of gas generation. In cases where hydrogen is produced slowly, the gas will diffuse through the bentonite layer and dissolve in groundwater. However, in cases where the hydrogen generation rate is too high, the hydrogen gas pressure at the container/buffer interface will increase until the gas breaks through the bentonite layer. Once the gas pressure is released, the sealing properties of the bentonite buffer will be restored. This process is anticipated to be repeated but the sealing and permeability properties of the bentonite are unlikely to be affected.

Hydrogen gas that has migrated through the buffer layer will permeate through the host rock. Gas migrating through the geological barrier may create potential pathways for the transport of radioactive contaminants into the environment. Extensive studies on hydrogen transport in

Opalinus clay have been performed by Nagra. In these studies, transport mechanisms that are relevant to gas releases from a repository were evaluated. Results indicate that hydrogen gas generated from steel corrosion at rates to $10 \mu m.yr^{-1}$ will not affect the long-term hydraulic characteristics of their host rock.

Hydrogen transport through the geological barrier requires further study in the Canadian program. The generation of hydrogen is particularly important in the case of a repository sited in sedimentary rock as a significant amount of hydrogen may evolve during its long unsaturated, anaerobic phase. A preliminary experimental study to evaluate the transport processes of hydrogen through different host rock types has recently been proposed. Studies on gas migration through sealing materials and rock are planned for the near future.

3.6 Hydrogen Degradation

Various degradation modes exist as a result of the detrimental interaction of hydrogen absorbed into steel, such as hydrogen embrittlement, blistering and hydrogen induced cracking. There is a wealth of information on the phenomenology of hydrogen degradation of steels from the oil and gas industry. Based on the existing information, none of the degradation modes are likely to cause a significant threat to the carbon steel used fuel container [30]. Hydrogen embrittlement is a concern for high-strength steels but not for the conventional steels that are being considered for the used fuel containers. Hydride formation affects metals such as titanium and zirconium, but is not a concern for carbon steels. Hydrogen blistering and hydrogen cracking are also not likely because unlike the earlier grades of steel with high levels of manganese and sulphide inclusions, modern steels of higher metallurgical quality have lower rates of hydrogen absorption and are therefore less susceptible to those processes [35, 36]. Further work is required, however, on the effects of hydrogen on the anaerobic corrosion of steel over the projected lifetime of the containers. Research studies to investigate adsorption rates, concentrations and distribution of hydrogen in the steel during the repository anaerobic phase are required to confirm that the risk of hydrogen-related failure of steel used fuel containers can be ruled out.

3.7 Corrosion Induced by Radiation

Gamma irradiation increases corrosion rate when above a threshold absorbed dose rate, the value of which depends on the environment [24]. In synthetic seawater, the threshold dose rate is ~ 3 $Gy.h^{-1}$, but effect remains minimal even at a dose rate of 1000 $Gy.h^{-1}$ in lower salinity groundwater. In high salinity brines, moderate dose rate (0.1-10 $Gy.h^{-1}$) have been reported to form more protective corrosion products resulting in a decrease in corrosion rate, but at higher dose rates (1000 $Gy.h^{-1}$), can significantly increase the corrosion rate [37].

4. CORROSION ALLOWANCE AND CONTAINER LIFETIME ASSESSMENT

4.1 Copper Used Fuel Container

In 2005, a preliminary estimate of the lifetime of copper containers in a deep geological repository in sedimentary formation was performed [6]. This assessment predicted a maximum depth of uniform corrosion to be 0.17 mm based on an initial oxygen inventory (102 moles of oxygen) in the repository. The uniform corrosion allowance did not take credit for the consumption of oxygen by microbial activity and reaction with Fe(II) minerals. For localized corrosion, a 0.1 mm pit depth is predicted based on the argument that distinct pitting does not occur. Recent reviews have generally agreed that this surface roughening argument is more realistic (i.e., used fuel container will not undergo pitting corrosion especially with the elevated chloride concentration in sedimentary groundwater). Stress corrosion cracking is not considered because of the limited period of tensile stress, the absence of SCC agents, the lack of oxidant during the anoxic phase, and the inhibitive effects of chloride ions in the pore water. Microbial activity was considered possible in the modelling but to be of limited impact. The allowance for MIC was estimated to be 1 mm after 10^6 years taking into account the findings of a recent Swedish analysis of copper corrosion in compacted bentonite clay [38].

The total wall loss due to corrosion after 10^6 years is estimated to be ~ 1.27 mm, resulting in predicted container lifetime to be more than 10^6 years.

4.2 Carbon Steel Used Fuel Container

Uniform corrosion is one of the major corrosion mechanisms for the carbon steel used fuel containers in the repository and the Canadian research program is continuing to study the mechanisms of uniform corrosion under both aerobic and anaerobic conditions in sedimentary rock. The program also aims to develop modeling capability to make long-term predictions of the lifetimes of carbon steel used fuel containers. A conceptual semi-empirical container lifetime model has been developed and preliminary lifetime predictions have been made [30]. Preliminary assessments have concluded that a carbon steel used fuel container will experience a total wall loss of 9 to 35 mm over 10,000 years and 18 to 125 mm over 100,000 years. The breakdown of the estimated thickness loss is shown in Table 1. With the current proposed wall thickness of 100 mm, a carbon steel used fuel container may meet the required design lifetime under the conditions of a suitable sedimentary rock environment.

Table 1: Carbon Steel Thickness Loss due to Corrosion

Phase	Corrosion rate	Thickness loss in 10,000 yrs	Thickness loss in 100,000 yrs
Aerobic (~ 50a)	20-200 $\mu m.a^{-1}$ (uniform) 160 -480 $\mu m.a^{-1}$ (localized)	9-34 mm	9-34 mm
Unsaturated, anaerobic (10,000 a)	0.01-0.1 $\mu m.a^{-1}$	0.1-1 mm	0.1-1 mm
Saturated, anaerobic (> 10,000 a)	0.1- 1.0 $\mu m.a^{-1}$	0 mm	9-90 mm
Total Thickness Loss		**~ 9-35 mm**	**~18-125 mm**

5. CONCLUSIONS

The corrosion behaviour of both copper and carbon steel has been reviewed with reference to the expected environments in a deep geological repository. Both copper and carbon steel are considered potentially suitable as used fuel container materials and the respective container conceptual designs may have sufficient corrosion allowance built in to endure their required lifetime. Overall, studies concluded that the used fuel container, both copper and carbon steel, in a deep geological repository will be primarily subject to general corrosion. The degree of localized attack, including pitting, microbiologically influenced corrosion and stress corrosion cracking will be less severe and can be controlled with sound engineering design and practices; the potential impact of these processes is also expected to diminish as the repository environment becomes anoxic.

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