

Contents lists available at ScienceDirect

Journal of Nuclear Materials



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

Overview of European concepts for high-level waste and spent fuel disposal with special reference waste container corrosion

D.G. Bennett^a, R. Gens^{b,*}

^a TerraSalus Limited, Orchard House, Church Lane, Bisbrooke, Rutland LE15 9EL, UK ^b Ondraf/Niras, Avenue des Arts 14, 1210 Brussels, Belgium

ABSTRACT

This paper provides a brief overview of current repository and engineered barrier system (EBS) designs in selected high-level waste (HLW) and spent fuel (SF) disposal concepts from European countries, with special reference to key metallic waste containers and corrosion processes. The paper discusses assessments of copper, iron and steel container corrosion behaviour under the environmental conditions expected, given likely repository host rocks and groundwaters, and comments on the significance of corrosion processes, the choice of waste container materials, and areas of research. Most of the HLW and/or SF disposal programmes in European countries are pursuing disposal options in which the primary waste container is designed, in conjunction with the surrounding EBS materials, to provide complete containment of the waste for at least the period when temperatures in the disposal system are significantly raised by radio-active decay.

© 2008 Elsevier B.V. All rights reserved.

1. European HLW/SF disposal programmes

The Belgian Agency for Radioactive Waste and Enriched Fissile Materials, Ondraf/Niras, is considering the feasibility of disposing of HLW and spent fuel, together with long-lived low and intermediate-level radioactive wastes, in a deep geological repository excavated in the Boom Clay formation. A key component of the EBS design for HLW and spent fuel is the supercontainer [1]. In the supercontainer, containment is achieved by placing the canisters of HLW or spent fuel assemblies in a carbon steel overpack and surrounding the overpack with a Portland Cement concrete buffer and an outer stainless steel envelope (Fig. 1). Carbon steel has been chosen for the overpack because its corrosion behaviour in the highly alkaline environment that will be conditioned by the surrounding cement is well known, and because carbon steel is expected to be much less prone to localised corrosion processes than other steels [2].

Both Finland and Sweden are moving towards geological disposal of SF using the KBS-3 concept. In the KBS-3 concept, it is planned that after 30 to 40 years of interim storage, SF will be disposed of at a depth of about 500 m in crystalline bedrock, surrounded by a system of engineered barriers (Fig. 2.). The principle barrier to radionuclide release is a cylindrical copper canister. Outside the copper canister is surrounded by a bentonite clay buffer, which is designed to provide mechanical protection for the canisters and to limit the access of groundwater and corrosive substances to their surfaces.

In May 2001, the Finnish Parliament accepted a decision in principle for deep geological disposal of SF in the bedrock at Olkiluoto, near the site of the existing nuclear power plant operated by Teollisuuden Voima Oy (TVO). Posiva, the Finnish company with responsibility for radioactive waste disposal, has published several key reports on its plans, including a plan for a repository safety case and an expected evolution report [3–5].

In Sweden, the Swedish Nuclear Fuel and Waste Management Company (SKB) has recently submitted a license application for the construction of a spent fuel encapsulation plant, and SKB plans to submit a further license application in 2009 for the construction of a final repository for spent nuclear fuel. In connection with the first of these applications, SKB published a safety report, known as SR-Can [6,7], in which the safety of a KBS-3 type spent fuel repository at two potential Swedish sites is assessed. A second safety report, SR-Site, will be published in 2009 as an essential component of the license application for construction of the repository. The two sites under consideration for the Swedish repository are at Forsmark and Laxemar.

The UK Government has recently transferred responsibility for radioactive waste disposal to the Nuclear Decommissioning Authority (NDA). The NDA has launched new Radioactive Waste Management Directorate, which is building on the work of the former organisation Nirex. In 2006, Nirex developed a 'UK reference HLW/SF geological repository concept' by adapting the KBS-3 concept in terms of canister length, diameter and structure of the

^{*} Corresponding author. Tel.: +32 2 2121079; fax: +32 2 2185165.

E-mail addresses: DavidBennett@TerraSalus.co.uk (D.G. Bennett), r.gens@nirond. be (R. Gens).

^{0022-3115/\$ -} see front matter @ 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jnucmat.2008.06.001



Fig. 1. Schematic diagram showing a cross section through a disposal tunnel (gallery) containing supercontainer with spent fuel (4 assemblies) [1].



Fig. 2. The KBS-3 concept for disposal of spent fuel [6].

insert to handle HLW and spent fuel from the UK's advanced gas cooled reactors (AGRs) and pressurised water reactor (PWR) [8].

The French national radioactive waste management agency, Andra, is investigating reversible and irreversible radioactive waste storage/geological disposal in deep granite and clay formations. According to a new French law, which was passed in June 2006, Andra should apply for licensing in 2015/2016 and a deep geological repository should be operational in 2025. The most recent published assessment of the French concept for disposal in clay is the Dossier 2005 Argile [9–12]. French investigations into disposal in clay have included development of an underground laboratory in the Callovo-Oxfordian Clay, at Bure. French concepts for HLW and SF disposal are illustrated in Fig. 3.

Carbon steel has been adopted as the first choice material for the overpack in France because, under the relevant geochemical conditions, it is less prone to localized corrosion than materials that passivate (e.g., stainless steels, nickel based alloys). The Swiss National Cooperative for the Disposal of Radioactive Waste, Nagra, has assessed the feasibility of siting a repository for SF, HLW and LL-ILW in the Opalinus Clay formation in northern Switzerland [13,14]. The Swiss concept for disposal of HLW involves containing the HLW glass within a stainless steel flask and placing the flask within a 250 mm-thick carbon steel canister. The Swiss reference design concept for SF canisters involves a cast carbon steel body, with a machined central square channel fitted with cross-plates to permit emplacement of either 4 PWR or 9 boiling water reactor (BWR) fuel assemblies (Fig. 4). Carbon steel was selected as a canister material because there is long industrial experience with its fabrication, it has high-strength, and it has a relatively low and predictable corrosion rate in anoxic environments. When emplaced in the repository, both the HLW and SF containers would be surrounded by a bentonite clay backfill.

Table 1 provides a summary of relevant aspects of the EBS and the physico-chemical conditions expected during disposal for the programmes described above.



Fig. 3. French concepts for disposal of HLW (left) and SF (right). Note the use of a bentonite clay buffer in the SF disposal arrangement [9,10].



Fig. 4. Swiss canister for the disposal of spent BWR fuel (the canister for PWR is similar in design, with channels to hold four of the larger PWR fuel assemblies [21]).

2. Corrosion processes

An extensive and detailed review of the scientific literature on the corrosion behaviour of a range of potential radioactive waste disposal container materials was undertaken as part of the European Commission's 5th Framework Programme in the COBECOMA project [15]. The fundamental data considered by that project remain relevant to current waste disposal plans, even though some of the disposal concepts have been revised since the project was completed. Various types of corrosion have been addressed in safety assessments and related research studies (Table 2). The types of corrosion that occur depend not only on the conditions within the disposal system but also on the materials in question:

- 1. Corrosion-allowance materials (e.g. carbon steel, low-alloy steels, cast irons and copper in oxidising environments) corrode actively under the conditions expected during geological disposal at significant but relatively easily predictable general corrosion rates.
- Corrosion-resistant materials (e.g. austenitic stainless steels, Ni–Cr–Mo alloys, titanium alloys) passivate in aqueous environments due to the formation of a protective oxide film, which

. . . .

ladie I		
Characteristics of selected dis	sposal	systems

Country	Waste type	Waste support/ inner container	Overpack	Buffer material	Buffer porewater pH	Host rock	Groundwater	Peak temperature at outer surface of overpack	Peak γ dose rate at outer surface of overpack
Belgium	HLW SF	Stainless steel and glass frit Cast iron and sand	3 cm carbon steel	Portland cement	12.5-13.5	Boom clay	Reducing NaHCO $_3$ waters, pH ${\sim}8.5$	~95 °C	$\sim 25~Gy/h$
Finland	SF	Cast iron	5 cm copper	Bentonite	7–8	Fractured crystalline basement	Brackish Na-Cl to saline Na-Ca-Cl waters. Eh –300 mV, pH 7.5–8	~70–90 °C	~0.33 Gy/h
France	HLW	Stainless steel	5.5 cm carbon	None	-	Callo- Oxfordian	Reducing Ca–Na–CO ₃ waters, near- neutral pH	~90 °C	<10 Gy/h
Sweden	SF SF	Cast iron Cast iron	steel 5 cm copper	Bentonite Bentonite	7–8 7–8	clay Fractured crystalline basement	Dilute Na-HCO ₃ waters, brackish Na- Ca-Cl waters and saline Ca-Na-Cl waters. Reducing Eh	~90 °C	<0.1 Gy/h
Switzerland	HLW	Stainless steel	25 cm carbon steel	Bentonite	7–8	Opalinus clay	Reducing, near-neutral, Na-Cl waters	~140-160 °C	
	SF	Carbon steel	15 cm carbon steel	Bentonite	7–8				\sim 0.035 Gy/h
UK	HLW SF	Cast iron	5 cm copper	Bentonite	7–8	Not determined	Assumed reducing	Assumed <100 °C	

considerably reduces the rate of general corrosion. For these materials, the risk of localised corrosion (e.g. pitting and crevice corrosion) has to be taken into account because the protective film may break down locally. Copper is thermodynamically stable in reducing environments free of complexing agents.

There may also be various couplings or feedbacks between processes. For example, corrosion, which depends on hydrologic saturation, may lead to the production of gas, which in turn, may displace water and reduce hydrological saturation and corrosion rates.

3. Corrosion in safety assessments

3.1. Disposal system evolution

Assessments of corrosion behaviour and waste package performance need to account for the fact that conditions within the disposal system will evolve with time. The descriptions of the disposal concepts, likely host rocks and groundwaters given above provide a very general outline of the initial state of each disposal system. However, for the conduct of thorough post-closure performance or safety assessments, more detailed considerations are necessary as there will typically be a period of some decades while the repository is being constructed and operated, during which a range of processes may affect the starting point for post-closure performance and safety assessment.

Processes that may occur during the operational phase include oxidation associated with hydrological drawdown and ventilation, localised water inflows, effects of grouting and other non-waste materials introduced to the repository during construction and operation, formation of a engineering disturbed zone (EDZ) and microbiological activity.

In the post-closure period, the conditions under which waste packages will need to perform will continue to evolve over time but the most significant changes are likely to occur relatively soon after closure. Most disposal systems are designed so that peak temperatures will rise to close to but not over ~ 100 °C, but some allow for temperatures greater than this (Table 1). The temperature rise

will decline as heat migrates away from the waste and as the radiation field decays. There may be a relatively complex process of hydrological re-saturation, and various mechanical and chemical effects may occur, particularly in the early post-closure period, as stresses and chemical gradients gradually relax. In particular, a common feature of the disposal systems considered in this paper is a fairly rapid return to reducing chemical conditions soon after repository closure and hydraulic re-saturation. In some systems, gas production is an additional complication. In the longer term it may be necessary to consider the potential influence of processes originating outside of the repository, such as glaciations and associated changes in groundwater chemistry.

3.2. The treatment of corrosion in recent safety assessments

This section provides examples of how some of the corrosion processes identified above have been considered in recent safety assessments for three types of disposal systems.

3.2.1. Copper-bentonite systems

In the KBS-3 concept a copper canister is protected by a buffer composed of bentonite clay. The following sections summarise the treatment of container corrosion in the most recent Swedish safety assessment.

3.2.1.1. Operational phase. At the time of disposal, the copper canister surface is assumed to be covered by a thin oxide layer which will have developed as a result of atmospheric corrosion [6].

Elevated temperatures may cause some redistribution and enrichment of salts on the canister surface, including chlorides and sulphates from the groundwater, and sulphates and carbonates from impurities in the bentonite. However, because the salt deposits are not electrically conductive, they are not expected to increase the risk of pitting corrosion [6]. Although an increase in chloride concentration would favour general corrosion over pitting corrosion, SKB [6] notes that the bentonite buffer will maintain slightly alkaline near-field conditions and the extent of general corrosion will, therefore, be determined by the amount of available oxygen, rather than by the availability of chloride. SKB [6] concludes that

Tabl	le 2	
Key	corrosion	processes

Process	Definition	Key factors
Atmospheric corrosion	Corrosion in air	Relative humidity, concentration of atmospheric pollutants, air flow rates
General (uniform) corrosion	Corrosion proceeding at almost the same rate over the entire surface of the metal when exposed to an aggressive aqueous environment	Presence or absence of oxygen, redox conditions and presence of other aggressive species
Crevice corrosion	Localised attack of a metal surface associated with, and taking place in, or immediately around, a narrow aperture or clearance formed between the metal surface and another surface	Geometry of crevice, size of cathodic area
Pitting corrosion	Localised attack of a metal surface resulting in pits, i.e. cavities extending from the surface into the metal	Geometry of pit, size of cathodic area
Stress corrosion cracking (SCC)	Cracking of a metal caused by the simultaneous action of corrosion and sustained straining of the metal (due to applied or residual stress)	Residual stresses, applied load, size of surface defects, presence of stress concentrators, mechanical properties of the material, chemical environment
Intergranular corrosion – grain boundary attack	Localised corrosion (dissolution) in or adjacent to the grain boundaries of a metal which otherwise exhibits corrosion resistance	Material properties
Galvanic corrosion	An electrochemical process in which one metal corrodes preferentially when it is in contact with a different type of metal and both metals are in an electrolyte	Material combinations, relative areas, differential aeration cells
Microbially influenced corrosion (MIC)	Corrosion caused or promoted by microorganisms, usually chemoautotrophs. Can occur under aerobic or anaerobic conditions	Viability of microbial population under prevailing conditions, the presence of water and availability of nutrients
Hydrogen embrittlement	A process by which various metals, most importantly high-strength steel, become brittle and crack following exposure to hydrogen	Size of surface defects, presence of stress concentrators, mechanical properties of the material, sub-surface defects
Radiation influenced corrosion	Corrosion caused or promoted by radiation	Strength of gamma radiation field
Stray current corrosion	Corrosion caused by an external source of direct current – effects are similar to, but in some case more severe than, those of galvanic corrosion	Presence and strength of electrical currents
Corrosion due to magnetic fields	Corrosion caused or promoted by electrical currents induced by magnetic fields	Strength of electrical currents induced by magnetic fields

the formation of salt deposits on the canister surface during the operational phase will not cause significant detrimental effects.

3.2.1.2. Early post-closure phase. Following repository closure, copper corrosion could potentially be caused by the introduction of [17]:

- 1. Oxygen from the buffer or groundwater.
- 2. Nitric acid formed by gamma radiolysis of nitrogen compounds in moist air in the gap between canister and buffer.
- 3. Sulphide from the buffer or groundwater.

SKB [6] argues that reducing conditions will be re-established shortly after closure because the amount of oxygen in the buffer is small and because oxygen infiltrating in groundwater will be consumed by microbial processes in soil layers or in the first few metres of bedrock fractures. Therefore, after closure no further corrosion due to oxygen is expected. During the unsaturated phase, nitric acid formed by gamma radiolysis of moist air will contribute to the corrosion attack, but the amount of nitric acid that could be formed corresponds to a corrosion depth of just a few microns [7].

After all of the oxygen has been consumed, sulphide will be the primary corrosive agent present in the repository, and corrosion will proceed with formation of copper sulphide and hydrogen gas.

$4Cu+2HS^- \rightarrow 2Cu_2S+H_2$

Sources of sulphide include the dissolution of sulphide minerals in the buffer and host rock, and microbial reduction of sulphates. Once the swelling clay of the bentonite buffer has re-saturated and developed a high swelling pressure, no microbial activity is expected in the bentonite buffer and the corrosion rate will be controlled by the dissolution and transport of sulphides present in the buffer [6]. Several studies of sulphate-reducing bacteria (SRB) in compacted bentonite have showed that SRB cannot survive if the bentonite achieves a swelling pressure of 2 MPa e.g. [22,23].

SRB may be active in the wetter parts of the buffer after the near-field has become oxygen-free but before the bentonite has developed sufficient swelling pressure, but SKB [6] indicates that this is unlikely at or very near the copper surface because by the time that the interface between the buffer and the canister becomes wet, the buffer will have developed its full swelling pressure.

Masurat [22] indicates that the maximum microbial sulphide production rate corresponds to a corrosion depth of 4 μ m in 1000 years. Hedin [24] has calculated that the contribution to corrosion of sulphides originating from pyrite in the buffer is between 15 and 35 μ m in 1000 years, depending on the composition of bentonite used. SKB [6] concludes that the total amount of copper corrosion during the excavation and operational phases and the first 1000 year period can be estimated to be in the range of 55–85 μ m.

3.2.1.3. Late post-closure phase. In the longer term, SKB [6] considers copper canister corrosion for two situations:

1. Intact buffer: For the case of an intact buffer, SKB [6] has used mass balance considerations to estimate the amount of corrosion due to sulphide from pyrite initially present in the buffer. If all of the pyrite initially present in the buffer surrounding the canister side attacks the canister side as sulphide, a general corrosion depth of between 0.1 and 0.7 mm is obtained, depending on the composition of the buffer assumed. The corresponding values for pyrite in the top part of the buffer attacking the canister lid are 0.5 and 3 mm, respectively. The time required for complete depletion of the pyrite has been estimated using a simple transport expression involving the diffusivity and the concentration limit of sulphide in the buffer [24]; using pessimistic values, corrosion times of 160000 and 3 million years were obtained. SKB [6] concludes that corrosion caused by pyrite initially present in the buffer will have a negligible effect on copper canister thickness.Sulphide concentrations in groundwater at the potential site at Forsmark are not expected to exceed 10–5 kmol/m³. Combining this sulphide concentration with the equivalent flow rates for the deposition holes at Forsmark, SKB [6] calculates that less than 1 mm of copper will be corroded in 100000 years, even for waste deposition holes exposed to the highest calculated groundwater flows. Similar results are obtained for the Laxemar site.

2. Partially eroded buffer: During future glaciations it is possible that low ionic strength glacial melt waters might cause erosion of the bentonite buffer and colloid release. Knowledge of these processes is uncertain and further research is being undertaken within the Swedish programme.SKB [6] indicates that, using cautious assumptions, substantial losses of buffer could occur that would lead to advective conditions in the waste deposition holes, enhanced canister corrosion and canister failure. For the Forsmark site this may lead to failures of some tens of canisters given the most pessimistic hydraulic model. Obviously, several significant uncertainties will affect the calculated rates of corrosion and canister failure, including the geometry of the eroded buffer and the possible role of corrosion by SRB-generated sulphate. For the Swedish groundwaters and conditions in question, SKB [6] suggests that microbial activity will be limited by the supply of methane which would be the primary electron donor in the system.SKB [6] notes, however, that even with this conservative assessment modelling approach, only deposition holes that experience the very highest flow rates would be penetrated during the one million year assessment period, and that it may be possible to avoid significant host rock fractures when selecting positions for the waste deposition holes.

3.2.2. Carbon steel-cement systems

In the Belgian Supercontainer, a carbon steel overpack is protected by a buffer composed of Portland cement concrete.

3.2.2.1. Operational and early post-closure phase. Conditions within the concrete buffer will initially be oxidising (the buffer itself will be fabricated at the surface under oxidizing conditions).

Radiolysis has the potential to prolong the period in which oxidising conditions will persist in the concrete buffer. Recent radiolysis simulations by Bouniol [25], which include consideration of Haber–Weiss peroxide/superoxide dismutation reactions and the effects of temperature, suggest that provided irradiation begins under oxidizing conditions, the level of oxygen in the concrete buffer will remain high and more or less constant as a function of time over ~300 years. The model suggests that this steady state condition will be reached fairly rapidly and should be relatively well poised, such that oxidizing conditions could be maintained even while the disposal environment surrounding the supercontainer is becoming anaerobic.

Experimental data on steel corrosion at different gamma radiation field strengths suggest that below a certain level (\sim 3 Gy/h) radiolysis has little effect on corrosion rate [27].

The initial strength of the gamma radiation field at the buffer/ overpack surface in the supercontainer is expected to be ~25 Gy/ h (Table 1). Although the gamma field strength will have declined quite significantly by the time that anaerobic conditions are established at the surface of the overpack, radiolysis could have a small effect on anaerobic corrosion rates, but this is not expected to be significant. Once the potential of the overpack falls to the hydrogen equilibrium potential, hydrogen gas will be produced by corrosion of steel. Experimental studies of carbon steel corrosion under a range of anerobic, high-pH chemical conditions, and at temperatures up to 90 °C, suggest that carbon steel is passivated relatively rapidly by the formation of a layer of magnetite, or magnetite and Fe(OH)₂, and that after passive film formation, long-term corrosion rates are low (typically <0.1 μ m/y) [26].

Initial results from calculations of gas generation and migration in the near-field suggest that the concrete buffer will re-saturate quickly, within just a few years of the liner becoming perforated. Following buffer saturation, and for overpack corrosion rates <0.1 μ m/y, calculation results imply that the rate of diffusive removal of hydrogen through the Boom Clay will exceed the gas production rate, and therefore no significant pressure build-up will occur.

3.2.2.2. Late post-closure phase. Eventually dissolved species from groundwaters outside the supercontainer will migrate through the buffer to the outer surface of the overpack and affect overpack corrosion.

The effect of chloride on the corrosion of carbon steel in concrete has been studied extensively as a result of the use of steel as reinforcement in many structures exposed to saline waters, including roads and buildings. Experience suggests that corrosion only becomes significant once chloride levels exceed approximately 500 mg/l. This value is valid for all redox conditions at 25 °C, and probably up to at least 50 °C, and is higher than the chloride concentrations that can be expected in the pore water of the supercontainer concrete as a consequence of interactions with Boom Clay pore fluids.

Bicarbonate could react with cement and lower the pH in the vicinity of the overpack. Based on the amount of bicarbonate available in the Boom Clay pore water, the diffusion coefficient of bicarbonate in concrete, and the initial composition of the concrete, scoping calculations of the time needed for pH reduction have been made [28]. These suggest that the pH of the buffer near the overpack, as influenced by carbonation due to the bicarbonate of the Boom Clay pore water, will remain >12.4 at 25 °C (corresponding to > ~11 at 100 °C) for several tens of thousands of years.

It is necessary to gain further knowledge concerning sulphideinduced steel corrosion to underpin the safety case [1].

3.2.3. Steel–clay systems

In the Swiss disposal concept, a carbon steel overpack is protected by a buffer composed of bentonite clay. The French disposal concept involves the use of carbon steel and a bentonite buffer is only present for SF; Andra [9] presents a concept in which carbon steel containers of HLW may be disposed of directly within the clay host rock.

3.2.3.1. Operational phase. During the operational phase Nagra [13,14] suggests that in the Swiss concept:

- 1. The initial moisture content of the bentonite backfill will be $\sim 2\%$ and that this corresponds to a relative humidity of $\sim 5\%$ well below the critical relative humidity for initiation of aqueous corrosion in bentonite of 30–40% (maximum temperature of the bentonite at the canister surfaces: 140–160 °C for both SF and HLW). In the case of HLW, the temperature at the canister surface will decrease to ~ 80 °C within 100 years, whereas the temperature at the surface of SF canisters will remain above 100 °C for almost 1000 years.
- 2. Moisture levels at the canister surface are unlikely to rise high enough for corrosion to occur for many years because of the high temperature gradient, which will maintain low moisture levels in the hottest part of the bentonite close to the container, even when saturation of the outer bentonite is approached.
- 3. Much of the oxygen initially present in the bentonite will be consumed by reaction with pyrite and siderite in the bentonite and in the Opalinus Clay immediately surrounding the tunnel and by other steel materials present in emplacement tunnels.

Nagra [13,14], therefore, concludes that the corrosion of the steel canisters is expected to be limited to $<100 \ \mu m$ for a period

Table 3

Summary of assessments and assumptions on key corrosion processes for differ	ent disposal systems
--	----------------------

Process	Copper-bentonite (e.g. Sweden, SKB [6])	Carbon steel-cement (e.g. [1])	Steel-bentonite (e.g. Switzerland, Nagra [13,14])
Aerobic general corrosion	Copper assumed to be initially passivated by oxide. Assessment pessimistically assumed that all oxygen corrodes copper, neglecting oxygen consumption by buffer pyrite and rock.	Assume aerobic corrosion will occur for a short period of up to a few years; thereafter, conditions become reducing.	Expect <100 µm of corrosion before closure. If any oxygen remains after closure assume this will be rapidly used up by corrosion at a rate of tens of µm/year.
Anaerobic general corrosion	Assessment model takes account of sulphide in the buffer and backfill, but neglects nitric acid, which will only be produced in small quantities, and chloride corrosion, which requires very low pH to proceed under reducing conditions.	Assumed rate of <0.1 μ m/year. Model neglects chloride, which is only present in low concentrations in Boon Clay groundwaters. Model neglects HCO ₃ ⁻ as it assumes cement will keep pH too high for >10000 years.	Assumed rate of ${\sim}1.0\mu\text{m/year.}$
Pitting corrosion	Pitting (oxygen corrosion) modelled as 'uneven general corrosion'.	Processes being assessed based on the exclusion principle [20].	Possible in the early post-closure phase but assessed as being of low consequence to disposal system performance.
Stress corrosion cracking	Process excluded on the basis of low concentrations of SCC-promoting agents and insufficient oxidants. Assumes that SCC cannot occur in reducing conditions.		Assessed as an unlikely process but cannot exclude a low probability of occurrence in the weld region.
Microbially influenced corrosion	Microbially generated sulphide in the buffer excluded for cases where the buffer develops high swelling pressures, but accounted for in cases where buffer density and swelling pressure are reduced by erosion.	Further R&D identified on sulphide corrosion.	Effect of microbially generated sulphide in the buffer assessed as insignificant in long-term because high swelling pressures limit microbial activity.
Radiation influenced corrosion	Process assessed as insignificant because radiation field intensity too low.	Radiolysis may prolong the period before anaerobic corrosion begins. Thereafter, radiolysis may have a small but probably insignificant effect on corrosion rates.	Process assessed as insignificant because radiation field intensity too low.

of some decades until the humidity increases sufficiently that a thin film of water can condense and initiate both local and general corrosion. Andra [11] reaches a similar conclusion for the French concept (that the extent of container corrosion during the operational period will be <1 mm and is, therefore, negligible), but expects higher humidity levels in the excavations and notes the progressive development of anaerobic conditions along the waste disposal tunnels after waste emplacement.

3.2.3.2. Early post-closure phase. After several decades or longer, water reaching the canister surface will initiate corrosion. If any oxygen still remains in the Swiss system at this time, it will cause rapid aerobic corrosion at a rate of tens of μ m per year until all the oxygen is consumed [13,14]. Nagra [13,14] suggests that because the amount of oxygen present would be limited to that trapped in the pore spaces of bentonite around each canister, consumption of any remaining oxygen would take just a few years. Nagra [13,14] also recognises that pitting corrosion is possible during this period of oxic corrosion and that penetration depths could be greater than in the case of general corrosion alone, but cites research on long-term field tests that indicates that the degree of localisation decreases as corrosion progresses. Nagra [13,14] suggests, therefore, that the overall effect of pitting corrosion over this short period would not be significant.

3.2.3.3. Late post-closure phase. Following consumption of all of the oxygen, anaerobic corrosion in the Swiss system is expected to proceed at a rate of $\sim 1 \mu m$ per year, based on data from Smart et al. [29]. Andra [11] give maximum rates for general corrosion of steel in clay under reducing conditions of 2–5 μm per year, and also emphasise the volume increase associated with the development of iron corrosion products.

Nagra [13,14] note that such low long-term corrosion rates are consistent with results of natural analogue studies of iron and steel archaeological artefacts, which yield rates of $0.1-10 \mu m$ per year, with the higher end of the range likely to be representative of steels exposed to aerated sediments. Based on these rates, and considering the short-term occurrence of pitting, Nagra [13,14] concludes that corrosion to depths of greater than a few cm in less than 10000 years appears very unlikely.

The effects of γ -radiation on corrosion of the Swiss SF canisters are expected to be insignificant, because the radiation field at the canister surface is only ~35 mGy h⁻¹ at the time of canister emplacement – well below the critical dose rate of 3 Gy h⁻¹, which the studies of Marsh and Taylor [27] suggest is the threshold for enhanced corrosion due to radiolysis. Swiss HLW containers have walls that are 10 cm thicker than those for SF.

Nagra [13,14] argues that canister corrosion due to the ingress of dissolved sulphide is extremely improbable in the long-term because of the inability of SRB to thrive and be mobile in bentonite backfill (see above). Even if a steady flux of sulphide to the canister surface was to be maintained as a result of SRB activity in the adjacent Opalinus Clay, Nagra [13,14] estimates this would lead to <1 mm of corrosion in 10000 years.

Nagra [13,14] suggests that stress-corrosion cracking of the steel in the weld region is highly unlikely, particularly because the pH conditions in the bentonite (\sim 7.3) do not fall in the range where SCC could occur. However, Nagra [13,14] notes that there is a remote possibility of canister breaching by SCC of the weld region after a period of perhaps a thousand years.

Table 3 provides a summary of the consideration of corrosion processes in the different assessments.

4. Conclusions and areas for investigation

Research within Europe has led to a very considerable body of expertise and data on the corrosion of potential materials for radioactive waste disposal containers. The extent of this data extends more broadly than has been possible to summarise in this short paper.

Currently most of the HLW and/or SF disposal programmes in European countries are pursuing disposal options in which the primary waste container is designed, in conjunction with the surrounding EBS materials, to provide complete containment of the waste for at least the period during which temperatures in the disposal system will be significantly raised by radioactive decay. Available understanding of corrosion processes has allowed the development of a high degree of confidence in several alternative proposed solutions to the waste containment and disposal problem, which have been tailored to the particular wastes and host rocks in question. This level of confidence also derives from the results of considerable programmes of work that have been conducted to assess the feasibility, performance and safety of waste disposal.

Johnson and Zuidema [16] discuss some of the various factors that may influence the motivation for and decisions on research to further support the development of safety cases for radioactive waste disposal. They correctly emphasise the point that research and development needs are specific to the disposal concept in question and to the stage that the particular disposal programme has reached. It should also be remembered that there are often alternative ways of addressing issues that arise when developing a safety case. For example, in some cases it may be possible to refine or modify the design of the repository or the EBS, instead of conducting detailed scientific research. Nevertheless, based on a review both of existing research findings on corrosion and recent safety assessments, it is possible to identify some topics that may warrant further consideration (e.g. microbially influenced corrosion may in some cases enhance uniform corrosion rate).

For programmes proposing the use of corrosion-resistant materials (e.g. the copper canisters in the KBS-3 concept), it is vital to eliminate the potential for localised corrosion and stress-corrosion cracking. At present there is some remaining uncertainty as to whether SCC of the KBS-3 copper canister can be ruled out as easily as has sometimes been assumed e.g., [18,19]. For example, Bojinov et al. [19] used an exclusion principle approach to determine whether different types of corrosion could be excluded under the disposal conditions of interest. They suggested that the risk of stress-corrosion cracking of copper in the presence of nitrite ions could be excluded, but that the risk of localised corrosion due to bicarbonate ions and the risk of general corrosion required further experimental work.

Similarly, for the Belgian concept, Gens et al. [1] noted that confidence might be improved by seeking further confirmation that the effects of localised corrosion of the carbon steel overpack will not pose a threat under repository specific conditions. In a companion paper to this workshop, Kursten and Druyts [20] outline a proposed methodology for improved estimation of the lifetime of the carbon steel overpack in the Belgian supercontainer.

Other corrosion topics where further work might be beneficial include gas generation and transport, and the feedbacks between gas (H_2) production, water saturation, corrosion and waste dissolution.

Also, while an assessment of waste container corrosion is central to the safety cases being developed, it is clearly important that the assessments consider the complementary roles of the surrounding engineered barriers (e.g., the bentonite or concrete buffer) as these protect the canister and provide chemical conditions that will limit corrosion. In this regard further studies could be conducted to improve understanding of the potential erosion of bentonite buffers and clay-based backfills in fractured rocks, and of the transport and effects on corrosion of aggressive species (e.g. sulphide) through concrete buffer materials.

Of course, the topics noted here do not form a comprehensive list, and it should be remembered that the various national organisations with responsibility for waste disposal are engaged in well-defined processes for defining R&D needs and conducting research, often with input from their respective governments and regulatory bodies.

References

- R. Gens, J. Bel, A. Pourbaix, M. Hélie, S.M. Wickham, D.G. Bennett, in: Proceedings NUCPERF 2006, Cadarache, France, 27–30 March, 2006, Journal de Physique IV, 136, 2006, 13–23.
- [2] ONDRAF/NIRAS, A review of corrosion and materials selection issues pertinent to underground disposal of highly active nuclear waste in Belgium, A report for ONDRAF/NIRAS prepared by the Corrosion Study Panel, Report NIROND 2004-02, 2004.
- [3] POSIVA, Plan for Safety Case of Spent Fuel Repository at Olkiluoto, POSIVA Report 2005-01, ISBN 951-652-133-9, ISSN 1239-3096, 2005.
- [4] POSIVA, Disposal Canister for Spent Nuclear Fuel Design Report, POSIVA Report 2005-02, ISBN 951-652-134-7, ISSN 1239-3096, 2005.
- [5] POSIVA, Expected Evolution of a Spent Nuclear Fuel Repository at Olkiluoto, POSIVA Report 2006-05, ISBN 951-652-145-2, ISSN 1239-3096, 2006.
- [6] SKB, Long-Term Safety for KBS-3 Repositories at Forsmark and Laxemar A First Evaluation, Main Report of the SR-Can project, SKB Technical Report No. TR-06-09, Swedish Nuclear Fuel and Waste Management Co., Stockholm, 2006.
- [7] SKB, Fuel and Canister Process Report for the Safety Assessment SR-Can, 2006, SKB Technical Report No. TR-06-22. Swedish Nuclear Fuel and Waste Management Co., Stockholm, 2006.
- [8] Nirex, Preliminary Post-Closure Assessment of a Reference Repository Concept for UK High-level Waste/Spent Fuel, 2006.
- [9] Andra, Dossier 2005 Argile: Évaluation de la Faisabilité du Stockage Géologique en Formation Argileuse. Document du Synthèsis. Andra, Paris, 2005.
- [10] Andra, Dossier 2005 Argile: Tome Architecture et Gestion du Stockage Geologique, 4/497, Andra, Paris, 2005.
- [11] Andra, Dossier 2005 Argile: Evolution Phenomenologique du Stockage Geologique, 13/520, Andra, Paris, 2005.
- [12] Andra, Dossier 2005 Argile: Tome Evaluation de Surete du Stockage Geologique, 232/737, Andra, Paris, 2005.
- [13] Nagra, Project opalinus clay, safety report, demonstration of disposal feasibility forspent fuel, vitrified high-level waste and long-lived intermediate waste (Entsorgungsnachweis), Nagra Technical Report NTB 02-05, Nagra, Wettingen, Switzerland, 2002.
- [14] Nagra, Project opalinus clay: models, codes and data for safety assessment, demonstration of disposal feasibility for spent fuel, vitrified high-level waste and long-lived intermediate-level waste (Entsorgungsnachweis), Nagra Technical Report NTB 02-06. Nagra, Wettingen, Switzerland, 2002.
- [15] B. Kursten, E. Smailos, I. Azkarate, L. Werme, N.R. Smart, G. Santarini, G. COBECOMA, State-of-the-art Document on the COrrosion BEhaviour of COntainer Materials. European Commission, Contract No. FIKW-CT-20014-20138, Final Report, 2004.
- [16] L.H. Johnson, P. Zuidema, Mat. Res. Soc. Symp. Proc. 932 (2005) 201.
- [17] F. King, L. Ahonen, C. Taxén, U. Vuorinen, L. Werme, Copper Corrosion under Expected Conditions in a Deep Geologic Repository, SKB, Technical Report TR-01-23, Svensk Kärnbränslehantering AB, 2001.
- [18] T. Saario, Stress corrosion analysis of copper progress Report 2006, VTT Research Report No. VTTR1121106.
- [19] M. Bojinov, J. Hinttala, P. Kinnunen, T. Laitinen, C. Lilja, K. Mäkelä, T. Saario, in: Proceedings of an International Workshop on Prediction of Long-Term Corrosion Behaviour in Nuclear Waste Systems, European Federation of Corrosion, vol. 36, 2003, pp. 62–72.
- [20] B. Kursten, F. Druyts, these Proceedings.
- [21] L.H. Johnson, F. King, Canister options for the direct disposal of spent fuel, Nagra Technical Report, NTB 02-11. Nagra, Wettingen, Switzerland, 2003.
- [22] P. Masurat, Potential for corrosion in disposal systems for high level waste by Meiothermus and Desulfovibrio, PhD Thesis, Göteborg University, ISBN 91 628 6773-3, 2006.
- [23] P. Masurat, K. Pedersen, Mat. Res. Soc. Symp. Proc. 807 (2004) 805.
- [24] A. Hedin, Integrated Near-field Evolution Model for a KBS-3 Repository.SKB, R-04-36, Svensk Kärnbränslehantering AB, 2004.
- [25] P. Bouniol, Radiolysis within the concrete of a supercontainer including two primary waste forms – simulation at the concrete/steel interface at variable temperatures, French Atomic Energy Commission (CEA), Report No: RT DPC/ SCCME 07-742-A, 2007.
- [26] N.R. Smart, D.J. Blackwood, G.P. Marsh, C.C. Naish, T.M. O'Brien, A.P. Rance, M.I. Thomas, The anaerobic corrosion of carbon and stainless steels in simulated cementitious repository environments: A Summary Review of Nirex Research, AEA Technology Report No. AEAT/ERRA-0313, 2004.
- [27] G.P. Marsh, K.J. Taylor, Corros. Sci. 28 (1988) 289.
- [28] L. Wang, G. Volckaert, P. De Cannière, A Scoping Calculation on the Evolution of pH within the supercontainer, SCK-CEN (2004) Technical Note, 04/LWa/TN-10.
- [29] 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.