Journal of Nuclear Materials 379 (2008) 9–15

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

# The effect of the evolution of environmental conditions on the corrosion evolutionary path in a repository for spent fuel and high-level waste in Opalinus Clay

L. Johnson [a,*], F. King [b]

[a] National Cooperative for the Disposal of Radioactive Waste (Nagra), Hardstrasse 73, 5430 Wettingen, Switzerland
[b] Integrity Corrosion Consulting Limited, Nanaimo, BC, Canada

## ABSTRACT

The corrosion evolutionary path (CEP) defines the time-dependent corrosion behaviour of canisters in a deep geologic repository. In turn, the CEP is largely determined by the evolution of the environmental conditions in the near- and far-fields. The evolution of environmental conditions in a repository for spent fuel and high-level waste in Opalinus Clay is described along with the impact on the corrosion behaviour of the canisters.

## 1. Introduction

Nagra (the Swiss National Cooperative for the Disposal of Radioactive Waste) has completed a study to evaluate the suitability of Opalinus Clay as a host rock for a repository for spent fuel (SF) and high-level waste from reprocessing (HLW) [11]. The potential repository host rock exists in several regions in northern Switzerland at depths of 450–900 m. Carbon steel canisters or copper/cast iron canisters as an alternative [19] have been proposed for the disposal of spent fuel. We present here a description of the evolution of the environmental conditions to which carbon steel spent fuel canisters will be exposed from the time of canister emplacement to the long-term steady-state conditions that will develop after many thousands of years, followed by an assessment of the expected corrosion behaviour associated with this evolution. The purpose of the evaluation is to identify the expected conditions in the repository, including the uncertainties, so as to provide input to the research programme that should be pursued for canister integrity studies, in relation to both improved coupled process modelling of the environmental conditions and corrosion-related investigations.

## 2. Repository design concept and safety functions

The proposed repository host rock is Opalinus Clay, a low permeability Jurassic claystone with a thickness of about 110 m. The carbon steel canisters, with a wall thickness of 13–15 cm, would be emplaced horizontally in excavated tunnels (diameter 2.5 m) and the voids around and between canisters filled with a combination of compacted bentonite blocks (on which the canisters would be initially placed) and a granular bentonite mixture prepared from dense bentonite pellets (Fig. 1). The bentonite would gradually take up water from the host rock, swell and form a low permeability barrier around the canisters. Rock mechanics and tunnelling experience in Opalinus Clay suggest that no ground support (e.g., shotcrete) is likely to be needed in the small diameter emplacement tunnels, although steel mesh and rock bolts are expected to be used.

The focus in the present study is on details of the conditions to which canisters of spent fuel are exposed, because they have the highest thermal output of the various wastes and thus result in the highest initial repository temperatures.

The safety concept relies on the canister as an absolute barrier to water contacting the waste for a minimum period of 1000 years. Long-term retention of radionuclides in the disposal system relies on slow release from the waste form and slow diffusive transport through the bentonite barrier and host rock, during which time the radionuclide content is greatly reduced by decay. As illustrated in safety assessment studies, the host rock plays by far the dominant role in attenuating the releases and estimated dose rates in the biosphere are not strongly influenced by canister lifetime [11].

## 3. Environmental conditions and their evolution

### 3.1. Relevant host rock characteristics

Opalinus Clay is a claystone comprising, on average, 40% clay minerals, 30% carbonates and 20–30% quartz plus minor accessory minerals. It has a porosity of about 12% and a hydraulic conductivity of $<10^{-13}$ m s$^{-1}$ in the siting area. Transport in the rock is diffusion controlled, providing effective hydraulic isolation from

---

* Corresponding author. Tel.: +41 564371234; fax: +41 564371317.
*E-mail address:* lawrence.johnson@nagra.ch (L. Johnson).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.06.003

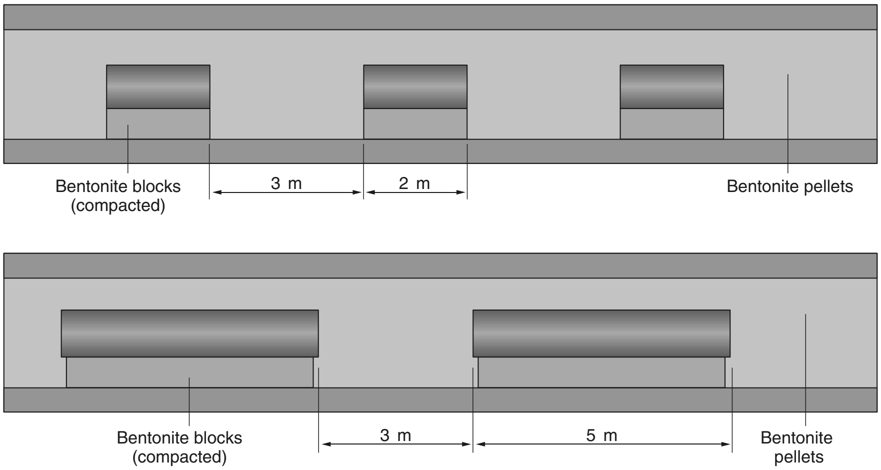


**Fig. 1.** Cross section of spent fuel and HLW emplacement tunnels for a repository in Opalinus Clay.

overlying and underlying rocks. Experiments in the Mont Terri underground laboratory have provided convincing evidence that Opalinus Clay has a self-sealing capacity, thus fractures in the excavation-damaged zone have been observed to gradually reduce in permeability with time and natural fractures in the clay have been observed to have the same permeability as the rock itself. The porewater chemistry in Opalinus Clay is brackish, with an ionic strength of 0.3 and with major ion chemistry dominated by Ca, Na, $SO_4$ and Cl. Redox conditions in the Opalinus Clay are considered to be strongly reducing as a result of the presence of pyrite (about 1%) and abundant siderite in the host rock [11].

### 3.2. Conditions at the time of emplacement of waste canisters

The initial low moisture conditions in the bentonite barrier and the low permeability of the Opalinus Clay, combined with the relatively high thermal output of spent fuel canisters, play an important role in dictating the evolution of moisture conditions at the canister surface. Nagra has proposed using bentonite blocks as a base for the canisters, with a granular bentonite mixture as a backfill that would be emplaced after the canisters are placed in position. This approach simplifies aspects of waste emplacement and sealing. SKB studies of bentonite have been used to define the properties of the blocks, which would have a saturation of about 50–60% and a dry density of 1.6 $Mg/m^3$. The properties of granular bentonite used for backfilling have been extensively studied in laboratory and field experiments [10]. The reference material is made from MX-80 bentonite by compacting dry bentonite powder (4–5% water content) at very high pressure to produce pellets with a density of 2.1–2.2 $Mg/m^3$. These pellets are then mechanically abraded and two sizes of resultant particles are mixed, along with bentonite powder. Full scale emplacement trials using this material give an average dry density of 1.45–1.50 $Mg/m^3$ [14]. The average thermal conduction characteristics and moisture content of the near-field are dominated by the granular backfill, as the blocks comprise only about 10% of the mass. The thermal output of a spent fuel canister is 1500 W at the time of emplacement.

### 3.3. Thermo-hydraulic evolution

The low average moisture content of the backfill leads to low thermal conductivity ($\sim$0.4 $W\,m^{-1}\,K^{-1}$), thus the canister surface temperature is expected to reach $\sim$150 °C within a few years after emplacement [4]. The subsequent temperature and moisture evolution have been explored using calculations with the TOUGH2 code by Senger [16], who has reported all the details of assumed input values for the calculations. In these calculations, the entire backfill was assumed to be granular, thus the higher density and higher moisture content of bentonite beneath the canister was not considered. As a first approximation, this is considered reasonable because the high thermal water vapour diffusivity in unsaturated bentonite will lead to rapid dryout of the blocks in the vicinity of the canister surface, with the water being redistributed to the granular bentonite which has a much higher suction. In addition the blocks comprise only about 10% of the entire backfill volume. These aspects will be explored in future calculations. The calculations confirm that the low hydraulic conductivity of the host rock controls the rate of water inflow, thus the saturation process is relatively slow. Fig. 2 illustrates the capillary pressure in the bentonite at the interface with the canister surface at times up to about 100 years. The capillary pressure values can be converted to relative humidity (RH) using the Kelvin equation [16], which gives the RH vs. time values in Table 1. The significance of this evolution of RH in relation to the corrosion evolutionary path is discussed in Section 4.2.

The evolution of temperatures at the canister surface is shown in Fig. 3. The maximum temperature is reached in about 10 years. The dashed line represents the temperature calculated considering only thermal conduction in the backfill. The solid line considers in addition the heat transferred by vapour flow, which becomes significant after 20–30 years.

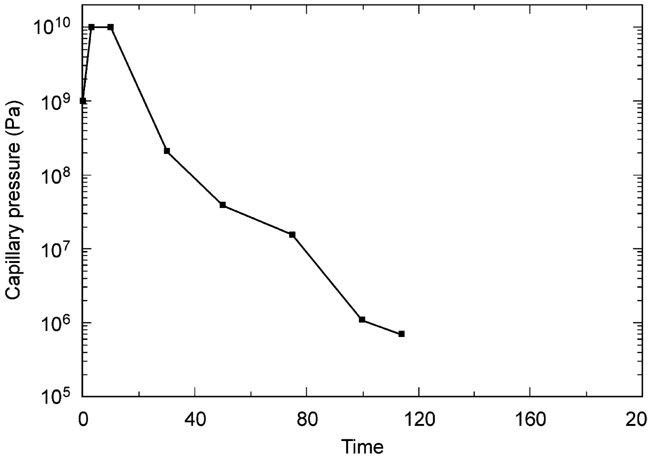


**Fig. 2.** Capillary pressure in the bentonite at the canister surface as a function of time [16]. Time in years following emplacement of the canister.

**Table 1**
Capillary pressures and relative humidity values as a function of time at the canister surface

| Time (y) | Capillary pressure (MPa) | Relative humidity (%) |
|---|---|---|
| 0 | $10^3$ | <5 |
| 3 | $10^4$ | <5 |
| 10 | $10^4$ | <5 |
| 30 | 200 | 35 |
| 50 | 40 | 80 |
| 75 | 15 | >95% |
| 100 | 1 | 100% |

Humidity values are calculated using the Kelvin equation [16].

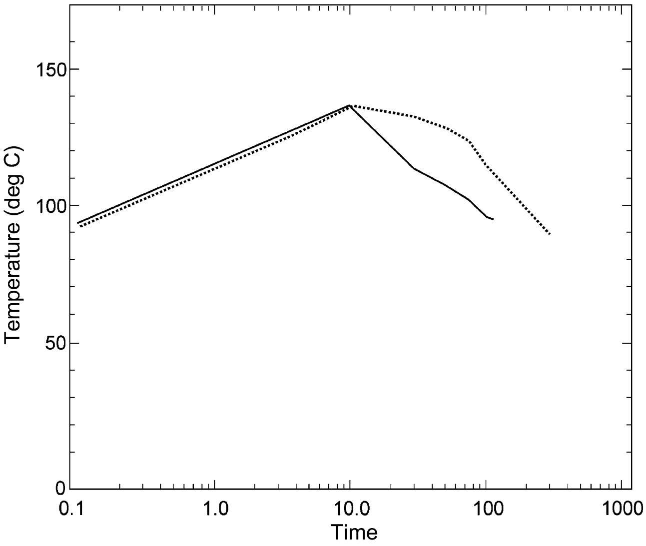


**Fig. 3.** Canister surface temperature as a function of time. Dotted line: temperature calculated considering only thermal conduction. Solid line: temperature calculated considering conduction and convection [16]. Time in years following emplacement of the canister.

The increase in thermal conductivity due to incoming moisture in addition to the decrease in heat output of the waste leads to the temperature at the canister surface declining to about 100 °C after 100 years. The canister surface temperature will then gradually fall to ambient host rock values (~35–40 °C) within 10000–20000 years.

### 3.4. Evolution of pore water chemistry and redox conditions

Redox conditions within the buffer are initially oxidising as a result of the entrapped air. The oxygen is expected to be used up within a few years, given the presence of siderite and pyrite in the Opalinus Clay and of steel mesh on the tunnel surface. Based on corrosion rates of steel and weathering rates of pyrite, the oxygen consumption time has been estimated to be a few years to a few decades [24].

Canisters will be exposed to bentonite pore water that is expected to have a composition similar to that of the Opalinus Clay pore water, with minor differences due to ion-exchange processes with the bentonite clay. The porewater pH is expected to be ~7.3, with a possible range of pH 6.9–7.9. In addition, there may be the transitory formation of thiosulphate due to the oxidation of pyrite in the excavation-damaged zone during the operational phase.

Microbial activity within the repository is expected to be severely restricted by the presence of compacted bentonite [21]. Microbial activity is the key to microbiologically influenced corrosion (MIC), since only active microbes produce aggressive metabolic by-products or the extracellular polymeric material (slime) that can form occluded regions on the surface. It is important to distinguish between microbial activity *on* the canister surface, which could lead to MIC, and that which occurs *further away* from the canister, for which aggressive microbial by-products would need to diffuse through the bentonite barrier in order to produce MIC. There is much evidence indicating that microbial activity will not occur in compacted bentonite with a dry density exceeding ~1.6 Mg $m^{-3}$, either because of low water activity or because of the effect of swelling pressures in excess of 2 MPa on the physiology of the microbes [21]. Such conditions will exist in the repository near-field, so there is expected to be limited MIC of the canister because the transport of metabolic by-products formed in regions of the repository more conducive to microbial activity to the canister surface will be minimal.

## 4. Corrosion aspects

### 4.1. Corrosion evolutionary path

The corrosion evolutionary path (CEP) defines the time-dependent corrosion behaviour of the canister and is closely tied to the evolution of environmental conditions. In general terms, the corrosion behaviour will evolve from a period of relatively rapid general corrosion and possible localised attack to a long-term phase of slow general corrosion. This CEP corresponds to the evolution of the repository environment from an initial period of hot, aerobic and unsaturated conditions, through a transition period to a long-term cool, anaerobic saturated phase.

A useful indicator of this evolution of the corrosion behaviour is the time dependence of the corrosion potential ($E_{CORR}$) of the canister. Fig. 4 shows a schematic illustration of how the $E_{CORR}$ of a canister would be expected to evolve with time in a sealed repository containing a limited amount of entrapped $O_2$. During the early aerobic phase, $E_{CORR}$ is relatively noble (positive) because of the cathodic reduction of $O_2$ and because of the possible spatial separation of anodic and cathodic processes, which also serves to increase the value of $E_{CORR}$. At long times, $E_{CORR}$ falls to a value determined by the relative rates of Fe dissolution and the reduction of $H_2O$, resulting in $E_{CORR}$ values close to the $H_2/H_2O$ equilibrium

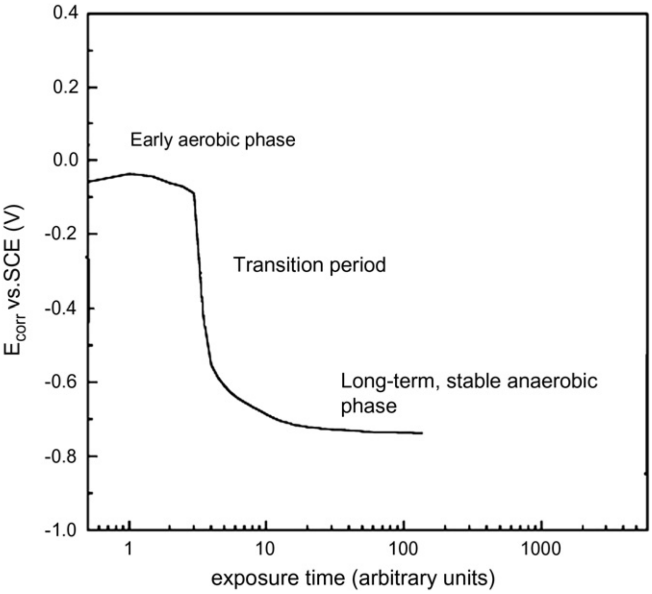


**Fig. 4.** Schematic of expected evolution of the corrosion potential of a carbon steel canister.

potential during the long-term anaerobic phase. Between these two periods, the value of $E_{CORR}$ undergoes a transition, during which Fe(III) corrosion products formed during the aerobic phase are reductively dissolved to Fe(II) species.

The evolution of environmental conditions within a repository in Opalinus Clay can be divided into the following phases:

- An initial period of hot, aerobic, but desiccated conditions, during which there is insufficient moisture to wet the canister surface.
- Gradual saturation of the near-field and the deliquescence of salts and other impurities on the canister surface as the canister cools and the relative humidity increases.
- A period of unsaturated conditions, during which the RH is sufficiently high that the surface is uniformly wetted and the repository redox conditions evolve from aerobic to anaerobic.
- A long-term anaerobic period characterized by cooler temperatures and saturated bentonite.

## 4.2. Expected canister corrosion behaviour

The canister corrosion behaviour is different for each of the four phases identified above.

### 4.2.1. Initial hot, aerobic, desiccated period

During this period there is insufficient water adsorbed on the canister surface to support aqueous corrosion processes. Based on the temperatures profiles in Fig. 3 and the RH data in Table 1, this period will last for 30–50 y following emplacement of the canisters.

Although oxidation in dry air is possible, the rate is expected to be low. Based on the rate of oxidation reported by Terlain et al. [23], the maximum oxide thickness (possibly comprising inner and outer layers of $Fe_3O_4$ and $Fe_2O_3$, respectively [3]) is predicted to be ~0.2–0.3 μm for the conservative ‘thermal-conduction’ temperature profile in Fig. 3.

During this period, some of the $O_2$ entrapped in the bentonite will be consumed by corrosion of steel rock support materials and by microbial processes in regions of the repository that are wetter and cooler than at the surface of the canister. As noted above, corrosion of the rock support materials could consume all of the trapped $O_2$ within a period of a few decades.

### 4.2.2. Initial saturation of the near-field and deliquescence of salts on the canister surface

As the temperature decreases and the RH increases (Fig. 3 and Table 1), the surface of the canister will start to wet due to deliquescence of surface impurities and condensation in the pores of the pre-formed oxide film. These impurities will include salts present naturally in the bentonite, such as NaCl (halite) and $CaSO_4 \cdot 2H_2O$ (gypsum), as well as contaminants picked up during handling and emplacement of the canisters (e.g., organic matter from exhausts and lubricants, airborne particulate matter). Each of these species will absorb moisture from the vapour-filled pores (deliquesce) at a specific RH. In general, the more soluble the species, the lower the RH (and, hence, the higher the temperature) at which deliquescence will occur [1].

Because these contaminants will be unevenly distributed over the canister, wetting of the surface will be non-uniform [25]. Droplets of water will form by deliquescence of individual salt crystals, or collections of crystals, with surrounding areas either dry or wetted by microdroplets or thin layers of moisture. If $O_2$ is still present in the bentonite at this time, the regions around the deliquesced droplets will tend to become cathodic because of the greater access of $O_2$. The droplets themselves will tend to become $O_2$ depleted and, hence, sites for the anodic process. In this manner, the initiation of localised corrosion is possible whilst the surface remains non-uniformly wetted.

Based on the predicted temperature profiles and, especially, the time dependence of the RH at the canister surface (Table 1), this period is expected to last for a few tens of years. During this period, the RH will increase from, say, 50–60% to close to saturation. The exact point at which deliquescence first occurs will depend on the nature of the surface contaminants, and the period before the surface is uniformly wetted will depend on the surface density of contaminants and the rate of increase in RH. However, some degree of localised attack can be expected during this period. Because of the possible presence of $O_2$ and because of the spatial separation of anodic and cathodic processes, the $E_{CORR}$ will be relatively positive during this period, corresponding to the early aerobic phase in Fig. 4.

### 4.2.3. Incompletely saturated bentonite, but uniformly wetted surface

As the near-field RH increases, the canister surface will become uniformly wetted. At this point, the driving force for the separation of anodic and cathodic processes will diminish, as any remaining $O_2$ will have equal access to all areas of the surface. Any propagating pits or crevices will tend to stifle as it becomes difficult to sustain the critical occluded chemistry. Overall, corrosion will tend to become more uniform in nature.

Several possible oxidants are present in the system during this period. Depending upon the rate of $O_2$ consumption by other processes, the repository may still contain some of the $O_2$ entrapped initially in the bentonite sealing materials. Transport of $O_2$ through unsaturated bentonite will be rapid [7] so, unlike in saturated bentonite, the corrosion rate will not be limited by the rate of $O_2$ supply to the canister surface. The importance of $O_2$ as an oxidant for the canister will diminish over time as the repository environment becomes anaerobic.

A second possible oxidant is Fe(III) produced during the early aerobic phase. Aerobic corrosion will result in the precipitation of various forms of hydrated Fe(III) oxyhydroxide and/or green rusts, which will become thermodynamically unstable as the repository $E_H$ becomes more reducing. The reductive dissolution of Fe(III) corrosion products can couple with oxidation of the underlying steel surface [15,18]. This electrochemical coupling is typically a transitory phenomenon and is characterized by a characteristic shift in $E_{CORR}$. In the early stages of the process, $E_{CORR}$ is controlled by redox processes between the precipitated Fe(II)/Fe(III) solids and dissolved Fe(II)/Fe(III) in solution. As the oxide dissolves and exposes the underlying C-steel substrate at cracks and pores in the film, the potential is partly determined by the rate of film reduction and of oxidation of the C-steel substrate. As more C-steel is exposed, the potential-controlling processes become oxidation of the steel coupled to $H_2O$ reduction, with characteristic potentials close to the $H_2/H_2O$ equilibrium line. Fig. 4 shows a typical transition in $E_{CORR}$ that is expected as the repository environment evolves from aerobic to anaerobic. From a corrosion viewpoint, the most aggressive period is that during the transition, at which time small areas of the underlying C-steel are polarized to relatively positive potentials and can dissolve locally quite rapidly.

The third possible oxidant during this period is $H_2O$. Depending upon the relative rates of $O_2$ consumption and repository saturation, it is possible that there will be a period of anaerobic corrosion under unsaturated conditions. There are relatively few studies of the corrosion of C-steel under such conditions, but corrosion is likely to be uniform in nature and there is no mechanistic reason for the separation of anodic and cathodic processes. Corrosion, of course, will be accompanied by the formation of $H_2$ gas.

This transition period in the evolution of the repository environment corresponds to a transition in the corrosion behaviour of the canister, characterised by the evolution in $E_{CORR}$ shown schematically in Fig. 4. In the early stages, relatively rapid general corrosion and/or localised corrosion is possible, depending upon the nature of the oxidants. Eventually, however, once the repository has become anaerobic, corrosion will be general in nature supported by the cathodic reduction of $H_2O$ and the evolution of $H_2$.

### *4.2.4. Long-term anaerobic saturated period*

Within a period of perhaps 100 y the repository environment will become water saturated and all of the entrapped $O_2$ (and the oxidised corrosion products) will have been electrochemically reduced. This phase of saturated anaerobic conditions is expected to persist indefinitely.

These environmental conditions are relatively benign for corrosion of the canister. The possibility of localised corrosion is much diminished because there is no process by which the anodic and cathodic processes may be spatially separated. Corrosion, therefore, is expected to be uniform in nature, proceeding at a rate determined by the rate of the anodic process. A precipitated corrosion product layer will develop, comprising either a duplex spinel/$Fe_3O_4$ layer (observed in bulk solution [2]) or a complex Fe, Ca-containing carbonate film (observed in compacted clay systems [12,13,22]) (Fig. 5).

The nature of the test environment is also found to affect the corrosion rate. In bulk solution, the corrosion rate is observed to reach a steady-state after 4–6 months exposure at a rate of $\sim$0.1 μm y$^{-1}$ (e.g., [9,20]). In compacted clay systems, no steady-state is observed after 4 y exposure, at which time the still-decreasing rate is $\sim$1 μm y$^{-1}$ (e.g., [13,22]). Knowledge of the precise corrosion rate is important for estimating the canister lifetime and the rate of $H_2$ generation. However, the observed corrosion rates are sufficiently high that $H_2$ cannot be transported away from the canister surface sufficiently fast by diffusion in the pore solution, so a separate $H_2$ gas phase will form in the repository. The occurrence of gas transport through the bentonite and Opalinus Clay host rock is not expected to compromise the safety functions of the barriers, as discussed in more detail elsewhere [11].

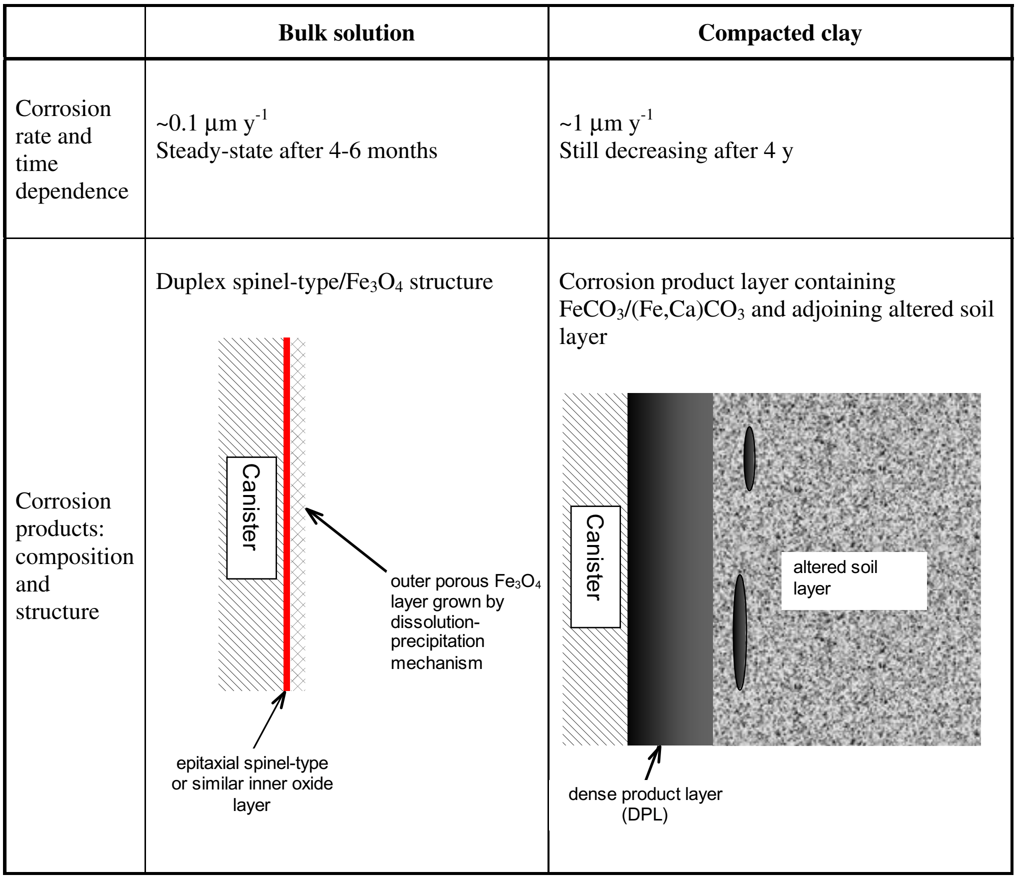
### *4.3. Predicted canister lifetimes*

### *4.3.1. Approach to lifetime prediction*

Different approaches have been used for predicting the long-term corrosion performance of nuclear waste canisters [17]. In all cases, a sound mechanistic understanding of how the corrosion processes change with time as the repository environment evolves is essential. In this regard, it is useful to define the CEP as briefly described above for a C-steel canister in the proposed repository in Opalinus Clay.

Given this detailed mechanistic understanding, it is then possible to make mathematical predictions based either on detailed process models or through relatively simple estimates of the extent of corrosion damage during each stage of the CEP. The particular approach taken is not important, since the important factor is not the level of mathematical sophistication used in arriving at a lifetime prediction but the underlying level of mechanistic understanding that is used to justify that prediction.

Here, a relatively simple mathematical treatment is used to predict the extent of corrosion of a C-steel canister in a repository in Opalinus Clay as a result of general and localised corrosion. The underlying mechanistic understanding is used to justify why these corrosion processes are, and why other corrosion processes are not, included in the lifetime assessment.



| | **Bulk solution** | **Compacted clay** |
|---|---|---|
| Corrosion rate and time dependence | ~0.1 μm y$^{-1}$<br>Steady-state after 4-6 months | ~1 μm y$^{-1}$<br>Still decreasing after 4 y |
| Corrosion products: composition and structure | Duplex spinel-type/$Fe_3O_4$ structure | Corrosion product layer containing $FeCO_3$/(Fe,Ca)$CO_3$ and adjoining altered soil layer |

**Fig. 5.** Summary of the anaerobic corrosion behaviour of C-steel in bulk solution and in compacted clay.

### *4.3.2. Corrosion processes not considered*

Before addressing those corrosion processes that are considered to determine the lifetime of the canister, it is necessary to justify the exclusion of those processes that are not considered. These processes include MIC, stress corrosion cracking (SCC), and hydrogen-related effects.

As discussed above, MIC requires that there be microbial activity at the canister surface or, in the case of remote microbial activity, that aggressive metabolic by-products diffuse to the canister surface. Based on the known effects of compacted bentonite [21] and elevated temperature on microbial activity, it is believed that significant microbial activity will not occur close to the canister surface. Therefore, colonization and biofilm formation are not possible on the canister surface and the aggressive forms of MIC generally associated with this form of corrosion will not occur. The extent of remote microbial activity in a deep geological repository with bentonite-based sealing materials has been estimated by King et al. [8]. (Although these calculations were performed for a copper canister, the estimate of the amount of aggressive microbial by-products is independent of the nature of the canister material). Because of the combined effects of compacted bentonite, low water activity, elevated temperature, and the lack of nutrients, the extent of MIC due to remotely produced sulphide and organic acids was equivalent to $\ll 1$ µm of additional wall loss. Therefore, it has been concluded that microbial activity will not significantly impact the lifetime of the canisters.

There are a number of forms of SCC of C-steel that must be considered when predicting the long-term performance of canisters [5]. Many of these, such as caustic cracking, cracking in high-temperature water, etc., can be discounted on the grounds that such environments will not be present in the repository. Pipeline steels are susceptible to SCC in carbonate-based solutions, however, and such environments could be present at the canister surface for some or all of the service life of the canister. However, these forms of cracking require a cyclic load to be present, either to rupture crack-tip films in the so-called high-pH form of pipeline SCC or as an inherent component of the corrosion fatigue mechanism for the so-called near-neutral pH form of cracking. Because of the absence of either a permissive environment or the necessary cyclic loading, therefore, SCC is not considered a credible failure mechanism for C-steel canisters in a deep geological repository [5].

Finally, some steels are susceptible to various forms of hydrogen-related damage. Hydrogen absorbed by the canister material during anaerobic corrosion can result in hydrogen-induced cracking, blister formation, step-wise cracking, and other forms of hydrogen damage [5]. Some of these forms of cracking require an externally applied tensile stress, whereas others result in internal stresses due to the absorption of hydrogen. Regardless, the susceptibility to this form of attack increases with increasing strength of the material [6]. In addition, older steels with high concentrations of MnS inclusions, especially of a given shape, are more susceptible to hydrogen damage than modern steels. Because of the use of a relatively low-strength modern steel for the canister, this form of corrosion is not expected to limit the service life.

### *4.3.3. Corrosion processes included in model and lifetime prediction*

The two forms of corrosion that are included in the lifetime prediction for C-steel canisters are general and localised corrosion. As noted above, a relatively simple empirical approach is taken to lifetime prediction, supported by a sound mechanistic understanding of the processes involved and how they are affected by the evolution of the repository environment.

General corrosion is predicted through a combination of mass-balance and corrosion rate estimates. The extent of aerobic corrosion is easily estimated based on the amount of atmospheric $O_2$ entrapped in the bentonite sealing materials upon repository closure. For the Nagra design of a repository in Opalinus Clay, this amount of $O_2$ is equivalent to <1 mm of general corrosion. Under anaerobic conditions, the extent of corrosion is based on an assumed steady-state corrosion rate of 1 µm/y, for which there is ample supporting evidence from the literature (see Fig. 5). Since the Opalinus Clay contains pyrite, an additional allowance is made for the transport-limited diffusion of $HS^-$ to the canister. Over a 10000-year period, sulphide-induced corrosion amounts to an additional 0.2 mm. (The implicit assumption is that sulphide causes additional corrosion over and above that which occurs under anaerobic conditions).

There are a number of possible mechanisms by which localised corrosion could initiate and propagate on C-steel canisters, including:

- non-uniform wetting of the surface by deliquescence of salt contaminants leading to the spatial separation of anodic and cathodic sites during the aerobic period,
- differential [$O_2$] cells, or
- electrochemical coupling of defected or cracked Fe(III) corrosion films to dissolution of the underlying steel.

Regardless of the mechanism by which localised corrosion initiates, the extent of propagation is treated using an empirical pitting factor derived from a mixture of long-term corrosion studies and short-term tests [6]. Fig. 6 shows the dependence of the pitting factor on the average depth of corrosion. It is clear from these data that the degree of surface roughening (it is misleading to refer to this as pitting since the aspect ratio is small except for the very shallowest of penetrations) diminishes significantly with increasing depth. This is an impressive set of data, comprising as it does a set of 1350 measurements from steel specimens exposed to various soil conditions and a further 50 or so measurements from controlled short-term laboratory experiments.

For the current analysis, a conservative value of the pitting factor of 10 has been selected. This factor is applied to the predicted depth of corrosion during the aerobic period only, as the presence of $O_2$ (or of Fe(III) produced by corrosion under aerobic conditions) is clearly a pre-requisite for localised corrosion. Since the extent of general corrosion during the aerobic phase is <1 mm, the maximum depth of surface roughening or 'pitting' that will occur during this period is estimated to be <10 mm. This surface roughening will

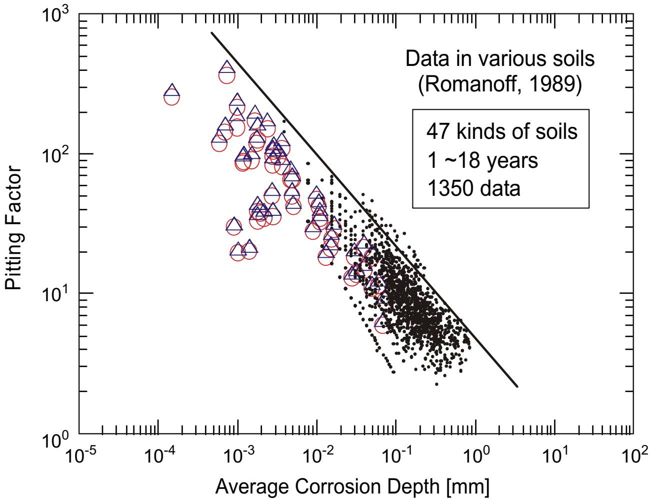


**Fig. 6.** Variation of the pitting factor for C-steel with the average depth of corrosion derived from long-term corrosion tests and short-term laboratory measurements [6].

diminish with time as the canister corrodes under anaerobic conditions, but it is conservatively assumed here that this roughening is maintained at all times.

Prediction of the extent of damage is then a simple matter of adding contributions for each of the proposed forms of corrosion. Over a 10 000-year period, the extent of damage during the aerobic period is <10 mm, with an additional ~10 mm due to general corrosion during the anaerobic phase at a rate of 1 μm/y (with an additional allowance for the transport-limited corrosion by sulphide). Therefore, the maximum wall penetration is predicted to be ~20 mm, significantly less than the proposed wall thickness of 150 mm.

## 5. Key future research issues

The evaluation of the corrosion evolutionary path provides some guidance in focusing future corrosion studies in support of lifetime assessment of canisters for disposal of SF/HLW in Opalinus Clay. The evolution of the canister surface over a period of decades from partially saturated conditions at a temperature of about 100 °C to reducing conditions at cooler temperatures suggests the need for studies of corrosion damage under these transitory conditions, including some in situ studies. In addition, the ability of compacted bentonite to maintain conditions that prevent MIC of canister materials requires further investigation, including long-term in situ corrosion measurements. Such studies would also provide insights into the possibility of any localised corrosion occurring under reducing conditions.

## 6. Summary

The concept of the corrosion evolutionary path has been used to assess the extent of corrosion of carbon steel canisters in a deep geological repository in Opalinus Clay. A key feature of this approach is the link between the evolution of the repository environment and the time-dependent corrosion behaviour of the canister.

A detailed mechanistic understanding is required of the corrosion processes that will, and will not, limit the service life of the canister. This mechanistic understanding is required as the basis of the mathematical model for calculating canister lifetimes as well as for the justification of the long-term predictions. Provided this sound mechanistic understanding is available, it does not matter whether corrosion predictions are based on detailed process models or on the basis of simple mass-balance arguments and empirical corrosion rates.

A carbon steel canister in a repository in Opalinus Clay will be subject to general and localised corrosion. Other corrosion processes, such as microbiologically influenced corrosion, stress corrosion cracking, or hydrogen-related damage, are not expected to occur, either because the environment is not supportive or because the material is non-susceptible. The maximum extent of wall penetration after 10 000 y is predicted to be ~20 mm, far less than the proposed wall thickness.

The canister lifetime assessment described here is based on a simple extrapolation of laboratory corrosion rates determined under repository-relevant conditions. Crucially, this prediction is supported by a sound mechanistic understanding of the corrosion behaviour of the canister and how it changes over time as the repository environment evolves.

## References

[1] BSC, In-drift precipitates/salts model, Report prepared for the US DOE by Bechtel SAIC Company, ANL-EBS-MD-000045 Rev 02, 2004.

[2] A.J. Davenport, L.J. Oblonsky, M.P. Ryan, M.F. Toney, J. Electrochem. Soc. 147 (2000) 2162.

[3] C. Desranges, N. Bertrand, D. Gauvain, A. Terlain, D. Poquillon, D. Monceau, in: Prediction of long term corrosion in nuclear waste systems, Proceedings of the Second International Workshop, Nice, September 2004, European Federation of Corrosion and Andra, 2004, p. 170.

[4] L.H. Johnson, M. Niemeyer, G. Klubertanz, P. Siegel, P. Gribi, Calculations of the temperature evolution of a repository for spent fuel, vitrified high-level waste and intermediate-level waste in Opalinus Clay, Nagra Technical Report NTB 01-04, Nagra, Hardstrasse 73, Wettingen, Switzerland, 2002.

[5] L.H. Johnson, F. King, Canister options for the disposal of spent fuel, Nagra Technical Report NTB 02-11, Nagra, Hardstrasse 73, Wettingen, Switzerland, 2003.

[6] JNC, H12: Project to establish the scientific and technical basis for HLW disposal in Japan, Japan Nuclear Cycle Development Institute, Supporting Report 2, Repository Design and Engineering Technology, 2000.

[7] F. King, M. Kolar, D.W. Shoesmith, in: CORROSION/96, NACE International, Houston, TX, Paper No. 380, 1996.

[8] F. King, M. Kolar, S. Stroes-Gascoyne, P. Maak, in: V.M. Oversby, L.O. Werme (Eds.), Scientific basis for nuclear waste management XXVII, Mater. Res. Soc. Symp. Proc., vol. 807, Materials Research Society, Warrendale, PA, 2004, p. 811.

[9] P. Kreis, J.P. Simpson, in: Corrosion Problems Related to Nuclear Waste Disposal, European Federation of Corrosion Publication Number 7, Institute of Materials, London, 1992, p. 57.

[10] J.C. Mayor, J.L. Garcia-Sineriz, E. Alonso, H.J. Alheid, P. Blümling, Engineered barrier emplacement experiment in Opalinus Clay for the disposal of radioactive waste in underground repositories, Enresa Publicaciones Tecnicas 02/2005, 2005.

[11] Nagra, Project Opalinus Clay – safety report, Demonstration of disposal feasibility for SF, vitrified high-level waste and long-lived intermediate-level waste (Entsorgungsnachweis), Nagra NTB 02-05, Nagra, Wettingen, Switzerland, 2002.

[12] D. Neff, P. Dillmann, L. Bellot-Gurlet, G. Beranger, Corros. Sci. 47 (2005) 515.

[13] F. Papillon, M. Jullien, C. Bataillon, in: Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems, European Federation of Corrosion Publication No. 36, Institute of Materials, Minerals and Mining, London, 2003, p. 439.

[14] M. Plötze, H.P. Weber, Emplacement test with granular bentonite MX-80, Laboratory results from ETH Zürich, Nagra Arbeitsbericht NAB 07-24, Nagra, Hardstrasse 73, Wettingen, Switzerland, 2007.

[15] Z. Qin, B. Demko, J. Noël, D. Shoesmith, F. King, R. Worthingham, K. Keith, Corrosion 60 (2004) 906.

[16] R. Senger, Thermo-hydrologic evolution of SF/HLW repository: scoping calculations in support of general THM process and system understanding, Nagra Arbeitsbericht NAB 06-13, Nagra, Hardstrasse 73, Wettingen, Switzerland, 2006.

[17] D.W. Shoesmith, Corrosion 62 (2006) 703.

[18] D.W. Shoesmith, W. Lee, D.S. Owen, Power Ind. Res. 1 (1981) 253.

[19] SKB, Fuel and canister process report for the safety assessment SR-Can, SKB Technical Report TR-06-22, Swedish Nuclear Fuel and Waste Management Co., Stockholm, 2006.

[20] N.R. Smart, D.J. Blackwood, L.O. Werme, The anaerobic corrosion of carbon steel and cast iron in artificial groundwaters, SKB Technical Report TR-01-22, Swedish Nuclear Fuel and Waste Management Co., Stockholm, 2001.

[21] S. Stroes-Gascoyne, C.J. Hamon, D.A. Dixon, C.L. Kohle, P. Maak, in: D.S. Dunn, C. Poinssot, B. Begg (Eds.), Scientific basis for nuclear waste management XXX, Mater. Res. Soc. Symp. Proc., vol. 985, Materials Research Society, Warrendale, PA, 2007.

[22] N. Taniguchi, M. Kawasaki, S. Kawakami, M. Kubota, in: Prediction of Long Term Corrosion in Nuclear Waste Systems, Proceedings of the Second International Workshop, Nice, September 2004, European Federation of Corrosion and Andra, 2004, p. 24.

[23] A. Terlain, C. Desranges, D. Gauvain, D. Féron, A. Galtayries, P. Marcus, in: Proceedings of the CORROSION/2001, NACE International, Houston, TX, Paper No. 01119, 2001.

[24] P. Wersin, L.H. Johnson, B. Schwyn, U. Berner, E. Curti, Redox conditions in the near field of a repository for SF/HLW and ILW in Opalinus Clay, Nagra Technical Report NTB 02-13, Nagra, Hardstrasse 73, Wettingen, Switzerland, 2002.

[25] J. Zhang, J. Wang, Y. Wang, Corrosion 61 (2005) 1167.