Radioactive Waste
Management

NDA Report no. DSSC/451/01

Geological Disposal

Waste Package Evolution Status Report

December 2016

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Conditions of Publication

ISBN 978-1-84029-564-1

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Abstract

The Waste Package Evolution status report is part of a suite of eight research status reports. The purpose of the research status reports is to describe the science and technology underpinning geological disposal of UK higher activity wastes by providing a structured review and summary of relevant published scientific literature and discussing its relevance in the UK context. The reports have been written for an audience with a scientific or technical background and with some knowledge of the context of geological disposal. The current suite of research status reports (issue 2) updates and replaces the suite produced in 2010 (issue 1).

The objective of the Waste Package Evolution status report is to summarise the scientific evidence relating to evolution processes of waste packages (wasteforms and waste containers) during periods of storage and after disposal in the GDF. The key message emerging from the analysis presented in this status report is that durable waste packages, able to withstand their storage and disposal environments for very long periods of time, have been produced or can be produced in the future for the wastes considered in the disposal inventory.

Executive Summary

The Waste Package Evolution status report is part of a suite of research status reports describing the science and technology underpinning geological disposal of UK higher activity wastes.

The report describes evolution processes of waste packages during periods of interim storage before emplacement in a geological disposal facility (GDF), during the operational period of a GDF, and after its closure. It considers all waste and potential waste currently considered in the disposal inventory, including intermediate level waste (ILW), some low level waste (LLW), high level waste (HLW), a variety of spent fuels, uranium (particularly depleted, natural and low enriched uranium, DNLEU), and plutonium (either in the form of spent fuel or immobilised plutonium residues). The report also considers a variety of packaging solutions currently adopted or envisaged for the disposal of radioactive wastes, including a variety of container types for ILW/LLW, HLW and spent fuel which may be also employed for the disposal of DNLEU and plutonium.

For HLW and spent fuel, waste containers have typically been manufactured with the aim of withstanding long time periods after closure of the GDF. A variety of container designs have been developed in many international programmes. Designs based on copper or carbon steel are typically considered as the most prominent candidates in a variety of disposal scenarios. Studies carried out in the UK programme indicate that our variety of container types is likely to provide high durability in the range of geochemical conditions applicable to the UK, giving flexibility to the disposal programme. In particular, the durability of designs based on copper and carbon steel is likely to depend only to a limited extent on the geochemical conditions at a disposal site; durability of the order of tens or hundreds of thousands of years can be achieved with these materials. The studies also indicate that, provided the environmental conditions are suitably controlled, many container designs will be able to withstand long periods of interim storage or disposal in un-backfilled disposal tunnels. This provides flexibility to upstream and downstream waste management options.

For ILW/LLW, waste containers have been manufactured with the aim of withstanding long periods of interim storage and operations in a GDF. The container designs most commonly employed in the UK (thin-walled, stainless steel) are expected to provide excellent durability in atmospheric conditions, provided that specific situations are avoided (particularly the deposition of marine aerosols). Other designs (thick-walled, cast iron or concrete) are also expected to provide good durability, provided that the environmental conditions are suitably controlled (particularly the relative humidity). In a cement backfilled GDF, the durability of ILW/LLW containers will depend on the container design and the geochemical conditions at the disposal site. In the case of stainless steel containers, either a relatively short (few years or decades) or long durability (greater than a thousand years) is expected, depending on the groundwater chemistry and rate of resaturation. A durability of greater than a thousand years is expected in the case of thick-walled cast iron and concrete containers, although further research is required to underpin durability estimates, particularly for concrete containers. In the case of ILW/LLW containers however, durability estimates are affected by substantial uncertainties. Key uncertainties include the state of containers at the time of disposal (after interim storage and GDF operational phase), the fact the current designs are not hermetically sealed, and the possibility heterogeneities in the backfill (for example, low pH niches) leading to specific corrosion mechanisms.

Once waste containers have become perforated, following exposure to groundwater, waste packages will start releasing radionuclides to the EBS. The rate at which radionuclide-release processes will occur depends on the wasteform in question.

For the majority of UK HLW (Magnox and Blend glass), radionuclide release is expected to be driven by long-term dissolution processes of the glass, and will occur over a timescale of tens or hundreds of thousands of years, somewhat faster than for HLW formulations

which do not contain magnesium. Faster dissolution processes, however, are expected to lead to a faster release of radionuclides initially (about 1% of the inventory being released over many decades). For some HLW streams (such as wastes arising from post-operational clean, radionuclide segregation processes may lead to a higher initial release of specific radionuclides, but this has not yet been evaluated and will depend on future product formulation development.

In the case of oxide spent fuels (existing AGR and PWR fuel), radionuclide release rates are expected to be driven by the long-term dissolution of the spent fuel matrix, and will occur on a timescale in excess of a hundred thousand years. An initial release of specific radionuclides, however, is expected to occur, leading to the rapid release of a fraction of the radionuclides inventory (0.1-10% of specific radionuclides). In the case of metallic fuel (some legacy fuel), should it be disposed of to the GDF, radionuclide releases are expected to be much faster, leading to dissolution of the whole inventory over periods of tens or hundreds of years after exposure to the groundwater.

Differently from HLW and (most) spent fuels, some of the wastes and encapsulation materials employed for the immobilisation of ILW/LLW possess sufficient chemical reactivity to require consideration during interim storage and the operational period of the GDF. Waste streams requiring particular consideration include those containing ‘reactive’ metals (Magnox, aluminium and uranium), organic wastes (such as plutonium-contaminated materials or some ion-exchange resins) and ‘mobile wastes’ (such as sludges and flocculants). These materials may require a suitable pre-treatment and selection/formulation of encapsulant (if any) to mitigate the potential for chemical alteration processes which might result in dimensional changes or other detrimental effects. Noteworthy developments in the upstream treatment of ILW/LLW (but also plutonium) include thermal-treatment processes able to reduce the waste volume and chemical reactivity and lead to the development of an inert and durable wasteform. For DNLEU, which will arise in the form of uranium oxide powders, wasteform evolution during periods preceding closure of the GDF are expected to be minimal.

After degradation of the waste container, and upon exposure to the groundwater, the release of radioactivity from ILW/LLW, plutonium and DNLEU will depend on the waste in question, the encapsulant and the geochemical conditions in the EBS. Relatively fast releases can be expected in the case of unencapsulated wastes containing reactive metals or organics. Lower release rates may occur in the case of less chemically-reactive wastes (such as corrosion-resistant metals, graphite or uranium oxides) and/or encapsulated wastes (particularly any thermally-treated wastes).

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List of acronyms

AGR	Advanced Gas-cooled Reactor
BFS	Blast Furnace Slag
BWR	Boiling Water Reactor
DNLEU	Depleted, Natural and Low Enriched Uranium
DSSC	Disposal System Safety Case
DI	Derived Inventory
EAC	Environmentally-assisted cracking
EBS	Engineered Barrier System
GDF	Geological Disposal Facility
HAL	Highly Active Liquor
HEU	Highly Enriched Uranium
HIC	Hydrogen-induced Cracking
HLW	High Level Radioactive Waste
IAEA	International Atomic Energy Agency
ILW	Intermediate level radioactive waste
IRF	Instant Release Fraction
ISG	International Simple Glass
LLW	Low Level Radioactive Waste
LWR	Light Water Reactor
MIC	Microbiologically-influenced Corrosion
MOX	Mixed Oxide (fuel)
MPC	Multi-purpose Container
NAPL	Non-aqueous Phase Liquid
OPC	Ordinary Portland Cement
PEM	Pre-fabricated Emplacement Module
POCO	Post-operational Clean Out
PCM	Plutonium Contaminated Material
PFA	Pulverised Fuel Ash
PWR	Pressurised Water Reactor
SCC	Stress Corrosion Cracking
UKRWI	UK Radioactive Waste Inventory
VES	Vinyl Ester Styrene
WVP	Waste Vitrification Plant

1 Introduction

1.1 Background

In order to build confidence in the safety of a future geological disposal facility (GDF) for the UK[1], in the absence of potential disposal sites, RWM is developing a generic Disposal System Safety Case (DSSC), which shows how the waste inventory destined for geological disposal could be safely disposed of in a range of geological environments. Background information on geological disposal in the UK can be found in the Technical Background Document [1].

The documents comprising the generic DSSC are shown in Figure 1 and include a number of research status reports ('knowledge base'). The purpose of the research status reports is to describe the science and technology underpinning geological disposal of UK higher activity wastes by providing a structured review and summary of relevant published scientific literature and discussing its relevance in the UK context. The current suite of research status reports (issue 2) updates and replaces the suite produced in 2010 (issue 1).

Figure 2 shows how research status reports underpin different safety cases. They include:

- reports on waste package evolution (this report), engineered barrier system (EBS) evolution [2], and geosphere [3], describing the understanding of the evolution of the specific barriers of the multi-barrier system
- reports on behaviour of radionuclides and non-radiological species in groundwater [4] and gas generation and migration [5], describing the release and movement of materials through the multi-barrier system, including the groundwater and any gas phase formed
- reports on criticality safety [6] and on waste package accident performance [7], describing the behaviour of waste packages and a GDF during low probability events
- a report on the biosphere [8], describing how we think the biosphere may evolve in the future and how radionuclide uptake might be expected to take place.

Research status reports need to be read in conjunction with other documentation, including:

- the Data Report [9], which describes the values of specific parameters used in the safety assessments based on scientific information presented in the status reports
- the Science and Technology Plan [10], which describes planned future research and development activities.

1.2 Objectives and scope

The objective of the Waste Package Evolution status report is to summarise the scientific evidence relating to evolution processes of waste packages (wasteforms and waste containers) during periods of storage and after disposal in the GDF. Available information is discussed with the aim of providing a sufficiently detailed evaluation of the implications of key processes to allow its direct use in the development of safety cases. Safety-related

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[1] Disposal of higher activity radioactive wastes in a GDF is current policy in England, Wales and Northern Ireland. Scottish Government policy is that the long-term management of higher activity radioactive waste should be in near-surface facilities. Facilities should be located as near to the sites where the waste is produced as possible.

considerations are excluded from the scope of this document and are provided solely in the safety cases.

The scope covers all materials currently considered in the inventory for disposal, including intermediate and low level waste (ILW/LLW), high level waste (HLW), spent fuels, uranium (particularly depleted, natural and low-enriched uranium, DNLEU) and plutonium.

Figure 1: Structure of the generic Disposal System Safety Case (DSSC). The suite of research status reports represents the knowledge base

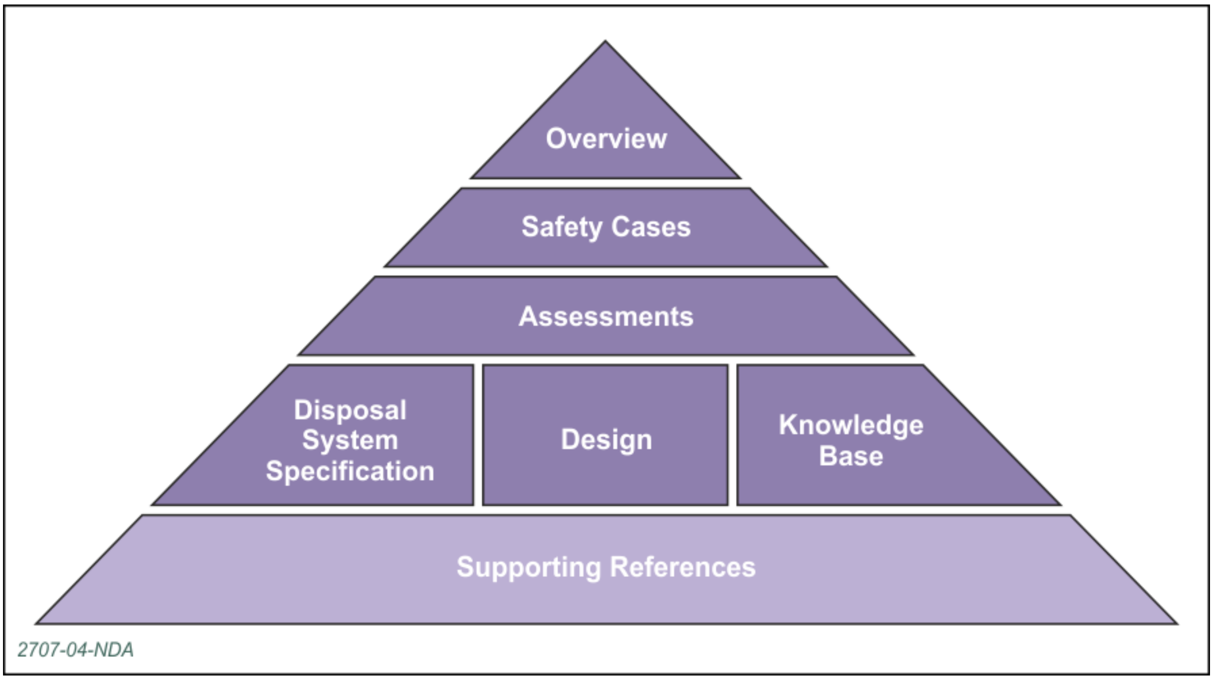
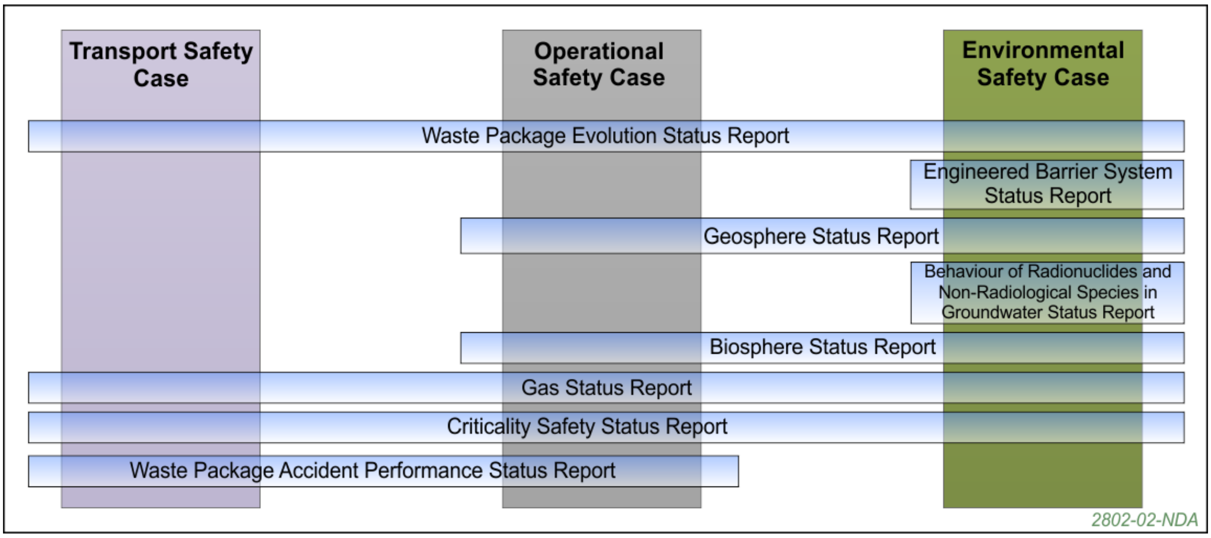


Figure 2: Safety cases and status reports in which underpinning information can be found



1.3 Audience and Users

The primary external audience of the status reports is our regulators. The audience is also expected to include academics, learned societies and stakeholders such as the Committee on Radioactive Waste Management (CoRWM) and Non-Governmental Organisations (NGOs). The reports have been written for an audience with a scientific or technical background and with some knowledge of the context of geological disposal. The primary internal user of the information presented in the status reports is RWM's safety case team.

1.4 Relationship with other status reports

There are important interfaces between this and other research status reports. Key interfaces with the Waste Package Evolution status report include:

- the chemical evolution of the buffer/backfill and the thermal evolution of the EBS as a whole (described in [2])
- the evolution of the geosphere; in particular, the groundwater geochemistry, the timescale of EBS resaturation, and the nature and magnitude of mechanical loads (described in [3]).

Information from the Waste Package Evolution that underpins other status reports includes:

- the evolution of the mechanical properties and physical condition of wasteforms and waste containers during interim storage and the operational period of the GDF, which can affect the accident performance of waste packages (described in [7])
- the release of specific radionuclides and other chemical species from wasteform degradation processes, which affects the quantities and timescales over which they are mobilised in the groundwater (described in [4]) and the criticality safety of the GDF (described in [6])
- the durability of waste containers, which affects the criticality safety of the GDF (described in [6])
- the release in groundwater, or any gas phase developed in the GDF, of specific non-radioactive species (e.g. hydrogen gas, non-aqueous phase liquids and metallic ions), which can affect specific aspects of the evolution of the GDF (described in [5] and [4]).

1.5 Changes from the previous issue

This document updates and replaces the 2010 Package Evolution Status Report [11], published as part of the 2010 generic DSSC suite. This issue includes the following developments:

- consideration of evolution processes for new wastes and potential wastes recently introduced to the inventory for disposal, including spent fuels from new reactors, spent fuel arising from the re-use of plutonium stockpiles, legacy metallic fuels, and uranium from various nuclear operations
- more detailed considerations of the evolution processes of HLW and spent fuels previously considered in the disposal inventory (oxide fuels), including the results of scoping studies on UK-specific fuels and HLW formulations
- additional understanding of the evolution processes of other ILW/LLW wasteforms, including consideration of reactive metals in cement, polymeric encapsulants, thermally-treated ILW, and non-encapsulated wastes

- additional consideration of the evolution processes of HLW and spent fuel containers manufactured from a variety of materials (copper, carbon steel, cast iron, titanium, stainless steel and nickel alloys), including the latest results from experimental studies and in situ experiments carried out in various international programmes
- additional consideration of the evolution processes of ILW/LLW containers manufactured from a variety of materials (stainless steel, other ‘steels’ and concrete), including the latest results from experimental studies, modelling studies and monitoring/practical operational experience
- initial consideration of the manufacture of waste containers to illustrate feasibility and understanding of the potential impact of the approach to manufacturing on the durability of waste containers (particularly for HLW and spent fuel), based on work carried out in other international programmes.

In line with the objectives of the document and in order to respond to previous feedback, contextual and safety-related information have been removed from the text. Contextual information is provided in [1], while safety-related information is described entirely in the safety case documentation.

1.6 Knowledge base reference period

The knowledge base described in this document contains scientific information available to RWM up to March 2016. Where, within RWM’s research programme, progress relative to important topics was made after such date, efforts have been made to reflect such progress up to the publication date of this document.

1.7 Terminology

For information about use of language and terminology in this and other RWM documents please refer to our Glossary [1]. When necessary, we have introduced specific terminology used in the document through the use of footnotes.

1.8 Document structure

The remainder of this report is structured according to the following format:

- section 2 describes the wastes and potential wastes
- section 3 describes the processing of radioactive wastes, including any immobilisation and other pre-treatment
- section 4 describes the environmental conditions to which waste packages will be exposed during periods preceding and following disposal
- section 5 presents our understanding of the evolution processes of HLW
- section 6 presents our understanding of the evolution processes of spent fuels
- section 7 presents our understanding of the evolution processes of wasteforms for ILW/LLW, plutonium residues, and DNLEU
- section 8 presents our understanding of the evolution processes of specific ILW wasteforms
- section 9 describes waste container materials for different types of wastes and potential wastes
- section 10 presents our understanding of the evolution processes of waste containers

- section 11 provides a description of the expected evolution of HLW and spent fuel packages during periods preceding and following closure of the GDF
- section 12 provides a description of the expected evolution of ILW/LLW, plutonium residues and DNLEU packages during periods preceding and following closure of the GDF
- Appendix 1 provides complementary information on the manufacturing and ongoing monitoring of waste packages.

We have used coloured boxes at the beginning of each section to provide a short summary of the key messages and help the reader in following the ‘golden thread’.

2 Wastes and potential wastes

The UK radioactive waste inventory considers a variety of wastes and other materials potentially requiring disposal in a GDF. Some wastes already arise as products with the required properties, such as Advanced Gas-cooled reactor (AGR) and Light Water Reactor (LWR) spent fuels)[2]. Other wastes may require specific treatment to obtain a product in a form suitable for disposal.

This section describes the quantities and characteristics of radioactive wastes and potential wastes as they arise. The nature of immobilisation processes and the key characteristics of encapsulants and embedding media are discussed in the next section. For convenience, whilst effectively resulting from the use of a specific immobilisation process (vitrification), HLW is described in this section since, given the nature of the waste requiring immobilisation and of the process currently used, the properties of the resulting wasteform are sufficiently well defined to consider the vitrified product effectively as the 'waste'.

2.1 Quantity and characteristics of wastes and potential wastes

ILW comprises a large variety of materials in substantial volumes. The volumes of HLW and spent fuel for disposal are much smaller. HLW and spent fuel generate substantial amounts of heat for hundreds of years. There may also be inventories of uranium and plutonium for disposal.

Detailed information about the nature and characteristics of radioactive wastes and potential wastes in the UK, including those currently planned for disposal in a GDF, is described in the UK Radioactive Waste Inventory (UK RWI) [12,13]. This information is subsequently enhanced by RWM with more detailed information, including assumptions on the nature of encapsulants and container types (in the so called 'Derived Inventory', or DI [14]). In this status report it is useful to consider the nature of materials present in different waste types, together with their expected volumes. This information can be used to gain an appreciation of the characteristics and relative significance of different waste streams. Information about the current arisings, projected volumes, degree of conditioning, assumed packaging material and overall volumes of wastes and potential wastes is also reported in [14].Table 1 gives indicative masses for wastes and other relevant nuclear materials based on figures presented in the Derived Inventory [14] for ILW/LLW, HLW and some spent fuels in the reference case. With some exceptions (notably HLW), the masses are those of the raw wastes and exclude any conditioning (such as encapsulant) and container materials that may be used to store or dispose of the wastes. Spent fuel from new power stations, spent fuel from the reuse of separated plutonium (MOX fuel), and uranium and plutonium from a variety of operations are not included in the table for the sake of simplicity. However, in terms of materials composition (but not in terms of overall expected volumes), spent fuel from new power stations and MOX fuel are currently assumed to have characteristics broadly similar to that of existing PWR fuel [14]. Additional information can be found in [14].

In general, the masses/volumes of HLW and spent fuels considered for disposal are much less than those for ILW/LLW. These materials are also less diverse in terms of their composition. However, HLW and spent fuels contain much higher levels of radioactivity per unit volume than ILW/LLW. As a result of the higher levels of radioactivity, HLW and spent fuel will generate heat for hundreds or even thousands of years, and are classified as high

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[2] Light Water Reactors (LWR) comprise a variety of reactor types, including Pressurised Water Reactors (PWR) and Boiling Water Reactors (BWR). A single LWR currently exists in the UK, the PWR at Sizewell B. New nuclear reactors currently considered in the UK, however, include LWR types other than PWR.

heat generating waste (HHGW). Conversely, ILW/LLW does not usually generate a substantial amount of heat and can hence be classified as low heat generating waste (LHGW). This classification is sometimes used in other recent RWM documentation but is not employed further in this document, in favour of a direct reference to the nature of the materials in question, which is more helpful when describing their likely evolution processes.

Table 1: Mass of main materials included in the Derived Inventory for LLW/ILW, HLW and some spent fuels (AGR, PWR and metallic spent fuel) for the reference case [14, Tables D2 and E4]. Figures include projected future arisings and do not include, unless explicitly noted, the mass of any conditioning and packaging medium

Material	**Unconditioned mass (tonnes)**				
	LLW/ILW(1)	**HLW(2)**	**spent AGR fuel**	**spent PWR fuel(3)**	**metallic spent fuel(4)**
Metals					
Stainless steel	38200	612	1020	36.3	318
Other ferrous metals	56000	1.18	0	0	0
Magnox[3]	6370	0	0	0	133
Aluminium	1750	0	0	0	0
Lead	1130	0	0	0	0
Zircaloy[3]	1280	0	0	269	0
Nickel alloys	53.1	20.6	0	15.1	0
Uranium	941	0	0	0	740
Other metals	1040	0	0	0	0
Organics					
Cellulose	2620	0	0	0	0
Halogenated plastics	4770	0	0	0	0
Non-halogenated plastics	2750	0	0	0	0
Organic ion exchange resins	3630	0	0	0	0
Rubber + other organics	2450	0	0	0	0
Inorganics					
Concrete, cement and sand	53900	0	0	0	0
Graphite	76800	0	0	0	0
Glass	235	2850	0	0	0
Ceramics	218	0	35.1	0	0
Sludges, flocs + aqueous liquids	31800	0	0	0	0

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[3] Magnox metal is an alloy of magnesium (99%) and aluminium (1%) used as a cladding material for Magnox fuel. Zircaloy is a zirconium alloy used as a cladding material for LWR fuel.

Ion exchange materials	5460	0	0	0	0
Heavy-metal oxides	0	0	5100	1190	0
Not assigned	1020	0	0	0	0
Total	292000	3480	6160	1510	1190

Notes:

(1) LLW includes only the fraction of this waste to be disposed of in a GDF. For both ILW and LLW, the materials reported represent the major components of the waste and not an exhaustive list. As a result, the total does not correspond to the sum of individual components. In some cases (when ‘+’ is used), materials have been grouped if considered meaningful from the perspective of likely encapsulation and resulting evolution processes.

(2) These figures include the glass used for conditioning and the stainless steel canister in which the glass is stored.

(3) These figures refer to PWR fuel from Sizewell B. However the nature of the materials and their relative amounts are broadly similar to those expected for spent fuels from new build power stations and MOX fuel.

(4) Metallic fuel refers to fuel made from uranium (or other heavy metal) in metallic, rather than oxide, form. The current assumption in the Derived Inventory is that it is mainly comprised of low burn-up Magnox fuel (uranium metal) which is unsuitable for reprocessing.

2.2 High Level Waste

HLW contains high concentrations of short and long-lived radionuclides; it is produced from the vitrification of nitric acid solutions containing fission products from the reprocessing of spent nuclear fuels. The resulting glass is stored in stainless steel canisters.

HLW contains concentrated radionuclides (both short and long-lived), as it is produced from the vitrification of nitric acid solutions (Highly Active Liquors, HALs) containing fission products from the primary stage of reprocessing spent nuclear fuel. The nitric acid solutions have been vitrified in an alkali borosilicate glass matrix at the Waste Vitrification Plant (WVP) at Sellafield. The resulting glass is stored in stainless steel canisters (Figure 3) prior to disposal in the future GDF.

Current plans are for the majority of HLW to be processed by the vitrification of mixtures of HAL and glass-forming substances. The typical waste loading of the glass product has been around 18-25 wt. % on an oxide basis. In most cases the product is a homogeneous glass with no discernible phase separation.

The canisters are unvented and made of a 5 mm thick grade 309 stainless steel envelope, which is welded remotely within the WVP. This grade (higher in chromium than other similar grades like 304 or 316)[4] has been employed due to its good corrosion/oxidation resistance at the high temperatures expected during vitrification and dry storage. However, its relatively high carbon content is expected to lead to the sensitisation of the weld region, making the canister unlikely to provide good corrosion resistance in aqueous environments (such as those expected in the GDF). Further packaging of HLW in a ‘disposal’ container is expected (see section 9.2).

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[4] Grade 309 contains higher levels of chromium and nickel than 304 (22-24 wt.% and 12-15 wt.% respectively, compared with 18-20 wt.% and 8-10 wt.% for 304) but, similarly to 304, contains no molybdenum (present in 316). The carbon content of 309 is reported to be 0.08-0.20 wt.%.

In general, most of the HAL derives from the reprocessing of Magnox and AGR spent fuels. Three other main families of glass or glass-containing products are also expected to arise: Butex glass, Post-operational Clean-out (POCO) glass, and technical wastes. All compositions are unique to the UK.

In particular most UK HLW contains, or will contain, significant quantities of magnesium, making it somewhat different from the vitrified HLW typically produced in other countries (see Box 1), for example the R7T7-type glasses produced in France (free of magnesium but richer in calcium). Differences in the chemical composition (particularly in the magnesium and calcium content) of these glasses are currently thought to be potentially responsible for differences in their experimental leaching characteristics, and hence their likely evolution in a GDF.

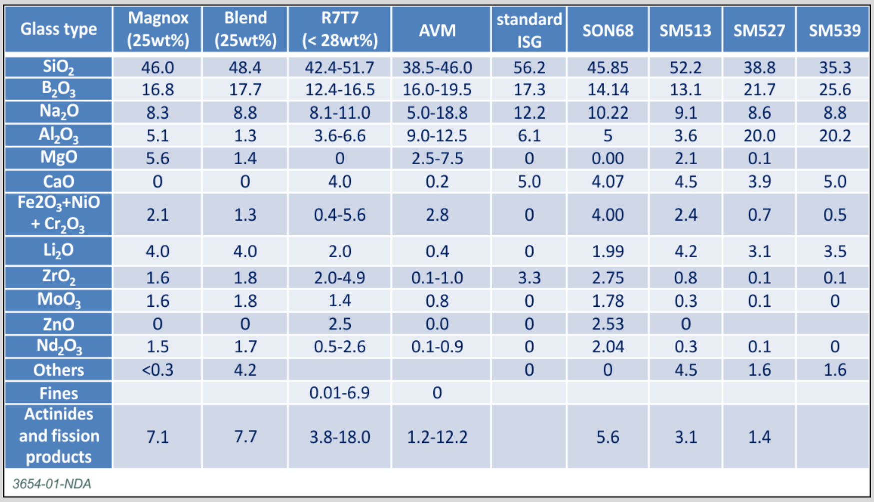
Figure 3: Simulant of vitrified High Level Waste in a stainless steel canister

Box 1 Comparison of HLW composition in the UK and other countries

In common with many of the vitrification processes adopted around the world, the vitrification process for HLW in the UK is based on the use of a sodium borosilicate glass. Most of the HLW arising in the UK includes a waste component derived from the reprocessing of Magnox spent fuel. As a result, most UK HLW (Magnox, blend and other glasses) contains, or will contain, significant quantities of magnesium. This distinguishes UK glasses from many of the HLW formulations produced in other countries, which usually contain calcium (absent from UK formulation) but contain lower amounts or no magnesium. Differences in the chemical composition (particularly in the magnesium and calcium contents) of borosilicate glass products are currently thought to be potentially responsible for differences in their likely evolution in a GDF, once the glass becomes exposed to water.

Table 2 shows the typical compositions of the standard UK Magnox and Blend products at a target waste loading of 25wt% (based on [20]), compared with compositional ranges (or targets) for vitrified products developed in France and in Belgium (based on [15, 16, 17, 18]). In common with UK glasses, the AVM glass produced in France and the SM513 glass developed in Belgium also contain magnesium. However, the majority of HLW glass produced in France, at the R7 and T7 plants at Le Hague, is magnesium-free. Compared to all other glasses, UK glasses contain virtually no calcium. The R7T7-type glasses have been the most studied internationally, with a large body of work on their chemical durability performed using the inactive simulant, SON68. Recently, a simplified six-component version of SON68 has been adopted internationally for fundamental studies of the mechanisms of glass dissolution. The target compositions for this International Standard Glass (ISG, [19]), as well as for SON68, are also included in Table 2.

Table 2: Typical target compositions or compositional ranges for vitrified HLW products developed in the UK (Magnox, Blend [20]), France/Belgium (R7T7/SON68, AVM, SM513, SM527, SM539 [15, 16, 17, 18]) and ISG [19][5,6]



Glass type	Magnox (25wt%)	Blend (25wt%)	R7T7 (< 28wt%)	AVM	standard ISG	SON68	SM513	SM527	SM539
SiO_2	46.0	48.4	42.4-51.7	38.5-46.0	56.2	45.85	52.2	38.8	35.3
B_2O_3	16.8	17.7	12.4-16.5	16.0-19.5	17.3	14.14	13.1	21.7	25.6
Na_2O	8.3	8.8	8.1-11.0	5.0-18.8	12.2	10.22	9.1	8.6	8.8
Al_2O_3	5.1	1.3	3.6-6.6	9.0-12.5	6.1	5	3.6	20.0	20.2
MgO	5.6	1.4	0	2.5-7.5	0	0.00	2.1	0.1	
CaO	0	0	4.0	0.2	5.0	4.07	4.5	3.9	5.0
$Fe2O_3$+NiO + Cr_2O_3	2.1	1.3	0.4-5.6	2.8	0	4.00	2.4	0.7	0.5
Li_2O	4.0	4.0	2.0	0.4	0	1.99	4.2	3.1	3.5
ZrO_2	1.6	1.8	2.0-4.9	0.1-1.0	3.3	2.75	0.8	0.1	0.1
MoO_3	1.6	1.8	1.4	0.8	0	1.78	0.3	0.1	0
ZnO	0	0	2.5	0.0	0	2.53	0		
Nd_2O_3	1.5	1.7	0.5-2.6	0.1-0.9	0	2.04	0.3	0.1	0
Others	<0.3	4.2			0	0	4.5	1.6	1.6
Fines			0.01-6.9	0					
Actinides and fission products	7.1	7.7	3.8-18.0	1.2-12.2		5.6	3.1	1.4	

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[5] The composition of 'Blend' glass has been evaluated based on information contained in [20] for a theoretical 'oxide' glass, and assuming a 75o:25m ratio.

[6] "Fines' refers to the insoluble phases which include platinoid metals, ruthenium dioxide and molybdate phases. 'Others' refers to other, predominantly minor, oxide components of the glass; in the case of the 'Blend' glass this includes about 4% Gd_2O_3 added as a neutron poison.

2.2.1 Magnox and Blend Glass

A vitrification process has been used to immobilise HAL arising from the reprocessing of both Magnox fuel and AGR fuel (Oxide HAL).

The vitrification process has been used, and will continue to be used, to immobilise HAL arising from the reprocessing of both Magnox fuel and AGR fuel (but not PWR fuel). In the case of Magnox fuel, vitrification of reprocessing liquor after calcination and blending with glass frit has generally been performed (‘Magnox’ glass). Conversely, in the case of AGR fuel, reprocessing liquor has been processed after blending with reprocessing liquor from Magnox fuel. Blending has been typically carried out in the ratio 75:25 Oxide:Magnox (75o:25m) on an oxide basis. This has led to the development of two families of products [20]:

- ‘Magnox’ glasses, which tend to contain relatively large quantities of magnesium and aluminium (5-6 wt.% for each element separately)
- ‘Blend’ glasses, which tend to contain lesser quantities of magnesium and aluminium (1-2 wt.% for each element separately), but slightly higher amounts of molybdenum and zirconium.

In recent years, to increase efficiency in vitrifying the remaining stocks of HAL, a large body of work has been undertaken to underpin plans to increase the waste loadings in both Magnox and blended glasses from 18-25 wt.% to 35 wt.% [21,22]. One constraint on these developments has been the potential for increased inhomogeneity of the glass product due to the separation of insoluble phases as the waste loading is increased. In particular, ‘yellow phase’, a complex mixture of alkali metal, alkaline earth and rare earth molybdates can separate from the glass melt under certain conditions [20]. Yellow phase is an unwanted by-product of vitrification because it is highly corrosive to the melter in the molten state and soluble in aqueous solution at ambient temperature [23]. The tendency to form yellow phase is greater for Blend glasses due to the higher molybdenum content of Oxide HAL. The vitrification flow sheets used on the WVP are designed to avoid yellow phase formation and, in general, only very small amounts of yellow phase are present in standard UK HLW products [20]. Yellow phase has also been reported in Japanese HLW [24].

Among the existing HLW products are canisters containing so-called ‘drain-pour’ products, that have arisen from the need to periodically drain the residual melts (‘heels’) that remain in the bottom of the melters at the end of each vitrification cycle. These products tend to be enriched with phases insoluble in the glass but soluble in groundwater, requiring specific consideration after disposal in a GDF.

2.2.2 Butex glass

The first fuel reprocessing plant at Sellafield used a solvent extraction process with di-butyl carbitol (Butex) resulting in reprocessing liquor of differing composition than Magnox or oxide liquor, which will result in a different HLW composition.

The first fuel reprocessing plant at Sellafield, which operated from 1952 to 1964, used a solvent extraction process with di-butyl carbitol (Butex) to separate uranium and plutonium in the reprocessing of irradiated fuel from the Windscale piles (comprising of natural uranium metal). The liquid waste arising was rich in uranium [25]. Sellafield Ltd. recently instigated research to underpin an operational strategy for the vitrification of this waste stream [26]. The characteristics of Magnox:Butex blend glasses of varying waste ratios and waste loadings are currently being investigated by the waste producer.

2.2.3 Post-operational clean-out (POCO) glass

A strategy for the immobilisation of any wastes resulting from Post-Operational Clean Out (POCO) is currently being developed at Sellafield.

Storage of reprocessing liquor over time has led to the precipitation of some insoluble compounds (barium-strontium nitrate, zirconium molybdate and caesium phosphomolybdate) in Highly Active Storage Tanks (HASTs). These compounds cannot be readily vitrified using the current alkali borosilicate glass formulation due to their high molybdenum content, which would result in the formation of yellow phase [23] and an unsatisfactory wasteform. The strategy for waste treatment is following a two-pronged approach [27, 28]:

- co-vitrification of POCO wastes with reprocessing wastes using the current borosilicate glass formulation
- development of a new borosilicate glass formulation containing calcium, which allows a higher incorporation of molybdenum through the formation of durable $CaMoO_4$ crystals in situ in the melt once the solubility of molybdenum in the melt has been exceeded.

To support the first approach, work has been undertaken to determine the levels of incorporation of POCO solids in current glass formulations when co-vitrified with reprocessing HAL [29].

The development of the second approach is intended for the vitrification of the remaining POCO waste once reprocessing HAL is no longer available for co-processing. In work to date, glasses containing up to 10wt% MoO_3 have been successfully manufactured at the laboratory scale without any detrimental yellow phase formation in the vitrified product [28, 30, 31]. The resulting product is a glass composite material with the $CaMoO_4$ phase evenly distributed throughout the glass. A good quality glass product containing ~8.7% MoO_3 has been successfully manufactured on the VTR without any operational problems, indicating the feasibility of the process for potential future implementation in the WVP.

2.2.4 Technical wastes

The main components of Highly Active Technical Waste (HATW) are melter bottoms and glass heels, melter necks, filters from the pour-extract system and miscellaneous piping associated with melters.

Highly Active Technical Waste (HATW) is a sub-category of non-standard HLW [27]. The main components of this waste are melter bottoms and glass heels, melter necks, filters from the pour extract system and miscellaneous piping associated with melters. Glass heels and other residue glasses from melters tend to be heterogeneous, with large quantities of nickel, iron and chromium spinels, ruthenium oxides and molybdates (yellow phase is commonly observed). The current waste management strategy for these wastes is to size-reduce the larger items and to consign them in shielded ILW flasks to the Miscellaneous Beta Gamma Waste Store (MBGWS). Waste that is too active for the MBGWS is placed in standard vitrification canisters, cut off at the shoulder to allow the addition of larger pieces. Once full, the shoulder and neck are welded back in position. The amount of HLW glass associated with these is around 6000 kg, which is equivalent to 15 WVP containers.

The other significant sources of HATW are pour extract filters (enriched in caesium compounds) and calcine/glass fines. The baseline strategy for these waste streams is to place them in stainless steel containers with the fines collected in open lidded tins. Although the inventory of this material is small it may contain a large soluble component and hence alternative disposal strategies may need to be considered.

2.3 Spent fuels

Spent fuel results from the occurrence in nuclear fuel of the radioactive processes that occur within a nuclear reactor. The inventory for disposal includes spent fuel from a number of different types of reactor (mainly AGR, PWR and fuels from new power stations). The form of the spent fuel may be metallic or oxide.

Spent fuel is the material that results from the occurrence in nuclear fuel of the nuclear processes that occur within the core of a nuclear reactor. In the UK different types of spent fuels have been generated, and will be generated in the future, due to the different designs of reactors that have been and will be operated.

The physical and chemical characteristics of different types of spent fuel, and consideration of their current and likely future state at the time of disposal, are reported below. In defining a 'wasteform' for disposal it is important to identify the nature of the fuel itself, and the nature of the cladding and other fuel assembly components requiring disposal. It is also important to define expected levels of enrichment, burn-up and power ratings (or operating temperatures) that the fuel has experienced. A detailed description of different types of fuels of relevance to the UK disposal programme is provided below. Additional information is provided in Box 2.

2.3.1 Advanced Gas-cooled Reactor (AGR) fuel

An AGR fuel element comprises 36 fuel pins, each made of UO_2 pellets confined in a stainless steel clad filled with helium and held together by a stainless steel grid and braces.

An Advanced Gas-cooled Reactor (AGR) fuel element comprises 36 fuel pins, each made of UO_2 pellets confined in a stainless steel clad (about 1 m long and 0.3 mm in thickness), filled with helium and held together by a stainless steel grid and braces[7]. The fuel assembly includes a graphite 'sleeve' which provides neutron moderation. The fuel assemblies are then irradiated in reactor piled up in a vertical 'stringer'. The fuel pellets are manufactured from enriched natural uranium or reprocessed uranium, typically to levels of 2.5-3.5 %.

The fuel pellet is ring-shaped (that is, it has an inner 'bore') to accommodate gases produced during fission (for example, helium, xenon and krypton). The reactor centreline temperatures and the thermal gradient across the fuel pellet are similar to those typically experienced in other UO_2-based fuels (such as LWR fuels). However, the geometry of the fuel pellet (ring-shaped as opposed to disk-shaped) and the nature of the coolant result in higher temperatures at the fuel cladding interface and of the cladding itself. This results in potential differences in the microstructure and chemical characteristics of spent AGR fuel compared with spent fuels typically generated in other reactor designs (such as LWRs). However some similarities exist with specific reactor designs. For example, ring-shaped fuel in used in Russian High Power Channel-Type Reactors (Figure 4). AGR fuel pellets have not been doped with either neutron poisons (for example gadolinium) or compounds used to control the grain size (for example chromium). An illustration of an AGR fuel assembly is provided in Figure 5.

AGR fuel has been typically irradiated to a burn-up of 20-30 GW day/tU. Reference values assumed in inventory calculations are 28 GWd/tU for current stocks and 33 GWd/tU for future arisings [14], but higher burn up values (up to about 40 GW day/tU) are possible.

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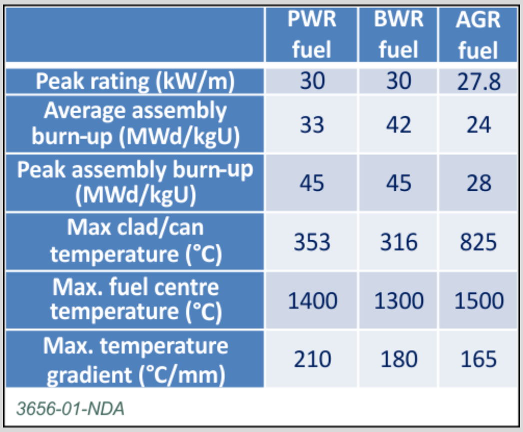
[7] The stainless steel used for the cladding and braces contains 20 wt% chromium and 25 wt% nickel (20/25 grade) 'stabilised' with niobium or titanium to prevent chromium carbide precipitation during welding (and possibly irradiation), hence mitigating the risk of intergranular corrosion.

Box 2 Typical AGR and LWR core parameters and irradiation conditions

The local thermal history is particularly important in evaluating the evolution of UO_2-based spent fuels in a GDF. The local thermal history of fuel during irradiation depends on the local values of power rating, thermal conductivity of the fuel matrix, the cladding and the pellet/clad interface, and the rate of thermal exchange between the external surface of the cladding and the coolant. The thermal characteristics of the fuel matrix, cladding and fuel/cladding interface change during irradiation due to the development of gas bubbles, the formation of surface oxides on the cladding and any geometrical changes that, depending on reactor design, may alter (typically reduce) any gap between the pellets and the cladding.

Typical characteristics of LWR and AGR fuel are reported in Table 3. In LWR fuels, peak (centreline) temperatures during reactor operations are of the order of 1,300 °C -1,400 °C, compared with maximum cladding temperatures as low as 300-400 °C. Peak assembly burn-up is typically as high as 45 GWd/tU. As a rule of thumb, local burn-ups are 50% higher than maximum assembly burn-up, up to 70 GWd/tU. In AGR fuels, peak temperatures (at the fuel bore) are of the order of 1,400 °C-1,500 °C and maximum temperatures at the cladding are as high as 800 °C (for the top elements of the fuel stringer). Typical maximum assembly burn-up is up to 28 GWd/tU (up to 34 GWd/tU estimated for future operations), resulting in maximum local burn-up of 50 GWd/tU. Thermal gradients are similar to those of LWR fuels or lower. An important consideration is that AGR reactors tend to display a higher thermal gradient along the direction of cooling (vertical) than LWR reactors. As a result, when evaluating the characteristics of spent fuel at the highest levels of burn-up and power rating, it is particularly important to test fuel elements in the hottest parts of the stringer (typically element 6 in AGR fuel).

Table 3 Typical AGR and LWR core design parameters and irradiation conditions at 2006, reproduced from [186], based on [32]



	PWR fuel	BWR fuel	AGR fuel
Peak rating (kW/m)	30	30	27.8
Average assembly burn-up (MWd/kgU)	33	42	24
Peak assembly burn-up (MWd/kgU)	45	45	28
Max clad/can temperature (°C)	353	316	825
Max. fuel centre temperature (°C)	1400	1300	1500
Max. temperature gradient (°C/mm)	210	180	165

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Notes:

(1) The peak temperatures and ratings reported correspond to ‘typical’ reactor conditions (in 2006). Higher temperatures and ratings have been reported in ‘atypical’ conditions.

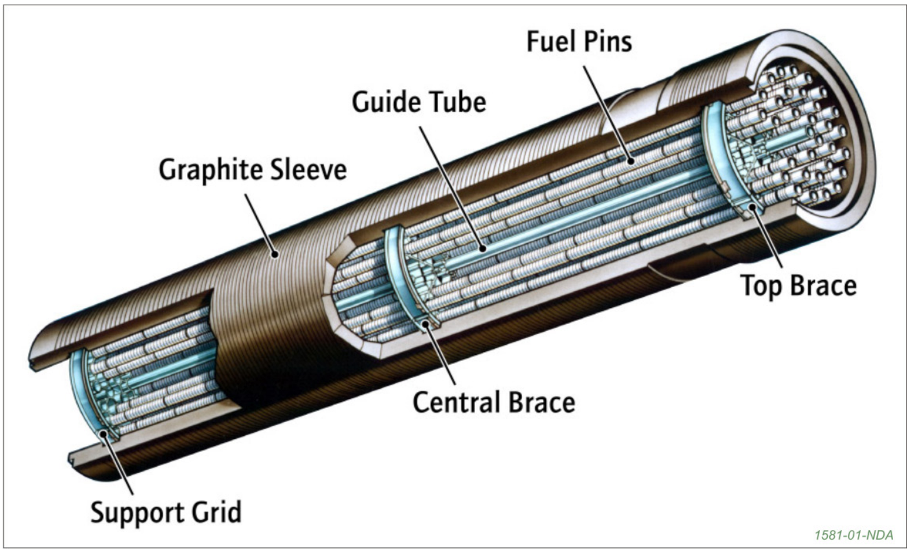
(2) The temperature gradients have been evaluated considering surface temperatures estimated on the basis of maximum clad/can temperature information plus a typical, beginning-of-life pellet-clad temperature drop at the tabulated peak ratings of 200°C. For the AGR, the pellet surface temperature was taken as the maximum can temperature (since the AGR can is pressurised onto the fuel pellets during manufacture).

In the case of AGR fuel requiring disposal, at least some fuel elements will have been dismantled before disposal. In this case (currently assumed as the baseline), the wasteform includes the fuel cladding (stainless steel) and the 'slotted can' in which fuel pins are consolidated during storage (stainless steel)[8]. In any case, at some point in the future, packaging in a dry storage and/or disposal container will have to take place.

Given the good corrosion resistance of stainless steel to both atmospheric and aqueous corrosion, our current expectation is that, at the time of containerisation for disposal, and following any additional period of interim storage, both the fuel and its cladding will remain in good condition. It is known, however, that some spent AGR fuel that has undergone pond storage at Sellafield has degraded, leading to localised perforation of the cladding and release of some radioactivity to the storage ponds. This is termed 'failed' fuel and may require specific consideration in waste management and disposal (see Section 11.1).

Figure 4: Image of (ring-shaped) fuel pellet used in Russian High Power Channel-Type Reactors. Ring-shaped pellets are also used in AGR fuel

Figure 5: Illustration showing an AGR fuel assembly, together with its graphite sleeve. Note that disposal of spent AGR fuel assumes removal of the graphite before containerisation in disposal containers, consistent with current storage practices at Sellafield. The length of the assembly is about 1 metre



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[8] During interim storage at Sellafield, spent AGR fuel is dismantled from its sleeve (graphite) and other assembly components (stainless steel). After dismantling, three fuel assemblies (36 fuel pins each) are consolidated within a single stainless steel 'slotted can' (108 fuel pins).

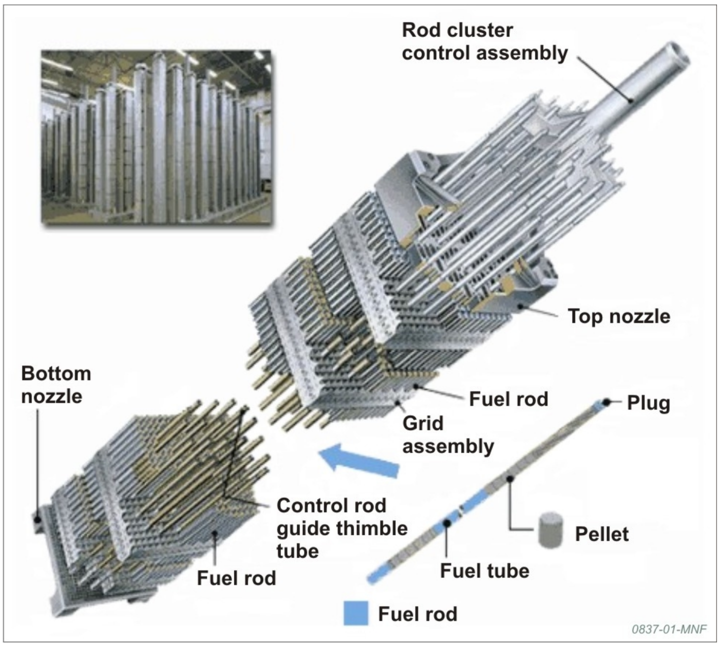
2.3.2 Light Water Reactor (LWR) fuel

A PWR fuel assembly from Sizewell B comprises 264 helium-filled fuel rods, each containing solid UO_2 pellets encased in a zirconium-alloy cladding, 24 guide tubes and an instrument tube in a square array.

In the UK, spent Light Water Reactor (LWR) fuel, in particular Pressurised Water Reactor (PWR) fuel, has arisen from the operations of the Sizewell B power station. LWR fuels may also arise from the operations of new nuclear power stations of either PWR or BWR (Boiling Water Reactor) design.

A PWR fuel assembly from Sizewell B comprises 264 helium-filled fuel rods, each containing solid UO_2 pellets encased in a zirconium-alloy cladding, 24 guide tubes and an instrument tube in a square 17 x 17 array. Other fuel assembly components are made from stainless steel or nickel alloys. Each assembly is fitted with top and bottom nozzles. Control rods and other non-fuel core components (NFCCs) are inserted into the guide tubes during reactor operations. For neutron control purposes, up to 24 rods in any one assembly contain gadolinium oxide up to 8wt%. Doping with compounds used to control the pellets grain size (for example chromium) is not currently used. An illustration of a PWR fuel assembly is provided in Figure 6.

Figure 6: Illustration showing an example of a PWR fuel assembly. The length of the assembly is about 4 metres



In the UK, PWR fuel has been typically irradiated up to a burn-up of 40-50 GWd/tU. Reference values assumed in the DI [14] are 45 GWd/tU for current stocks and 55 GWd/tU for future arisings.

Similarly to PWR fuel used at Sizewell B, LWR fuel from new nuclear power stations will also use a zirconium alloy as a cladding material and stainless steel or nickel alloys for other fuel assembly components. Our current assumption is that these fuels may achieve a higher burn-up, up to 65 GWd/tU [14].

In all cases, fuel elements may not be dismantled before disposal, so the wasteform includes both the fuel cladding and other components of the fuel assembly, plus potential NFCCs and neutron absorbing rods. At some point in the future, packaging in a dry storage and/or disposal container will have to take place for Sizewell B fuel. Current plans are for all PWR fuel assemblies to be packaged and dry stored in ‘Multi-Purpose Containers’ (MPCs), making use of an inner containment vessel and interchangeable external ‘overpacks’ to meet requirements for storage, transport and disposal [33].

Given the excellent corrosion resistance of Zircaloy to aqueous and atmospheric corrosion, and the plans for packaging fuel assemblies into MPCs in the near future, our current expectation is that most PWR fuel (as well as future LWR fuels) will remain in excellent condition at the time of transport to a disposal facility.

2.3.3 Magnox and Metallic fuel

Magnox fuel comprises rods of metallic uranium, encased in a magnesium-aluminium alloy cladding. This fuel is currently destined for reprocessing, but legacy fuels with similar composition will require disposal.

Magnox fuel comprises rods of metallic uranium, encased in a magnesium-aluminium alloy cladding (Magnox cladding). The fuel was manufactured from natural uranium, thus requiring the choice of a cladding material with a low neutron cross-section such as magnesium. Magnesium alloys (and Magnox in particular), however, present relatively poor corrosion resistance, so any management of the fuel requires storage in highly controlled conditions. An illustration of Magnox fuel (only the cladding) is provided in Figure 7.

Figure 7: Illustration showing an example of a Magnox fuel element (cladding). The element is typically 1 metre in length

Magnox fuel is currently managed under the Magnox Operating Programme (MOP) [34]. The current baseline for this fuel is reprocessing. It is possible, however, that some Magnox fuel will not be reprocessed and may require disposal.

Additionally, the UK has accumulated significant quantities of legacy fuels, some of which are in metallic form (‘metallic fuel’), currently stored in water ponds. Sufficient information is not currently available to determine the precise composition of these fuels. However, it is currently assumed that their composition is similar to that of Magnox fuel. It is likely that such fuel will have been subjected to low burn-up. Values of less than 5 GWd/tU are currently assumed [14].

It is presently unclear in what form disposal of any metallic fuel may take place. Options being evaluated include disposal of un-dismantled fuel (that is, the fuel and its cladding), immobilisation in a suitable encapsulant, or processing into a more stable chemical form, followed by packaging in suitable disposal containers.

Given that metallic fuel elements will have been stored in aqueous conditions for a long time, it is likely that will they have experienced some corrosion of the cladding and possibly of the fuel itself. This may have to be considered in the development of packaging solutions for this waste.

2.3.4 Exotic fuels

The UK also has a series of spent fuels and nuclear material arising from experimental reactor programmes and, to a lesser extent, military defence programmes.

The UK has a series of spent fuels and nuclear material arising mainly from experimental reactor programmes, termed ‘exotics’ [35]. These materials include:

- Dounreay Fast Reactor (DFR) breeder fuel, with characteristics similar to that of Magnox fuel (metallic) and for which, like Magnox fuel, the current preferred waste management option is reprocessing
- irradiated fuels, comprising oxide and carbide fuel consisting mainly of Prototype Fast Reactor (PFR) fuel and the HELIOS material that was irradiated in experimental work.
- fuels consisting of plutonium, mixed uranium and plutonium oxide and mixed uranium and plutonium carbide fuels;
- unirradiated high enriched uranium (HEU) fuels consisting of uranium oxides, uranium metal, uranium alloy, uranium tetrafluoride, uranium hexafluoride[9] and other miscellaneous enriched uranium fuels; and

The exotics inventory includes Ministry of Defence (MOD) used fuel (previously called ‘submarine’ spent fuel).

The DI currently assumes only disposal of PFR fuel (assumed to be in the form of a mixed oxide, rather than carbide) [14]. PFR SF comprises intact sub-assemblies and separate fuel pins. The sub-assemblies contain driver fuel and additional breeder material. The driver fuel is a $(U, Pu)O_2$ solid solution, with plutonium content typically 25 – 33% by mass. The breeder material comprises depleted UO_2. Spent PFR fuel assemblies have a wide range of irradiation histories with cumulative burn-ups ranging from 21 GWd/tHM to 230 GWd/tHM. A burn-up of 189 GWd/tHM has been assumed in the DI [14]. Some unirradiated material also exists.

From the point of view of evolution processes of the fuel during storage and eventual disposal in a GDF, important characteristics of the fuel include its basic chemistry (that is, whether the fuel is based on a metallic, oxide, or carbide system), the nature of the cladding (and other assembly components) and its irradiation history. Due to their high chemical reactivity, disposal of metallic, carbide-based, or oxide fuels irradiated at high burn-up and power ratings is expected to be more challenging than that of other fuels.

2.3.5 Fuels from the reprocessing of the existing plutonium stockpile

The UK Government’s current preferred option for the management of plutonium recovered during the reprocessing of spent nuclear fuel is to use it in the manufacture of plutonium-rich reactor fuels.

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[9] Materials arising in gaseous form are likely to require conversion into a fully-immobilised wasteform for disposal.

In the UK, plutonium (Pu) has been recovered during the reprocessing of spent nuclear fuel. The UK Government's preferred option for its management is to use it in the manufacture of plutonium-rich reactor fuels as a mixture of uranium and plutonium oxide (mixed-oxide, MOX) fuel for use in LWRs [36]. Options for reuse of plutonium in other fuel/reactor types are also being considered [36]. Such options would result in the use of plutonium in MOX fuel or in fuel in the form of a metallic uranium-plutonium-zirconium alloy.

Broadly speaking, from a chemical perspective, MOX fuel is likely to possess similar characteristics to more conventional UO_2-based fuels (such as AGR or PWR fuel). The main physical difference between spent MOX fuel and conventional spent LWR UO_2 fuels is the presence, in spent MOX fuel, of plutonium-rich agglomerates [37]. Due to the presence of plutonium, MOX fuels have higher αβγ-decay activities (due to the ingrowth of americium daughters) and higher decay heats (at a given burn-up) than UO_2 fuels, as well as higher fission gas release (due to higher reactivity and in-reactor temperatures).

Fuel in metallic form is likely to possess physical and chemical characteristics similar to some exotic, plutonium-bearing fuels.

2.4 ILW and LLW

ILW and LLW are diverse in nature, ranging from large solid items to small particulate materials and sludges. Major constituents of ILW include metals, organics and concrete. The main fraction of LLW that may require geological disposal is graphite.

ILW and LLW form the majority of the waste inventory by mass that is to be disposed of in a GDF. These wastes comprise a large variety of materials with varied physical and chemical characteristics, but which can be described as materials (generally solids) that have been either contaminated due to direct contact with radioactive materials or activated due to their proximity to neutron sources (normally reactor cores). The major mass fraction of ILW/LLW is currently unconditioned [38].

The major components of the ILW/LLW inventory are metals (mostly stainless steels and other ferrous metals), graphite[10], concrete, cement and rubble, and sludges and flocs. Additional detail about the nature of these materials is provided below:

- steel items arise from a variety of sources, including reactor components and plant and equipment that were used during reactor and reprocessing operations
- most graphite arises in the form of moderator blocks from final stage reactor dismantling at Magnox and AGR power stations
- the concrete and rubble waste arises mostly from building decommissioning; although, in the case of ILW already packaged, cements used in waste immobilisation contribute a substantial volume for disposal
- most ion-exchange resins, sludges and flocculants arise from the treatment of liquid effluents and from the corrosion of stored Magnox fuel cladding ('swarf').

Other materials include various other metals (including Magnox, aluminium, Zircaloy and lead), and organics (particularly plastics, cellulosics and rubbers).

The materials more likely to be susceptible to evolution processes are those which present a degree of chemical reactivity, for example reactive metals such as Magnox, aluminium, uranium, and those that can decompose in the presence of environmental stressors, for

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[10] The major component of LLW that, due to its carbon-14 content, is unsuitable for surface disposal is reactor graphite.

example plastics or cellulosic materials. Examples of organic materials which are particularly important from the point of view of potential evolution of the wasteform include:

- plutonium contaminated materials (PCM), which typically include plastic gloves, metallic and plastic tools, filters, items of equipment, containers and protective clothing, all wrapped in polyvinyl chloride (PVC) [12]
- organic ion-exchange resins (used to filter and purify pond water where spent fuels are stored), including: polystyrene divinylbenzene resins (used to remove borate and treat AGR/Sizewell B pond waters), phenolic resins (used to remove caesium and strontium from Magnox pond waters), and acrylic resins [12].

Some of the materials described above are illustrated in Figure 8.

Figure 8: Examples of ILW: a) The cladding of Magnox fuel elements after size reduction (Magnox swarf); b) Parts of PWR fuel elements after size reduction (hulls and ends); c) Plutonium-contaminated materials (PCM)

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2.5 Uranium and Plutonium

There exists a large inventory of uranium and plutonium which may require disposal.

Uranium and plutonium exist, and are currently stored, in a variety of chemical forms. From the point of view of the evolution of waste packages, the chemical form is particularly important and is described in some detail in this section.

2.5.1 Uranium (DNLEU)

The uranium inventory consists mainly of large quantities of depleted uranium, significant quantities of natural and low-enriched uranium, and a small amount of highly-enriched uranium. The majority is likely to be disposed of as uranium oxides.

The great majority of the uranium currently considered for disposal in a GDF is depleted uranium (DU). Currently, DU stocks are mainly in the form of uranium hexafluoride (UF_6), a by-product of the uranium enrichment process used in the manufacture of nuclear fuels for AGR and PWR power stations. Current plans [39] are for conversion of UF_6 into a less chemically reactive form more suitable for storage and disposal (U_3O_8). Significant quantities of DU are also stored as UO_3, the form arising from reprocessing of spent Magnox and AGR fuel.

Natural and low-enriched uranium (LEU)[11] are also present in the inventory. These materials are used in their metallic form in Magnox reactor fuel (typically at natural enrichment, ~0.7 %). LEU is also used as uranium dioxide (UO_2) in the manufacture of AGR and PWR fuels (typically at an enrichment of 3-5 %) and arises as triuranium octoxide (U_3O_8) during reprocessing of these fuels. Natural uranium is in the form of UO_3, the form in which it is usually imported into the UK for the manufacture of nuclear fuels (before conversion to UF_6, enrichment and further conversion to UO_2). Together with depleted uranium residues remaining after the enrichment process (known as ‘tails’), these materials are sometimes referred to as depleted, natural and low-enriched uranium (DNLEU). The term DNLEU is employed in this report to describe this category of waste, while the term uranium is generally used to denote the uranics contained in other waste streams (such as ILW or metallic fuel).

Highly-enriched uranium (HEU) comprises residues from the manufacture of specialist nuclear fuels (such as those irradiated in research reactors), and their reprocessing, with enrichment levels greater than 20%. This material represents a small fraction of the disposal inventory and may either be used for other purposes or disposed of in a GDF. Currently, HEU is considered within the inventory of exotic fuels (section 2.3).

Overall, the majority of uranium is either in the form of a ceramic oxide (UO_2, UO_3 or U_3O_8) or as a gas (UF_6) which, before disposal, will have to be converted to a more stable form (current plans are to convert it into U_3O_8).

2.5.2 Plutonium

One option for the immobilisation of any plutonium that requires disposal (‘plutonium residues’) is incorporation in a ceramic or glass-ceramic wasteform.

Plutonium is currently stored in the UK in the form of PuO_2. In line with the NDA’s Plutonium Strategy [36], the current assumption is that any plutonium used in the manufacture of MOX fuel (currently the bulk of the inventory) will be irradiated in a new generation of nuclear reactors and will arise as spent fuel with the characteristics described in section 2.3. Other options for the management of plutonium include disposal in a suitable wasteform, including a glass/glass-ceramic product or as un-irradiated MOX fuel in a form not suitable for irradiation in reactor (‘storage’ or ‘low-specification’ [40])[12].

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[11] LEU is defined as uranium with a level of enrichment in the U-235 isotope below 20% (by mass). It is typically used in reactor fuel at enrichment levels below 5%. Highly enriched uranium (HEU), conversely, is enriched to levels higher than 20%.

[12] The pins and assemblies used for ‘storage MOX’, also referred to as ‘low specification MOX’, can be of a simpler design than those for ‘reactor specification’ MOX fuel, the purpose of ‘storage MOX’ being to immobilise for disposal rather than use in reactor.

Additionally, given the chemical and physical condition of some of the plutonium inventory (contaminated with a variety of other materials, generally referred to as ‘plutonium residues’), it is likely that at least a small fraction of this material will require immobilisation in a glass/glass-ceramic product. Research has been carried out to develop suitable wasteforms for plutonium in order to support future decisions over the disposition of this material. This is discussed in further detail in section 3.1.3.

In this document the evolution of plutonium in the form of (MOX) spent fuel is considered within the discussion of oxide spent fuel, whilst the evolution of plutonium in the form of a glass, glass ceramic or ceramic wasteform is discussed in the context of ‘plutonium residues’ as thermally-treated waste.

3 Processing of radioactive wastes

When required to achieve the desired characteristics, waste is conditioned using a suitable encapsulant and embedding medium[13]. For ILW, encapsulants such as cements and polymers have been used, or are being considered for future applications. Embedding in glass or glass ceramic materials through high temperature processes is also being considered. For HLW, embedding through a vitrification process has been used. Most spent fuels, on the other hand, do not require treatment as they already arise as solid, durable products. Some wastes may be disposed of without encapsulation if suitably robust waste containers are used. In general, the approach that should be used to treat, condition and package different types of radioactive wastes is described in the generic waste package specifications [41,42].

This section describes the media and processes used to immobilise some wastes, as well as the nature of any accompanying treatment (such as drying). The discussion focusses on ILW, for which a variety of immobilisation processes has been employed or is being considered. Spent fuels, DNLEU and plutonium residues are also discussed in some detail. HLW (including vitrification processes) was described in the previous section and is not considered further herein.

3.1 Encapsulation and embedding processes

For wastes requiring encapsulation or embedding, the choice of medium may include consideration of: immobilisation of radioactivity; chemical compatibility; radiation tolerance; stability; amount of voidage; and strength of the resulting wasteform.

When required (for example, if they arise as liquids or sludges), wastes have to be treated with suitable encapsulation or embedding processes to ensure their effective immobilisation. Encapsulation and embedding media are selected to ensure that the required product characteristics are achieved in an efficient manner. The characteristics that packaged waste need to achieve in order to meet the requirements for disposal in a GDF are described in the Waste Package Specifications [41,42]. A key consideration, reflecting international standards [43], is that wastes should be dried as far as practicable before containerisation in storage or disposal containers. This minimises the potential for detrimental evolution processes such as corrosion and pressurisation. Important characteristics of encapsulation and embedding media are described in Box 3.

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[13] In this document, the term ‘encapsulation media’ and ‘encapsulants’ are used to describe materials that can be employed to immobilise solid or liquid wastes through their flow and setting properties (for example, cement and polymers). The term ‘embedding media’ is used to describe materials which, through their physical and chemical properties, can be used to immobilise the radioactive content of wastes at a microstructural level (for example, glass or glass-ceramics). For the sake of simplicity, unless required for the sake of precision, we will generally use the term ‘encapsulants’ to describe media used for waste immobilisation.

Box 3 Factors considered in the choice of ILW immobilisation media

Immobilisation of radioactivity. The wasteform should immobilise radionuclides physically and/or chemically in a product able to contain them during interim storage, transport to a GDF and throughout its operational period, including accident conditions [7]. For the GDF post-closure period it is particularly advantageous if the wasteform is also able to immobilise the waste chemically, either in a durable product (for example, in a microstructure with low leaching rates), by creating chemical conditions limiting the solubility of the radionuclides in the groundwater, or by limiting the access of water to the waste.

Chemical compatibility. Any encapsulant or embedding medium used should be chemically compatible with the wastes being treated. Reactions that may affect the evolution of the wasteform on relevant timescales should be considered. Encapsulation and embedding media should also be chemically compatible with the materials used for waste containers and other components of a GDF (such as buffer and backfill).

Radiation tolerance. Ionising radiation may induce the chemical breakdown of materials through radiolysis. Any encapsulant or embedding medium used should be tolerant of radiation doses that may arise from the radioactive constituents of the waste and from surrounding waste packages. The nature of any products formed (for example, radiolytic gases) needs to be considered.

Stability, voidage and strength. The resulting wasteform should be stable and display physical integrity over the timescales required, and over the range of environmental conditions (including temperature) that may be experienced. The resulting wasteform should also have low voidage and adequate strength.

Flow properties. The encapsulating or embedding materials should be free-flowing at the time of treatment to give good penetration of waste materials with complex geometries. In the case of cements, the presence of superplasticisers may need to be controlled to avoid potential complexation with radionuclides [4].

Cost/resource usage. The materials used should provide a cost-effective approach to immobilising the radioactive wastes. The cost of waste packages is likely to represent a significant fraction of the overall disposal costs, and the availability of natural resources has important economic and ethical implications.

3.1.1 Cement-based wasteforms (ILW)

Cement has been extensively used for the immobilisation of ILW. Typical formulations use mixtures of ordinary Portland cement, together with other inert components, to obtain products with the required mechanical, flow and thermal properties. Three commonly used designs for waste packages are characterised by: in-drum mixing (typically for sludges), in-container grouting (for solid wastes), and wasteforms with a grouted annulus (for wastes previously subjected to compaction).

Encapsulation in cement has been used for the majority of ILW packaging that has been undertaken to date in the UK [38]. Cement encapsulation is also used for many wastes in overseas waste management programmes [44]. The cement encapsulation processes developed by the nuclear industry for ILW immobilisation fall into three broad categories [42, 45], as illustrated by the examples of the resulting wasteforms in Figure 9.

- **Category 1:** In-drum mixing of liquid or sludge wastes with the cement constituents, to form a relatively homogeneous wasteform which is then allowed to set

- **Category 2:** In-container grouting, where solid waste items are placed in a waste container and then in-filled with a fluid cement-based material
- **Category 3:** Annular grouted wasteforms, where the waste, often in the form of high-force compacted drums (or ‘pucks’), is surrounded by an inactive protective annulus of cement.

This set of conditioning processes, coupled with an appropriate cement formulation, allows many types of ILW to be immobilised successfully.

Different cement compositions can be used to achieve different flow properties to infiltrate and immobilise a variety of materials in a wide range of geometries. Encapsulation in cement is particularly suitable for the immobilisation of sludges, fine particulate and, in general, materials that do not undergo detrimental chemical reactions in contact with the cement porewater. Given that waste containers for ILW are typically designed in steels (see Section 9), the use of cement also mitigates the potential for internal corrosion of the waste container.

Cement-based materials used for the conditioning of radioactive waste in the UK are usually based on formulations containing blast furnace slag (BFS) or pulverised fuel ash (PFA), mixed with ordinary Portland cement (OPC) ([46], see also Box 4). Such wasteforms are characterised by a relatively high pH at room temperature (typically > 11.5)[14]. These formulations are used because they are :

- tolerant to a wide range of chemical constituents
- tolerant to substantial doses of radiation
- stable over the relevant range of temperature
- suitable for immobilisation of solid, slurry and liquid wastes
- capable of being designed to be free-flowing when freshly mixed, so they give good penetration into voids in drummed solid waste
- cost-effective
- able to produce (after curing) wasteforms that have low voidage, combined with adequate strength and low permeability
- able to slow the release of a number of radionuclides in groundwater, due to their effect on the solubility and sorption of relevant chemical species
- well understood, as they have been employed as construction materials for very long times (many millennia).

Lower pH formulations are also being investigated as possible encapsulants for those wastes that may undergo evolution reactions in the more alkaline environments provided by current OPC-based formulations (see Box 5).

A number of UK waste producers have considered the use of organic superplasticisers in grout formulations for ILW but, so far, these compounds have not generally been used due to concerns over their effects on the solubility of radionuclides in a GDF [4]. Recently, however, we have accepted the use of superplasticisers for some solid ILW and for the manufacture of concrete containers for ILW/LLW [4, 47].

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[14] In this document pH values described always refer to room temperature values, unless noted otherwise.

Figure 9: Different means of encapsulation of ILW in cement-based encapsulants

Category 1: In-drum mixed wasteform

Category 2: In-container grouted wasteform

Category 3: Annular grouted wasteform

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Box 4 Conventional cement encapsulants

In the UK, two types of cement encapsulants are used for the immobilisation of ILW: blends of Ordinary Portland Cement (OPC) with Blast Furnace Slag (BFS), or blends of OPC with Pulverised Fuel Ash (PFA).

OPC is the material most widely used in the construction industry. Its chemical composition can vary depending upon the source of the raw materials and the particular manufacturing plant. It consists essentially of calcium oxides, silicates and aluminates.

BFS is a by-product of the manufacture of iron. It is formed by the fusion of limestone (and/or dolomite) and other fluxes with the ash from coke and the siliceous and aluminous residues from the iron ore after reduction and separation of iron. This material is subsequently ground to produce a powder with a similar particle size to OPC.

PFA is a waste material produced during the burning of pulverised coal in a power station. After combustion, the ash is separated from effluent gases. The finer particle fraction, removed by electrostatic precipitation, is normally used for concreting and cementation purposes. The main chemical constituents are silica and alumina.

BFS and PFA are included in cement encapsulants because they produce cements with longer curing times, minimising the temperature increase that is associated with curing.

Box 5 Alternative cementitious encapsulants

Alternative cement formulations are also being considered for the encapsulation of ILW, particularly when concern exists that the alkalinity associated with OPC-based cements may be detrimental for some GDF components (such as clays). Examples of alternative, ‘low pH’ cement materials include [48]:

- calcium sulfoaluminate (CSA) cement, widely used for ~40 years in the construction industry worldwide. This type of cement has been used in China to encapsulate borate-contaminated ion-exchange resins and evaporator concentrates arising from PWR power plants, since borate inhibits the curing of OPC cements.
- calcium-aluminium cement (CAC), also widely used in construction industries worldwide.
- magnesium phosphate cement (MPC), produced by mixing fine-grained periclase (MgO) with phosphoric acid or monopotassium phosphate; the product is sometimes referred to as a cold ceramic.
- geopolymers, including SIAL®, made by mixing sodium silicate (hydrate) with metakaolin. In Slovakia, SIAL® has been used to treat radioactive sludges and sludge/resin mixtures from four nuclear power stations.
- chemically-bonded phosphate ceramics (CBPCs), used in South Africa for the immobilisation of wastes containing radionuclides such as iodine isotopes and ^{14}C.

3.1.2 Polymeric wasteforms (ILW)

Polymer encapsulants have been used or considered for the immobilisation of specific types of ILW. Advantages include their ability to infiltrate complex geometries and to provide a dry environment in contact with the waste.

For most ILW, encapsulation in a cement-based material is considered suitable, provided that detrimental reactions between the waste and the encapsulant do not occur. Such reactions can occur for some types of wastes due to the ‘wet’ environment provided by the cement porewater. For those wastes for which this may be an issue, such detrimental reactions can be avoided by providing a dry environment, using a water-free encapsulant such as an organic thermosetting polymer [49]. In particular, polymeric encapsulants can limit the corrosion of reactive metals such as aluminium, magnesium and uranium, which may present an issue for the stability of cement-based wasteforms over long timescales. Additional advantages offered by polymers include their capability to infiltrate fine voidage and immobilise fine particulate before any polymerisation reaction, which may be important for wastes that present a relatively complex geometry. However, ionising radiation can degrade many polymers (specifically, organic polymers), potentially compromising their immobilisation properties. Further details on these materials are provided in Box 6.

To date, in the UK, vinyl-ester styrene (VES) and epoxy resins have been used for the immobilisation of some wastes including ion exchange resins, radium-containing wastes and aluminium-clad fuel elements from the Harwell GLEEP[15] reactor. Examples of the use of polymeric encapsulants in the UK nuclear industry are provided in Figure 10.

Box 6 Polymeric encapsulants

Organic polymers are often classified into two groups, thermoplastics and thermosets. The main difference between the two groups is that thermoplastics become soft, re-mouldable and weldable when heated, whilst thermosets, once formed, cannot be welded or remoulded when heated. Once a thermoset has cured it tends to be more rigid and stronger and is therefore less flexible than a thermoplastic.

A number of polymers have been considered internationally for packaging radioactive wastes; bitumen, polyethylene, epoxy resins, polyester resin and urea formaldehyde have been the most extensively investigated [50]. Each has particular properties which may offer benefits in some applications. For example, bitumen has low leach rates and high resistance to radiolytic degradation, epoxy resins have good mechanical properties and are highly impermeable, polyester and vinyl ester resins can immobilise wastes containing considerable amounts of water. However, there are also some specific issues with their use, for example flammability or swelling in the presence of concentrated solutions (bitumen), hazards from individual constituents (for example, styrene) or the generation of potentially corrosive free liquids during curing (urea-formaldehyde). Bitumen and urea-formaldehyde resins have not been employed for general waste encapsulation in the UK.

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[15] Graphite Low-energy Experimental Pile.

Figure 10: Examples of polymeric encapsulants employed for the immobilisation of some ILW. Top: simulants of radium-contaminated waste encapsulated in VES. Bottom: heating block simulating effect of heat release from graphite (Wigner energy) on encapsulant (epoxy) and ability to infirm any heat-generated crack with further (yellow-coloured) resin

3.1.3 Glass and ceramic wasteforms (ILW and plutonium)

High-temperature processes are being considered for immobilising some ILW and plutonium. The resulting glass, glass-ceramic and ceramic materials can make a particularly durable wasteform.

In the UK, high temperature processes are being considered for the immobilisation of some types of ILW as well as for plutonium residues. The resulting glass, ceramic and glass-ceramic materials are less susceptible to degradation than cements or organic polymers and are likely to result in a particularly durable wasteform.

Wastes currently considered as potential candidates for high temperature processing include:

- solid wastes containing large quantities of organic materials, for example some plutonium contaminated materials (PCM) containing poly-vinyl chloride (PVC)
- solid wastes containing metals that tend to corrode in cement (such as Magnox and uranium), for example from legacy fuel skips
- sludges from radioactive liquid effluent treatment facilities (such as the ‘clinoptilolite/ sand’ wastes from the SIXEP plant at Sellafield), or recovered from spent-fuel storage ponds (for example, the Magnox Swarf Storage Silo at Sellafield)

- chemically-contaminated plutonium oxide and other associated materials unlikely to be used in the manufacture of fuel (plutonium residues).

Due to the high temperatures experienced during processing, some wastes are expected to undergo chemical reactions resulting in the loss of large quantities of volatile species, often leading to a large volume reduction. This contrasts with typical encapsulation processes, in which substantial volumes of encapsulant are added to immobilise the waste, leading to an increase in total volume. An overall reduction in chemical reactivity is also expected. In the case of streams containing large volumes of organic materials, removal of organic components will eliminate the risk of formation of water-soluble radionuclide complexants, non-aqueous phase liquids and gases, which may have detrimental effects on a GDF.

Thermally-treated wastes can be obtained through the addition of glass- or ceramic-forming materials to the waste. In some cases, the wastes themselves contain glass- or ceramic-forming materials. Feedstocks of glass-forming materials currently considered for use in ILW thermal treatment processes vary depending on the type of waste and the specific process under consideration. For example, soda-lime glasses and alumino-silicate materials, have been used in process trials. The resulting glassy products differ from the borosilicate glasses typically employed for HLW. In most cases, given the diverse nature of ILW and the co-existence in the same waste stream of different components, the application of high temperature processes to ILW is likely to lead to the formation of heterogeneous glass or glass-ceramic materials, in which crystalline solids are embedded in a glassy or crystalline matrix. In other cases, processes leading to the development of fully ceramic wasteforms may be considered. Examples of thermally-treated glass or ceramic products obtained from the treatment of ILW simulants are presented in Figure 11 and Figure 12.

In the case of plutonium residues, options for high temperature processes currently focus on Hot Isostatic Pressing (HIP), conceived to either embed the wastes in a ceramic/glass-ceramic matrix (zirconolite- or pyrochlore-based, see [51, 52, 53]) or a metallic matrix[16].

Additional details about these processes are provided in Box 7.

Figure 11: Borosilicate glass incorporating surrogates of Magnox sludge and plutonium-contaminated waste. The glass block is about 15 cm by 10 cm

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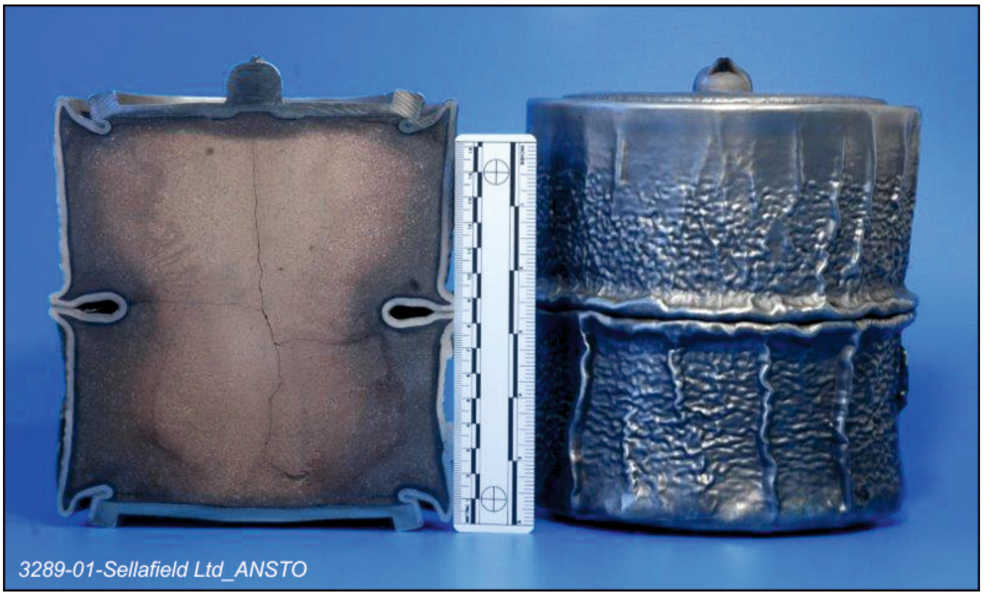
[16] For plutonium residues, waste encapsulated in a metal matrix (aluminium or copper-based) is also being considered. This is not discussed further in this report as it is at a very early stage of development.

Figure 12: Ceramic from Magnox sludge surrogate (magnesium silicates and titanates), formed by Hot Isostatic Pressing (HIP) – see Box 7. The length of the scale is 15 cm



Box 7 High temperature processes for the immobilisation of ILW and plutonium

A variety of potential technologies for high temperature processes is currently being considered to treat specific ILW streams and plutonium residues. These have been summarised [54] as:

Joule-heated ceramic melters (ILW) in which, after mixing with glass frit and additives inside a refractory-lined reaction vessel, the waste is melted by the insertion of reusable electrodes. Application of a 'cold cap' reduces the loss of volatile radionuclides from the melt. The process generally requires a homogeneous waste feed such as a slurry.

In container vitrification / in situ vitrification (ILW) in which sacrificial electrodes are inserted into contaminated ground (in-situ) or inside a vessel containing radioactive wastes (in-container). In common with the previous process a high electrical current is applied, generating a very high temperature (of the order of 1800 °C) that melts the waste/soil, creating a melt pool. To 2012, over 26,000 tonnes of waste had been processed in the US, Australia and Japan using this process.

Induction melters (ILW) in which an external radio frequency field is used to create induction currents inside a metallic reaction vessel containing waste and ceramic or glass additives. In a variant called the 'cold crucible melter concept', the inner surface of the metallic container is deliberately cooled to form a protective non-reactive layer (a 'skull'), allowing corrosive or refractory wastes to be processed. A plant utilising the 'cold crucible' concept was built in Russia in 1999 and was used to vitrify LLW/ILW evaporator concentrates and reboiler residues into a borosilicate glass product, suitable for packaging and disposal [55].

Plasma Melters (ILW) in which an electrical discharge between an anode and cathode (called 'torches') melts the waste, forming a melt pool. Typically the plasma temperatures may be as high as 5000 °C and require an additional plant to capture the off-gases generated. The systems are either referred to as 'transferred' (in which the melt pool acts as the cathode - also referred to as 'Plasma Torch' technology), or 'non-transferred' (in which the electric arc created utilises an ionising gas to transfer heat into the melt pool - also referred to as 'DC Plasma Arc' technology). The Zwilag plant in Switzerland has been operating this technology as a commercial facility since 2004. To the end of 2013, this plant had treated 1300 tonnes of waste (~8000 drums) [56].

Hot Isostatic Pressing (plutonium) in which the waste is calcined (to remove volatile components), then placed inside a metallic container with a homogeneous feed of ceramic or ceramic-glass additives. The vessel is heated at temperatures up to 1300 °C and is pressurised at 10-200 MPa under an inert cover gas. The solid components melt or undergo solid state reactions to form a ceramic or glass-ceramic wasteform with minimum internal voidage/porosity as the metal walls deform inwards to produce a packaged product of nearly theoretical density [54]. The technology has been trialled at Sellafield for the treatment of plutonium residues (ILW), using waste simulants doped with uranium and other relevant radionuclides, for example Tc-99 and Cs-137 [57].

3.2 Non-encapsulated waste (ILW/LLW, spent fuels)

Some wastes will be packaged without encapsulation. This is suitable when the radionuclides are contained within large solids of chemically-stable material, but may also be acceptable for other wastes provided a robust container is used. The use of void fillers may also be required in this case.

When the waste arises as a bulk, stable solid, the waste itself can provide immobilisation of the radionuclides without additional treatment. Examples of waste which may not require encapsulation are oxide spent fuels, LLW graphite blocks, and large metallic neutron-activated ILW items.

Potentially, other wastes (including those which may degrade over relevant timescales or which arise as items of relatively small size) could also be packaged without encapsulation. For this option to be viable, a particularly robust container may need to be used to provide durability and accident performance [7]. It may be also important to fill waste packages void fillers to limit the introduction of voidage in a GDF, which may affect its mechanical stability.

In general, for non-encapsulated wastes, the evolution of the waste will need to ensure that the functionality of the container is not compromised. For this reason, ensuring that waste materials are dry is an important factor. In specific circumstances (typically to drive hazard reduction in specific facilities), the UK nuclear industry is pursuing containerisation of wet, non-encapsulated wastes, which may present specific challenges when considering their likely evolution processes.

3.2.1 Spent fuel

Spent fuels arising as stable solids require drying if they have been stored in water for cooling. Fuel that has degraded to various degrees may need further immobilisation.

Upon discharge from a reactor, spent fuels arise as solids requiring cooling. For the vast majority of fuels the UK has pursued a ‘wet storage’ strategy, with fuel stored in water (cooling) ponds.

AGR fuel is stored in cooling ponds at reactor sites before being transferred to Sellafield for further (longer) periods of storage, pending reprocessing or disposal. Such fuel has been generally stored in controlled chemical conditions. Upon retrieval from cooling ponds (either for dry storage and/or disposal) such fuel will need to be dried.

PWR fuel has been stored in water ponds at its site of arising (Sizewell B). Upon retrieval and containerisation for dry storage (currently planned) and subsequent disposal, this fuel will also need drying.

Metallic and exotic fuels have been stored in a variety of conditions (including water ponds) and, over time, have been subjected to various degrees of degradation. Upon retrieval and containerisation, due to their state and inherent reactivity, some of these fuels may require further treatment.

Waste management strategies for other spent fuels that may arise in the future (including any LWR fuel from new power stations and fuel from the reuse of plutonium) are currently not well defined, but are likely to be similar to those currently in place for other spent fuels.

3.2.2 Graphite and other ILW

Graphite, assumed to arise in large blocks during final stage decommissioning of gas-cooled reactors, is a stable and durable wasteform; further immobilisation processing before storage and disposal is unlikely to be required. Other large-size components (ILW) may be also packaged without further immobilisation.

Graphite, assumed to arise in large blocks, represents a significant fraction in volume of the UK ILW inventory. Graphite also comprises the largest volumes of LLW currently planned for disposal in a GDF. With some exceptions, graphite is generally dry and, as such, may not require any pre-treatment before storage and/or disposal. Additional information about the nature of the UK graphite inventory is provided in Box 8. A variety of large-sized, neutron-activated, plant items or components (ILW), especially when made in corrosion resistant materials such as stainless steel, may also be suitable for non-encapsulation.

Box 8 Graphite

In the UK, irradiated graphite wastes comprise six main types:

- Magnox reactor core graphite
- AGR reactor core graphite
- graphite sleeves (Hunterston A and AGR reactors)
- graphite struts (Berkeley)
- core graphite from research reactors, for example, GLEEP at Harwell
- core graphite from the Windscale Piles.

Graphite is a stable and durable wasteform and further immobilisation before storage and/or disposal is unlikely to be required.

3.2.3 DNLEU

Uranium is likely to arise or to be transformed to solid powders which may not require immobilisation due to their low hazard potential.

Any DNLEU destined for disposal is likely to arise either as a solid powder (uranium oxides), or to require processing into a solid (mainly in the case of UF_6, which is likely to be converted to U_3O_8). A range of disposal options for DNLEU is currently being evaluated [58], including overpacking of the current storage mild steel containers (containing DNLEU in the form of powders) in more robust and durable waste packages. Despite the fact that powders are potentially mobile, the low toxicity of these materials is such that further immobilisation treatments may not be required.

Among alternatives, the use of cement grouts to intimately immobilise the waste followed by packaging in stainless steel containers is also being evaluated. In alternative, a wasteform comprising uranium oxide powder in its existing storage containers but subsequently entombed in cement could be employed to reduce the amount of voidage likely to be present in disposal concepts envisaging the use of existing storage containers.

4 Environmental conditions during waste management

This section describes the environmental conditions to which waste packages will be exposed during periods preceding and following disposal. This information is necessary to evaluate the processes likely to operate on waste packages during those periods.

The description of environmental conditions present during periods of interim storage is largely presented for completeness and to provide confidence in the feasibility of preserving waste packages in good condition, able to meet future conditions of acceptance of the GDF. Information about the environmental conditions in specific surface facilities is beyond the scope of this report and is not described in detail.

Environmental conditions during the operational and post-closure period of a GDF are central to the evolution of waste packages in a GDF. However, in the absence of a specific disposal site, and considering the range of disposal concepts currently considered in the UK, the information presented provides a general description of key environmental factors and their anticipated ranges. In particular, key environmental parameters such as the timing of resaturation and the chemical composition of groundwater will depend on the nature of the disposal site, whilst the temperature of waste packages and the nature of the buffer/backfill materials employed will depend on the disposal concept and the design of the GDF.

Information herein focuses on HLW, spent fuel and ILW/LLW, for which waste management strategies are more advanced. It is likely that the environmental conditions for plutonium residues and DNLEU will be similar to that for HLW/spent fuel and ILW/LLW respectively.

4.1 Environmental conditions during interim storage and the operational period of the GDF

Prior to closure of the GDF, the key environmental conditions affecting the evolution of waste packages are the temperature and chemistry of the environment, and the relative humidity.

The key factors affecting the potential evolution of wasteforms and waste containers during periods preceding closure of the GDF (such as, exposure to atmospheric conditions or to controlled water chemistry in the case of some spent fuels) include the temperature, the chemistry of the environment and, in the case of atmospheric conditions, the relative humidity. These are discussed in some detail below.

For wastes packaged in containers intended for both interim storage and disposal (typically ILW/LLW and possibly DNLEU), these factors largely affect the degradation of waste containers, unless a vented container is used (generally ILW/LLW). For materials which are likely to require further containerisation before disposal in the GDF (HLW and spent fuels), conditions during interim storage are likely to affect the evolution of the wasteform and any storage containers, while conditions during the operational period of the GDF are likely to affect the evolution of the disposal containers/overpacks[17].

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[17] When a difference exists (for example in the case of HLW and, where appropriate, spent fuels), this document refers separately to the case of ‘storage containers’ and ‘disposal containers’. In the case of ILW/LLW (where the same container is typically envisaged for both purposes), when generalising or discussing together the case of ILW/LLW and HLW/spent fuels, or at times when describing HLW and spent fuel disposal, this document refers to ‘waste containers’. In specific cases, particularly to emphasise aspects of specific design featuring internal and external containers, the text refers to ‘overpacks’. As a general rule, when discussing disposal, the text often refers interchangeably to ‘waste containers’ or ‘disposal containers’.

4.1.1 HLW and spent fuel

The HLW store is designed to limit corrosion of the canisters. High temperature and low relative humidity are expected. Spent fuel may be stored under water to limit degradation, or alternatively in dry conditions using overpacks, again limiting degradation. Conditions during the operational period of the GDF are currently not fully defined and will largely depend on the site and disposal concept(s) envisaged.

Environmental conditions for HLW and spent fuel during periods preceding closure of the GDF will largely depend on the waste management routes considered for these materials.

HLW is currently stored in dry conditions in a purpose-built facility, the Vitrified Product Store (VPS) at Sellafield. Due to the heat-generating nature of the waste, high temperatures arise and will be maintained throughout the interim storage period. The WVP canisters are stored in vertical channels (containing up to 10 canisters), cooled by natural air convection currents around the outside of the channels [20]. As a result of cooling, the external temperature of each canister (about 100 °C in absolute terms) is significantly lower than the core temperature of the glass (which may be as high as 480 °C upon emplacement). These elevated temperatures result in a low surface relative humidity during storage, expected to limit corrosion of the stainless steel canisters in which the HLW is packaged.

The majority of spent fuels are currently stored in cooling ponds, either at the site at which they arise or at Sellafield. AGR fuel is stored in ponds with controlled water chemistry, typically with alkaline pH (around 11.4), controlled chloride levels (<0.1 ppm), and a temperature below 23 °C. Some legacy fuels, including some metallic and exotic fuels, have been stored in open ponds with poorly controlled chemistry. In these conditions, some fuel has degraded substantially.

Some spent fuels (predominantly PWR fuel) have been, or will be, stored in dry conditions pending disposal. It is also possible that, in the future, AGR fuel may be transferred to a dry storage regime. During dry storage, at least for PWR fuel and any AGR fuel, environmental conditions are not expected to be conducive to promoting alteration processes in the wasteform.

Both HLW and spent fuel will require over-packing into a disposal container before emplacement in the GDF. The environmental conditions experienced during the GDF's operational period will largely depend on the packaging and disposal concept pursued, particularly the packing density inside the disposal containers, the age of the wasteform at the time of emplacement (hence, the decay time), and the nature of operations at the GDF.

In concepts envisaging prompt emplacement in deposition holes in contact with a buffer, environmental conditions will be similar to those expected in the early post-closure period (see Section 4.2), although the ingress of oxygen inside unsealed tunnels may be an important factor in evaluating the likely evolution of waste containers in conditions of prolonged operations.

In concepts envisaging underground storage in vaults for long periods before backfilling and closure of the GDF conditions will be similar to those expected during any preceding periods of dry storage, although the temperature, relative humidity and composition/level of surface contaminants may differ between surface storage facilities and the GDF. The current specification for the GDF prescribes a maximum air temperature of 50 °C and a maximum relative humidity of 90% to ensure the long-term operability of the electrical equipment (for example, the cranes) and to mitigate the degradation of the waste packages and infrastructure [59]. The temperature of waste packages will however be much higher, and largely dependent on the time of disposal and the nature of the disposal concept. In relatively bounding situations (disposal in Multi-Purpose Containers containing twelve PWR assemblies), temperatures up to 300 °C have been evaluated [60].

4.1.2 ILW/LLW

Surface stores for ILW and LLW are typically designed to limit degradation of the waste packages. Temperature between 0-30 °C and relative humidity around 20-90% are expected. Conditions during the operational period of a GDF are currently not fully defined and depend on the site and concept.

During surface storage and the operational phase of a GDF, ILW/LLW packages will remain in indoor facilities, where the potential exposure to water, high temperatures, corrosive chemical species (such as acids and marine aerosols) and nutrients able to sustain microbial activity will be relatively limited.

In the UK, as well as in other countries, ILW/LLW stores are generally designed to keep the temperature of the environment above the dew point, thus preventing the potential for 'bulk' condensation of water to occur [61, 62]. The absence of a bulk water phase on the surface of waste packages is particularly important since, in these conditions, the potential for degradation to occur is limited.

Some surface stores (especially modern ones) may also be designed to filter the inlet air (to remove aerosols) and to minimise contamination of the packages with organic materials. Guidance developed by the UK nuclear industry [63] describes how minimisation of contamination by chlorides and organic species can be achieved by appropriate operational procedures (for example, empty containers and contact-handled packages should only be touched with gloves) and store design (such as, filtering of inlet air with high efficiency HEPA filters).

Initial studies of the environmental conditions (particularly the nature of surface contaminants) present and likely to develop in some interim stores in the UK have been recently completed [64, 65]. The results of these studies indicate that temperature and relative humidity are likely to be subject to daily and seasonal fluctuations, with temperatures typically in the range 0-30°C and relative humidity in the range 20-90%, and averages of the order of 10-15 °C and 60-70% respectively. A variety of ionic species are typically found on surfaces (mainly chlorides, sulfates, nitrates and carbonates), with deposition densities (for each species) typically below 10 μg cm^{-2}. These values are lower than the values expected to be potentially conducive to the onset of degradation of the stainless steel typically employed for the manufacture of ILW containers [63] (based on info presented in Box 31).

Broadly similar conditions are expected in GDF disposal vaults, although higher temperatures (due to the geothermal gradient) and higher relative humidity (due to the humid nature of some underground environments) may be present in this case. Requirements on control of the environmental conditions in a GDF are included in the facility specification [59], including the operational temperature, relative humidity and aerosol filtration. The current specification for the ventilation system requires the temperature to be maintained below 50 °C, the relative humidity below 90%, and the use of HEPA filters to control aerosol contamination [59].

Specific information about environmental conditions in a UK GDF is likely to be site-specific and is hence currently unavailable. One of the studies described above, however, included measurements in underground facilities potentially relevant to an operational GDF [65].

4.2 Environmental conditions during the post-closure period of a GDF

Following closure of the GDF the key environmental conditions affecting the evolution of waste packages are temperature, groundwater chemistry, redox potential and mechanical stresses.

The key factors affecting the potential evolution of wasteforms and waste containers during the period following closure of a GDF (including initial exposure to unsaturated and, later on, saturated conditions) include the temperature, the chemistry of the environment (groundwater chemistry and nature of buffer/backfill material), the redox potential and, depending on the characteristics of the host rock and the disposal concept, mechanical stresses. These are discussed in some detailed below.

4.2.1 HLW and spent fuel

Following closure, HLW and spent fuel packages will be in fairly benign chemical conditions. Upon resaturation, in certain host rocks, the environment may become more corrosive due to the chloride and sulphide content of groundwater. It is anticipated that the UK GDF for HLW and spent fuel will be designed with a maximum temperature limit of about 100-200 °C.

At GDF closure disposal containers may experience either relatively dry conditions (such as in an evaporite host geological environment, where a rock backfill material will be used) or will be in contact with wet buffer materials (if cement or bentonite is used). In either case, the corrosivity of the environment towards waste package materials will be very limited, either due to the lack of water, or to the benign chemical conditions, respectively. Typical compositions of bentonites used in HLW and spent fuel disposal concepts are described in [66].

Some oxygen is likely to be entrapped in the facility at this time, leading to redox conditions initially similar to those of naturally aerated systems. Estimates of the maximum amount of oxygen potentially trapped in the GDF after closure can be used to evaluate the maximum amount of corrosion expected on waste containers during this period (often referred to as the ‘early post-closure period’). For HLW and spent fuel containers, for example, values of the order of 500 moles O_2 per waste container have been estimated in a specific disposal concept [67]. Values of the order of 1-10 mol per m^2 surface area of the container, amounting to a maximum depth of corrosion of the order of 10-100 µm if uniformly distributed over the container, were estimated in another study [68]. Over time, however, anoxic conditions will be established [69].

Upon resaturation, the salinity of the inflowing groundwater is likely to increase the corrosivity of the environment. The timescales over which resaturation is expected to occur are highly site-specific [3]. In some environments (for example an evaporite rock), resaturation may not occur at all [3]. The chloride and sulphide content will be particularly important to its corrosivity towards most metals, whilst sulfate is likely to be important for concrete containers. The chloride content of UK groundwater can range very substantially depending on location, from relatively low values up to values of the order of 10,000-100,000 mg L^{-1} (10,000-100,000s of ppm) [70]. The concentration of trace species (such as sulfide) of particular interest to the degradation of some materials is likely to be much lower, with current estimates of the order of less than 0.1 mg L^{-1} (< 0.1 ppm) [70,71].

In the case of high heat generating wastes the temperature of the environment during the post-closure period will be determined by the thermal output of waste packages, their packaging density, the thermal characteristics of the EBS materials and the host rock and the host rock’s natural temperature. We have recently developed a thermal dimensioning tool to enable us to evaluate likely temperatures in a UK GDF, taking into account the thermal characteristics of UK wastes and disposal concepts under consideration [60].

This tool is being used to guide the design of the GDF to take into account specific thermal limits required to retain the properties of some buffer materials, particularly clays. Current thermal limits at the container/buffer interface range from 100 °C (for an EBS employing a swelling bentonite clay), to 125 °C in the middle of the buffer (for an EBS employing a bentonite buffer, but allowing for some thermal alteration), up to 200 °C (for disposal in an evaporite rock employing a crushed salt backfill) [59, 60]. Limits on cement buffers that may be employed in other disposal concepts are not currently defined in the UK [59, 60], although a recent review of the performance of cement at high temperature indicated that it may be possible to design cements able to withstand relatively high temperatures (>100 °C) [72]. Whilst the designs of waste containers and disposal tunnels will need to comply with such limits, they will also need to ensure that, other constraints being achieved (such as rock mechanics requirements on tunnel spacing), packing efficiency and layout of a GDF are optimised to accommodate as much heat as possible in the available space. As a consequence it is likely that waste packages will experience temperatures relatively close to the thermal limits of the disposal concepts in question.

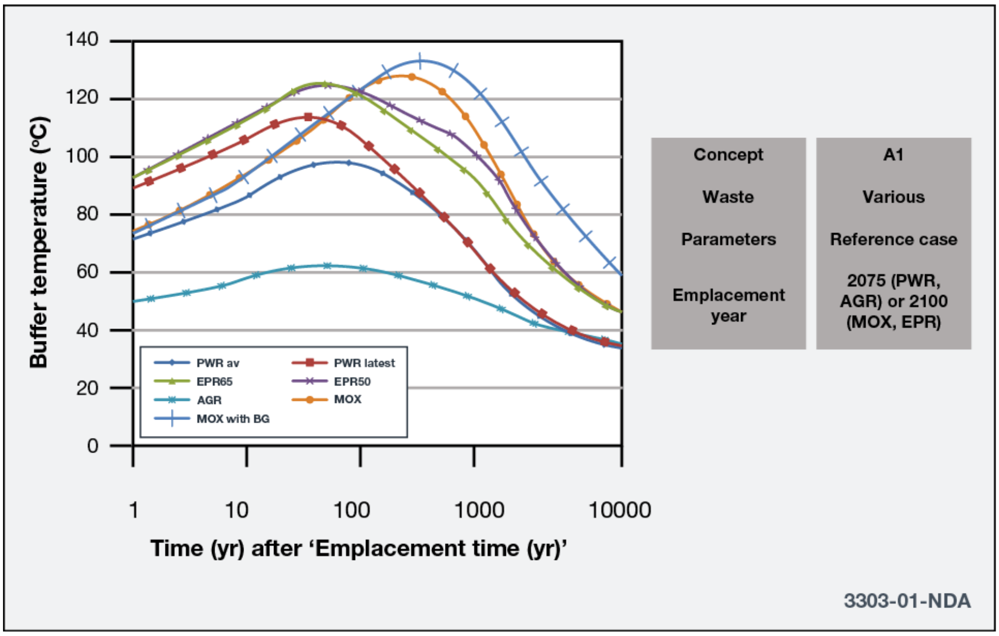
Detailed calculations of the likely thermal evolution of disposal modules containing HLW and a variety of spent fuel have been carried out for a number of disposal concepts, based on the thermal characteristics of UK wastes [60]. These calculations indicate that temperatures in the range 80-200 °C are expected on the surface of disposal containers in the early post-closure period, depending on the nature of the waste, disposal concept and GDF design. An example of such calculations, aimed at illustrating the effect of different types of wastes on the temperature of a GDF, is illustrated in Figure 13. The figure shows the evolution of the temperature at the container surface for a variety of spent fuels in a concept envisaging disposal in a copper disposal container in bentonite-filled vertical boreholes (see Section 9.2).

Whilst high temperatures will be retained in the EBS for long periods of time and will start to decrease significantly only after radioactive decay has substantially decreased the radionuclide inventory of the wastes, the redox potential of the environment will decrease over a shorter timescale. As an illustration, Figure 14 shows an example of the conceptual evolution of temperature and redox conditions evaluated in the Canadian programme [73]. The figure shows how the temperature remains relatively high for about 1000 years, before slowly starting to decrease. This period, often described as the ‘thermal period’, is particularly important for heat generating waste (such as HLW and spent fuel) and the current specification of a UK GDF requires waste packages to maintain their integrity at least over this period [59]. The decrease to ambient levels will generally require of the order of 10,000 years. A period of the order of at least 10,000 years is typically expected before perforation of the waste container occurs (see Section 11.2). As a result, temperatures up to 40 °C (the temperature assumed at the assumed depth of disposal) are expected at the time of container breach. This is important for evaluating the likely behaviour of the wasteform upon exposure to groundwater.

The redox conditions, conversely, are expected to become reducing over periods of tens to hundreds of years and then remain reducing over the foreseeable future. Waste containers for HLW and spent fuel are currently designed to ensure that dose rates outside them are below 1 Gy h^{-1} [74, 67]. At this level, effects on container materials are expected to be negligible. Dose rates inside waste containers, however, may be important in evaluating the evolution of the wasteform once the container has been breached. The doses rate of HLW and spent fuel diminishes substantially (by a factor of about 1,000) over a period of approximately 300 years, corresponding to ten half-lives of the major γ-emitters ^{137}Cs and ^{90}Sr. Alpha activities of the order of 10^{13}-10^{14} Bq/teU are nevertheless expected after thousands of years [75], the minimal lifetime generally expected from HLW/SF containers (see Section 10). Conversely, the influence of gamma or beta radiolysis on the creation of any oxidized species in contact with waste package materials is expected to be negligible, due to the large amounts of hydrogen dissolved in the water as a result of the corrosion of steels present inside disposal containers [76, 77, 78]. Hydrogen pressures of the order of 1-10 MPa are generally expected [78,79].

In disposal concepts for HLW and spent fuel employing cement-based materials, the pH of the system and its evolution with time will be important. Understanding of the evolution of a cement buffer in the geochemical conditions expected in the Belgian disposal programme [80] suggests that the pH will remain high (above pH 12.5, at 25°C[18]) for tens of thousands of years[19]. These estimates are similar to those developed in the UK programme relative to the likely evolution of cement-based backfills for ILW [2].

Figure 13: Illustration of thermal calculations for a variety of spent fuel types (including different levels of burn-up), following disposal in a copper-based container emplaced in a bentonite-filled vertical borehole [60][20]



Mechanical loads may also be important when evaluating the evolution of waste packages, particularly for disposal containers. Mechanical factors are particularly important for disposal concepts in which creep (copper-based systems) and hydrogen embrittlement (carbon steel or titanium-based systems) may be expected.

After closure of the GDF the most significant sources of mechanical loads are likely to be the hydrostatic loads associated with resaturation and the lithostatic load associated with creep of the host rock (particularly for some rock types), as well as any loads that may be associated with the swelling of specific buffer materials (such as bentonite clays). In some cases (for example, spent fuels in which entrained water is present, see below), internal loads from gas pressurisation could also arise. The magnitude and timing of the mechanical loads on waste containers will depend on the disposal concept, the host geological environment, and its likely evolution. Work recently carried out in the UK programme to evaluate the implications of voidage in a GDF considers the expected mechanical loads in a variety of geological environments [81].

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[18] Unless otherwise stated, pH values quoted in this report are the values that would be measured at 25°C.

[19] The calculations did not consider the potential for pore clogging, which may have an important effect on the rate of pH evolution.

[20] The calculations assume different times of emplacement for different fuel types (2075 for AGR/PWR and 2100 for EPR/MOX fuel) and different fuel loadings inside a disposal container (48 AGR fuel elements, 4 PWR fuel elements, 3-4 EPR fuel elements, or 1 MOX fuel element) as well as other specific design parameters (such as tunnels spacing). Concept A1 refers to disposal in a copper-based container emplaced in a bentonite-filled vertical borehole.

The likely mechanical loads on a disposal container in a Swiss GDF are shown in Figure 15 for a single-shell carbon steel HLW/SF container located at a maximum depth of 900 m in Opalinus clay [82, 83]. In the analysis shown in Figure 15, disposal tunnels tends to close prior to saturation due to creep of the host rock, resulting in a lithostatic load of 1.8-2 MPa. Saturation of the bentonite subsequently results in an additional load of a maximum of 4 MPa, assumed to develop over a period of approximately 100 years. Over relatively long timescales, the Opalinus clay gradually deforms and compacts the bentonite, resulting in a maximum isotropic load of 22 MPa for tunnels aligned parallel to the direction of maximum stress in the rock (lower red diamond in Figure 15). As an extreme bounding case (unlikely scenario), for tunnels aligned perpendicular to the maximum rock stress, and assuming a bentonite stiffness equal to that of the rock, an anisotropic load between 22 MPa (vertical) and 29 MPa (horizontal) was evaluated.

Figure 14: An illustration of the evolution of temperature and redox conditions in the EBS in the Canadian disposal concept for spent fuel [73]

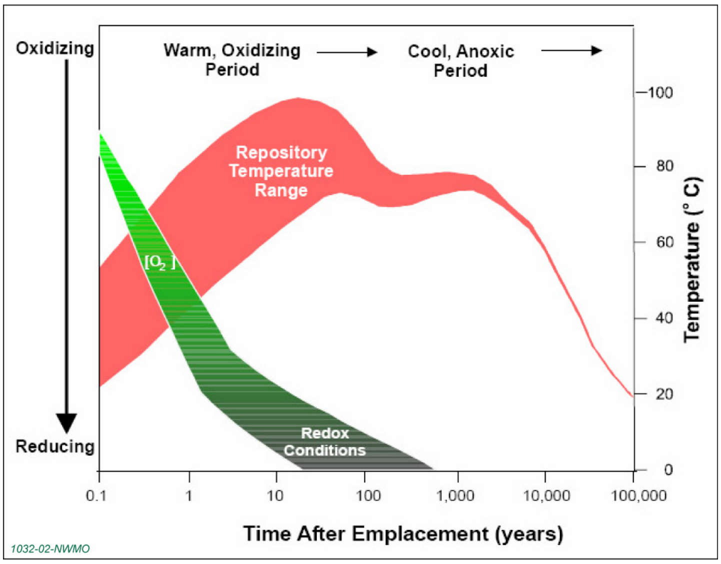
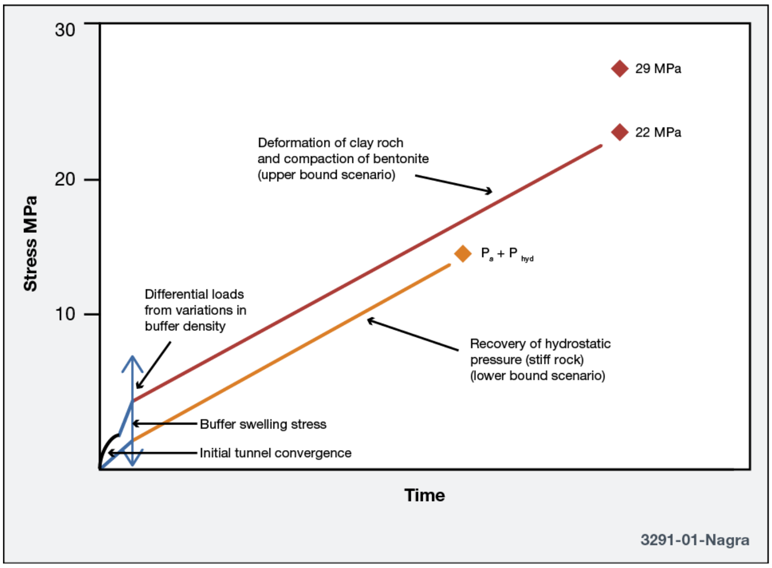


Figure 15: Possible evolution of stresses experienced by a disposal container emplaced within a bentonite backfill in an Opalinus clay repository at a depth of 900m [83]



Overall, particularly from a chemical point of view, the initial period after groundwater resaturation is likely to be the most challenging for the durability of waste containers and (if they were to degrade) for the wasteforms contained therein, as saline water and relatively high temperatures may be present in the system. The redox conditions present at this time will depend on the rates of resaturation and oxygen consumption. As oxygen is consumed, and as the temperature decreases, the corrosivity of the environment will decrease substantially. Apart from these factors, degradation processes will depend on specific chemical species being available in the groundwater or produced by the metabolism of viable micro-organisms in the vicinity of waste packages.

4.2.2 ILW/LLW

Following closure, resaturation will take place and more corrosive conditions will develop. In concepts employing a cement backfill the groundwater is expected to be buffered to (room temperature) pH levels above 12.5 for tens of thousands of years. Thermal guidance levels currently assume average long-term maximum temperatures of 50 °C, with peak temperatures up to 80 °C (for five years) for particularly hot areas of the backfill.

Broadly speaking, the chemical conditions experienced by ILW/LLW packages post-closure are likely to be similar to those of HLW and spent fuel packages. Important differences however may be associated with the use of buffer/backfill materials and expected thermal profiles.

Following closure but before resaturation with groundwater, waste packages may experience either relatively dry conditions (if dry backfill materials are used) or wet, benign conditions (if cement is used as a backfill). Porewater compositions expected in ILW cement backfills are described in [84], with typical pH levels (at room temperature) greater than 12.5-13 and low chloride concentrations. In either case, the corrosivity of the environment towards waste package materials (such as steels and concrete) will be very limited, either due to the lack of water, or due to the benign effect of low-salinity, alkaline conditions. Some oxygen is likely to be entrapped in the facility at this time, leading to redox conditions initially similar to those of naturally aerated systems. Over time, however, anoxic conditions will be established.

After resaturation, the salinity of the groundwater is likely to increase the corrosivity of the environment. Information on the chemical composition of UK groundwaters is provided in Section 4.2.1. The chloride and sulphide/thiosulfate content will be particularly important in determining the corrosivity towards steels, while the sulfate content may affect the evolution of concrete packages.

The temperature of ILW vaults after closure of a GDF will largely depend on the rock temperature, as well as on the heat generation associated with the curing of cementitious materials that may be employed to backfill disposal vaults. Thermal models of the evolution of ILW vaults backfilled with cement indicate short-term peak temperatures of 40-50 °C (depending on depth and host rock temperature), developed and gradually dissipated over periods of the order of ten years [2, 85]. These models also indicate long-term peak temperatures associated with radiogenic heat of the order of 40 °C in the case of packages generating levels of heat representative of the average UK inventory at the time of disposal (of the order of 0.5 W m^{-3}) and between 50-60 °C for particularly hot packages, developed over a few hundreds of years [85]. Thermal targets of 80 °C for periods up to five years are currently considered in the GDF specification [42,59]. These values are compatible with vaults in which the average heat output is one order of magnitude higher than the average heat output of waste packages (about 6 W m^{-3}, currently used as a screening level for waste packages [42]), or with vaults in which particularly hot packages (up to about 100 W m^{-3}) are dispersed among packages generating lower amounts of heat [42].

Overall, the corrosivity of the environment towards metallic waste containers will depend on the use (or not) of cement-based backfills and on whether, at the time of resaturation with saline groundwater, aerobic conditions will or will not be present in the system. Estimates of groundwater resaturation in ILW vaults, in the case of rock with relatively high permeability, indicate that full saturation of a vault is expected to occur over tens or hundreds of years [2]; a timescale over which low (anaerobic) redox conditions may or may not yet have been established. However, emerging research indicates that, in cement-backfilled ILW modules, resaturation may not be immediately accompanied by increase in salinity in contact with waste packages, since low-salinity water present in the backfill may be 'pushed' towards waste containers as the resaturation front progresses [86]. This may be particularly important since, even in a host rock in which resaturation processes were fast, contact of saline water with waste packages may occur long times after disposal (of the order of a thousand years based on [86]), at a time in which oxygen may have been consumed by other evolution processes. For concrete containers, the redox conditions are less important; groundwater salinity (particularly the sulfate content) being the most important factor.

In the long-term, once anaerobic conditions have been established, the corrosivity of the environment will largely depend on the pH evolution of the system. It is likely that the pH will be buffered to values above 12.5 for tens of thousands of years, maintaining a benign chemical environment for waste containers. Models of the pH evolution are described in detail in [2].

As for HLW and spent fuel packages, mechanical stresses on ILW packages will largely depend on the host rock and the disposal concepts. In concepts envisaging the use of porous cement-based backfills, however, mechanical stresses may be largely hydrostatic and hence more uniform and lower in intensity than in concepts employing clay backfills, typically considered in HLW and spent fuel disposal systems [81].

4.3 Environmental conditions inside waste packages

The environmental conditions inside a waste package will largely depend on the type of waste and how it has been processed. Key factors include the temperature, the radiation dose rate and the presence of water.

The evolution processes that may occur within a waste package, and the factors affecting them (abundance of water, oxygen, pH, etc.), are the same as those relevant to the outer surface of the container. However, the chemical conditions inside a package can be different from those outside, so the relative importance of the different factors may differ too.

The potential for evolution processes to occur inside a waste package depends in the first place on the availability of water inside the package. Wasteforms based on the use of glass (for example, HLW) or polymers (some ILW) are inherently dry, so are at low risk of internal corrosion. ILW wasteforms based on the use of cement contain some porewater; this is available for corrosion reactions, but bulk, free liquids are not present.

Spent fuel previously stored under water will require drying before containerisation for dry storage and disposal [87], resulting in little (if any) residual water remaining inside waste containers. For some spent fuels however, the amount of residual water is currently thought to be potentially significant. In particular, for spent AGR fuel the potential for entrained water is thought to be higher than for LWR fuels, due the higher incidence of cladding perforation. For AGR fuel, volumes of entrained water of the order of 50 g have been estimated for a slotted can containing 'intact' fuel. Conversely, values of the order of 600-700 g have been estimated for a slotted can containing, together with intact fuel, a single fuel element in which the cladding was perforated ('failed' or 'damaged' fuel) [88]. Due to its location (inside the annulus of fuel pins), this water may be difficult to remove. Conversely, levels of 50 g of water have been estimated in the Swedish programme ([89], section 3.5.1)[21] for water entrained in a BWR fuel element containing a single perforated fuel pin. On this basis, conservative estimates of water inside a disposal container of 1400 g for AGR fuel ([88] and Section 11.1.3) and 600 g (BWR fuel [89]) have been obtained.

Significant quantities of water may also be retained inside specific ILW streams. In this case, there may also be a need to consider the potential effect of residual water inside waste packages, particularly for waste containerised without encapsulation. Estimates of water in these instances would need to be made on a case-by-case basis, but volumes of the order of a few litres (for example, 10 litres) are considered in the subsequent sections for scoping purposes.

Specific considerations for cement ILW/LLW packages are associated with the pH and redox conditions expected inside waste packages. Cement formulations employing BFS/OPC mixtures typically possess higher pH (generally above 13) and tend to lead to the development of particularly reducing conditions inside waste packages (Eh ~ -300 mV or less), associated with the presence of reduced sulphur species (see Section 7.2.1). Formulations employing PFA/OPC mixtures tend to display lower pH (generally above 12) and less reducing conditions (see Section 7.2.1).

Inside waste packages, radiation levels will be higher than outside and, depending on the type of wastes, may or may not have a significant effect on evolution processes. Dose rates of the order of 0.01-1 Gy h^{-1} are typically present inside ILW packages at the time of packaging, although higher dose rates are possible in specific instances. Much higher rates are expected inside HLW and spent fuel containers.

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[21] These estimates assume that the fuel is sufficiently old to not be self-drying and that any water collected at the base of a slotted can (estimated to be of the order of 1200-1300 g) is drained. Estimates of entrained water in a single (sensitised) AGR fuel element are based on the assumption that 50% of the fuel pins may have been perforated by corrosion and consideration of the geometry of the fuel pins (about 1 m long, containing hollow, ring-shaped, fuel pellets). Estimates of water entrained inside BWR fuel elements are based on assumptions of water filling the volume of the ‘plenum’ (that is, the gas expansion volume) of a single perforated fuel pin.

5 Evolution of vitrified HLW

This section presents scientific and technical information relevant to the expected evolution processes of HLW, particularly dissolution processes in groundwater. It analyses the available information to evaluate the likely durability of the wasteform in relevant conditions, in particular its ability to immobilise radionuclides over long timescales. Key sources of information include work carried out by waste management organisations in other countries at universities and research institutes, as well as a number of EC-funded projects (for example, NF-PRO [90]), and the proceedings of conferences such as the Scientific Basis for Radioactive Waste Management Symposia [91].

The information presented summarises some of the evidence on this topic produced in the UK and worldwide in the last 20-30 years. Typical studies include:

- research on inactive simulants, whose compositions have been selected to closely approximate the chemical composition of the (active) wasteform
- modelling aimed at supporting the development of a mechanistic understanding of microstructure and dissolution properties
- natural and anthropogenic analogues
- decades of industrial experience in the use, handling and storage of these materials.

The information presented focuses on HLW compositions which, to date, have been considered in the disposal programme (Magnox and Blend glasses as well as, for comparative purposes, glass compositions relevant to other disposal programmes). Information on other HLW compositions (POCO and Butex glasses) has not yet been considered in our research programme [10, task 538] and is not described in this document.

An overview of evolution processes is presented, followed by a more detailed description of specific ones. The overall impact of such processes on the evolution of UK HLW is discussed in Section 11.4, largely based on work carried out on non-UK formulations.

5.1 Overview of HLW evolution processes

5.1.1 Initial state and pre-closure period

Key characteristics of the initial state of HLW include the level of cracking and the level of micro-segregation. During interim storage periods, the main degradation process is likely to be the atmospheric corrosion of the stainless steel canister in which the waste is packaged.

After pouring into vitrification canisters, the cooling of the glass following solidification is likely to lead to the formation of cracks, which will affect its surface area and its subsequent leaching properties. The density of cracks present in the structure, at least at a macroscopic level, is expected to be unaffected by glass evolution processes, but is an important characteristic of the initial state of HLW. In addition, a small quantity of crystalline material invariably separates from the glass products on cooling due to the relative insolubility of some waste elements in the glass. The level of segregation of some specific radionuclides into separate phases, which may lead to their preferential leaching, is a second important characteristic of the initial state of the glass.

During the subsequent storage (and disposal) period the elevated temperatures associated with the radiolytic heating and radiation damage associated with radioactive decay itself can potentially lead to microstructural alterations of the glass, for example, due to the formation of crystalline structures (a process known as de-vitrification). The effect of radiogenic heating on devitrification is considered in the context of the initial state of the glass in Section 5.2, whilst the effect of radiation damage is discussed in the context of the microstructural alteration and dissolution properties of the glass in Section 5.5.

Atmospheric corrosion of the stainless steel HLW vitrification canister could also lead to degradation of its structural integrity during pre-closure operations, potentially affecting its confinement properties. This is discussed briefly in this section, but further details of the atmospheric corrosion processes of relevant stainless steels are described in Section 10.

Evolution processes and their effects are described in Table 4.

5.1.2 Post-closure period

After disposal in a GDF, and upon contact with groundwater, the main degradation processes of HLW are the aqueous corrosion of the vitrification canister and, once the canister is breached, glass dissolution in groundwater. Glass dissolution processes are likely to be affected by microstructural changes associated with radioactive decay.

During the post-closure period, there will be an initial period in which the integrity of the disposal container ensures that dry conditions are present in contact with the wasteform. During this period, evolution processes are expected to be minimal. Once exposed to groundwater (that is, after any disposal container has been breached), vitrified HLW is likely to undergo dissolution/leaching reactions leading to a release of radionuclides in the EBS. In key waste streams (Magnox and Blend glasses) this release of radionuclides is expected to occur congruently with the dissolution of the matrix (resulting from the high homogeneity of the wasteform). This process is expected to be particularly important in long-term safety assessments and is described at length in this document.

Table 4: Processes of general relevance to HLW

Period	**Evolution Process**[22]	**Effect**	**Section**
Initial state	Solidification of the melt and initial cooling	Surface area (amount of cracking) Level of micro-segregation	0
Pre-closure and post-closure	Corrosion of vitrification canister (air and groundwater)	Change in structural integrity of the vitrification canister	0
Post-closure	Dissolution of glass (groundwater)	Leaching of radionuclides in groundwater	5.3 and 5.5[23]
Pre-closure and post-closure	Microstructural evolution due to self-irradiation	Leaching of radionuclides in groundwater Level of micro-segregation Gas generation (He)	5.5[23]

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[22] The table presents a simplified description of key processes likely to affect the evolution of HLW. Other important processes include their thermal and radioactive decay processes, which are central to many other evolution processes and are discussed in Section 4 in the context of the environmental conditions in which evolution processes will take place.

[23] In the context of HLW, the effects of radiation on both microstructure and dissolution and leaching behaviour are discussed together in Section 5.5. In the context of spent fuels, conversely, the effects of radiation on the dissolution behaviour and microstructure of the fuel are discussed separately.

Corrosion processes of the vitrification canister employed for storage are also relatively important. Beyond being precursors for the exposure and subsequent dissolution of the underlying glass in the groundwater, these processes are also likely to control the interaction between the glass and species able to affect its dissolution behaviour (such as ferrous corrosion products and chemical species in the clay buffer). Theoretically, corrosion of the vitrification canister could also lead to the release of specific radionuclides which may have been generated in the metal by neutron-activation processes during storage periods, but these will be in negligible amounts are not considered further in this document.

Evolution processes and their effects are described in Table 4.

5.2 Initial state

The initial state of the glass is determined by the composition of the melt and the rate of cooling of the solid glass product.

The initial state of the glass is determined by the composition of the melt and the rate of cooling of the solid glass product after casting into the WVP canisters. Properties of the initial state that may be important in determining glass durability and leaching behaviour are the potential presence of cracks within the glass matrix, affecting the surface area, and the segregation of specific radionuclides in separate phases, which may lead to faster, preferential leaching of specific species. These aspects are discussed below.

5.2.1 Cracking

Substantial cracking is expected in HLW upon cooling, with estimates of the resulting surface area ten times higher than the nominal geometric area.

Cracks are generated in HLW during the glass production process (following casting of the molten glass into WVP containers) as a result of differential shrinkage and fracturing of the glass block during cooling. Additional cracking may arise during the handling and transport of HLW containers. Although any handling of HLW will be carried out with care, it is possible that, for a small fraction of the inventory, cracks may be generated by mechanical damage during storage and transport operations (for example, in an impact). Cracks in the glass matrix increase the surface area available for dissolution [92], providing pathways for groundwater to access the wasteform and for soluble or gaseous radionuclides generated by dissolution processes to migrate out of it.

Work has been carried out to evaluate the amount of cracking expected in typical UK glass formulations as a result of solidification processes [20]. Comparative information is available from other vitrification programmes (summarised in reference [92]). Available information indicates that a substantial amount of cracking occurs during glass manufacture, with the overall surface area of the glass being about ten times larger than the nominal, geometric surface area of the glass block [20]. The ratio between the total surface area of the glass accessible for dissolution and the nominal, geometric surface area is sometimes referred to as the ‘effective cracking factor’ [92] or ‘effective fracture ratio’ [93].

5.2.2 Micro-segregation

The level of micro-segregation in the majority of HLW products is expected to be very low. In the case of waste feeds containing high concentrations of molybdenum, segregation of a ‘yellow phase’ has been observed, potentially leading to a relatively fast release of some radionuclides upon contact with groundwater.

Vitrified HLW is largely a homogeneous material, with the highly-active waste fully dispersed in solid solution and chemically bound (‘embedded’) within the glass matrix. However, there is always a small component of crystalline phase present as small inclusions in the glass (typically <2% by volume), due to the relatively low solubility of some elements in the glass matrix. Simulant UK Magnox glasses at 25 wt% waste incorporation usually contain at least 1% ruthenium oxide crystalline material and spinel phases[24]. Other commonly observed phases include metallic platinoid (ruthenium, palladium and/or rhodium) or platinoid oxide phases and zirconium-rich phases [20]. As-cast UK blend glasses also contain cerium oxide. Such crystalline phases tend to be evenly distributed throughout the glass monolith, with no evidence for settling during cooling.

Storage conditions in the VPS at Sellafield have been designed to ensure that the glass products, once emplaced, cool sufficiently rapidly such that further growth of separated phases (devitrification) is minimised[25]. Work undertaken to assess the potential impact of storage at high temperatures for a transient period during cooling on standard UK HLW products has confirmed that the extent of devitrification, if any, will be small [20]. For example, a fully active 25 wt% Magnox glass heated at 650 ºC for two weeks (an extreme case) showed an increase in crystallinity to 11.8% ± 7.1% by volume (compared with typical values of less than 2%). In contrast, a simulant 75:25 (oxide:Magnox) Blend glass at 25% waste incorporation, heat treated at 700°C for two weeks, exhibited crystallisation of less than 5% by volume. Overall, should elevated temperatures occur leading to devitrification for a small number of canisters, the extent of devitrification is not expected to exceed 15% and typically would be less than 5% by volume. Additional crystalline phases observed in heat-treated products include silicon- and lanthanide-rich phases [20].

Under some conditions, a low density ‘yellow phase’ is observed on the top surface of glass following pouring and cooling [23]. This phase, made of about 80% soluble alkali molybdates and 20% insoluble alkaline earth and rare earth molybdates, may act as a potential host for a number of radionuclides, such as the long-lived nuclides ^{99}Tc and ^{135}Cs and, potentially, the higher actinides ^{241}Am and ^{237}Np. Conditions that favour the production of yellow phase are high calcination temperatures, low melter temperatures, poor mixing in the melter, and high concentrations of molybdenum and sulfate in the feed. Yellow phase has also been observed in some Japanese HLW glasses [24].

A small proportion of the WVP canisters stored in the VPS at Sellafield contain glass originating from non-standard ‘drain pours’ that were performed periodically during earlier vitrification campaigns at the WVP. Drain pours were required to drain the residual melt (the heel) from the bottom of a melter at the end of each vitrification cycle. These products can be enriched in phases that may have either settled into the base of the melter (in particular spinels, ruthenium and cerium oxides and platinoid metals) or have floated on the surface of the melt (yellow phase), and tend to have a higher fraction of waste oxides than standard glasses. The nature of the heels is, in large part, dependent on the efficiency of mixing and the uniformity of the melts during the preceding vitrification cycle. The use of four-sparge melters with improved mixing efficiency (compared to the single-sparge melters used

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[24] Spinel phases observed in Magnox glasses have a composition of the form M-II(M-III)$_2$O$_4$ where M-II = Mg or Ni and M-III = Al, Fe or Cr.

[25] De-vitrification of glass, that is, the growth of crystalline phases within the matrix, is a process that may occur if the glass is stored at temperatures above the glass transition temperature, T_g (the temperature at which a molten glass hardens into a more brittle solid on cooling), which is typically in the range 505 to 535 °C for standard UK HLW glass products. The VPS at Sellafield has been designed to ensure that the centre-line temperature of the glass in any individual WVP canister will remain below T_g. Even at the maximum predicted heat output on emplacement, the centreline temperature will cool to less than 400 °C within one year and the external temperature of the glass container will be significantly lower once the heat from glass manufacture has dispersed. Owing to this large temperature gradient within the glass wasteform, devitrification will be limited to only a small volume of the glass and for a relatively short time period (days).

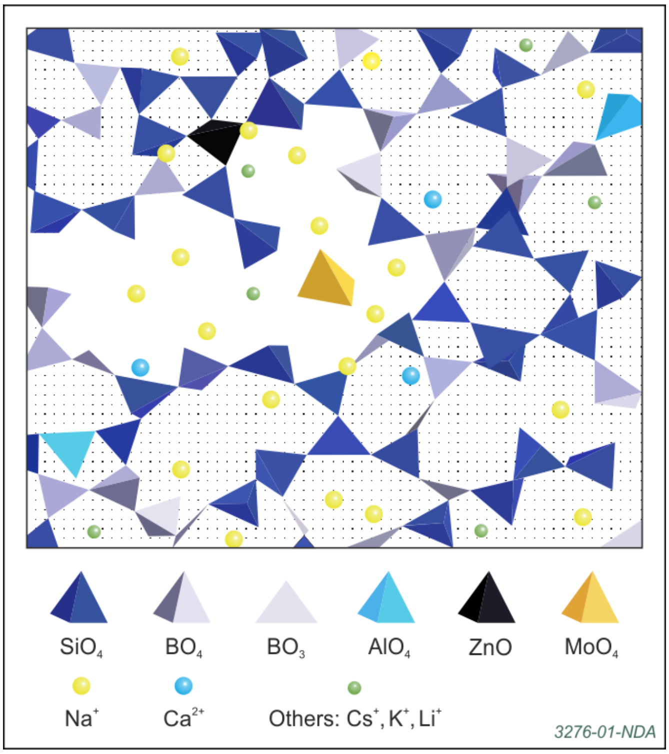
originally at the WVP) has largely alleviated the problem of heel enrichment, and drain pours are no longer required during routine operations.

5.3 Glass dissolution

Borosilicate glasses are likely to undergo very slow long-term dissolution processes in conditions relevant to geological disposal. However, UK HLW compositions may exhibit higher long-term dissolution rates than formulations developed in some other countries.

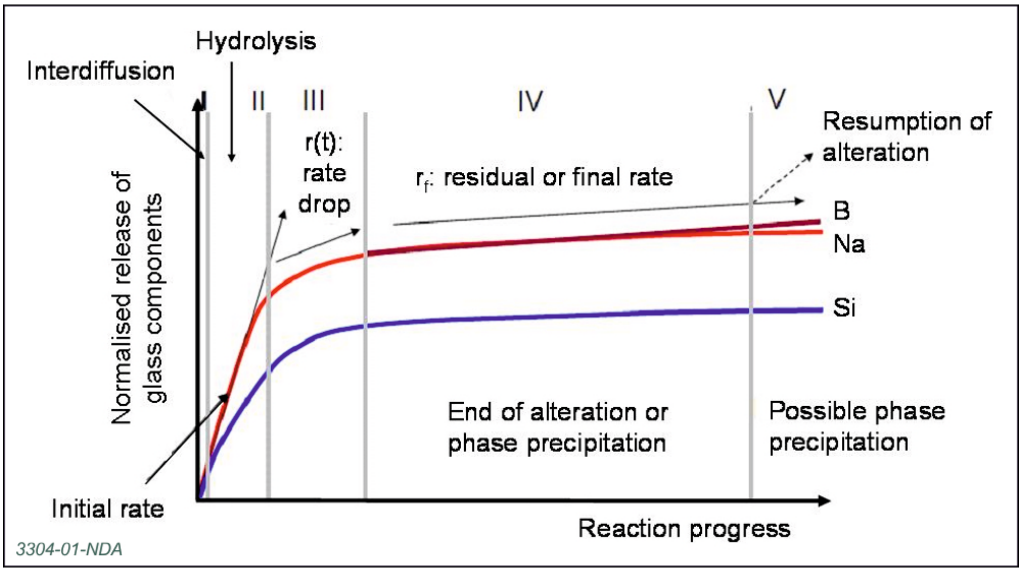
Common glasses are typically made of oxides of silicon and other elements (such as boron), termed network formers, that are capable of forming a continuous network structure cross-linked by bridging oxygen atoms. The continuous network can be modified by the presence of other oxides that may be categorised as either network modifiers or intermediates. Network modifiers (for example, sodium or potassium) reduce the connectivity of the network structure as, being monovalent, they can link to just one network cation. Intermediates (such as aluminium or zirconium) cannot form glass networks on their own, but can contribute to the connectivity of the network structure, usually in conjunction with a charge-balancing modifier species. The resulting network is characterised by short-range order, but lacks the long-range order typical of crystalline solids. A schematic illustration of the microstructure of glasses typically employed for HLW immobilisation (borosilicate glasses) is shown in Figure 16. Although glasses are not thermodynamically stable compounds, they are characterised by excellent chemical stability in a range of environmental conditions.

Figure 16: Schematic illustration showing the microstructure of borosilicate glass (based on [94])



For HLW (borosilicate glass), the dissolution and leaching behaviour of the glass is an important process determining the release of radionuclides from the EBS once, after a very long time, corrosion processes have led to the breach of the disposal container and inner canister. The mechanisms of glass dissolution are relatively well understood [95, 96] and are shown schematically below in Figure 17 [97]. As dissolution of the silica network (the glass matrix) proceeds, different chemical elements present in the glass (including embedded radionuclides) are released at different rates.

Figure 17: Different rate regimes for glass dissolution in near-neutral pH conditions [97]



In conditions of near-neutral pH, when glasses come into contact with water, the initial stages of dissolution (Stages I and II in Figure 17, generally defined as the ‘initial’ or ‘forward’ rate regime[26]) are characterised first by inter-diffusion (diffusion of water molecules into the glass surface layer) and ion-exchange of network modifier elements (Stage I) and then by the hydrolysis of the borosilicate glass network (Stage II), resulting in the release of boron and silicon [98]. This leads to the formation of an altered surface layer that is depleted in soluble components. As dissolution proceeds, a very substantial reduction in the rate of release of both soluble and insoluble components (three or four orders of magnitude) is usually observed (Stage III in Figure 17, known as the ‘rate drop regime’) until the rate of glass alteration achieves a much lower long-term rate (Stage IV in Figure 17, known as the ‘residual rate’ regime). In some cases, a resumption of alteration processes at rates higher than the residual rate can also occur (Stage V). This representation is widely established in the relevant technical literature although, in some instances, the treatment is simplified to a smaller number of key stages (see for example [96]. From a mechanistic stand-point, an important question is whether the decrease in alteration rate is associated with:

- the progressive saturation of insoluble phases (such as silicates) in solution, leading to an increase in the rate of ‘backward’ reaction (precipitation) which slows down the net rate of alteration (as per classical Chemical Affinity theory [99], albeit applied to an out-of-equilibrium system such as a glass)
- the formation of kinetic (for example, physical) barriers at concentrations much lower than expected levels of saturation, hindering the rate of the ‘forward’ reaction (referred to in the literature as the Gel Protective Layer theory [100]).

The Near-Field PROcesses (NF-PRO) project, the latest collaborative project funded by the European Commission in this area [90], concluded that a gel layer acting as a kinetic barrier to dissolution is likely to be responsible for the observed phenomenology. It also concluded

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[26] The term ‘forward rate’ is generally used for tests in pure water (where the initial silicon concentration and the resulting rate of the backward reaction is negligible), while the term ‘initial rate’ refers to tests in waters with a non-zero silicon background concentration (like most ground waters).

that the rate controlling process is determined by which of the following is the slowest: silicon release from the glass-gel interface (chemical control); or silicon diffusion through the gel layer and then transport into the EBS (diffusion control, illustrated in Figure 18). This project also highlighted how silicon sorption onto available minerals (such as ferrous corrosion products from the container and clays from any bentonite buffer or host rock) can promote the dissolution of the glass, inhibiting the establishment of a long-term residual rate [101].

Available evidence from relatively long-term experiments indicates that, in many circumstances, once the residual rate regime (Stage IV) has become established, the glass will continue to dissolve at a residual rate. Under some circumstances, however, there can be a resumption of alteration; a sudden increase in the glass alteration rate (Stage V in Figure 17). In the case of French R7T7-type glasses, this is usually observed at high pH (>10.5) and/or high temperature (> 90 °C), and is associated with the precipitation of secondary, alumino-silicate-based phases (zeolites) or, in some cases, calcium silicate hydrate alteration products [102, 103]. The proposed mechanism for the resumption of alteration in this case is that the precipitation of secondary phases consumes aluminium and silicon from solution and, as a result, from the gel layer in equilibrium with it, leading to a decrease in its protective properties. The composition of the glass (in terms of the aluminium and alkali contents) and of the solution are considered important in determining both the timing and the magnitude of the resumption of alteration, but currently these effects are not well-understood. Species released by the dissolution/corrosion of other components of the EBS (particularly iron), are also thought to be potentially important in the resumption of alteration [90].

The rate of borosilicate glass dissolution (particularly Stage II) is dependent on the solution pH. Under both acidic and alkaline conditions the glass matrix dissolves more quickly than under near-neutral conditions and the mechanisms controlling the actual dissolution rate may be different. The effects of pH on measured glass dissolution rates under conditions representative of the initial rate regime (Stage II) are illustrated in Figure 19. The figure shows steady-state dissolution rates for a simple five-component borosilicate glass[27] over the pH range 1-13 (deionised water with dilute buffers) at 25, 50 and 70 °C, measured using a flow-through methodology [104]. At alkaline pH values between 8 and 11, dissolution of the glass was found to be congruent, but at lower pH, dissolution was incongruent. An aluminium- and silicon-rich gel layer was formed on the surface of the glass at pH 3 to 7 and a silicon-rich layer under strongly acidic conditions (pH 1 to 3). The data presented in Figure 19 indicate that the dissolution rates can increase by two to three orders of magnitude between near-neutral and a very alkaline system (pH around 12). A more limited increase (one order of magnitude) is observed in the case of mildly alkaline systems (pH around 10).

Beyond considerations relative to the ‘overall’ dissolution/leaching rate (assuming that such a quantity could be meaningfully defined), it is also important to understand the behaviour of specific elements - whether they tend to behave like soluble components or not. In the case of borosilicate glasses used for radioactive waste immobilisation, for example, the silica-rich gel layer is thought to preferentially incorporate radionuclides such as plutonium and americium, which are of low solubility and are strongly sorbed. Recent work carried out in the UK programme indicates that potentially more soluble elements like caesium can also be retained in the gel layer under certain conditions [105]. In general, it is important to note that, for radionuclides that are adsorbed or retained in the gel layer or secondary solids, measured glass dissolution rates based on the release of weakly or non-sorbing elements define an upper limit for the rate of radionuclide release [106].

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[27] The glass composition was about 56 wt% SiO_2, 8 wt% B_2O_3, 12 wt% Al_2O_3, 18 wt% Na_2O and 6 wt% CaO.

Figure 18: Glass alteration in near-field conditions according to a diffusion-controlled model of the gel-layer [108]

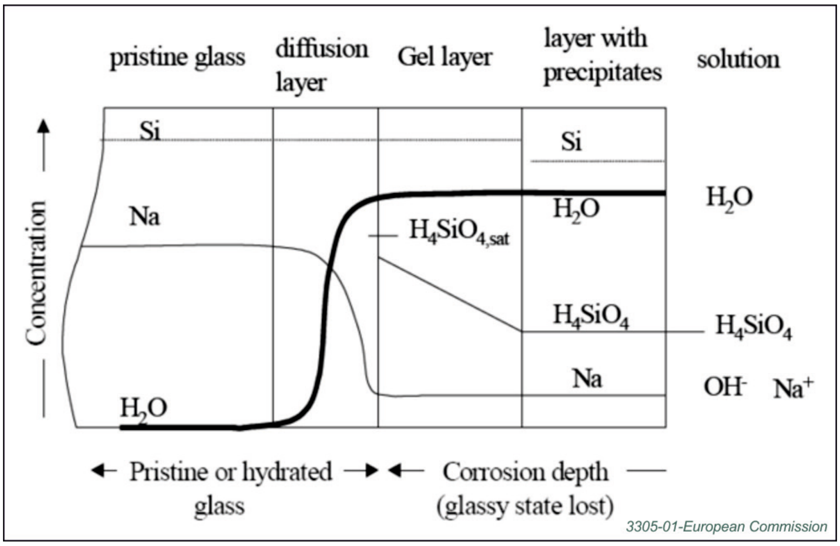
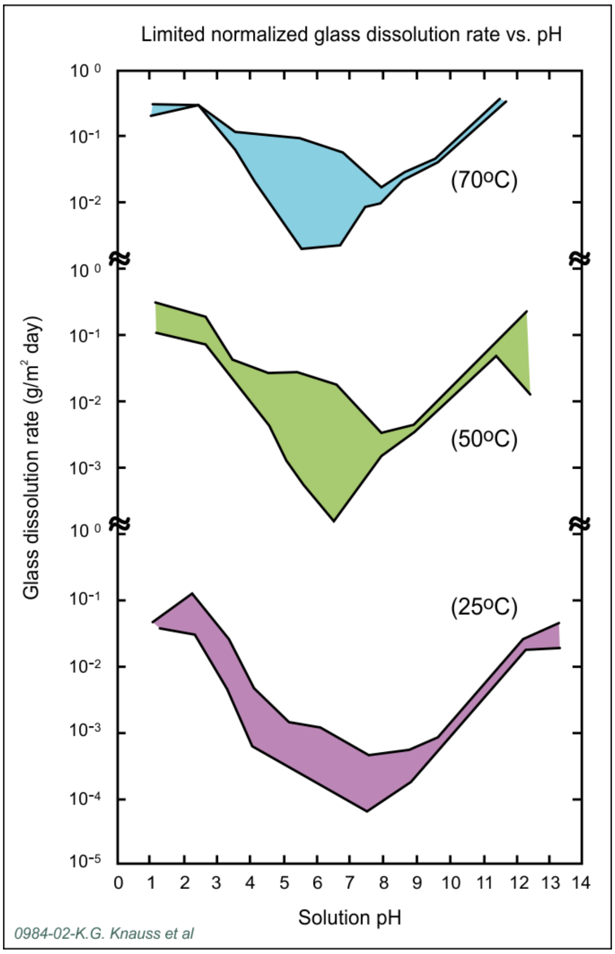


Figure 19: Steady-state dissolution rates of a simple five-component borosilicate glass in deionised water containing dilute buffers over the pH range 1-13 and at different temperatures measured in dynamic leaching tests [104]. The shaded areas represent the measured ranges for different glass components (typically B, Na and Ca at the top and Si and Al at the low end)

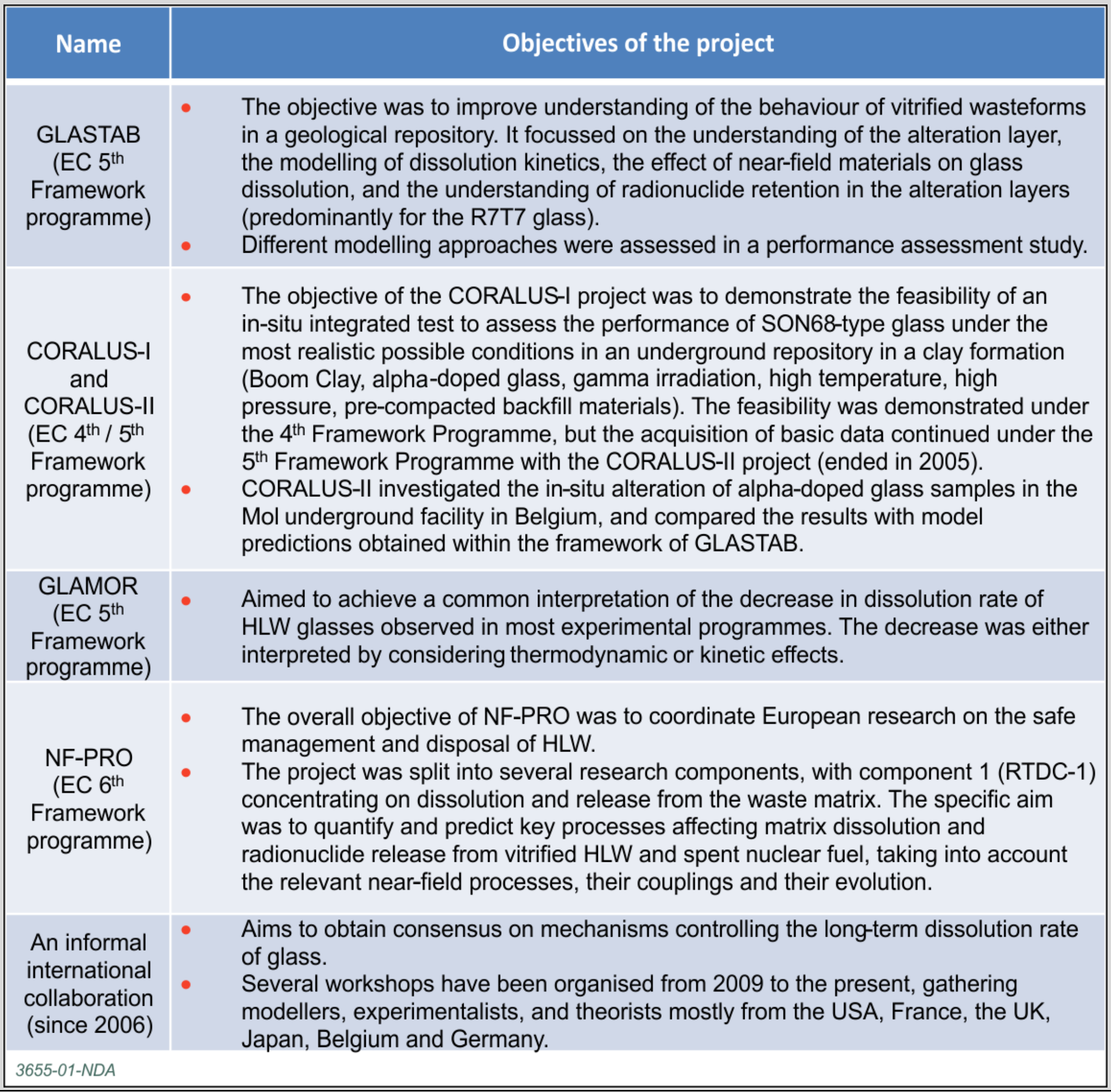


Many worldwide experimental and modelling studies have tried to evaluate and underpin the likely evolution of borosilicate glasses of compositions relevant to the immobilisation of HLW. These include many international collaborations (see Box 9).

Box 9 International collaborative projects on HLW glass dissolution

The dissolution of HLW in the context of waste disposal (primarily French and Belgian-type glasses) has been studied by major research programmes funded by the European Commission: GLASTAB [107], GLAMOR [108], CORALUS [109, 110] and, more recently, the EC 6th Framework Programme's NF-PRO [90, 111]. An informal international collaboration has been also operating since 2005 [115]. A summary of the scope of these projects is reported in Table 5, reproduced from [112]. These and other projects have produced a mature understanding of the likely dissolution and leaching behaviour of HLW (especially for compositions relevant to other waste management programmes) to enable safety assessments to undertake a robust evaluation of the likely evolution of these glasses. For example, relatively long-term in situ measurements (up to ten years) with active glass samples, performed under the CORALUS project [109], were found to agree well with results from laboratory tests and model predictions, confirming the understanding of glass alteration phenomena.

Table 5: International collaborative projects on glass dissolution, reproduced from [112]



Name	Objectives of the project
GLASTAB (EC 5th Framework programme)	• The objective was to improve understanding of the behaviour of vitrified wasteforms in a geological repository. It focussed on the understanding of the alteration layer, the modelling of dissolution kinetics, the effect of near-field materials on glass dissolution, and the understanding of radionuclide retention in the alteration layers (predominantly for the R7T7 glass). • Different modelling approaches were assessed in a performance assessment study.
CORALUS-I and CORALUS-II (EC 4th / 5th Framework programme)	• The objective of the CORALUS-I project was to demonstrate the feasibility of an in-situ integrated test to assess the performance of SON68-type glass under the most realistic possible conditions in an underground repository in a clay formation (Boom Clay, alpha-doped glass, gamma irradiation, high temperature, high pressure, pre-compacted backfill materials). The feasibility was demonstrated under the 4th Framework Programme, but the acquisition of basic data continued under the 5th Framework Programme with the CORALUS-II project (ended in 2005). • CORALUS-II investigated the in-situ alteration of alpha-doped glass samples in the Mol underground facility in Belgium, and compared the results with model predictions obtained within the framework of GLASTAB.
GLAMOR (EC 5th Framework programme)	• Aimed to achieve a common interpretation of the decrease in dissolution rate of HLW glasses observed in most experimental programmes. The decrease was either interpreted by considering thermodynamic or kinetic effects.
NF-PRO (EC 6th Framework programme)	• The overall objective of NF-PRO was to coordinate European research on the safe management and disposal of HLW. • The project was split into several research components, with component 1 (RTDC-1) concentrating on dissolution and release from the waste matrix. The specific aim was to quantify and predict key processes affecting matrix dissolution and radionuclide release from vitrified HLW and spent nuclear fuel, taking into account the relevant near-field processes, their couplings and their evolution.
An informal international collaboration (since 2006)	• Aims to obtain consensus on mechanisms controlling the long-term dissolution rate of glass. • Several workshops have been organised from 2009 to the present, gathering modellers, experimentalists, and theorists mostly from the USA, France, the UK, Japan, Belgium and Germany.

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The current state of knowledge is summarised in a number of recent reviews [96, 113, 114]. Studies have often been carried out at relatively high temperatures (usually 90 °C), typically at near-neutral or alkaline pH in deionised water and simulated groundwater, or in simpler solutions. There is a general consensus about the phenomenology (stages) of glass dissolution (as shown in Figure 17), but there are still uncertainties about important questions, including [115]:

- the mechanisms which control the change from the forward rate regime to the residual rate regime
- the effects of exposure to groundwater and its more complex chemistry, as opposed to simplified solutions
- changes in pH (in most experimental programmes the leaching solution is deionised water, in which alkali borosilicate glasses tend to buffer the pH to around 9)
- the effect of glass composition on dissolution rates
- the mechanism(s) by which the formation of secondary products formed on the glass surface can lead to a resumption of glass alteration at rates close to the forward rate.

To address these uncertainties, the international scientific community (Belgium, France, Japan, UK and the USA) have started to work collaboratively to study the long-term behaviour of HLW [19]. This has involved the adoption and common usage of the International Simple Glass (ISG), a simplified six component oxide borosilicate glass based on the composition of the French simulant SON68, for studying glass-dissolution mechanisms and kinetics (Section 2.2, Box 1).

Results obtained so far with the International Simple Glass (ISG), at 90 °C in a KOH solution, indicated a similar behaviour to that described above. It was found that, over an initial 209 days where the pH was fixed at 9, the glass corrosion rate fell continuously from the forward rate to a residual rate, three orders of magnitude lower - due to the formation of a uniform, homogeneous, amorphous alteration layer on the glass surface. Over the duration of the experiment, incongruent dissolution of the network-forming elements was observed. When additional KOH was added and the pH increased to 11.5, the rate increased dramatically (almost as high as the forward rate) and congruent dissolution of Si, Al, B and Na was observed, indicating the rapid dissolution of the glass. At pH 11.5, the mechanism of dissolution was controlled by the hydrolysis of the silicate network promoted by OH^- and driven further by the precipitation of crystalline calcium silicate hydrates (CSHs) and zeolites [115]. The dissolution behaviour in conditions of high pH is particularly important in evaluating the likely durability of an EBS were it to employ a cement-based buffer, or be co-located with ILW modules employing a cement-based backfill.

The effect of different environmental parameters on the dissolution rates of typical glass formulations studied in worldwide disposal programmes is discussed in detail in Box 10. Based on the substantial mechanistic understanding produced by research studies in this area, a detailed semi-empirical model of the likely dissolution behaviour (and resultant radionuclide leaching) has been developed for R7T7-type glass formulations relevant to French HLW, the Glass Reactivity with Allowance for the Alteration Layer (GRAAL) model. This model has been used to simulate the behaviour of SON 68 glass in relatively short-term experiments and has been compared with the results of experimental studies in similar conditions [116].

Box 10 Effect of environmental conditions on HLW glass dissolution

Effect of pH

The effect of pH on glass dissolution in simple acidic and alkali hydroxide media is well understood. Normally, higher rates are observed under acidic (pH <4) and alkaline (pH >10) conditions. At higher pH the entire glass network dissolves and, with it, any embedded species [97]. Data for Magnox glass 'forward rates' as a function of pH at 18 °C are reported in [148] and increase by an order of magnitude from about 10^{-3} g m^{-2} d^{-1} to 10^{-2} g m^{-2} d^{-1} from pH 7.8 to pH 9.9. Data on the effect of pH on the forward rate of blend glasses is also available [117]. For SON68 the initial dissolution rate at 25 to 100 °C and from pH 6 to pH 10 has been found to vary according to a power law (proportional to $10^{0.4pH}$) [17]. However, the residual dissolution rate has been found to be almost independent of pH for values between pH 7 and pH 10.5, regardless of temperature [118]. The pH also affects the composition of the alteration layer and secondary phases that form on the glass. The behaviour in high-pH cementitious waters has been found to be different from that in simple high-pH solutions [119].

Effect of Temperature

The dissolution rate of glasses increases with temperature. For SON68, different activation energies have been measured in deionised water, with an activation energy of 76 kJ mol^{-1} observed for the initial rate [17] and 53±5 kJ mol^{-1} for the residual rate [120] (constant from 50 °C to 180 °C and independent of the SA/V ratio). The activation energy for the initial dissolution rate of simulant 25 wt% waste loading Magnox glass was determined to be between 56-64 kJ mol^{-1} under high pH conditions (pH 12.1) over the temperature range from 30 to 90 °C [148] and of the same order of magnitude for blend glasses in similar conditions [117]. In NF-PRO, the activation energies measured for a 25 wt% 75:25 Oxide/Magnox Blend glass were 77.9 kJ mol^{-1} (pH 8.8), 56 kJ mol^{-1} (pH 7) and 44.2 kJ mol^{-1} (pH 2.2) after 14 days at 60 °C and 90 °C [90]. The values at near-neutral pH are indicative of a dissolution rate controlled by surface reaction. With these activation energies, a 10 °C rise in temperature results in a doubling of the dissolution rate.

Effect of Groundwater and EBS Composition

At a first approximation, silicon-rich solutions tend to inhibit glass dissolution, while magnesium-rich solutions tend to result in relatively fast glass dissolution. Calcium may have an inhibiting effect on glass dissolution at neutral to weakly basic pH [153] but at high pH can trigger glass dissolution by the formation of C-S-H phases [121]. Materials present in the EBS, particularly a clay buffer and container corrosion products, may also be important by acting as sinks for silicon due to their high sorption capacity. However, these effects may be mitigated by the presence of high concentrations of silica naturally present in the system. For example, SON-68 showed a residual rate of 0.024 g m^{-2} d^{-1} in contact with 'unsaturated' magnetite, compared with a rate of 3 10^{-4} g m^{-2} d^{-1} if the magnetite was pre-saturated with silica (all the sorption sites filled), after 300 days [90]. In a similar manner, the addition of glass frit to a clay buffer material in contact with SON68 glass was found to reduce the alteration rate of SON68 by about two orders of magnitude [109]. In the long-term the effects of solution chemistry and EBS materials on glass dissolution are rather complex because the precipitation of secondary minerals can determine alteration rates.

Effect of Redox Conditions and Radiolysis

In general, glass dissolution rates are independent of redox conditions because most of the major glass-forming elements in HLW are not redox sensitive. However, the rates of release of some redox-sensitive species within the glass (such as ^{99}Tc, see [122]) may be affected by the redox conditions, due to differences in the solubility of different technetium oxidation states. The formation of minerals affected by the redox conditions can also affect glass dissolution. This may be particularly important in the case of ferrous materials.

Box 10 (cont.'d) Effect of environmental conditions on HLW glass dissolution

Glass dissolution rates are typically independent of radiation levels. The few experimental data in radioactive conditions show that the glass corrosion rate does not appear to be significantly affected by either external radiation fields or self-irradiation [20]. Leach tests showed a factor of 2-3 increase in the initial dissolution rate in the presence of radiation. However, disposal containers will be sufficiently long-lived that water will only come into contact with the wasteform after long times, when dose rates will have substantially reduced.

In support of laboratory tests and modelling studies, a series of *in situ* tests have been performed, in which samples of glass were buried in the ground (near-surface) and subsequently analysed [41]. The oldest such ongoing test is at the Ballidon burial site, which is a near-surface limestone site in Derbyshire (UK) [123]. Simulants of radioactive waste glasses, primarily from Savannah River National Laboratory [124], have been buried there since 1986. Other examples of near-surface burial studies of simulants of HLW glasses include Russian K26 glass at a site north-east of Moscow [125] and US glasses at Savannah River (South Carolina) [126] and Hanford (Washington State) [127]. Perhaps more relevant to geological disposal, examples of glasses buried underground at depth include samples at the Waste Isolation Pilot Plant (WIPP) in New Mexico, at Stripa in Sweden, and at Mol in Belgium [124].

Under the EU 5th Framework Programme known as CORALUS, samples of SON68 and DWK/Pamela glass, doped with α–emitting radionuclides, were placed in Boom Clay at the HADES underground research facility. Tests were carried out at temperatures of 30 °C and 90 °C for 1.3 to 10 years. These tests showed that once sorption sites in the Boom Clay became saturated with silicon the rate of glass dissolution slowed considerably. Adding glass frits to the backfill to provide an alternative source of silicon to the HLW glass reduced glass alteration by two orders of magnitude or more [110].

Further evidence for the stability of glasses in geological conditions is also available from natural and anthropogenic analogues (see Box 11). Ancient glasses (dating up to a few millennia) demonstrate the great stability of such materials in a variety of chemical conditions [128,129].

Box 11 Evidence from natural analogues of glass

A high level summary of natural analogues of HLW glasses and their relevance to geological disposal is available in [130]. Examples of such analogues are provided in Figure 20. Examination of natural, basaltic glasses that have been exposed to aqueous (commonly seawater) environments for millions of years have been performed [131, 132]. These studies show that the surface of glasses tends to become coated with secondary mineral phases, known collectively as palagonites. A synthetic basaltic glass tested under laboratory conditions behaved in a similar fashion to the SON68 glass [133], suggesting that observation of natural glasses is likely to provide useful insights into the behaviour of HLW.

A study of medieval potassia-lime-silica glasses buried for about 800 years and soda-lime-silica glasses buried for about 1100 years found that, together with highly hydrated surface crusts, there was a significant water content throughout the bulk glass, indicating diffusional ion-exchange had occurred [134].

Studies on glasses from both pre-history and the classical period were also carried out. The alteration profiles were successfully fitted using a reactive chemical transport model of glass dissolution [127]. The findings indicated that, in the longer term, overall alteration rates of glass wasteforms are likely to be lower than those previously estimated based on models that assume a uniform rate of glass dissolution from all accessible surfaces.

A Roman glass block that had lain in a shipwreck in the Mediterranean for 1800 years was also recently studied [135].This sample showed alteration products on all crack surfaces, identified as mainly a magnesium-rich smectite. However, the depth of alteration layers tended to be less within cracks away from the surface directly exposed to the seawater, indicating that the dissolution rate of the glass in internal cracks had been much less than the dissolution rate at the external surface [136]. These observations highlighted the importance of both geometric (e.g. crack aperture, distance from surface) and transport parameters (rate of diffusive exchange of alteration solution) in determining dissolution kinetics. The precipitation of secondary phases also resulted in the sealing of cracks.

The alteration profiles were successfully fitted using a reactive chemical transport model of glass dissolution [136]. The findings indicated that, in the longer term, overall alteration rates of glass wasteforms are likely to be lower than those previously estimated based on models that assume a uniform rate of glass dissolution from all accessible surfaces.

Figure 20: Left: 60 million years old obsidian showing, despite the age, limited extent of devitrification (grey-white zones) [130]. Right: photograph of a 14.5-centimetre-long Egyptian fish-shaped glass vessel (3,300-3,400 years old), buried at low depth in non-well characterised conditions [137]

3451-01-Bedrock Geoscience/British Museum

5.3.1 Long-term Dissolution

Glass formulations containing calcium, but free of magnesium, typically show very low long-term dissolution rates. Formulations containing magnesium, both from the UK and other countries, typically display dissolution rates higher than magnesium-free formulations (but still relatively low in general terms). Calcium and magnesium are believed to participate in the formation of phases affecting the behaviour of the glass.

There is a large body of research available from the French programme on SON68 glass, the inactive analogue of the R7T7 HLW product. This glass contains significant quantities of calcium (about 4 wt.%) and aluminium (about 5 wt.%), but no magnesium. Much of the work, summarised in [17], has focussed on understanding the kinetic regime of glass dissolution (outlined above) and the effects of glass composition on dissolution behaviour. More recent studies have been concerned with the wider effects of the disposal environment on glass dissolution, including the effects of a clay host rock and groundwater [138, 139, 140], and the presence of canister corrosion products [141]. In addition to work on R7T7-type glasses, a number of chemical durability studies have been performed in the French programme on simulants of the magnesium-containing AVM glass [18, 142]. This glass contains about 2.5-7.5 wt.% magnesium and 9-12.5 wt.% aluminium, but little calcium (about 0.2 wt.%) and is hence particularly relevant to UK HLW.

There is also a large body of data from the Belgian programme which has focussed on other glass compositions (SM513, SM527 and SM539) related to the PAMELA HLW products. These glasses contain both calcium (4-5 wt.%), aluminium (5-20 wt.%) and, in some cases, magnesium (0.1-2 wt.%). In some cases (for example, SM527) very high quantities of aluminium (20 wt.%) are present in the glass. The Belgian research programme has focussed on disposal in Boom Clay, a potential host geology for Belgian high-level or long-lived radioactive waste [143, 144].

The longer-term dissolution rates of AVM- and R7T7-type glasses have been compared in high SA/V powder leaching tests at 50 °C in deionised water [18]. These studies used a range of 27 simulant R7T7-type and 25 simulant AVM-type glass compositions within the production envelope for the two vitrified products (see Box 1). Typical long-term dissolution rates for R7T7 and AVM glasses are reported in Table 6. Dissolution rates for the AVM glasses were on average higher and covered a broader range than those measured for the R7T7 glasses. In the longer-term tests, the rates of alteration of the R7T7 glasses generally decreased by at least four orders of magnitude to a low apparent residual rate. In contrast, many of the AVM glasses were found to continue to alter at a higher long-term rate, which was related to the extensive formation of phyllosilicate phases rich in magnesium. Additionally, no secondary phases were observed on the surface of the magnesium-free R7T7-type glasses, where more protective altered gel layers were formed.

Table 6: Variability in the longer-term alteration rate from 4 months to 1 year (r_{1y}, measured at 50 °C) for simulant AVM- and R7T7-type glass compositions in deionised water (based on data presented in [18])

	residual rate ($g\ m^{-2}\ day^{-1}$)			
Glass type	Maximum ($r_{1y\ max}$)	Minimum ($r_{1y\ min}$)	Average ($r_{1y\ mean}$)	Max/Min ratio ($r_{1y\ max}/r_{1y\ min}$)
AVM	7.20E-03	1.40E-04	1.79E-03	51.4
R7T7	3.20E-04	2.70E-05	1.46E-04	11.9

Overall, in all of these studies, an acceleration of glass alteration was observed in the presence of magnesium-containing clay groundwater, in the proximity of claystone, or in the proximity of magnetite to the glass. In each case, the acceleration of SON68 glass dissolution was associated with the formation of silicon-containing secondary phases (magnesium silicates, analcime and iron silicates, respectively). In particular, the addition of magnesium to a SON68 dissolution experiment in deionised water in the rate drop regime was found to induce a resumption of glass alteration at a higher rate compared with tests in the absence of magnesium [145].

A more limited amount of work has been performed on HLW compositions of specific relevance to the UK programme. These compositions contain magnesium (1-6 wt.%) and aluminium (2-5 wt.%), but no calcium. Specific studies on the leaching properties of 25 wt.% Magnox glass have been published over a number of years, either abroad [106, 146, 147] or in the UK [148, 149, 150, 151]. These included batch leaching tests on powdered glass in water at 50 and 90 °C [151, 106, 146, 147], and single-pass flow-through (SPFT) tests at 40 °C [149, 150]. The latter studies were designed to study the initial stages of glass dissolution in alkaline media [149, 150] (see Section 5.3.2). The effects of pH and temperature on the dissolution rate were also investigated [148]. Recent work included studies on Blend glasses [117].

Among the few studies aimed at evaluating the long-term leaching behaviour of UK-relevant glass compositions in groundwater a long-term study (12 years), comparing the dissolution behaviour of simulants of a Magnox glass (25 wt% waste loading) with the French R7T7-type glass (SON68) in water at 90 °C, found that the residual rate was an order of magnitude higher for the Magnox glass [106]. The faster alteration of the Magnox glass was associated with the formation of magnesium-containing clay minerals, whereas only small amounts of clay minerals were formed as secondary alteration products of SON68.

We have undertaken some more recent tests [152, 105] to directly characterise the dissolution behaviour of UK-specific HLW compositions at temperatures closer to those expected in a GDF at the time of container perforation (40 °C). These tests are still ongoing so a full analysis of their implications, including an analysis of long-term dissolution/leaching rates is planned for the future. Tests were carried out in static conditions, and in six different solutions, including three illustrative groundwaters, two alkaline solutions[28] (sodium and calcium hydroxide) as well as deionised water. The results of initial measurements on a 25 wt.% waste incorporation Magnox glass after about 90 days of leaching were published in reference [152]. Subsequent work [105] extended measurements on the Magnox glass to longer durations (up to 400 days) and included measurements on a 75:25 Oxide:Magnox blend glass (25 wt.% waste loading) up to 180 days, and both a 50:50 Oxide:Magnox blend glass (38 wt.% waste loading) and the ISG up to 90 days. The results of these studies indicated that the leaching behaviour of a variety of UK HLW glass compositions in a variety of chemical conditions is broadly similar. Glasses with typical (that is, 25 wt.%) incorporation rates showed higher dissolution rates (a factor of three) than their 'equivalent' calcium-containing simulants (ISG). Higher waste incorporation rates substantially decreased the rate of glass alteration (to values similar or lower to that of the ISG).

Different simulated groundwaters (near-neutral pH) had a relatively minor effect on the leaching rates of each glass formulation (typically within a factor of 2-3), with short term rates generally affected by the pH (typically between 8 and 10) and longer term rates affected by the pH - as well as by the presence of specific species in solution, particularly calcium and magnesium. When present/released, these species were found to be gradually removed from solution, indicating a reaction with the glass. Higher quantities of magnesium in solution tended to correlate with faster leaching rates. In contrast, the presence of calcium has been

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[28] Tests in alkaline solution were aimed at evaluating the potential effects of alkaline plumes associated with cement and concrete used in a GDF, as well to support the overall interpretation of the alteration mechanisms, particularly the influence of calcium.

correlated with lower leaching rates; a reduction in dissolution rates has been observed at in calcium-rich solutions using a 'simplified' SON68-type glass simulant [153].

Additional experimental studies were carried out with 'simplified' glass formulations in order to develop a good mechanistic understanding of the role of magnesium in UK HLW [154]. In this work, glass simulants containing silicon, boron, sodium, aluminium, lanthanum, and systematically substituting magnesium with calcium, were tested in deionised water at 90 °C. After 112 days leaching, dissolution rates about 1 order of magnitude higher were observed for the magnesium-containing glass simulant relative to the calcium-rich simulant, consistent with previous observations on Magnox and SON68 simulants [106]. The dissolution rates of the simplified glasses were also broadly similar to those of their more complex equivalents (Magnox simulant and SON68). Estimates of the size and nature of the alteration layer indicated a much thicker layer in the case of the magnesium-containing simulant (about one order of magnitude), suggesting that a faster dissolution process is accompanied by faster re-precipitation processes. Indications of two different silicate phases were found for magnesium-containing glasses. Overall, the conclusions of this study suggest that a less protective gel-layer may be responsible for the higher dissolution rates observed in the case of magnesium-containing glasses [154].

In addition to leaching studies focusing on 25 wt% Magnox and Blend glass, and specifically aimed at evaluating the likely behaviour of HLW in a GDF (including work at lower temperatures and in a variety of chemical conditions), a substantial amount of work has been carried out by Sellafield Ltd. to support the identification of suitable glass formulations and to confirm the quality of products produced by the vitrification plant [155, 156, 157, 158, 159]. In particular, this work has been concerned with underpinning the development of higher waste-loading Magnox and Blend glass products, up to a limit of 38 wt.% [160]. Work on glass durability has consisted of monolith and powder leaching studies, typically at high temperature (90 °C) in deionised water. For Magnox glasses, the extent of glass alteration and the alteration rate decreased as the waste incorporation increased. Further work on the effects of temperature and groundwater composition on the dissolution of glasses is planned to test materials in conditions more relevant to disposal [10, tasks 537 and 538].

The effect of settled solids and the potential enrichment of certain species in the melter heel on the durability of non-standard drain-pour products has also been investigated in recent trials [156]. In general, the heel residues did not show significantly increased elemental releases compared to standard 25 wt.% Magnox product, despite higher waste loadings (29.5, 49 and 57 wt%) and increased concentrations of chromium, nickel, ruthenium and molybdenum.

5.3.2 Initial Release

Early release of radionuclides from glass wasteforms is possible due to the dissolution of highly soluble phases (in particular yellow phase) and due to the faster initial ('forward') rates of glass dissolution, before longer-term dissolution rates are established.

Two types of early release of radionuclides from glass wasteforms, once they become exposed to groundwater, are possible:

- releases arising from the dissolution of highly soluble phases, in particular yellow phase, that may separate from the glass matrix
- releases arising from the faster, initial/forward rate phases of glass dissolution (Stages I and II in Figure 17) before longer-term dissolution rates are established (Stage IV).

The dissolution of any yellow phase directly exposed to the groundwater and the release of it associated radioactive inventory is likely to occur within very short periods (years). The release of radioactivity due to the initial dissolution rate of the glass is likely to be occur over decades or centuries. From the point of view of safety assessments such processes are relatively fast compared to radionuclide transport and their associated release of radioactive inventory can be treated like an instant release fraction (IRF), similar to the case of spent fuels (see Section 6). However, it is important to note that the dissolution and subsequent radionuclide release of any yellow phase entrapped within the glass matrix is likely to occur over the timescales in which the glass matrix is expected to dissolve, which are relatively long. As a result, any evaluation of such IRF based on the expected inventory of yellow phase is likely to be pessimistic and experimental work would be required to measure more realistic release rates (like in the case of spent fuels, see Section 6.3.1).

Initial release due to yellow phase

As noted in Section 5.2, the composition of yellow phase in standard UK HLW products is complex; in general it comprises about 80% water soluble alkali molybdates and about 20% insoluble alkaline earth and rare earth molybdates [20]. Yellow phase may act as a host for a number of radionuclides such as the long lived fission products ^{99}Tc and ^{135}Cs, and potentially for the higher actinides ^{241}Am and ^{237}Np (although to date, the presence in this phase of actinides has not been verified experimentally). In a recent study of whole pours of 75o:25m Blend glass produced at Sellafield on the Vitrification Test Rig, the glass was broken up and leached in deionised water for 24 hours to dissolve soluble yellow phase. Chemical analysis of the leachate found that caesium made up 10 ± 2 % by mass of the cations present; the quantity of technetium present in yellow phase was assessed to be small (0.4% by mass) [20].

An attempt to quantify the yellow phase associated with standard WVP product concluded that it amounted to 0-5g per 190 kg pour. During full-scale trials of the vitrification process, an assessment of yellow phase on some 75 trial pours for standard 25wt% incorporation Magnox glass found that 64 contained less than 0.4 g, and a further 6 less than 1 g; the largest amount found was 5.6 g [20]. Owing to the tendency of yellow phase to float on the melt surface, much of the yellow phase is retained in the melter crucible when the melt is poured. As a result, higher amounts of yellow phase have been found in drain pours, but these have been assessed to amount to only a few tens of grams [20].

Chemical durability experiments on active and inactive UK glasses containing yellow phase have shown a rapid dissolution of the alkali molybdates, which is complete within a few hours, but the elemental concentrations in the leachate after a few months is similar to a glass that does not exhibit any obvious yellow phase [20, 24]. Given the relatively small quantity of yellow phase associated with the standard (25 wt% waste loading) HLW containers, we currently do not consider its associated early release significant compared to releases that will arise in the short term from the initial dissolution of the glass matrix. The potential for higher levels of yellow phase associated with future products (POCO glasses, Technical Wastes) has not been considered at this stage, but is part of the future R&D programme [10, task 538].

Initial release due to short-term dissolution rate

The previous section has focused on the long-term release rates of glasses and their effect on radionuclide release. As discussed in Section 5.3, however, glasses typically display a higher initial dissolution rate (Stage I and II). In the absence of mechanisms leading to the removal of silicon (and possibly other species) from solution, this regime is expected to be relatively short, leading to a release of a very small fraction of the radioactive inventory of the glass. However, as noted in section 5.3, work on European collaborative projects has shown how the presence of EBS materials (in particular ferrous metal corrosion products and clay buffer materials) can promote the dissolution of the glass, inhibiting the establishment of a longer-term residual rate [101]. A number of more recent studies found that the presence of claystone [139] and magnetite [141] accelerated the long-term leaching rate of SON68 when compared to experiments in simple solution.

A similar finding has recently been reported in cementitious environments. In recent studies, the presence of OPC has been found to trigger the dissolution of both SON68 and SM539 glasses at a relatively fast rate [15]. In these tests, powdered glasses were intimately mixed with cement and subjected to leaching at 30 °C and a pH of 13.5. The rate of glass dissolution was found to increase with the amount of cement present until the rate reached that measured for the initial glass dissolution rate in dynamic tests under similar conditions, but in the absence of cement. The key reactions driving glass dissolution were postulated to be the reaction of silicate released from the glass with calcium hydroxide to form calcium silicate hydrate phases (C-S-H) and the further conversion of C-S-H phases with aluminium to form calcium-aluminium silicate hydrate phases (C-A-S-H). It was further anticipated that once the calcium hydroxide component of the cement had been consumed the rate of glass alteration would decrease.

Overall these findings indicate that, as a result of interactions with EBS materials in close proximity to the glass, there is potential for a period of faster release of radionuclides from HLW glasses on exposure to groundwater; the rate may in fact be as high as the initial dissolution rate. The duration of this period of accelerated leaching may be limited by the capacity of the reactive EBS materials to sorb or react with silicon to form secondary phases, currently estimated to occur over periods of decades or centuries. However, a crucial factor that has emerged from recent French studies concerns the proximity of the EBS material to the glass. It has been found that the effects of EBS materials (clay or corrosion products) are attenuated when there is a diffusion barrier between the glass and the reactive material [161], indicating that the presence of an impermeable barrier such as the stainless steel vitrification canister could be important in determining the glass behaviour.

Initial dissolution rates in deionised water of glass formulations relevant to the French and Belgian disposal programmes are presented in Table 7. Compared with long-term release rates (Table 6), initial release rates are typically three or four order of magnitude higher. Studies of the initial stages of glass dissolution of Magnox and blend glass in alkaline media are reported in [149, 150, 117], complementing recent studies focusing on long-term release rates [105, 152, 154]. Recognition of these potential effects of the initial dissolution rate on radionuclide release from HLW was taken into account in the source term model for HLW glasses in [162], which is discussed further in section 11.4.

Table 7: Variability in the initial alteration rate (r_o, measured at 100 °C) for simulant AVM- and R7T7-type glass compositions in deionised water (based on data presented in [18])

	initial rate ($g\ m^{-2}\ day^{-1}$)			
Glass type	Maximum ($r_{o\ max}$)	Minimum ($r_{o\ min}$)	Average ($r_{o\ mean}$)	Max/Min ratio ($r_{o\ max}/r_{o\ min}$)
AVM	9.8	1.3	5.3	7.4
R7T7	4.1	1.3	2.4	3.2

5.4 Corrosion of the vitrification canister

During interim storage corrosion of the vitrification canister is likely to be very limited, provided good control of the environmental conditions is achieved. Upon exposure to groundwater general corrosion is likely to be very slow, but localised corrosion is likely to occur, leading to relatively fast perforation of the vitrification canister.

The vitrification canister in which HLW is initially emplaced for interim storage is made of stainless steel (grade 309). The corrosion behaviour of stainless steels is described at length in Section 10, since this type of material has been considered for the manufacture of waste containers for both ILW and, to a lesser extent, HLW and spent fuels.

During the vitrification process, the vitrification canister is exposed to molten glass at very high temperatures (>1000°C). This leads to the rapid oxidation of both the internal and external surfaces of the metal, resulting in the growth of surface oxides and the formation of a so called ‘heat tint’. This effect, however, does not lead to any substantial damage to the bulk metal (this grade, which is higher in chromium than other austenitic grades, is employed for its high resistance to elevated temperatures).

Following vitrification, and upon exposure to atmospheric conditions (relevant to dry interim storage), the vitrification canister is likely to be exposed to relatively high temperatures for prolonged periods. In these conditions, dry oxidation is likely to continue at a very low rate. Even under aggressive marine exposure conditions the atmospheric corrosion rate of grade 309 stainless steel is less than 0.025 μm year^{-1} [163]. As the system cools down, depending on storage conditions, deliquescence of moisture may become possible. In these conditions, and if chloride salts are present in the environment, pitting and SCC could become possible (see Section 10).

Upon exposure to groundwater, after perforation of the disposal container, aqueous corrosion of the vitrification canister is likely to occur. At the temperatures expected during disposal, general corrosion rates would be expected to be very low (<0.1 μm year^{-1}, see Section 10). At this rate, the very low levels of activation products present in the canister are such that any radionuclide release associated with corrosion will be minimal.

However, depending on the nature of the buffer employed, groundwater chemical composition and temperature/redox conditions at the time of resaturation, localised corrosion may occur. The resistance of this grade to localised corrosion is expected to be similar to that of other austenitic grades used for ILW (304) [164, Table 2.1]. Additionally, the material grade employed in the manufacture of vitrification canisters is known to contain levels of carbon too high to prevent sensitisation upon welding (it is not an ‘L’ grade) and, as a result, it is expected to be susceptible to intergranular corrosion - even in conditions in which the bulk of the material would not suffer localised corrosion.

Given these considerations, after relatively short periods following penetration of any long-lived disposal container (overpack), it is very likely that localised corrosion of the vitrification canister will occur upon exposure to near-neutral pH groundwater. Pitting corrosion, and, even more likely, intergranular corrosion and stress corrosion cracking near the weld region are expected to occur and propagate at a relatively fast rate. However, the very small perforations that may be generated by these processes are such that, even after perforation, the canister will provide a transport barrier between the groundwater and the HLW glass, which is important in evaluating the dissolution behaviour of the glass (see Section 5.3).

The use of a cementitious buffer could potentially inhibit localised corrosion, but any protection that may be afforded to such a system has not been assessed in detail. This however would need to be balanced against the desire to ensure a low dissolution rate of the vitrified wasteform which, as described in Section 5.3, may (or may not) experience higher rates of glass dissolution in the presence of cementitious buffers.

Overall, given these and other considerations, it is likely that HLW will be disposed of with an overpack likely to provide substantial robustness during any periods preceding closure of the GDF and higher durability for many thousands of years following its closure. In suitable dry geological conditions (such as an evaporite) however, direct disposal of HLW without further over-packing may still be an option.

5.5 Effects of radiation on glass stability

The accumulation of damage arising from alpha decay has been identified as the main source of change in the macroscopic properties of borosilicate glasses over long times. However, at least for non-UK glass compositions, there is no apparent effect of accumulated alpha decay dose on either the initial or the residual dissolution rates.

HLW glasses incorporate significant concentrations of fission products and smaller amounts of higher actinides (such as curium) which undergo radioactive decay. This produces a significant radiation field within the glass that results in radiation damage (which heats the glass), transmutation of decaying radionuclides into daughter elements and the generation of helium atoms within the glass matrix. The potential impacts of radiation effects on the microstructure, properties and long-term performance of HLW glasses have been studied for over 40 years (see for example the historical reviews [165, 166, 167]). Recently, a comprehensive review of work on the effects of alpha decay and helium build-up on the radiation stability of French R7T7-type HLW glasses has been published [168].

The principal sources of radiation in HLW glasses are the beta-decay of fission products (in particular ^{137}Cs and ^{90}Sr) and alpha-decay of long-lived actinides (such as some isotopes of uranium and neptunium). The effects of α-, β- and γ-irradiation on glasses have been investigated for a range of HLW glass compositions, including UK glasses [165]. This research has often used simulant waste glasses that have either been doped with short-lived radioisotopes (such as α-emitting curium-244, half-life 18.1 years [169]) or irradiated using external sources, such as bombardment with electrons, ion beams (of potassium ions [170][29]) or gamma sources (Co-60) to accelerate the impacts of radiation. More recently, molecular dynamics modelling techniques have been used to study high-energy nuclear interactions and the resulting radiation damage in HLW glasses [171].

5.5.1 Effects of beta decay and radiolysis

In general, beta decay is the primary source of irradiation during the first few hundred years of storage and disposal as it arises from relatively short-lived radionuclides with a consequent high specific activity; alpha decay becomes the dominant source of irradiation at longer times. Disposal containers, or overpacks, are expected to be sufficiently long-lived that water will only come into contact with the glass wasteform after a long time, once beta dose rates have substantially reduced. Studies simulating the effect of beta-decay, using either gamma irradiation or high energy electrons, have found no appreciable increase in leach rates for the glasses tested. For example, recent studies of SON68 glass leaching under gamma irradiation found no significant effects on glass alteration rates up to doses rates as high as 5 kGy h^{-1} [172].

5.5.2 Effects of alpha decay and alpha recoil

The results of a comprehensive international review of the state of understanding of self-irradiation effects in nuclear waste glasses and ceramics, published in 1997 [167], identified alpha decay of the minor actinides as the main source of change in glass properties. Subsequently, a significant body of research has been undertaken on the impact of alpha decay on the properties of R7T7-type glasses in the French programme [168]. The principal findings of these studies are summarised below.

The French studies used SON68, doped with varying concentrations of the short-lived actinide ^{244}Cm, to investigate the effects of alpha-radiation dose on glass properties. It has

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[29] Bombardment with helium and heavier ions (such as potassium or lead) has been used to simulate the effects of α-irradiation and the recoil of the decayed nucleus (α-recoil) respectively.

been found that some macroscopic properties of the curium-doped glass vary with the accumulation of alpha decay, but then stabilise after cumulative doses of about 4×10^{18} alpha-disintegrations per gram ($\alpha\ g^{-1}$) [168]. For example, the glass density diminishes by about 0.6%, its Young's modulus by about 15% and its hardness by about 30%, whereas its fracture toughness increases by around 50%. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that the glass is still homogeneous; no phase separation, crystallisation or bubble formation were apparent up to an alpha decay dose of $10^{19}\ \alpha\ g^{-1}$ (corresponding to an accumulated dose equivalent to several thousand years after disposal for an R7T7-type HLW glass[30]).

To study the origin and nature of the structural changes that underlie the observed macroscopic changes in glass properties, in the same study [168] specimens of (inactive) SON68 were irradiated with both light (helium, krypton) and heavy (gold) ions. In addition, molecular dynamics simulations have been performed to investigate the underlying nuclear reactions. Comparison of the macroscopic properties of the curium-doped glass with those obtained for SON68 specimens irradiated with light or heavy ions (from experimental and molecular dynamics studies respectively) suggests that the macroscopic evolution is induced by the nuclear interactions resulting from the recoil nuclei of alpha decay.

Spectroscopic examination of irradiated glasses has detected small changes in the local order around some cations and in the medium-range order of the glass network[31], indicating an increase in disorder of the glass structure. This structural evolution appears to be driven by the reconstruction of the glass damaged by the displacement cascades of the recoil nuclei, resulting in a glass structure with a higher degree of disorder than the as-cast glass. At doses around $4 \times 10^{18}\ \alpha\ g^{-1}$ the entire sample volume was affected by this process at least once (i.e at least one displacement per atom), which explains why the macroscopic properties stabilise at this dose.

Helium accumulation also occurs in HLW glasses as a result of electron capture by alpha particles released during alpha decay [167]. Detailed work carried out in the French programme, (summarised in reference [168]) has found that the capacity of the borosilicate-based matrix of SON68 simulant glass for helium dissolution is significantly larger than the amount of helium produced by α-decay in a glass package. Furthermore, the aforementioned SEM and TEM investigation [168] of ^{244}Cm-doped glass damaged by an alpha decay dose of around $10^{19}\ \alpha\ g^{-1}$ (equivalent to the cumulative radiation dose over several thousand years after disposal) showed a homogeneous glass without crystallisation, phase separation or bubbles with a size greater than the limit of spatial resolution of 10 nm. A major conclusion of the French programme is that high helium accumulation in the SON68 glass has no macroscopic consequence on glass integrity.

To evaluate the effects of accumulated alpha decay on the chemical durability of glass, a series of ^{244}Cm-doped SON68 glasses, and glass specimens irradiated with gold ions, were subjected to Soxhlet tests in water at 100 °C for 28 days [173]. It was found that there was no significant variation in the initial dissolution rate of the curium-doped glasses with accumulated alpha dose, up to $2 \times 10^{19}\ \alpha\ g^{-1}$, within the 20% measurement uncertainty. Likewise, there was no change in the alteration rate with fluence for the gold-irradiated samples, despite some induced changes in the glass density and mechanical properties.

In addition, no significant effect of alpha dose on the residual dissolution rate was found in static leach tests at 90 °C in water over 1200 days for a plutonium-239 doped SON68 glass

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[30] Similar or lower levels of α damage are currently expected in UK HLW.

[31] Changes in medium-range order involve both changes in the bond angles between network formers (fro example in mean Si-O-Si angle) and broadening of the size distribution of the ring structures that form the glass network.

with an alpha dose rate of 150 Gy h^{-1} (equivalent to an HLW glass after about 1500 years) compared to inactive glass [174]. In addition, plutonium was found to be strongly retained (95%) in the glass alteration layer.

The results of recent studies (mostly on SON68) are in accord with historic studies on alpha-doped glasses carried out in the UK during the 1970s (summarised in reference [165]), which showed that any changes in leach rate due to accumulated alpha-decay damage were modest and no more than a factor of 2 to 3.

6 Evolution of spent fuels

This section describes scientific and technical information relevant to the expected evolution processes of spent fuels, particularly dissolution and leaching processes in groundwater. Key sources of information include work carried out by waste management organisations in other countries at universities and research institutes, as well as a number of EC-funded projects (for example, SFS [175]; MICADO [176]; FIRST-Nuclides [177]; and REDUPP [178]), and the proceedings of conferences such as the Scientific Basis for Radioactive Waste Management Symposia [91].

The information presented summarises the available evidence on this topic produced in the UK and worldwide in the last 20-30 years. Typical studies include:

- research on real spent fuel samples
- research on simulants, with compositions selected to closely approximate the chemical composition of spent fuel (the so called ‘SIMFUEL’, as well as UO_2 doped with high specific activity alpha-emitters such as ^{233}U)
- modelling aimed at supporting the development of a mechanistic understanding of microstructure and dissolution properties
- natural analogues and decades of industrial experience in the use, handling and storage of these materials.

In situ experiments in underground laboratories have received little attention because of the difficulties in implementing emplacement and retrieval of UO_2 or SIMFUEL specimens under the reducing conditions required to preserve the surface redox conditions of samples.

The information presented focuses on spent fuels which, to date, have been considered in more detail in our research programme (AGR and LWR fuels). A more limited amount of information relative to the behaviour of metallic fuel is also presented, largely based on the behaviour of (un-irradiated) uranium. Metallic and other spent fuels (such as exotics and MOX fuel) have not yet been investigated in RWM’s research programme (they will be the subject of future studies [10, tasks 550 and 554]), but their behaviour is expected to be relatively similar to that of the spent fuels described herein[32].

An overview of evolution processes is presented below, followed by a more detailed description of specific processes. The overall impact of such processes on the evolution of UK spent fuels is discussed in Section 11.5, largely based on work carried out on LWR fuels.

6.1 Overview of spent-fuel evolution processes

6.1.1 Initial state and pre-closure period

Characteristics of the initial state of spent fuel include its degree of porosity and cracking, its level of micro-segregation and its water content. During interim storage, degradation processes requiring consideration include corrosion of the cladding, the underlying fuel, and any dry storage container. If residual levels of water are present, internal pressurisation can also occur.

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[32] The matrix dissolution of fuels based on metallic or carbide systems may be similar - characterised by relatively fast dissolution processes, albeit yielding different gaseous products (such as methane, acetylene and other hydrocarbons). Conversely, the dissolution behaviour of fuels based on oxide systems (including MOX fuel) may be similar to that of other UO_2-based fuels, at least in comparable irradiation conditions. The behaviour of oxide systems characterised by much higher burn-up (PFR fuel) would need to be specifically evaluated.

Irradiation of fuel in nuclear reactors leads to substantial microstructural and chemical alteration of the fuel and its cladding, arising from nuclear reactions (particularly fission and neutron capture) as well as physico-chemical processes (particularly thermal and radiation-enhanced diffusion). The fuel develops extensive cracking (oxide fuels) and/or porosity (oxide and metallic fuels) as well as substantial chemical changes associated with fission, activation and radioactive decay. Particularly for oxide fuels, the formation of cracks (which will affect the surface area of the fuel) and chemical changes associated with the generation and microstructural segregation of a variety of radioactive (and stable) elements in the structure will affect the leaching properties of the fuel and are very important characteristics of its initial state.

During the subsequent storage (and disposal) period, the microstructure of the fuel is expected to continue to evolve at a much reduced rate, associated with reduced temperatures and the much more limited extent of nuclear reactions compared with a nuclear reactor (processes of radioactive decay, as opposed to fission and neutron capture). Some microstructural evolution (such as helium generation due to alpha decay) is however expected to occur.

Corrosion of the fuel cladding, fuel, and other fuel assembly components during interim storage in water ponds or, in the case of dry storage, of any dry storage container can lead to degradation of the immobilisation properties of the wasteform. For spent fuels stored in cooling ponds these processes may also lead to a decrease in the radioactive content of the wasteform (due to in-pond leaching) and potential alteration of its chemical properties, with a consequent impact on the post-closure behaviour.

In the case of spent fuel previously stored in cooling ponds and subsequently packaged in storage/disposal containers, generation of hydrogen gas from any water that may be retained in fuel assemblies after drying may result in a degree of pressurisation of the container through radiolysis and/or internal corrosion. Any air present inside a disposal container may also lead to the radiolytic generation of nitric acid, potentially increasing corrosion rates or leading to the corrosion of components particularly susceptible to nitric acid corrosion. This can be effectively mitigated by employing an inert gas (for example, argon) at the time of container sealing.

Evolution processes and their effects are listed in Table 8.

6.1.2 Post-closure period

After disposal in the GDF the most important degradation processes are likely to be dissolution of the fuel matrix and leaching of specific, micro-segregated radionuclides. Corrosion of the metallic components of the fuel assembly (such as cladding) will also occur. In the case of oxide fuel, these processes can, in turn, be affected by microstructural changes likely to occur as a result of radioactive decay.

During the post-closure period, there will be an initial period in which the integrity of the disposal container ensures that dry conditions are present in contact with the wasteform. During this period, evolution processes are expected to be limited to slow microstructural evolution processes (including generation of helium gas) and not result in release of radioactivity to the EBS nor adverse effects on the disposal container. Once exposed to groundwater (following breach of the disposal container), spent fuel is likely to undergo leaching and dissolution/corrosion reactions leading to a release of radionuclides in the EBS. Leaching involves preferential release of some fission and activation products that may have segregated during irradiation of the fuel in the reactor. In the case of oxide fuels, in oxidising conditions, electrochemical oxidation of the matrix from U(IV) to U(VI) may lead to the fuel matrix to dissolve at a relatively fast rate (a process described herein as ‘oxidative dissolution’ and by some authors as ‘corrosion’), much faster than the chemical dissolution (as U(IV)) which tend to dominate its behaviour in strongly reducing potentials. Different types of oxide spent fuel are likely to exhibit different dissolution and leaching behaviours. However, the release of much of the inventory of key radionuclides is expected to occur congruently with the matrix. The leaching behaviour of some spent fuels (particularly oxide fuels) is likely to be affected by the formation of gas bubbles or soluble phases containing specific radionuclides (such as caesium and iodine isotopes). In the case of metallic fuel, its dissolution (in this document also referred to as ‘corrosion’ for analogy with processes characteristic of metallic materials) is expected to be particularly fast, resulting in a relatively congruent radionuclide release as well as gas generation.

Corrosion of the fuel cladding and other fuel assembly components also requires consideration. Beyond being precursors for the exposure and subsequent leaching of the underlying fuel to groundwater, these corrosion processes are also likely to lead to the release of specific radionuclides which may have been generated within the clad by neutron activation. In particular, clad and fuel assembly corrosion may lead to a release of gases and low molecular weight compounds containing ^{14}C; this is currently being studied in a large international research programme being led by RWM [10, tasks 201 and 206]. In the case of metallic fuel, corrosion of the cladding is expected to be particularly fast in contact with water. However, given that the corrosion of the fuel itself may also be relatively rapid, corrosion of the cladding may have limited impact on the release of radionuclides from the wasteform; cladding corrosion may however be particularly important in contributing to the rate of bulk gas generation which can drive gaseous radionuclide releases from the GDF [5].

Microstructural evolution of spent fuel over the timescales associated with geological disposal requires due consideration of its contribution to dissolution and leaching behaviour. In the longer-term, any helium gas generated by α-decay may result in internal pressurisation of the fuel grains, potentially leading to cracking and an increase in the surface area available for leaching. Over long-enough timescales, if cracking of the grains was considered possible, pressurisation of the waste container could also result from this process.

Generation of hydrogen gas from corrosion of internal waste container furniture or, for metallic fuel, of the fuel assembly itself, may also be important. The hydrogen gas generated will contribute to the development of reducing conditions in proximity to the fuel, which can decrease the dissolution rate of oxide fuels. Eventually, any gas generated will be released to the EBS upon perforation of the waste container.

Evolution processes and their effects are listed in Table 8.

Table 8: Processes of general relevance to spent fuels

Period	Evolution Process[33]	Effect	Section
Initial state	Irradiation in reactor	Surface area (driven by the level of cracking/porosity) Level of micro-segregation	6.2
Pre-closure	Evaporation of entrained water[34]	Gas generation (water vapour)	6.6
Pre or Post-closure period	Leaching and dissolution/corrosion of fuel (pond water or groundwater)	Release of radionuclides Relocation of fissile materials	6.3
	Corrosion of cladding (pond water, atmosphere or groundwater)	Release of radionuclides Relocation of fissile materials Gas generation (H_2)[35]	6.4
	Microstructural evolution due to self-irradiation	Release of radionuclides Gas generation and effect on fuel grains (He)	6.6
	Corrosion of internal container furniture[34]	Gas generation (H_2)	6.6

6.2 Initial state

Enhanced cracking, porosity and micro-segregation are expected in spent fuels upon discharge from the reactors. Entrained water may also be present in some fuel.

Factors that may be important in assessing spent fuel evolution processes are the degree of cracking and porosity within the matrix, affecting the surface area, and the level of micro-segregation, which may lead to faster leaching of specific species and an increase the overall rate of dissolution of the fuel matrix.

For spent fuels that, before containerisation in a storage and/or disposal container, were stored under water, the amount of residual water may also be important (see Section 4.3).

These factors are considered in turn below.

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[33] The table presents a simplified description of key processes likely to affect the evolution of spent fuels. Other important processes include their thermal and radioactive decay processes, which are central to many other evolution processes and are discussed in Section 4 in the context of the environmental conditions in which evolution processes will take place.

[34] This process is relevant only to fuel which was not completely dried before containerisation.

[35] In the case of metallic fuel, corrosion of the cladding may lead to the generation of hydrogen gas.

6.2.1 Cracking/porosity and surface area

Irradiation in a reactor produces a substantial amount of cracking and/or porosity. Estimates of resulting surface areas are needed where the absolute corrosion rate is required, for example in comparing to rates from other experiments. However, they are not essential for deriving fractional dissolution rates if spent fuel fragments in their normal state are directly tested.

In-reactor processes produce a substantial degree of cracking (oxide fuels) and/or porosity (for oxide and metallic fuel). Porosity is generated by fission gases and cracking is largely generated by differential thermal expansion. Higher levels of porosity and cracking are usually observed as the burn-up increases, while cracking is enhanced by the thermal cycling experienced by fuel pellets during reactor refuelling.

The nature and degree of cracking and porosity are likely to affect the dissolution behaviour of the fuel by controlling the surface area. Nonetheless, at least for oxide fuels, the dissolution behaviour is typically evaluated on the basis of experimental measurements on real (cracked) spent fuel samples and rates are often reported as fractional dissolution rates (fraction of the sample inventory dissolving per unit time). As a result, a detailed understanding of this parameter may not be required when estimating fuel dissolution rates for safety assessment calculations. However, in order to make comparisons to dissolution rates of fuel simulants (SIMFUEL, UO_2 or metallic uranium) in experiments performed under the same conditions, specific surface areas can be estimated (see for example, [179]).

6.2.2 Micro-segregation

Micro-segregation is particularly important for oxide spent fuels, since it determines the extent of initial release of important radionuclides and the long-term dissolution rate of the fuel matrix upon exposure to groundwater. Levels of micro-segregation for specific radionuclides have been characterised in a number of fuels and reactor conditions.

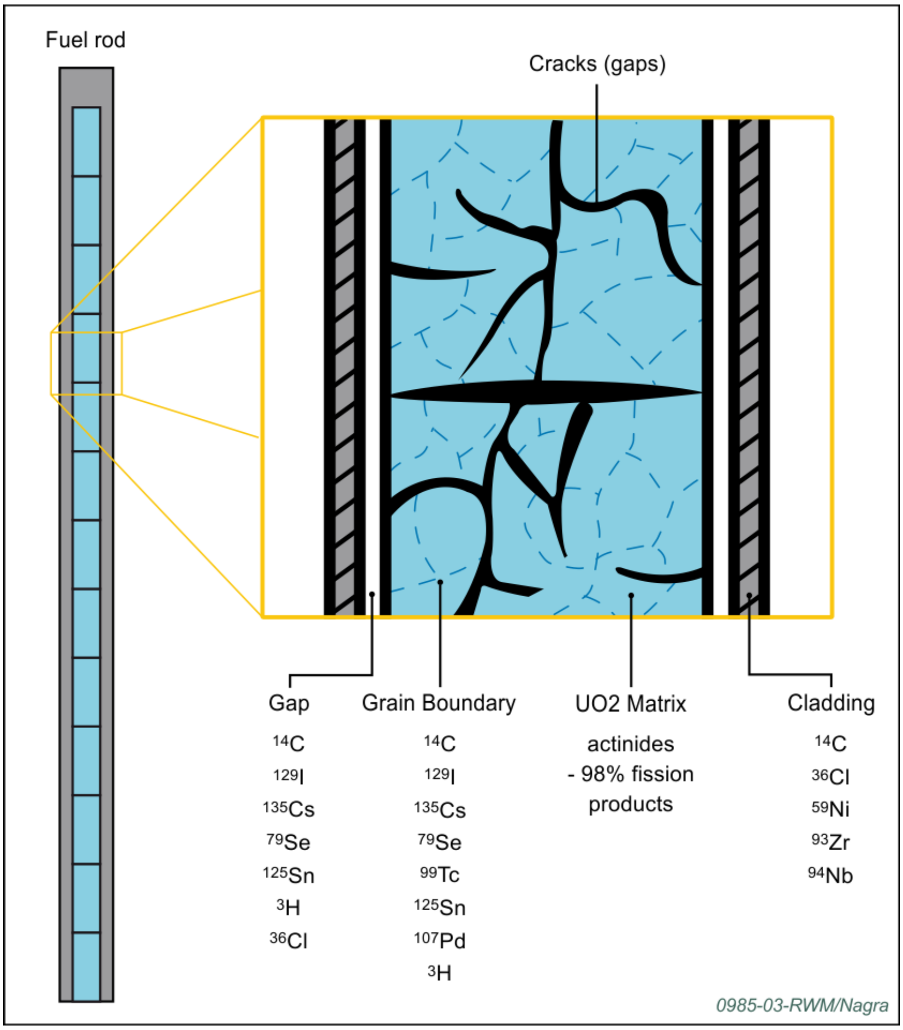
The level of micro-segregation is expected to be particularly important for oxide fuels since, given the very low dissolution rate of the fuel matrix, dissolution of segregated, soluble phases is a key contribution to the release of radioactivity from the wasteform upon exposure to groundwater. The level of micro-segregation in metallic fuels may also have an effect on the dissolution behaviour of the fuel but has not yet been evaluated in our research programme and is not currently covered in this document ([10], task 554).

Oxide fuel is a heterogeneous material, consisting of a matrix of nearly stoichiometric uranium dioxide in which the higher actinides produced by capture of epithermal neutrons are generally viewed as forming solid solutions with UO_2. The same holds for the majority of the fission and activation products (such as strontium and the lanthanide oxides). At the temperatures relevant to the operations of nuclear reactors Kleykamp [180] divided the fission products into four classes, depending on their chemical state in the fuel:

- fission gases and other volatile fission products: Kr, Xe, Br, I
- metallic precipitates: Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te
- oxide precipitates: Rb, Cs, Ba, Zr, Nb, Mo, Te
- dopants in the fuel matrix: Sr, Zr, Nb, Y, La, Ce, Pr, Nd, Pm, Sm.

A small percentage of elements which are volatile at the temperatures experienced in the hottest parts of the fuel during irradiation (for example, Cs and I) migrate, by varying degrees, to the fuel-clad gap or to grain boundaries; others (such as Mo, Tc, Pd, Tc) form separate metallic alloy phases (ε-particles) [180, 181, 182]. A schematic representation of these effects is presented in Figure 21. The extent of segregation is a function of power rating and burn-up [183]. In the case of species which are highly soluble in groundwater, segregation can affect the leaching behaviour of the fuel, resulting in a relatively fast release of specific isotopes.

Figure 21: Conceptual distribution of radionuclides in spent fuel [182]. The illustration (focusing on LWR fuels but likely to be relevant also to AGR fuel) shows the location of key radionuclides in different parts of a fuel pellet, including the matrix, grain boundaries, the cladding, and the 'gap' (formed by the easily accessible spaces, including pellet/pellet and pellet/cladding interface, cracks, and open fission-gas tunnels)[36]



Not all micro-segregation processes, however, have the same impact on dissolution and leaching processes. For example, for insoluble inclusions, such as metallic particles ('ε-particles'), or particles made of barium and zirconium oxides ('grey phase'), segregation has little impact on the leaching behaviour of the radionuclides segregated in the particles themselves. However, segregation may affect oxidative dissolution processes, particularly in the case of metallic particles. Since micro-segregation processes are very strongly associated with the dissolution and leaching behaviour of the fuel, they are described in more detailed in the section dedicated to such processes (Section 6.3).

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[36] Note that, in LWR fuel, while a physical gap initially exists between the fuel pellets and cladding, as burn-up increases the gap progressively closes.

It is important to understand that, due to the relatively poor thermal conductivity of UO_2, the differences in temperature experienced across a fuel pellet (across a distance of few mm) are very substantial, with peak temperatures of the order of 1,400 °C in the fuel centre and 300 °C at the cladding interface for LWR fuels, and 1,400°C at the fuel bore and 800°C at the cladding interface for AGR fuel (see also Box 2). The variations in diffusivity of many elements are typically very large within this temperature range. This effect results in substantial differences in the level of micro-segregation observed in the hotter (centre/bore) and colder (cladding) parts of the fuel.

6.3 Fuel dissolution and leaching (oxide fuels)

After release of a fraction of the inventory of specific radionuclides (the Initial Release Fraction, IRF), dissolution of oxide spent fuel and the associated radionuclide release rate are controlled by the rate at which the matrix itself dissolves.

Most spent fuel of relevance to the UK inventory for disposal consists of heterogeneous fractured ceramic UO_2 pellets. Dissolution and leaching of radionuclides from the UO_2 ceramic pellets is relevant to understanding the behaviour of spent fuel.

The reactor operating conditions have an important impact on heterogeneity of the fuel, in particular the segregation of fission and activation products from the UO_2 grains (see Section 6.2.2), which in turn affects the leaching behaviour of specific radionuclides. Fission gases, ^{129}I, ^{36}Cl and isotopes of caesium diffuse rapidly in UO_2 at the high temperatures of the central region of the fuel. Thus they may accumulate at grain boundaries and other heterogeneities (such as cracks) present in the system.

- The inventory of radionuclides present in ‘accessible’ parts of the fuel is generally referred to as the ‘gap inventory’ (the ‘gap’ representing the interconnected volume of the fuel to sheath gap, fractures in the fuel pellets and open fission gas tunnels[37], Figure 21).
- Conversely, the inventory present at grain boundaries is referred to as the ’grain boundary’ inventory (Figure 21).

In safety assessments the gap inventory, and sometimes the grain boundary inventory, are assumed to be released ‘instantly’ upon contact with the groundwater, resulting in the so called ‘Instant Release Fraction’ (IRF) - sometimes divided into an IRF_{Gap} and an IRF_{GB} [184]. It should be noted, however, that some fission products that are segregated from the matrix are highly resistant to dissolution at low redox potentials (for example Tc-99), thus a distinction should be made between the fractions of radionuclides segregated and the fractions likely to be released.

The IRF can be related explicitly to the properties of the fuel itself and its magnitude depends on many factors, including the initial fuel composition, the chemistry of the relevant fission products and burn-up history during reactor operations. When fission gas bubbles at grain boundaries interconnect to create tunnels, this may create a pathway to a crack in the fuel, leading to an increase in the accessible (gap) radionuclide inventory and a consequent release of the IRF_{Gap}. Since the interconnectivity of gas bubbles has been shown to be strongly dependent on fuel thermal history, the IRF_{Gap} increases with the linear power rating, which affects the fuel centreline temperature, as well as with burn-up, which affects the overall yield of fission products and other changes in the fuel microstructure.

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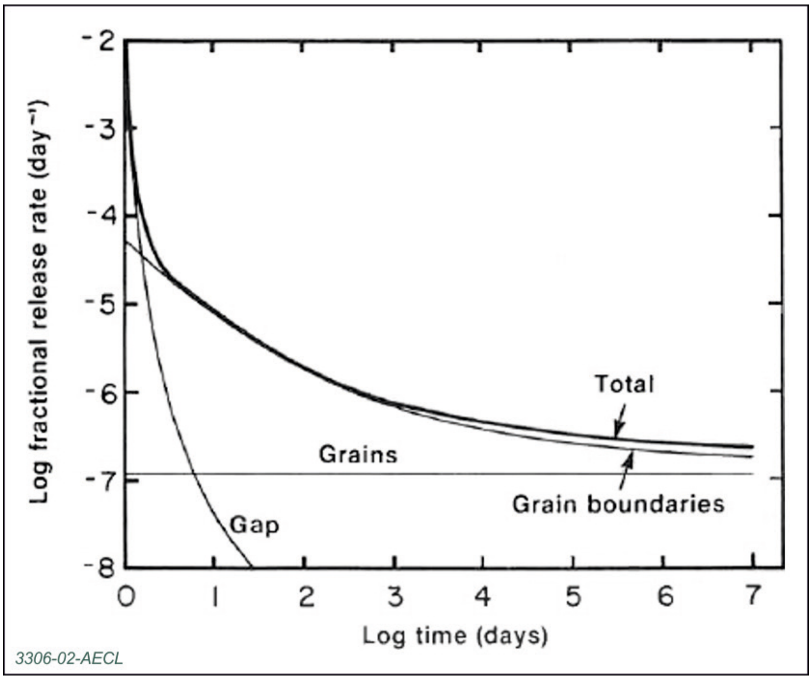
[37] Tunnels generated within the fuel microstructure by the coalescence of initially-closed porosity, typically observed at sufficiently high burn-up and power rating.

After release of the IRF, dissolution of the spent fuel and the associated radionuclide release rate are controlled by the rate at which the matrix itself dissolves. A conceptual illustration of radionuclide release from spent fuel is shown in Figure 22. Matrix dissolution is influenced by a variety of factors, such as fuel burn-up, the radiation field and the chemistry and redox potential of the water contacting the fuel. The key influence on dissolution rate is the redox chemistry of the aqueous/solid phase system. Significant dissolution of the spent fuel would only occur at high redox potentials, where the relatively stable UO_2 (solid) matrix is oxidised to the more soluble U(VI) form. Fuel matrix dissolution is much slower under reducing conditions because, in these conditions, oxidation to U(VI) does not occur and the dissolution of the matrix is driven by the chemical dissolution of UO_2, which has a much lower solubility and slower dissolution kinetics than higher oxidation compounds (usually denoted as UO_{2+x}). In geological systems it is highly unlikely that such highly oxidising conditions would develop, even if glacial conditions affected groundwater hydrochemistry at depth.

Overall, studies of the dissolution and leaching behaviour of LWR fuels have been carried out in many international programmes (for example, [184]). These studies are directly relevant to the disposal of PWR fuel from existing (Sizewell B) and, potentially, future UK power stations. There is less information about the dissolution behaviour of spent AGR fuel. Initial desk-based studies were completed between 2009 and 2011 [185, 186], followed by direct experimental studies [187]. These studies indicate that, although some differences in the behaviour of the fuel are seen, the knowledge base developed for LWR spent fuels is largely applicable to AGR fuels. More detailed information is provided below.

Figure 22: Conceptual illustration of aqueous radionuclide release from spent fuel in aerated water [188]



6.3.1 Instant release

In oxide spent fuels a small fraction of radionuclides is likely to be released over relatively short timescales upon contact with the groundwater – this is the Instant Release Fraction.

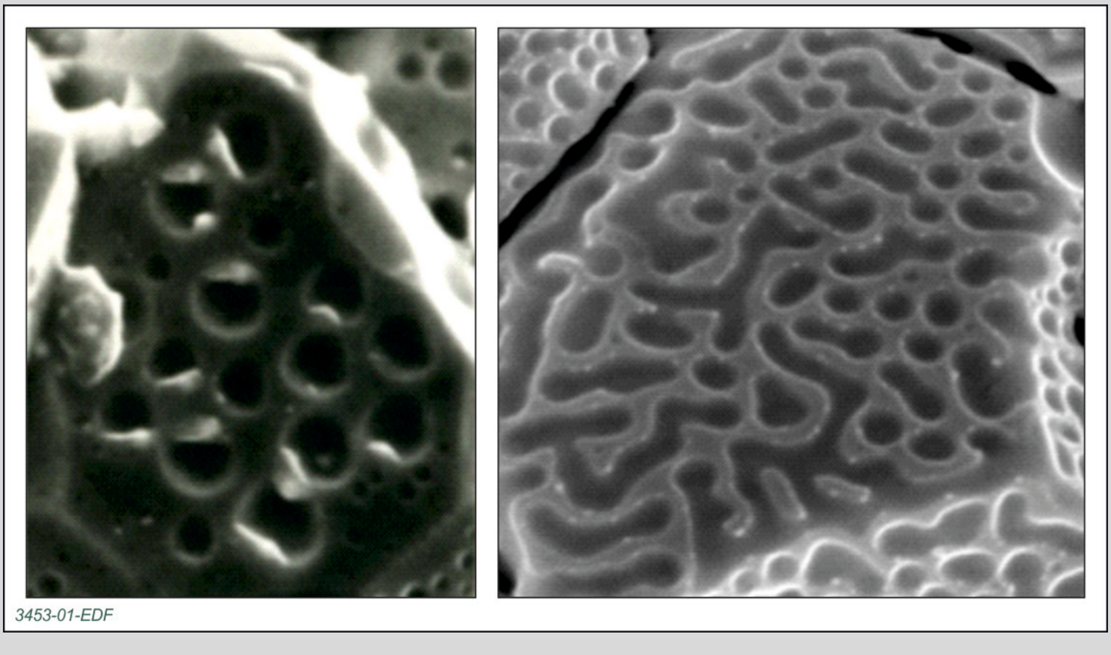
Studies on LWR fuels (typically carried out in oxic conditions) have demonstrated a correlation between the inventory of caesium and iodine 'immediately' leached by spent fuel in contact with water (the IRF_{Gap}) and the inventory of gases released inside fuel pins after reactor irradiation (the fission-gas release, FGR) [189, 190, 193] – see Box 12. This correlation is based on the observation that fission gases, such as xenon and krypton (measured during post-irradiation examination by puncturing a fuel pin), display similar characteristics to relatively volatile elements. As a result, a predictable fraction of the overall inventory of the fission gases is released in the gas phase (as xenon and krypton) to that released to the liquid phase via the IRF_{Gap} (predominantly caesium and iodine). One of the key advantages of being able to correlate IRF_{Gap} with FGR is that the FGR is more easily measured than the IRF_{Gap}. Furthermore, being an important parameter for the operations of nuclear reactors, the FGR is both routinely measured and calculated with well-qualified models [192].

Box 12 The correlation between IRF and FGR

The correlation between the IRF of caesium and iodine isotopes and the FGR is well established for LWR fuels [193]. This is based on considerations of the thermal diffusivity of caesium, iodine, xenon and krypton at the temperatures of interest and with observations of the morphology of spent fuel at different levels of irradiation and power rating. Two regimes for the FGR have been identified [185, 186, 193]: a low temperature / low burn-up regime, in which release of gas (and volatile elements) is characterised by a-thermal recoil-driven release (ratio between FGR and caesium/iodine equal to 1:1), and a high temperature / high burn-up regime, in which release of gas (and volatile elements) is characterised by diffusion-driven processes associated with the formation of a network of interconnected pores (ratio between FGR and caesium equal to $(1:3)^{0.5}$ and between FGR and iodine equal to 1:1). An example of gas bubble networks in spent AGR and LWR fuel approaching an interconnected regime is presented in Figure 23 [186]. The figure also shows that, after irradiation in similar conditions, grain-face bubbles in AGR tend to me more vermicular than in LWR fuel. This is the result of the lower morphological relaxation experienced in AGR reactors, which is associated with the lower hydrostatic stresses experienced in reactor [186].

In AGR fuel, temperatures typically below 1100 °C and FGR below 1%, levels of average rod burn-up below 20-30 GW day te^{-1} and levels of FGR <1% were proposed to distinguish the two regimes [185, 186].

Figure 23: Grain boundary gas bubbles in irradiated LWR fuel (left) and AGR fuel (right). Reproduced from [186] (originally from [191])



At low linear power ratings (or in cooler parts of the fuel at higher ratings), relatively little fission gas accumulates at grain boundaries, thus gas bubbles do not interconnect and limited local FGR occurs. In these conditions a relatively low IRF is observed. In LWR fuel however, the trend to extend burn-ups to 50-65 GWd/tHM and to up-rate reactor power over the last decade has led to generally higher fission-gas release (FGR) and IRF_{Gap} values (~4-12%) [192, 193]. An important observation is that at burn-ups exceeding about 45 GWd/tHM, the rim of the fuel restructures, resulting in a ~100 μm thick layer with small grain size and a high concentration of fission gases in closed pores [194]. Given this consideration, some studies have focused on evaluating the likely characteristics of the rim, including any potential rapid release ([195] and references therein). Consequently, it is known that as much as 4-8% of the total fission gas inventory in a fuel rod may reside in the rim at a burn-up of 60 GWd/tHM [195].

In order to capitalise on this understanding of LWR fuels we have investigated the relationship between FGR and the IRF of AGR fuel. This work has confirmed that the correlation applies to spent AGR fuel, with the formation of a network of interconnected porosity, associated with the coalescence of worm-like fission gas bubbles at grain boundaries [186]. In these conditions experimental measurements indicate substantial mobilisation of gases and volatile elements, particularly in the bore of the fuel, due to the high temperatures experienced in these regions [186]. However, at the maximum levels of burn-up expected in AGR fuel (a local maximum of 65 GWd/teU can be estimated for the rim region) the formation of a high burn-up structure (with potential effects on FGR and IRF) is not expected [186]. At the power ratings and levels of burn-up expected from past operations of AGR reactors (before 1985), fission gases, volatile species (for example, iodine, caesium and tellurium) and other less mobile elements (barium, molybdenum) are expected to remain entrapped within the bulk of the fuel (largely in poorly-interconnected gas bubbles), thus resulting in a very limited FGR (< 0.1%) [186]. At higher ratings/temperatures and burn-up, representative of modern reactor operations, more significant segregation of fission gases, volatile species (particularly iodine, but also caesium and tellurium) and, to a lesser extent, less mobile species has been shown to occur in the fuel. This has led to higher FGR (~0.1-5%) [186] and a divergence from the anticipated relationship.

We recently confirmed the expected similarities between the leaching behaviour of AGR and LWR fuel in an experimental study directly measuring the behaviour of spent AGR fuels [187]. Spent-fuel fragments from 'hot' parts of the reactor (stringers 6 and 7) were leached in simplified groundwaters (10 mM NaCl and 2 mM $NaHCO_2$)[38] in naturally aerated conditions. Samples with average rod burn-ups of 27 GWd/teU, 30 GWd/teU and 37 GWd/teU and FGR of about 0.2%, 1.1% and 8.4%, respectively, were tested. After two years leaching, values of the release of caesium and iodine isotopes from the sample with the lowest FGR (0.2%) were broadly similar to the FGR [187]. For the higher burn-up/FGR samples, the release of caesium was about one third of the FGR value [187] but the release of iodine showed much lower values than those expected on the basis of FGR [187][39]. Subsequent analysis of the bottom end cap region of the highest burn-up/FGR sample indicated that a macroscopic relocation of caesium, iodine and tellurium had occurred in this fuel element, leading to an accumulation of these species in the end cap [187]. This effect, already discussed in previous desk-based studies [75,186], may be relatively specific to AGR fuel, and is likely to be associated with the ring-shaped geometry of the fuel pellets, allowing migration and condensation of volatilised species in the cooler parts of the fuel pin in the conditions of

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[38] Similar groundwater compositions were employed in other studies on high-burn up LWR fuels and, to a lesser extent, MOX fuel carried out as part of the EC Project 'First-Nuclides'.

[39] Care must be taken when interpreting these results since, after two years testing, leaching rates have not yet reached a steady state.

particularly high operating temperatures. A refined analysis of the cumulative releases, taking into account the release from the end cap, resulted in minor increases in the values of caesium but substantially higher values for iodine. A value of 3.5% was evaluated [187] compared with FGR values of 8.4%, which is closer to values expected from previous studies [186].

Although the maximum operating temperatures within the fuel are similar, a key difference between AGR fuels and LWR fuels is the deposition of carbonaceous species on the cladding surface, in some circumstances, which effectively insulate the element and impede its heat transfer to the coolant gas. This may contribute to the higher FGR/IRF ratio at relatively low nominal linear power and burn-up [186][40].

The lower levels of burn-up typically associated with AGR fuel, however, suggest that, overall, the FGR and IRF_{GAP} of AGR fuel are likely to be similar or lower than (bounded by) that measured for LWR fuels (given their typically higher burn-up) [186]. The presence of the internal bore is not expected to result in substantial differences between AGR and LWR fuels, since differences in geometric surface area are expected to be much smaller than those associated with the amount of cracking present in fuel pellets after reactor irradiation [186]. This is supported by a comparison of LWR FGR data with data from a fuel of Russian LWR design (VVER) containing a bore similar to that present in AGR fuel [186].

The inventory of relevant isotopes of caesium, iodine and other radionuclides trapped in the grain boundaries is sometimes referred to as IRF_{GB} based on the conservative assumption that this material is also rapidly released upon contact with water. This trapped intergranular inventory of fission gas (and mobile radionuclides) has been studied by Pontillon et al. [196], who measured the release of fission gas by controlled sequential air oxidation methods. For PWR UO_2 fuel with a burn-up of 49 and 69 GWd/tHM and a total FGR of 1.6 and 2.6% respectively, the measured intergranular grain boundary inventories of fission gas were about 10%. The measurement process involved collecting fission gas released during air oxidation and concurrent cracking of grain boundaries. The results suggested that the total IRF (IRF_{Gap} plus IRF_{GB}) would be about 12% for the fuel in question. Applying this to the case of spent fuel dissolution in a GDF is clearly pessimistic, as the process analogous to cracking grain boundaries open through air oxidation would be rapid preferential dissolution of all grain boundaries in the fuel, which is at least partially dependent on a supply of oxidant (see discussion of redox chemistry below).

An activation product that falls into the category of radionuclides that are volatile under in-reactor conditions is ^{36}Cl, produced by neutron activation of trace stable chlorine contaminants in the fuel pellets and cladding. Information about its inventory in fuel is in [197]. Studies by Tait et al. [198] show that the aqueous release is several times the FGR, indicating that in-reactor segregation of ^{36}Cl and subsequent leaching is thermally driven to an extent greater than that observed for other relatively volatile elements (such as iodine).

In contrast to release of nuclides of Cs, I and Cl, the release of ^{14}C, produced principally by neutron activation of ^{14}N, has been suggested to be independent of fuel power rating, based on studies of CANDU fuel [199].

The release of the long-lived fission product ^{79}Se from spent fuel has proven difficult to study because of the low fission yield and limitations in analytical techniques. Recent studies suggested that the rapid release fraction of ^{79}Se is small (less than about 1%). This behaviour has been attributed to selenium substituting for oxygen in the UO_2 lattice [200].

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[40] Another difference is the lower ‘morphological relaxation’ expected in AGR intergranular bubbles due to the lower hydrostatic stresses present during reactor operations. This difference is unlikely to induce substantial changes in the FGR (and IRF) unless interconnected porosity is developed (at high FGR).

The above discussion focused principally on the aqueous release of semi-volatile radionuclides and their relationship to FGR. There is another category of fission products that are not volatile under in-reactor conditions, but are nonetheless segregated from the fuel matrix because they are insoluble in UO_2. For example, the segregation of some metallic radionuclides in the fuel matrix (as ε-particles, an alloy of Tc-Rh-Ru-Mo-Pd), has been extensively documented in oxide fuels [181]. As these are noble-metal inclusions significant dissolution is not expected, nor is it observed [201].

6.3.2 Matrix dissolution

For oxide spent fuels in non-oxidising conditions, the dissolution rates for the spent fuel matrix are very low, resulting in a very slow congruent release of the vast majority of radionuclides present in the fuel.

A variety of studies have been carried out on LWR fuel to evaluate the dissolution mechanisms of the spent fuel matrix and the subsequent (congruent) release of radionuclides in solid-solution (typically actinides), or trapped in the microstructure (in intra-granular gas bubbles, grain boundaries, etc.). As noted in Figure 21 the significant majority of the fission product inventory, and indeed the entire actinide inventory, are contained within the UO_2 grains, so understanding the behaviour of the fuel matrix is very important in evaluating the likely release of radionuclides to the EBS in the long term. Experimental studies have employed real spent fuel samples, as well as inactive analogues of spent fuel (for example, SIMFUEL) and relatively pure (unirradiated) UO_2. Under the reducing conditions typical of deep groundwaters, U(IV) is the dominant species and the solubility of UO_2 is a minimum of four orders of magnitude lower than under oxidizing conditions, where U(VI) is the stable oxidation state [179]. The dissolution rate is also substantially reduced, the process being driven by the relatively slow chemical (non-oxidative) dissolution of U(IV). Additional details on the effect of a variety of environmental parameters on the dissolution behaviour of oxide fuels (based on work on LWR fuels) are reported in Box 13.

Many studies of the kinetics of UO_2 oxidative dissolution in aerated solutions have also been performed, often in the presence of carbonate, a known complexant for U(VI). For example, the dissolution rate at 25 °C is reported [202, 203] to be in the range of $\sim 10^{-3}$ g m^{-2} day^{-1} ($\sim 1\ 10^{-3}$ mol m^{-2} $year^{-1}$) in naturally aerated 0.01 M $NaHCO_3$/0.1 M NaCl solution. In the absence of oxygen, even in the presence of carbonate, oxidative dissolution does not occur and the rate drops by a factor of more than one hundred. Solutions simulating groundwater typically result in somewhat lower dissolution rates as a result of the blocking of surface sites [179, 202].

Although low redox potentials are expected in a GDF at the time of container failure, the presence of alpha radiation inside spent fuel containers can affect the redox potential of solutions in contact with the spent fuel surfaces [179][41]. In particular, it is important to understand whether alpha radiolysis is likely to generate oxidants, such as hydrogen peroxide (H_2O_2), which may in sufficient quantities increase the dissolution rate of the spent fuel, for example by locally increasing the redox potential. The effect of radiolytic oxidants (in particular H_2O_2) and reductants (predominantly H_2 from container corrosion and radiolysis) on un-irradiated UO_2 and spent fuel dissolution have been studied extensively [179, 204]. In oxygenated water, radiolysis products such as H_2O_2 further accelerate the oxidative dissolution of UO_2 [205]. In the absence of oxygen the dissolution rate is significantly lower; nonetheless, there is still evidence for some impact of radiolytic oxidants on dissolution.

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[41] After a few hundred years, a period over which the waste container is expected to remain intact, the dominant contribution to radiolysis product formation is alpha radiation from the decay of actinides.

A method of studying alpha-radiolysis effects without the complication of high gamma radiation fields is to add alpha-emitters to un-irradiated UO_2 [206, 207]. These studies have shown that at the alpha activity levels typical of fuel that has decayed for about 3000 to 10000 years, the radiolytic driving force is low, leading to dissolution rates in anoxic conditions of ~10^{-7} $year^{-1}$.

Box 13 Effects of environmental conditions on oxide spent fuel dissolution

With the possible exception of some redox sensitive species, the IRF associated with spent fuel is likely to show relatively little dependence on a number of environmental variables. The dissolution rate of the fuel matrix, however, is dependent on environmental variables such as temperature and redox potential. Other important parameters include the groundwater/buffer content of specific complexants (particularly carbonate) and corrosion products of the waste container and other components, particularly hydrogen gas.

Effect of pH

The dissolution rate of UO_2 under aerated conditions is pH independent in the range 5-10, whereas it is first order with $[H^+]$ in the pH range 3-5 [189].

Effect of Temperature

The dissolution rate of UO_2 under aerated conditions increases by about a factor of ten between 35 and 75 °C, whereas the spent fuel dissolution rate increases by only a factor of three in the same temperature range [198, 208]. The effect of temperature on UO_2 dissolution under reducing conditions has received limited attention. Nonetheless, under strongly reducing conditions, there is little temperature dependence of the solubility of UO_2 between 100 and 300 °C [209], thus the effect of temperature is likely to only be relevant in the event of oxidation (likely to occur only in oxic conditions). A study [210] observed negligible oxidation of UO_2 at 100 °C in anoxic water containing low concentrations of hydrogen using un-irradiated UO_2 samples in close proximity (30 µm separation) to alpha sources of various strengths.

Effect of Groundwater and EBS Composition

The most important complexing agent for U(VI) is carbonate and there have been extensive studies of its role in dissolution [179]. The influence of carbonate on fuel dissolution decreases with decreasing potential, thus in the context of the reducing conditions in a GDF, carbonate becomes unimportant. The most probable alteration product from UO_2 dissolution under anoxic/reducing conditions is coffinite ($USiO_4.2H_2O$), although the slow kinetics of UO_2 dissolution under reducing conditions make this difficult to study on a laboratory timescale. However, there is evidence of coffinite formation in uraninite deposits, e.g. at Cigar Lake, although studies of uraninite ores suggest coffinite formation occurred principally at temperatures above about 130 °C [211]. This makes it an unlikely conversion product of UO_2 at anticipated GDF temperatures.

Effect of Redox Potential and Radiolysis

Many studies of spent fuel dissolution performed recently have shown that the presence of significant amount of hydrogen and the absence of oxygen result in a complete suppression of oxidative dissolution [179, 212, 213, 214].

Such an environment is expected in a breached waste container from the corrosion of ferrous materials present in the system, in the form of cast iron or steel likely to be used in the fabrication of waste containers, especially in systems which in the corrosion rate of steel components is expected to be high (for example in a clay buffer compared with a cement buffer). Corrosion of iron produces significant quantities of hydrogen, which is likely to build up because of the slow transport rate in a sealed GDF.

Desk-based studies comparing the likely characteristics of AGR and other spent fuels (particularly LWR fuels) have suggested that, although less characterised than LWR fuel, the oxidation state (i.e. degree of hyper-stoichiometry) of the fuel matrix is likely to be similar in both fuels[42], suggesting a similar dissolution behaviour of the fuel matrix [186]. In particular, given the typical dose rates and expected yield of α-radiolysis of AGR fuel compared to fuel with higher burn-up, rates of dissolution of the AGR fuel matrix have been suggested [186] to be similar to, or potentially lower than, those expected in other fuels (depending on whether the dissolution rate is controlled by the production of oxidising radiolytic species). The effect of hydrogen in suppressing the dissolution of the spent fuel matrix is also expected to apply to AGR fuels [186].

Our recent experimental work on AGR fuel has confirmed that relatively low matrix dissolution rates can be expected in oxidising conditions [187]. Analysis of the release of uranium, lanthanides and actinides indicated steady-state values of the matrix dissolution rate (reached after about one year of leaching) of the order of $5\ 10^{-8}$ day^{-1} (about 10^{-5} year^{-1}), which is consistent with rates previously measured in oxic conditions on LWR fuels. Analysis of the release rates in anoxic conditions is planned for the next stages of the experimental programme [10, task 551].

Because of the difficulty of performing detailed mechanistic studies of spent fuel dissolution on real spent-fuel samples, much of the relevant knowledge has been developed through studies of un-irradiated UO_2 and SIMFUEL, the latter being UO_2-doped with specific stable elements to simulate the chemical effects of in-reactor burn-up. Important properties of spent fuel that are simulated with this material include the rare earth doping of the matrix, the presence of noble metal particles and the creation of residual non-stoichiometry [179]. The actinide-lanthanide doping that occurs as burn-up increases stabilises the fuel to some degree against air oxidation [215] and other studies on SIMFUELs and rare earth-doped UO_2 suggest a similar effect in aqueous environments [216].

Electrochemical studies show (Figure 24) that the surface composition of UO_2 (here in the form of SIMFUEL containing 1.5 wt% fission products) shifts towards U(VI) as the corrosion potential increases [179]. These studies also show that metallic particles formed by the segregation of noble metal fission products (such as palladium, ruthenium and rhodium) in phases insoluble in the UO_2 matrix (the ε-phase) are likely to be particularly important in supporting electrochemical reactions driving (via hydrogen peroxide reduction) or inhibiting (via H_2 oxidation) dissolution.

Electrochemical studies of SIMFUEL have demonstrated that the mechanism of suppression of oxidative dissolution in solutions containing H_2 is the oxidation of H_2 to H^+ on the alloy particles. Because SIMFUEL is a rare-earth doped semiconductor this reaction is galvanically coupled to the cathodic reduction of U(VI) species on the fuel surface [217]. This results in a very low electrochemical potential on the fuel surface, preventing oxidative dissolution (Figure 25). Studies of alpha-doped UO_2 have shown a similar suppression of fuel oxidative dissolution despite the absence of catalytic noble metal particles [206]. The dissolution of irradiated MOX fuel at high hydrogen concentrations has also been studied and similar suppression of oxidative dissolution occurs [218].

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[42] Differences, if any, may be associated with differences in peak temperatures, burn-up and neutron spectrum and, more likely, with any differences in reactivity of the fuel cladding.

Figure 24: The fraction of various oxidation states of uranium in a 1.5 wt% SIMFUEL surface as a function of applied electrochemical potential [179]

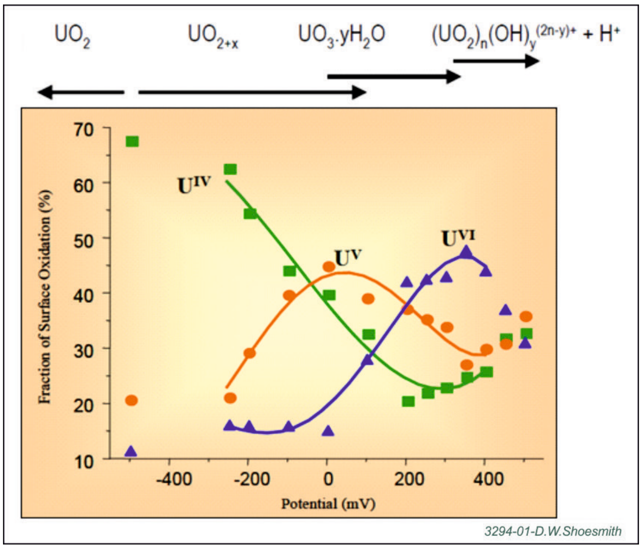
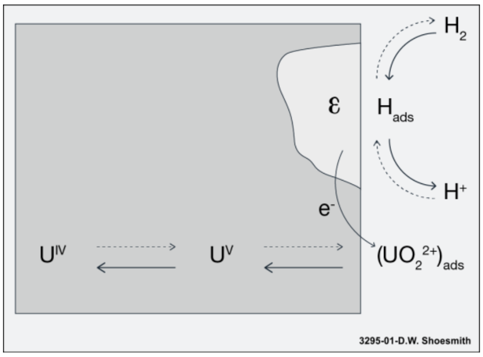


Figure 25: Illustration showing the galvanic coupling of fission product alloy (ε-particles) to the fuel matrix in H_2-containing solutions [217]



Additional SIMFUEL studies have also been carried out to evaluate whether the typical chemical composition expected in spent AGR fuel is likely to yield a different reactivity of the fuel. These studies comprised leaching of SIMFUELs manufactured to replicate the expected composition of typical spent AGR fuels after long periods of radioactive decay [219, 220, 221, 222], as well as modelling studies aimed at evaluating the likely partitioning of fission products in the matrix [223, 224, 225].

These experimental studies generally indicated that the behaviour of AGR SIMFUEL is similar to that of LWR SIMUFUEL, as illustrated by similar electrochemical characteristics upon polarisation [222]. This is not surprising given the limited differences between the chemical composition of LWR and AGR fuels, on which SIMFUEL formulations are based (see Table 2 in [219]). However, these measurements indicated higher dissolution rates for AGR SIMFUEL doped with high levels of fission product simulants (representative of higher burn-up). This has been interpreted as a being a result of greater lattice distortion and a greater density of defects introduced by fission products in the UO_2 crystal structure. Measurements of galvanic coupling between the AGR SIMFUEL and stainless steel[43] in oxic, saline groundwaters (brines) also indicated that corrosion of the cladding may afford

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[43] The steel used was of the same grade as that employed in the cladding, known as niobium-stabilised 20/25 grade, with 20/25 referring to the chromium and nickel content respectively (wt%).

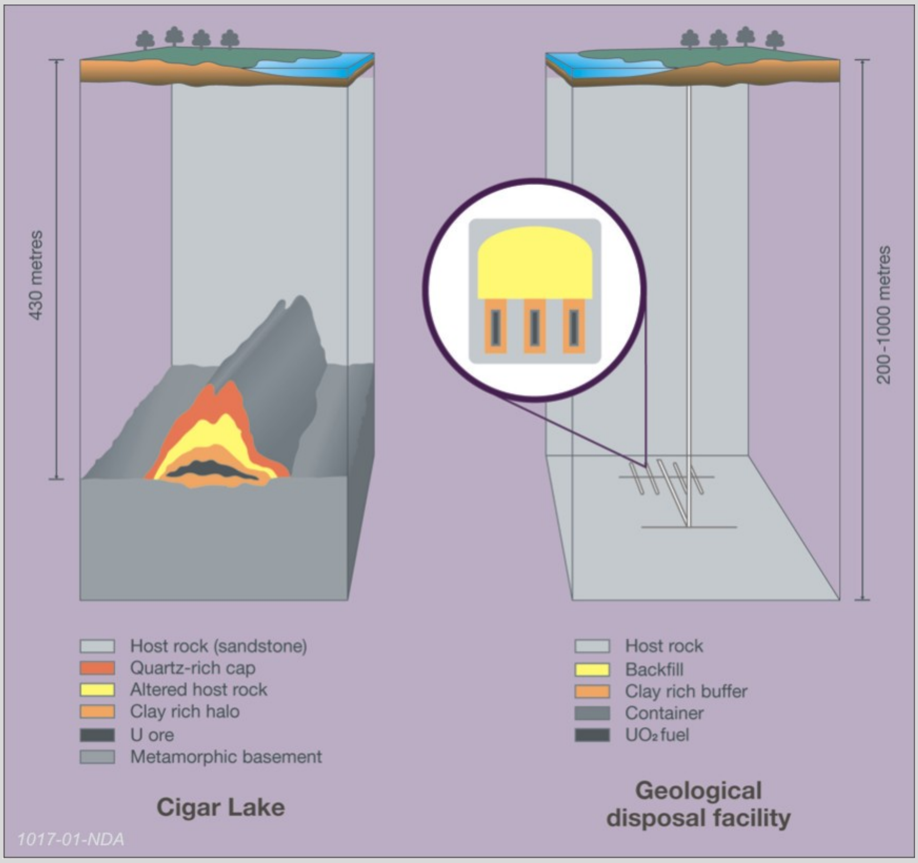
sacrificial protection to the fuel, reducing its likely dissolution rate [222]. This effect, however, may be weaker than the effect expected to be associated with the reducing effect of hydrogen gas and may be even less important in less saline conditions, in which the stainless steel may corrode very slowly. Further work on SIMFUELs with characteristics relevant to UK fuels is planned in our R&D programme [10, task 552].

An additional source of information is provided by the mineralogy of uranium minerals in contact with reducing groundwater, which can be considered natural analogues for spent fuel. This information shows that such deposits are very stable over geological timescales. Further information about natural analogues for spent fuels is provided in Box 14.

Box 14 Natural analogues of spent fuel

An extensive literature exists on natural analogue studies related to uraninite deposits and the conditions influencing their preservation and alteration over geological timescales. There are clear similarities between natural uraninites and spent fuel [226] and as a result, uraninites can provide understanding of the alteration behaviour of spent fuels over these timescales. The discovery of the Oklo natural reactors in Gabon provided an opportunity to examine uraninite ores in which fission product and actinide production occurred almost two billion years ago. In addition, several international projects have focused on understanding the conditions of formation and alteration of various uraninite deposits in crystalline and sedimentary rocks. One of the most thoroughly studied is the Cigar Lake deposit, a massive deposit of predominantly uraninite and coffinite ($USiO_4{\cdot}2H_2O$) in Saskatchewan, Canada (Figure 26). As discussed in [227] and [228], various attempts have been made to assess the impact of radiolysis on the Cigar Lake ore body and to test these models against observations from analysis of the ores. The overall conclusion has been that the radiolytic models tend to over-predict the extent of alteration of the ores. Bruno and Spahiu [228] have attributed this to the effective recombination of oxidants and reductants produced by radiolysis, leading to stability of the ore body over more than one billion years. There is nonetheless some evidence [211] for alteration of uraninite to coffinite under reducing conditions, including the presence of high silica concentrations [227].

Figure 26: A schematic representation of the Cigar Lake uraninite ore deposit compared to a GDF. The deposit, located in Canada and ~ 1,300 million years old, is rich in uranium and other safety relevant radionuclides, making it a relevant analogue for a GDF containing spent fuel



6.4 Fuel dissolution/corrosion (metallic fuels)

The dissolution/corrosion of metallic spent fuels is expected to be relatively fast in a GDF. It is possible, however, that a substantial fraction of the radioactive inventory initially released will be retained in the uranium corrosion product.

The corrosion of uranium leads to the development of uranium hydride which, due to its potentially pyrophoric nature, requires specific consideration in the operations preceding closure of a GDF.

Part of the UK inventory includes fuels made of metallic rods of uranium or uranium alloys. Dissolution/corrosion processes of the fuel rod are important in safety assessments considering this type of fuel. The dissolution behaviour of metallic spent fuel has not yet been reviewed in our research programme, but is planned in the future [10, task 554]. As a result, the information presented herein should be considered as an initial, scoping analysis.

We have not yet reviewed any experimental studies of the dissolution behaviour of metallic spent fuel in conditions representative of a GDF (if any exists). Currently, we are not aware of any direct studies of the dissolution of metallic spent fuels in conditions representative of a GDF. There have been, however, a relatively large number of studies evaluating the corrosion behaviour of uranium [229, 230, 231, 232, 233]. In particular, a detailed review of corrosion mechanisms and rates in oxygen, water vapour, oxygenated water vapour and water is available in [234].

The corrosion of metallic uranium fuel through its reaction with water is a relatively fast process and is expected to occur even faster under anoxic conditions [234]. This is because a protective oxide layer forms under oxidizing conditions, contributing to a lower rate of metal corrosion [234]. The corrosion rate increases with the temperature; in reducing conditions (expected to be present inside disposal containers featuring substantial quantities of steel, such as those considered in the UK [78]), and for temperatures between 10-60°C, a corrosion rate of the order of 10^{-3}-10^{-1} mg cm^{-2} h^{-1} can be estimated (see Figure 16 in [234]), corresponding to a rate of 4-400 μm year^{-1} (0.2-20 g m^{-2} day^{-1} for comparison with rates for HLW or UO_2 spent fuels). With a corrosion rate of 100 μm year^{-1}, a uranium bar of the diameter of 3 cm would loose its inventory over periods of the order of a hundred years.

Given the temperature dependence and the exothermic nature of the corrosion reaction, it is important to understand whether an increase in temperature associated with the corrosion reaction itself is expected. In reducing conditions the corrosion of uranium in water produces a nearly stoichiometric UO_2 phase ($UO_{2.004}$, see [235]). Assuming stoichiometric UO_2 as the corrosion product, a value for the enthalpy of reaction of the order of -500 kJ mol^{-1} can be obtained using data from [236]. Based on a corrosion rate of 10^{-1} mg cm^{-2} h^{-1} (estimated at 60 °C) a power output of the order of 0.5 W m^{-2} can be expected[44], which is too low to lead to a significant increase in temperature.

The corrosion rate is relatively high and over a few decades to centuries all metallic uranium is expected to be transformed into UO_2. However, given the relatively low flow of groundwater expected in the GDF it is likely that the solubility limit of uranium will be reached [4], leading to in situ precipitation of corrosion products. Whilst some highly-soluble fission products such as caesium and iodine isotopes will be, very likely, released completely to the groundwater and not incorporated in the corrosion product, for other radionuclides it is likely that a fraction will be trapped in the newly formed uranium dioxide phase, especially for

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[44] A corrosion rate of 10^{-1} mg cm^{-2} h^{-1} is equivalent to 10^{-6} mol m^{-2} s^{-1}. The power output can be calculated as the product of the enthalpy of reaction (500 kJ mol^{-1}) and the corrosion rate (10^{-6} mol m^{-2} s^{-1}), leading to a power of 5 10^{-4} kJ s^{-1} m^{-2} = 0.5 W m^{-2}.

species unlikely to undergo oxidation processes themselves (such as technetium or neptunium isotopes). For example, in the presence of air-saturated solutions, a substantial retention of actinides such as americium and plutonium and, to a lower extent, of fission products such as strontium and technetium, was observed during the so called “stage 2 corrosion” [237]. Less information, however, is currently available to evaluate whether, and to what extent, these effects may also take place in reducing conditions.

In addition to promoting the release of radioactivity from the fuel during the post-closure period of a GDF, in reducing aqueous/humid conditions the corrosion of uranium is known to lead to the formation of uranium hydride. Given the high reactivity of the hydrides, even at ambient temperature, this process can raise safety concerns during packaging of metallic fuels and the subsequent storage and disposal of waste packages.

The nature and quantity of hydrides formed is likely to depend on the redox potential of the environment, as well as on its relative humidity and temperature. Corrosion of uranium by hydride formation is well-known to occur in enclosed environments [230], where initial corrosion by water can lead to the formation of hydrogen gas, which reacts further with the fuel. The formation of uranium hydride by the reaction of uranium metal with hydrogen gas is a diffusion-controlled process with an activation energy of 26.6 kJ mol^{-1} [231]. Totemeier [238, 239, 240] indicates that the presence of hydrides is associated with a localised corrosion process (requiring limited access of air/water and hydrogen trapped in proximity to U). In specific conditions, the morphology of the products formed (powders) leads to pyrophoric behaviour in air at room temperature; this is considered to be the source of several incidents [238, 241].

6.5 Corrosion of fuel cladding and other assembly components

In wet or dry storage conditions, corrosion of metallic components of AGR and LWR fuels is expected to be minimal. Upon exposure to groundwater, general corrosion is also likely to be very slow. Localised corrosion and other degradation processes are however likely to result in relatively fast perforation of the cladding. In the case of metallic fuel clad in Magnox, corrosion during storage in water ponds or humid conditions and in a GDF will be relatively fast, leading to a rapid degradation of the cladding.

The current assumption is that all spent fuels destined for the GDF will be disposed of with their cladding. In some cases (for example, LWR fuel), the fuel will also be disposed of with other components of the fuel assembly. Understanding corrosion processes of such components during periods preceding closure of the GDF is important, particularly if the fuel is stored without additional containerisation (bottling), as is current practice during wet storage.

Once disposed of in a GDF, the cladding may provide an additional barrier to the release of radionuclides to the EBS once the waste container has been breached. For non-standard spent fuels (particularly Dragon fuel), the fuel design features specific components that are likely to affect its long-term evolution (see Box 15). Beyond that however, corrosion of the cladding and other fuel assembly components is important in evaluating the long-term release of specific activation products (such as some nickel or zirconium isotopes, as well as ^{14}C from the neutron activation of nitrogen impurities), which are likely to be released as such components corrode. There is some indication that ^{14}C may be present in the oxide film on Zircaloy [242, 243]. Our current expectation is that the stainless steel cladding of AGR fuel [244] and, to a lower extent, the Magnox cladding of metallic fuel [245] also contains significant quantities of ^{14}C (see also [5]).

In the case of AGR and LWR fuel, the cladding and other fuel assembly components are made of corrosion-resistant metals (Zircaloy, stainless steel or nickel alloys) which may provide an additional barrier to the release of radionuclides contained within the fuel and fuel assembly components. In the case of metallic fuel (Magnox-clad), this is unlikely to be the case.

The rate of atmospheric corrosion of stainless steels, nickel alloys and Zircaloy (relevant to any dry interim storage) is known to be slow. For these materials, general corrosion is likely to be minimal over foreseeable storage periods. Other degradation processes, however, are likely to be potentially important. For stainless steels, chloride-induced localised corrosion and stress corrosion cracking may occur if these materials are exposed to chloride-containing (marine) aerosols in specific ranges of relative humidity, particularly at relatively high temperatures (>30°C). These processes are discussed in detail in section 10.8. For Zircaloy, an important degradation process is associated with the presence of brittle hydride phases, formed by the permeation of hydrogen through the cladding during reactor operations [246, 247]. The corrosion properties of stainless steel and Zircaloy in atmospheric conditions have been briefly reviewed [248]; largely based on the need to limit the potential degradation of Zircaloy during dry storage (due to hydride reorientation and its subsequent impact on cladding brittleness and the potential for creep rupture), this study recommended a storage temperature limit of 400 °C for the cladding. Temperature limits for the stainless steel cladding during storage have also been proposed, but are less well underpinned [248].

In aqueous conditions, the corrosion rate of Zircaloy, stainless steel and nickel alloys is also very low. For example, a study of the corrosion rate of irradiated Zircaloy pressure tube material at 90 °C in aerated Hanford River water by Johnson [249] gave an estimated rate of 3 to 5 nm year^{-1}. In dilute and saline groundwaters (relevant to disposal), the general corrosion rate of stainless steel and Zircaloy has been evaluated in [250, 251]. Recent work on stainless steel [252, 253] indicated general corrosion rates lower than 0.01 μm year^{-1} at temperatures below 80 °C in high pH solutions (NaOH solution at a room temperature pH of 12.5). Thus, for both stainless steel and Zircaloy clad fuel, radionuclide release as a result of general corrosion in groundwater will occur over thousands of years following perforation of the disposal container. The potential for localised corrosion to occur on stainless steel (see Section 10.9.2) and the potential for delayed hydrogen cracking (DHC) to occur on Zircaloy [246], however, provide limited confidence in the ability of the cladding to act as a lasting containment barrier over and above that provided by a long-lived disposal container.

The corrosion behaviour of magnesium alloys is described in [254]. Additional detail on its corrosion behaviour in cement (relevant to ILW as well as to the management of metallic fuel in cement-based disposal systems is provided in section 8.2.4). Unless very low relative humidity (during any dry storage) or alkaline conditions (during wet storage or disposal) are present (for example associated with the use of cement buffers), the corrosion rate is expected to very fast. As an example, corrosion rates greater than 8 mg cm^{-2} day^{-1} (about 1,500 μm year^{-1}) are reported for magnesium alloyed with less than 2 wt.% aluminium (similar to Magnox) in (aerated) 5% NaCl solution [254, Figure 15 in Section 44]. Corrosion rates are expected to be somewhat less in reducing conditions, but remain relatively high. As a result, if Magnox fuel is disposed of to the GDF, it is likely that it will exhibit moderately or substantially degraded cladding at the time of disposal. Once in a GDF, upon exposure to groundwater, corrosion of the fuel will lead to a fast release of activation products and exposure of the underlying fuel.

Box 15 Wasteform evolution for non-standard spent fuels – Dragon fuel

The Dragon reactor, funded by the Organisation for Economic Co-operation and Development (OECD) and operated in the UK between 1965 and 1975, was an experimental, high-temperature, gas-cooled reactor. The disposability of dragon fuel in the GDF is being evaluated.

Dragon fuel is a non-standard fuel comprising uranium fuel kernels with coatings of pyrolytic carbon in a graphite matrix. Much of the uranium in the fuel was highly enriched (up to 93 wt.% ^{235}U), although other enrichments, including low-enriched and depleted uranium, were also used. The fuel was subjected to a wide range of burn-ups. After unloading from the reactor, it was initially placed in mild steel containers for storage at the Winfrith site. Subsequently it was repackaged into stainless steel containers, planned to be cement-grouted and further packaged in standard 500-litre drums for disposal as ILW[45]. This is contingent on demonstrating that criticality safety can be assured (see Criticality Safety status report [6]).

To address this issue, a package-specific Criticality Safety Assessment was produced for Dragon fuel, which concluded that the long-term, post-closure behaviour of the wasteform was important in determining the safe fissile mass. In particular, the assessment concluded that, in order to assure the long-term criticality safety of the waste packages, credit had to be taken for the presence and persistence of carbon, which acts as a diluent, in these waste packages. The persistence of carbon is also expected to play an important role in retaining radioactivity within waste packages after degradation of the waste container.

A study aimed at identifying the factors affecting the long-term behaviour of bulk carbon, including pyrolytic carbon and graphite, and evaluating the likely evolution of the carbon to ^{235}U mass ratio over timescales relevant to the post-closure period of the GDF was recently completed [255]. The study indicated that sufficient carbon will remain in the waste packages, along with the ^{235}U, to ensure that they meet the criticality safety carbon to uranium mass ratio criteria over relevant timescales.

6.6 Processes leading to microstructural changes and gas generation

The effects of microstructural evolution processes on the long-term properties of spent fuel are expected to be limited. In the long term, modest internal fuel-pin pressurisation with helium due to alpha decay can occur.

Spent fuel will be placed in disposal containers that will prevent contact with water for a very long period of time. Under such conditions only solid state mechanisms could lead to changes in fuel properties. Any changes, however, could potentially affect the dissolution processes described in the previous sections.

The effect of radiation-enhanced solid state diffusion of fission products due to alpha recoil from actinide decay (the main radioactive process expected to affect the fuel microstructure after discharge from the reactor) has been addressed in several studies. In principle, such a process could cause the inventories of fission products at grain boundaries to increase over time. Ferry et al. [195, 256, 257], however, indicate that the radiation-enhanced diffusion

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[45] Packaging as ILW is possible because of the modest heat output, associated with the small amount of α-emitters (compared with β/γ emitters) present in the fuel.

coefficient is less than 10^{-26} m^2/s, which would lead to an average atomic displacement of only (0.5 μm), or about 10% of the diameter of a fuel grain, after 1 million years [89]. Whilst self-irradiation effects are likely to be insignificant for iodine and other fission products, they may be more relevant for relatively small atoms such as chlorine [90, 195]. Any increase in IRF associated with these effects could be modelled based on the approach reported in [256, 257].

Together with any radiation damage, an important process likely to occur inside the cladding of spent fuel is the generation of helium gas produced by alpha-decay. This is likely to lead to microstructural alteration of the fuel, including formation of gas bubbles, which may have an impact on the IRF and the long-term release of other radionuclides associated with the dissolution of the matrix by increasing the surface area available for leaching. In the long term, these processes may also lead to pressurisation of the fuel pin and, after pin failure, pressurisation of the disposal container. Pressures expected from this process in a disposal container (due to its relatively large void volume) are expected to be relatively low over periods of hundreds of thousands of years [258, 259].

Microstructural studies of UO_2 and MOX fuel have shown that their fluorite structure will be retained, but that high stresses will arise as a result of the formation of helium gas bubbles [260]. As a result, some fracturing of grains may eventually occur, in particular for higher alpha-activity MOX fuel. The overall increase in pressure, and the timescale over which any pressurisation is likely to occur (hundreds of thousands of years) make these effects unlikely to be particularly important. However, any effects on the dissolution behaviour of the fuel, in particular on whether the formation of gas bubbles is likely to lead to a gradual fragmentation of grain boundaries and subsequent exposure of some of the radionuclide inventory associated with grain boundaries (IRF_{GB}) remains an uncertainty.

For fuel that has been previously stored in pond water, it is also possible that, upon containerisation for dry storage and/or disposal, some water may remain entrained inside disposal containers, depending on the efficiency of the fuel drying processes. Such water may lead to the corrosion of internal components of the disposal container. Perhaps more importantly, water evaporation, radiolysis and corrosion of ferrous materials present in disposal containers may lead to pressurisation of the disposal container. Any pressurisation associated with this process will depend on water inventory, temperature and container design (in particular its free volume). Levels of pressurisation associated with this process in the context of current UK spent fuel container designs are described in Section 11.1.3.

7 Evolution of ILW/LLW, DNLEU and plutonium wasteforms

This section describes scientific and technical information relevant to the expected evolution of immobilisation media for ILW (cement, polymer, glass or glass ceramics) and plutonium residues (glass, glass ceramic or ceramic wasteforms). It also describes expected evolution processes of un-encapsulated wastes, including DNLEU. The evolution of such media in contact with specific waste types is described in Section 8. The section analyses the available information to evaluate the ability of the wasteform to immobilise radionuclides over long timescales.

Key sources of information in this area are typically UK studies, although relevant information includes the RILEM workshop series (for example, [261]), the Scientific Basis for Nuclear Waste Management Proceedings [262], proceedings of the Migration Conference [263], and publications in journals such as Cement and Concrete Research (for example, [264]).

The information presented summarises some of the studies produced in the UK and worldwide in the last 20-30 years. Studies include:

- experimental work on encapsulation/ embedding media and wasteform simulants
- models of the evolution of encapsulation/embedding media and the resulting wasteform
- archaeological analogues and experience with the use of cements in the nuclear and other industries (such as the construction industry for cements).

The information presented focuses on encapsulation media which have already been employed in the UK programme to immobilise ILW (largely cements and, to a lesser extent, polymers). Consideration is also given to thermal treatment processes, which may be employed in the future to immobilise some ILW and/or plutonium residues, and to non-encapsulated wastes. Information relative to thermally-treated ILW and plutonium has only been considered recently in our programme and is considered in greater detail in the future work programme [10, tasks 603/604 and 616]. The need for further work on cement-based and polymeric wasteforms, DNLEU and graphite will also be evaluated in the future [10, tasks 573, 586, 631, 636 and 637].

An overview of evolution processes is presented for different types of encapsulation and embedding media, followed by a more detailed description of specific processes.

7.1 Processes of general relevance to ILW/LLW, DNLEU and plutonium wasteforms

During pre-closure periods, a variety of evolution processes may occur in cement-based and polymer-based encapsulants, including gas generation, changes in chemical properties, and changes in mechanical properties. After closure of a GDF, evolution processes include leaching and chemical degradation. Good tolerance to leaching is a key characteristic of glass and glass-ceramic wasteforms.

The main evolution processes for typical encapsulants employed or considered for the immobilisation of ILW/LLW, DNLEU and plutonium residues are expected to be largely dependent on the waste and the encapsulation/embedding media in question (if any). These processes are described in turn below for different types of encapsulants/embedding media, as well as for un-encapsulated wastes.

The presence of water is a pre-requisite for many evolution processes to occur. Wasteforms made with cement contain water (as cement porewater); therefore certain reactions are of particular importance to those wasteforms.

7.1.1 Cements (ILW/LLW and DNLEU)

The initial state of a cementitious encapsulant is characterised by its strength, porosity/permeability and alkalinity. During periods preceding closure of a GDF, evolution processes in cement-based wasteforms include hydration, carbonation and radiolytic degradation. During the post-closure period, chloride and/or sulphate attack, as well as leaching of the cement and encapsulated waste, are also likely to occur.

Important characteristics of the initial state of a cement-based wasteform are its mechanical strength as well as its initial alkalinity, porosity and permeability. The initial mechanical strength affects the immobilisation properties of the wasteform, whilst alkalinity and porosity/permeability affect chemical processes able to affect the immobilisation properties. Additionally, the high pH of cementitious materials affects the ability of the wasteform to protect the internal surfaces of the waste container from corrosion.

During the pre-closure period the main evolution process intrinsic to cement encapsulants is their hydration, the process by which they cure to form a solid. Hydration results in evolution of the structure of the cement that, although predominantly occurring on relatively short timescales, continues at a slower rate for several years after the cement has set. This process can affect the immobilisation properties of the resulting wasteform and needs to be considered in understanding its long-term evolution.

When cements are exposed to carbon dioxide they react to form calcium carbonate (carbonation). Carbonation initially takes place on the surface, and will subsequently migrate deeper into the cement upon continued exposure to carbon dioxide. The carbon dioxide may be present in the atmosphere, or it may be formed from the degradation of organic materials in the waste. This reaction tends to increase the compressive strength of cements, potentially enhancing their immobilisation properties. It also has the potential to retain some of the radioactivity that may be associated with gaseous carbon dioxide (as ^{14}C) released from some wasteforms (see [5] for further details). However, carbonation also reduces the alkalinity of the cement, thus potentially affecting the corrosion behaviour of encapsulated metals and waste containers, as well as the solubility of radionuclides typically insoluble in highly alkaline conditions [4]. Carbonation of cement is also discussed in Section 10.4.3.

Radiolysis of water in the cement phase can induce gas generation in the wasteform. Gas generation introduces the potential for mechanical damage of the wasteform (such as cracking), pressurisation of the waste container (if unvented), and may enhance the release of any gaseous radionuclides (such as ^{222}Rn from radium-containing wastes) [5].

During the post-closure period, additional degradation processes of the wasteform can only occur after perforation of the waste container and exposure to groundwater. In particular, chloride and sulfate attack can change the chemical characteristics of cements. Chloride and sulfate are likely to be present in UK groundwater and their reaction with cement-based encapsulants is likely. The potential for chloride and sulfate attack in the context of a cement-based backfill are also discussed in [2].

Leaching of alkalinity from cements due to prolonged exposure to groundwater will also result in a gradual evolution of the cement. This will occur only if there is significant diffusion or advection (particularly in a cracked grout) of water between the cement and the surrounding environment.

Beyond the cement-alteration processes described above, processes of radionuclide release will be largely dependent on the nature of waste encapsulated in the cement, the ability of water to access it (which may depend by the extent of wasteform cracking) and by the chemistry of the environment.

Evolution processes and their effects are summarised in Table 9.

Table 9: Processes of general relevance to cement-based encapsulants

Period	Evolution Process[46]	Effect	Section
Initial state		Alkalinity Mechanical strength Porosity / permeability	7.2.2
Pre or post-closure	Hydration	Change in mechanical strength	7.2.2
	Carbonation	Change in mechanical strength Container corrosion Decrease in alkalinity Capture of ^{14}C	7.2.2
	Radiolytic degradation	Change in mechanical strength Gas generation	7.2.4
Post-closure	Chloride and sulfate attack (groundwater)	Formation of expansive phases	7.2.5
	Leaching of cement (groundwater) [47]	Decrease in alkalinity	See [2]
	Leaching of waste (groundwater)	Release of radionuclides in groundwater	7.2.6

7.1.2 Polymers (ILW/LLW)

The initial state of a polymeric encapsulant is characterised by its strength and chemical characteristics. During periods preceding closure of the GDF evolution processes are mainly associated with thermal and radiolytic degradation. During the post-closure period leaching is also likely to occur.

Important characteristics of the initial state of a polymeric wasteform are its mechanical strength and its chemical characteristics, including the nature of the chemical bonds forming its cross-linked structure and the presence of specific additives. The initial mechanical strength affects the immobilisation properties of the wasteform. The chemical characteristics affect important processes able to affect the immobilisation properties as well as the ability of the wasteform to protect the internal surfaces of the waste container.

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[46] The tables present a simplified description of key processes likely to affect the evolution of ILW/LLW encapsulants and wasteforms. Other important processes include their thermal and radioactive decay processes, which are central to many other evolution processes and are discussed in Section 4 in the context of the environmental conditions in which evolution processes will take place.

[47] Leaching of ILW/LLW wasteforms and subsequent radionuclide release are not discussed in detail in this report, but are discussed in greater detail in the Engineered Barrier System status report. This is because, during the post-closure phase, the performance and evolution of individual ILW/LLW packages becomes less important than the behaviour of the EBS as a whole.

In the presence of environmental stressors such as high temperatures, microbiological activity, and particularly radiation, polymers can undergo degradation which gradually alters their structure. Depending on the nature of these changes, a polymer may either become less solid (gluey) or brittle. For radiation-induced processes (expected to be the main concern for this type of encapsulant) the extent to which this occurs will depend on the radiation dose, the particular polymer and the environmental conditions.

During the pre-closure period these processes can lead to a reduction in compressive strength and gas generation, thus affecting the immobilisation properties of the wasteform. Chemical stability may also be important, since the species released by degradation, while not affecting the strength of the encapsulant, could affect the evolution of the waste container if water was present (typically not the case).

During the post-closure period, once groundwater is in contact with waste containers, these processes may lead to the release of corrosive species (such as chlorides or organic acids, depending on the type of polymer and any specific additives employed during its manufacture and curing), potentially affecting the confinement properties of the waste container[48]. In addition, the release of specific organic species has the potential to affect the performance of a cement-based EBS. For example, the formation of complexants through the degradation of cellulosic materials can increase the solubility of some radionuclides (see [4]). Non-aqueous phase liquids (NAPLs) may also form from the degradation of some polymers; however, it has been shown that NAPLs will continue to degrade and will not migrate from the GDF [265, 266].

Leaching of polymeric wasteforms in the presence of groundwater can affect the release of radionuclides in the EBS in a way similar to that expected for cement-based wasteforms.

Evolution processes and their effects are described in Table 10.

Table 10: Processes of general relevance to polymeric encapsulants

Period	Evolution Process[46]	Effect	Section
Initial state		Mechanical strength Chemical characteristics	7.3.1
Pre or post-closure	Radiolytic and thermal degradation (dry)	Change in mechanical strength Gas generation	7.3.2
Post-closure	Radiolytic and thermal degradation (groundwater)	Release of corrosive species Gas generation Release of non-aqueous phase liquids (NAPLs)	7.3.2
	Leaching of waste (groundwater)	Release of radionuclides in groundwater	7.3.3

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[48] In principle these processes may also lead to the risk of internal corrosion of the waste container during periods preceding closure. However, the use of a polymeric encapsulant is likely to result in a dry wasteform, with very limited potential for corrosion.

7.1.3 Glasses, glass ceramics and ceramics (ILW and plutonium residues)

The initial state of a glass, glass-ceramic or ceramic wasteform is characterised by its strength and heterogeneity. Before closure of the GDF, evolution processes are expected to be very limited. During the post-closure period leaching may occur.

Important characteristics of the initial state of a glass, glass-ceramic or ceramic wasteform for the immobilisation of ILW or plutonium residues include its mechanical strength, surface area (primarily its degree of cracking) and its level of heterogeneity and micro-segregation. The initial mechanical strength affects the immobilisation properties of the wasteform. Surface area, level of heterogeneity and micro-segregation affect the leaching behaviour of the wasteform once exposed to groundwater.

Glasses and glass-ceramic materials are chemically very stable and unlikely to undergo evolution processes affecting the key characteristics of waste packages during pre-closure periods. However, if wastes with higher activity (such as plutonium residues) are immobilised in a glass or glass-ceramic material, microstructural evolution processes (for example, gas generation or metamictisation[49] for wastes with alpha-emitting radionuclides) may occur, potentially affecting the mechanical and chemical properties of the material.

During the post-closure period, once exposed to groundwater, glasses, glass-ceramics and ceramics may undergo dissolution reactions, leaching radionuclides more or less congruently with the dissolution of their matrix. However, depending on their solubility, specific radionuclides may be either leached preferentially or retained in solid form as the matrix dissolves. Of specific relevance to ILW wasteforms is the likely level of heterogeneity, at a macroscopic level, of any solid phases formed upon solidification. Any radionuclide leached preferentially (if partitioned in phases of high solubility) may be particularly important in the evaluation of the radiological impact of a GDF after closure[50].

Evolution processes and their effects are described in Table 11.

Table 11: Processes of general relevance to thermally-treated ILW and plutonium residues

Period	Evolution Process[46]	Effect	Section
Initial state	Solidification of the melt and initial cooling	Surface area (cracking) Level of heterogeneity and micro-segregation	7.4.1
Post-closure	Dissolution of glass/ceramic (groundwater)	Leaching of radionuclides in groundwater	7.4.2
	Microstructural evolution due to self-irradiation	Leaching of radionuclides in groundwater Gas generation (He)[51]	7.4.2

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[49] The process by which alpha radiation breaks down a crystalline structure, leading to an amorphous structure.

[50] For thermally-treated ILW, options considering disposal with backfill materials other than cement are currently being considered. For this type of disposal concept the leaching properties of the glass wasteform and its compatibility with the backfill may be particularly important.

[51] This process is expected to be relevant only for waste containing α-emitters, for example plutonium residues.

7.2 Evolution of cement-based wasteforms (ILW/LLW)

Evolution processes of cements are generally well understood. Hydration, carbonation and radiolytic degradation are unlikely to have a detrimental effect on the immobilisation properties of the wasteform during storage. Upon exposure to groundwater, cements are likely to undergo chemical and mineralogical changes. At this time, the mobility of encapsulated radionuclides will be affected by their sorption and solubility in the EBS.

This section describes evolution processes of cement-based encapsulants employed in the immobilisation of ILW/LLW (typically OCP/BFS and OPC/PFA cements)[52]. Information relevant to the evolution of other cement-based systems employed for other components of a GDF (particularly buffer/backfill materials) are described in greater detail in [2]. Relevant information is also available in [267].

Beyond studies of specific processes, additional understanding, as well as overall confidence in the expected long-term behaviour, can be gained from practical experience with the use of cement grouts to immobilise ILW in the UK nuclear industry (see Box 16) as well as studies of natural and man-made analogues of cement (see Box 17).

Box 16 Practical experience with the use of cement-based encapsulants in the UK nuclear industry

The earliest waste packages destined for geological disposal in the UK were manufactured at Sellafield around 1990. To date, inspections of waste packages in interim storage at Sellafield have shown that the vast majority undergo no visible changes up to 20 years [288].

As waste packaging plans are developed it is typically necessary to produce small-scale samples containing inactive simulants of the real waste to demonstrate that the processing and as-manufactured properties of the encapsulant and wasteform are adequate. Common examples of relevant work are the monitoring of dimensional stability and changes in the mechanical strength of suitable samples. Samples from some research and development programmes have been retained, stored under controlled conditions, and continue to be monitored on a frequency that allows changes in their physical and mechanical properties to be identified. These archived samples also allow for more detailed and/or destructive investigations such as micro-structural analyses when a need for such studies is identified.

Monitoring of these types of samples indicates that changes in the dimensions and mechanical properties of encapsulants based on BFS/OPC and PFA/OPC are very slow once the cements are about 1 or 2 years old (once the majority of the cement has undergone hydration) [268]. Compressive strength continues to increase, and permeability to decrease, as hydration progresses. Although such samples are only currently about 20 years old, this gives some confidence that the important performance characteristics of these materials will persist over the timescales that are associated with waste package transport and GDF operations.

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[52] Formulations based on low-pH cements are also potential candidates for use in the immobilisation of particular waste types.

Box 17 Natural and archaeological analogues of cement

Confidence in understanding the evolution of cementitious materials can be increased through studies of natural and anthropogenic analogues for Portland cement [130, 282, 269, 270].

Some examples of anthropogenic analogues of cement are shown in Figure 27. Cements and concretes with some similarities to modern formulations have been used since Roman times; they were widely used in many types of buildings, some of which remain in good condition today. As with many analogues, it is not possible to use these materials to build a quantitative picture of the likely durability of cements used for the immobilisation of ILW/LLW; cement formulations were different from those used in ILW/LLW packaging and it is difficult to know what fraction of the buildings originally constructed degraded due to their natural evolution rather than other causes. In general, however, the existence of such analogues is a good indication of their long-lasting strength, if suitably formulated and manufactured. An example is Hadrian's Wall in Northern England, where the cements are ~2,000 years old. Archaeological analogues also provide evidence for the longevity of other cement physical properties such as permeability. For example, ancient lime mortars have retained their high permeability and porosity even when carbonated, whilst concretes in Roman Baths have retained their low permeability [282]. There is less information available on analogues for low pH cements which are currently under consideration for specific applications [271].

Natural analogues that have similar mineralogy to cements that have formed under specific geological and environmental conditions, and afford another opportunity to study the evolution of important components of cement such as C-S-H [272, 273]. This provides evidence for the longevity of chemical properties. For example, field observations from the site at Maqarin in Jordan support the outcomes of cement leaching/groundwater buffering models used in safety assessments [282, 271, 272]. Sites in Maqarin and Oman [282, 274] also show that trace elements are incorporated into cement gels and minerals, indicating a high sorptive capacity for key radionuclides - which is a key driver for the use of cement backfills in a GDF. Samples from Scawt Hill in Northern Ireland show that amorphous cement gels can persist for millions of years [282].

Figure 27: Examples of anthropogenic analogues of cement [275]: (left and centre) Hadrian's Wall (~ 2,000 years old) and details of cement from the wall, Northern England (the scale on the photograph is 22 centimetres across); (right) the dome of the pantheon (~ 2,000 years old), made in concrete (Italy)

7.2.1 Initial state

Once set, cements typically employed for the immobilisation of ILW display good compressive strength, low permeability and relatively high alkalinity.

Cements typically employed to immobilise radioactive wastes are described in section 3.1.1. These cements have porewater compositions similar to many other cements used in the construction industry. Examples of typical porewater compositions are reported in the tables below. Typical room temperature pH values for encapsulation / embedding grouts are approximately 12-13 and compressive strengths are typically in excess of 40 MPa for a mature cement containing no waste [276]. The porosity is of the order of 10 to 20%, the gas permeability of the order of 10^{-17} to 10^{-16} m^2 and the water permeability of the order of 10^{-20} to 10^{-18} m^2 [276]. Information about key properties of cement grouts used in waste encapsulation are reported in Table 12 and Table 13, which illustrate the effect of curing temperatures on the system.

7.2.2 Hydration

When well formulated, cements are unlikely to experience a decrease in the mechanical properties due to hydration and are likely to retain their structural integrity over long times.

Ordinary Portland Cement (OPC) hydrates to form a variety of hydration products, depending on the cement formulation. Calcium silicate hydrate (C-S-H) phases are the main hydration product and the main source of cement strength. Other products include calcium hydroxide, ‘AFt’ phases such as ettringite, ‘AFm’ phases such as monosulfate (this typically forms later in the hydration process), hydrotalcite and hydrogarnet.

Cements continue to hydrate over time, leading to an evolving microstructure and hydration product composition. The ageing processes are associated with the distribution of water within the system (water of hydration, water absorbed in fine porosity, and free water in large pores). For example, the free water in a 3:1 BFS/OPC w/c=0.35 cement decreases from 100% at mixing, to 70% at 28 days and 36% by 2 years. This decrease is dependent on formulation and is less for a PFA/OPC w/s=0.42 cement, where it decreases to 90% at 28 days and 75% by 2 years [277,278]. The state and amount of water within the cement system will control its propensity for shrinkage and cracking (as well as its contribution to gas generation as a result of radiolysis) [277, 278]. Hydration products, and therefore the properties of the cement, are dependent on temperature and cement composition [279].

Figure 28 shows how C-S-H phases exhibit an increased tendency to polymerise and ultimately form crystalline minerals such as jennite and tobermorite as the temperature is increased. The relative stabilities of various hydrated calcium aluminate phases are modified at elevated temperatures.

Studies of the evolution of the microstructure of cements over relatively long periods (20 years) without any acceleration of ageing have been carried out in order to develop understanding of evolution processes and interactions that may not be observed macroscopically [280]. These include, for example, changes in elemental composition of cement phases, the degree of carbonation, and the extent of reaction of blast furnace slag when added in varying proportions. In other studies, samples of cements have been tested in conditions intended to induce changes that would otherwise take many hundreds of years to develop (i.e. accelerated ageing) [281]. Overall, the understanding gained from these studies indicates that such information can be used to inform the development of predictive models of cement evolution.

Crystallisation of C-S-H gels can be accelerated in the laboratory. In particular, ageing at 80 to 120 °C induced the formation of minerals similar to those found in nature, indicating that in this temperature range the use of high temperatures to accelerate evolution processes is an appropriate means to study the long-term natural evolution of cements [279]. Although the mineralogy of the C-S-H phase differs depending on the grout used (BFS/OPC or PFA/OPC), this type of study indicates that confidence in understanding evolution processes in a variety of wasteforms can be obtained with these tests.

The construction industry has been utilising Portland cements for longer than the nuclear industry. These materials provide an opportunity to gain further understanding of the likely evolution processes at a large scale and without the potential for experimental artefacts that may be introduced by accelerated testing. However, there are also limitations associated with the information we gain by studying these materials. In particular:

- materials used in the construction industry are often concretes (that is, they contain aggregate) rather than the cement pastes used in the nuclear industry
- for available materials, there is rarely any information about the specification of the original components or their proportions in the cement/concrete mix
- the environmental conditions which these materials have been exposed to (particularly outdoors) are often different from the conditions that prevail in ILW stores and in a GDF.

Notwithstanding these limitations, reviews of the properties of aged OPC-based structures (such as [282]) have shown that these cements can, when well formulated, retain structural integrity over long periods, with slow but continued hydration of cement grains resulting in the development of a denser matrix that affords lower permeability and greater strength.

Table 12: Typical physical and chemical properties of cement grouts used for ILW/LLW immobilisation after 360 days curing at ambient temperature (reproduced form [276])

Property	**Grout**		
	3:1 BFS/OPC **W/C[53] = 0.35**	**9:1 BFS/OPC** **W/C = 0.35**	**3:1 PFA/OPC** **W/C = 0.42**
Compressive strength (MPa)	75	65	40
Dimensional stability (μ strain)	-1600	-1500	-1800
Gas permeability (m^2)	$1.5\ 10^{-16}$	$2\ 10^{-16}$	$2\ 10^{-16}$
Water permeability (m^2)	$1\ 10^{-20}$	$2\ 10^{-18}$	$1\ 10^{-19}$
Porosity (%)	10	10	19
pH	13.3	13.6	12.5
Eh (mV)[54]	-360	-400	-130
Na (mM)	130	70	50
Ca (mM)	1	<0.3	<0.3
K (mM)	140	90	90
SO_4^{2-} (mM)	5.5	3	33
S_2O_3(mM)	3	0.7	0.5
S^{2-} (mM)	<0.02	<0.03	<0.02
SO_3^{2-} (mM)	0.15	0.5	<0.01

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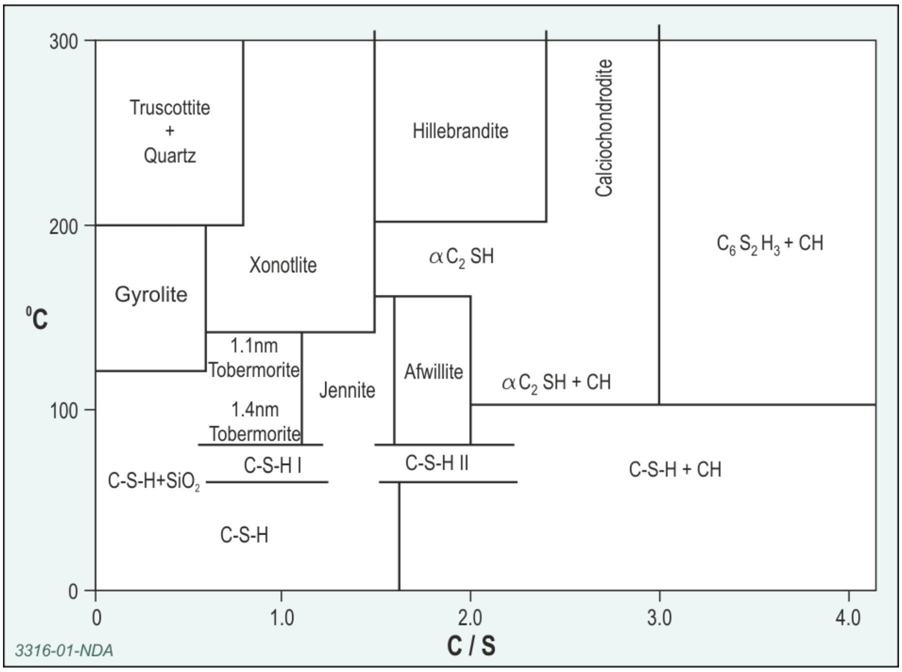
[53] W/C is the ratio of water to cement powders (OPC and BFS, or OPC and PFA) by weight.

[54] The term Eh refers to the redox potential

Table 13: Typical physical and chemical properties of cement grouts used for ILW/LLW immobilisation after 200 days curing at 80 °C (reproduced form [276])

Property	**Grout**		
	3:1 BFS/OPC **W/C = 0.35**	**9:1 BFS/OPC** **W/C = 0.35**	**3:1 PFA/OPC** **W/C = 0.42**
Compressive strength (MPa)	62	40	47
Gas permeability (m^2)	$2.7\ 10^{-17}$	$4.4\ 10^{-17}$	$5.7\ 10^{-17}$
Water permeability (m^2)	$1.4\ 10^{-20}$	$1.9\ 10^{-19}$	$7.3\ 10^{-20}$
Porosity (%)	19	20	13
pH	13.1	13.1	12.0
Eh (mV)	-	450	10
Na (mM)	121	42.4	93.5
Ca (mM)	1	0.5	6.1
K (mM)	163	55.1	109
SO_4^{2-} (mM)	56.5	20.8	83.3
S_2O_3(mM)	1.5	2.32	0.04
S^{2-} (mM)	-	0.03	-
SO_3^{2-} (mM)	1.5	0.06	0.06

Figure 28: Phases in the CaO-SiO_2-H_2O system as a function of CaO/SiO_2 (C/S) and temperature [279]



7.2.3 Carbonation

For cements with low permeability, the rate of carbonation is slow and decreases with time. Carbonation is expected to increase the strength of cement and decrease its alkalinity, potentially leading to the corrosion of metallic materials in contact with the porewater.

Carbonation of cements is relatively well understood. Carbon dioxide dissolves in the cement pore water, or is present in groundwater as carbonic acid, and reacts with calcium ions from the cement to form calcium carbonate. This process is one of the key mechanisms responsible for the degradation of concrete infrastructure in urban areas and has been extensively researched [283, 284]. Carbonation of cement formulations employed in the UK nuclear industry to immobilise radioactive wastes has also been specifically studied [285, 286]. The rate of carbonation is limited by diffusion, and is therefore dependent on the permeability of the cement, which is dependent on its formulation (BFS or PFA content). Investigation of the extent of carbonation in aged cement samples has shown that the depth of cement affected by carbonation is of the order of 1 to 2 mm after about twelve years [287] or up to 14 mm for a capping grout [288]. It is probable that the rate of carbonation penetration will fall with time, because the carbonation itself slows the ingress of further carbon dioxide by reducing the cement’s permeability.

Studies of materials used in the construction industry can also be used to observe long-term rates of carbonation and the effects that carbonation has on cement micro-structure and chemistry [282]. This information can also be used to support the extrapolation of results obtained from the younger, more directly relevant samples identified above.

Carbonation lowers the local pH of the cement and has the potential to locally increase the solubility of radionuclides [277, 278], which is an important aspect to consider after waste packages are emplaced in a GDF. However, the occurrence of this process in a wasteform is unlikely to affect overall GDF conditions due to the presence of a large excess of highly alkaline backfill [2]. Further detail about this process in the context of concrete containers is provided in Section 10.10.

7.2.4 Radiolytic degradation

At doses expected in ILW, the presence of radiation is unlikely to result in a reduction in the mechanical properties of cements. This process, however, is likely to result in the generation of hydrogen gas.

Accelerated dose rates have been used to infer the continued radiation stability of cementitious wasteforms over very long timescales [277, 278, 285]. This type of work demonstrates the stability of BFS/OPC and PFA/OPC cement formulations when exposed to lifetime gamma doses; gamma irradiation does not cause them to swell or crack to an extent that will significantly reduce the performance of the waste package. Such lifetime doses are typically of the order of 10 MGy maximum, and changes in the cement are typically not noticed until 9 MGy. Cements and concretes containing no radioactive wastes are generally considered to be resistant to gamma radiation doses of up to 100 MGy [289]. Beyond this dose, degradation in properties, particularly a decrease in strength has been reported [289]. Relevant information is also available in [290, 291].

The majority of changes to cement under irradiation are due to radiolysis of the pore water. This causes the evolution of hydrogen gas and, potentially, oxidation of reactive materials contained in the waste by radiolytically-produced oxidising radicals such as peroxides (described in more detail in Section 8). Gas generation can cause cracking of cement, especially if the water content is high. This process is also dependent on the cement composition. Generally BFS/OPC grouts produce more hydrogen than pure OPC cement paste, which in turn produces more than PFA/OPC grouts [277, 278].

7.2.5 Chloride attack, sulfate attack and leaching of cement

Chloride and sulfate attack are expected to occur once waste packages are exposed to groundwater. Leaching of cement is also expected to occur. However, alteration of the wasteform itself will not affect the overall performance of the EBS as long as the properties of the backfill are retained

During the storage and GDF operational periods, exposure of typical grouted ILW wasteforms to external sources of chloride or sulfate, or liquids, is unlikely to occur. Exposure to chlorides and sulfates, however, can occur as a result of the degradation of specific wastes, typically organic, leading to expansive processes (for example ettringite formation associated with sulfate attack).

After closure of the GDF, in disposal concepts employing a cement-based backfill, the ability of the EBS to provide an environment in which the solubility of key radionuclides (particularly actinides and lanthanides) and other chemotoxic species is limited will rely on the presence and persistence of the hyperalkaline chemical environment [2]. The backfill also provides a high sorption capacity [2]. Processes of chemical alteration of cement (for example sulfate attack or leaching of cement) can occur once the cement comes into contact with groundwater. These processes (discussed in section 3.10.5 of [2]) may result in alteration of the cement phases, affecting the solubility and sorption of radionuclides and chemotoxic species. In the case of expansive processes (such as sulfate attack) cement cracking may also increase the ability of water to come into contact with the waste.

Given that alteration of the wasteform itself will not affect the overall performance of the EBS as long as the properties of the backfill are retained, there is limited emphasis in our R&D programme on the evolution of cemented wasteforms after closure of a GDF. There has been, however, substantial work on the chemical evolution of the cement backfill (particularly its pH, see [2]) and the solubility and sorption of radionuclides in the EBS, including solubility studies at a range of pH values encompassing that of typical ILW wasteforms (see [4]). In situ experiments aimed at providing confidence in the 'chemical containment' provided by cemented systems ([10], task 424) are also planned in our R&D programme. Overall, these processes are particularly important for the backfill (and for concrete containers), as discussed in [2] and in Sections 8.3 and 10.11.2 of this document.

7.2.6 Release of radionuclides and toxic species from waste

Cementitious wasteforms will start releasing radionuclides (and any toxic species present) once the container has been breached, at a rate that depends on the specific wasteform in question. At this time, whatever, the rate of release from the wasteform, the mobility of radionuclides will be limited by their solubility and sorption in the EBS.

During the post-closure period of a GDF, once the waste container is breached, cement-based wasteforms will start releasing radionuclides (and any toxic species present) into the EBS. The rate at which this occurs is likely to depend on the nature of the waste, the extent of any previous degradation of the cement and the waste, and the overall chemical conditions in the vicinity of the waste (dependent on the chemistry of the incoming groundwater and on the conditioning provided by the backfill and the wasteform). Given the broad range of wastes involved and the timescales over which release processes from the wasteform can occur, post-closure evolution models do not typically take into account of the release of radionuclides from specific wasteforms and, as a result, these processes have not always been subjected to detailed R&D. Conversely, there has been a great focus on understanding the sorption and solubility of radionuclides in the EBS, assuming that, over short timescales, such radionuclides would become available in the groundwater [4]. In some cases (for example, steel and other corrosion-resistant metals, see Section 8.2.1), however, slow degradation processes and slow associated radionuclide release rates can be expected. For example, assuming a corrosion rate of 0.01 μm year^{-1}, a 2 mm thick bar of a corrosion-resistant material (such as stainless steel or Zircaloy) would release its radioactive inventory (if uniformly distributed through its thickness) over a period of hundreds of thousands of years. Analogous considerations may apply to the case of chemotoxic species (for example lead, see section 8.2.3). As a result, for some ILW, it is likely that relatively slow release processes of radionuclides and toxic species may control their concentration in the EBS and their subsequent transport. The release of such species due to some of these processes can be estimated on the basis of information presented in this report (Section 8.2) and [4].

In the case of a cement-backfilled ILW concept, however, it is likely that, beyond any control associated with leaching from the waste, the mobility of radionuclides and chemotoxic species will be limited by their solubility and sorption in the EBS, which are discussed in [4].

7.3 Evolution of polymeric wasteforms (ILW/LLW)

Radiolytic and thermal degradation can affect a variety of polymeric encapsulants, leading to a decrease in strength and the release of species potentially able to induce corrosion processes on the waste container or complexation of radionuclides.

This section describes evolution processes of polymeric encapsulants considered as potential candidates for the immobilisation of some ILW. Examples include vinyl ester styrene (VES) and epoxy resins.

7.3.1 Initial state

Upon curing, polymeric encapsulants display excellent mechanical properties and chemical stability.

Upon curing, polymeric encapsulants display the characteristics of a solid, homogeneous and dry product. Characterisation of three candidate polymer encapsulants (two epoxy resins, APS™ and Huntsman™) and a VES polymer has been carried out[55]. Compressive strengths of the order of 80-200 MPa and ~120 MPa were measured for the two epoxy resins and for the VES polymer respectively [292]. Flexural strengths ranged from 35-96 MPa for the epoxy resins to 108 MPa for the VES polymer [292].

7.3.2 Radiolytic and thermal degradation

On exposure to radiation in conditions relevant to the immobilisation of ILW, many polymeric encapsulants display a reduction in compressive or flexural strength. In the presence of radiation and/or high temperatures, upon exposure to an aqueous phase, they also release organic acids and other electrolytes, including chloride.

Initial assessments of the structural integrity and chemical stability of the three resins described above, when aged at elevated temperatures and in the presence of gamma radiation (in air or in aqueous solutions), were carried out [292]. For the VES polymer, exposure to a 10 MGy dose of gamma radiation at a dose rate of 4 kGy h^{-1} in dry conditions (depending on their location within the GDF, some ILW waste packages are expected to be exposed to cumulative gamma radiation doses of approximately 10 MGy over a period up to

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[55] The resins tested were: APS™ epoxy resin (Advanced Polymer System process from Diversified Technology Services in the USA), Huntsman™ epoxy resin, D formulation, produced by mixing 100 parts of LY 1564 Bisphenol A resin and with 35 parts XB 3403 polyetheramine hardener, and a vinyl ester styrene (VES), also known as Dow Polymer, originally manufactured by the Dow Chemical Company and used in the ‘vinyl ester resin in situ (VERI)’ encapsulation process. Both the APS™ epoxy and the VES have been developed for use in radioactive applications, whereas the Huntsman™ resin is a commercially available “off the shelf” resin.

500 years) had little or no effect on its flexural and compressive strength [292]. Long-term aging at lower dose rates, however, showed that the compressive strength of samples comprising organic ion-exchange resins and encapsulated using a VES polymer decreased slightly between eight and eleven years when exposed to uncontrolled outdoor conditions, including natural freeze-thaw cycles [293]. In contrast to VES, both epoxy resin formulations showed an 80-100% decrease in flexural strength, but no decrease in compressive strength [292].

The three candidate polymers described above and a third epoxy resin formulation called Alchemix 4760™ [56] were also tested in subsequent experiments in a broader range of conditions, including tests at high temperature with radiation [292, 294]. Samples of the resins were irradiated to a total gamma dose of ~10 MGy at a dose rate of 3.2 – 4 kGy h^{-1}, and to a total gamma dose of 120-157 kGy at dose rates ranging from 50 Gy h^{-1} (Alchemix 4760™ only) to 48 kGy h^{-1}. Irradiation was carried out in deionised water (pH ~7-8) or in saturated $Ca(OH)_2$ (where the pH was effectively buffered ~ 12.4) at ~20 °C. Both APS™ and Alchemix™ 4760 epoxy resins were tolerant to radiation in both solutions up to the maximum dose tested (10 MGy), with relatively low Total Organic Carbon (TOC) release observed (<5ppm). A previous study of VES has shown that only very low levels of organic species were generated from this material at 10 MGy in both deionised water and $Ca(OH)_2$ solutions [293]. In contrast, the third epoxy resin, Huntsman™, was less stable and TOC values of 320 and 910 ppm were observed in deionised water and saturated $Ca(OH)_2$, respectively, at a dose of 10 MGy (lower values were observed at lower dose/dose rate).

Experiments to test the polymers' thermal stability were carried out in the same solutions at 20 and 80 °C with no radiation [292, 294]. The thermal stability of APS™ at 80 °C was less than observed for the other three resins (~400-500 ppm TOC in solution after 108 days, compared with about 95-180 ppm TOC for VES and 50-65 ppm TOC for Huntsman and Alchemie after 108-113 days). More chloride was also released from the APS™ sample (60-105 ppm compared with levels less than 10 ppm for the other polymers). In the deionised water tests, for all resins with the exception of Huntsman (in which the pH increased), the pH dropped from 8 to values as low as 3-4 in both the irradiated samples and those heated to 80 °C. This was interpreted as the result of organic acids being released into solution [294]. Benzyl alcohol was the most abundant degradation product identified from the three epoxy resins; for VES it was dimethylaniline.

Radiolytic degradation of the polymers also led to the generation of gas (H_2, CO and CO_2). Tests on APS and Alchemix 4760™ showed that the nature of the gaseous species and amounts generated were generally independent of irradiation dose rate and composition of the atmosphere, with H_2 being the most abundant gas formed. Based on these experiments, a G-value[57] ranging from ~ 0.08 to 0.6 molecules per 100 eV was calculated for H_2 for the three epoxy resins [292]. For VES, H_2 was not the most abundant gas (the yields of CO and CO_2 were higher), and $G(H_2)$ appeared to follow an inverse relationship with dose [292]. Supporting evidence indicating the stability of epoxy resins after irradiation in air was found in a separate study [295], which indicated potential embrittlement, but good stability after several years of storage at dose rates substantially higher than those expected in ILW.

Studies on the same materials were also carried out in aqueous conditions (deionised water and $Ca(OH)_2$) to evaluate the effect of acidic species and chloride released by thermal and radiolytic degradation on the corrosion resistance of stainless steels (grade 316L) typically

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[56] A formulation developed by Alchemie in the UK and trialled at Sellafield as a potential encapsulant for some ILW waste streams.

[57] The amount of gas or other species produced as a result of radiolysis is usually represented by the G-value, which represents the quantity of gas produced per unit of energy absorbed, traditionally represented as the number of molecules produced per 100eV of energy absorbed.

employed in the manufacture of waste containers [296]. Tests were carried out with and without irradiation (dose rates at 10 Gy h^{-1}) and at temperatures of 80 °C. The results of tests in deionised water indicated that for some of the resins tested, over periods of months, a decrease in pH to values of the order of 3-4 and concentrations of chloride up to about 1,000-2,000 ppm occurred both in the presence and in the absence of radiation. In one case, exposure of stainless steel to the solution generated led to the development of localised corrosion (pitting) over a period of six months. No corrosion, however, was found in the $Ca(OH)_2$ solution, which was attributed to its high pH buffering capacity (release of chloride was still observed).

Overall, this studied indicated a good radiolytic and thermal resistance of some potential polymeric encapsulants, in the presence of γ radiation at comparatively high dose rates. The presence of α-emitters in specific wastes is only expected to lead to localised damage (few tens or hundreds of microns), thus not affecting the overall wasteform stability.

Further studies have also considered the effects of thermal and radiolytic degradation on polymers, including the potential for the formation of NAPLs [297, 298, 299, 300]. These may arise from degradation of the polymers themselves (due to the release of low molecular weight species such as ketones, aldehydes, alcohols, hydrocarbons and carboxylic acids, that nominally contain 5-22 carbon atoms and are often insoluble in water), or from the release of plasticisers and stabilisers which are used in the manufacture of rubbers and PVC (generally liquid esters and oils that have limited solubility in water and low specific gravity [58]). A study of potential NAPLs generated from waste streams containing polymers and other organic wastes was also carried out [265, 301]. The impact of NAPLs on radionuclide mobility in the GDF is covered in [4] and is not assessed further here.

7.3.3 Leaching of radionuclides from waste

Polymeric wasteforms will start leaching radionuclides once the waste container has been breached.

During the post-closure period of a GDF, once the waste container has been breached by corrosion, polymeric wasteforms will start leaching radionuclides into the EBS. Given the limited amount of waste streams already encapsulated or planned for encapsulation in polymer, and the likely complexity and diversity of behaviour associated with different waste streams, only a limited amount of R&D has been carried out to understand their likely evolution and resulting radionuclide release to the EBS. Information concerning the radiolytic and thermal degradation processes (such as TOC values, Section 7.3.2), however, could be used to allow an initial evaluation of the likely rate of degradation of the encapsulant.

In the case of a cement-backfilled ILW concept, however, it is likely that, beyond any control associated with leaching from the waste, the mobility of radionuclides will be determined by their solubility and sorption in the EBS, which are discussed in [4].

7.4 Evolution of thermally-treated ILW and plutonium residues

Wasteforms resulting from the thermal treatment of ILW or plutonium residues with very good durability and leaching properties can be obtained with a variety of processes and wasteform formulations.

This section describes the initial state and evolution processes of potential wasteforms which may arise as a result of the thermal treatment of ILW and plutonium residues. No thermally-

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[58] Once released, these species may further degrade to form lower molecular weight species that may be either water soluble or gaseous.

treated waste (other than HLW) has been produced to date in the UK, so initial studies have aimed at scoping the characteristics of a range of potential ‘non-optimised’ wasteforms rather than underpinning the disposal of specific formulations. Potential wasteforms considered so far include borosilicate glasses, alumina-silicate glasses, vitrified ground blast furnace slag, phosphate glasses and single and polyphase ceramics such as pyrochlore or zirconilite.

7.4.1 Initial state

After processing, wasteforms resulting from high temperature processes display excellent mechanical and chemical properties. Depending on the nature of the raw waste and the thermal process, they are likely to display different levels of heterogeneity. For wastes with a high content of α-emitters, microstructural alteration processes may also occur.

The initial state of any thermally-treated ILW will largely depend on the nature of the waste being treated and the specific thermal process employed. In any case, a dry, solid and inert product is likely to be formed. A key characteristic of thermally-treated waste is likely to be the chemical nature of the glass/glass-ceramic material obtained upon solidification, including its level of heterogeneity, together with its low chemical reactivity.

The amount of cracking may also be important in understanding the leaching behaviour of the wasteform. In addition, internal radiation damage due to alpha particles from actinide decay can lead to lattice defects in some crystalline ceramic materials; these may start to lose their crystalline structure (via metamictisation[49] / amorphisation [302]), which can lead to potential decreases in wasteform durability and increased radionuclide release rates.

An issue of relevance to plutonium wasteforms (similar to the case of spent fuel) is the formation of helium gas due to alpha decay inside the matrix; this may cause stresses and pressure build-up, leading to mechanical disruption of the matrix and the potential release of radionuclides previously structurally bound [303, 304]. Another relevant issue is the need to control the potential for criticality, as discussed in [6].

7.4.2 Dissolution processes – glasses

Low dissolution rates can be expected for a variety of glass wasteforms for the immobilisation of ILW and plutonium residues. Dissolution rates depend on the type of formulation employed, on the waste to be immobilised, and on the level of heterogeneity of the resulting wasteform.

Information about the dissolution behaviour of glasses in contact with aqueous solutions has been provided in Section 5.3, particularly in the context of borosilicate glass formulation typically employed for the immobilisation of HLW. Such information is generally relevant to the behaviour of ILW immobilised in glass or glass-ceramic materials, although there is a need to consider wastes and glass formulation specific to ILW.

Experimental work on a variety of glasses and glass ceramics relevant to the immobilisation of ILW and plutonium residues has been carried out in a variety of contexts. Information is available from studies on borosilicate glasses [105, 305, 306, 307, 308], alumino-silicate glasses [105, 305], vitrified Ground Granulated Blast-furnace Slag (GGBS) [309] and phosphate glasses [310].

Recent work carried out in our programme focused on the effect of cement porewater on the likely dissolution behaviour of the glass, as well as the effect of glass dissolution (such as the release of silicates) on a cement backfill [97, 105, 305][59].

A laboratory-based borosilicate simulant (LBS) ILW glass has been studied alongside two full-scale, inactive vitrified ILW simulants (a PCM/Magnox slag and a zeolite/sand glass [105, 305]). The composition of the LBS ILW glass was based on formulations of full-scale products developed by Bingham et al. [311] for immobilisation of wet ILW from Hinkley Point A[60]. Compared to these, the LBS glass produced in the laboratory was homogenous and contained boron. Initial tests with powdered glass samples [305] were carried out at temperatures ranging from 30 to 90 °C in $Ca(OH)_2$ solution over a period of 168 days. Subsequent tests [105] were carried out in deionised water, NaOH (to assess the effect of calcium on glass dissolution rates) and a $CaCl_2$ solution with a similar calcium concentration to the previously used $Ca(OH)_2$ solution (to assess the effect of pH at the same calcium concentration) at 50 °C, but for longer durations.

The highest dissolution rate was measured in the NaOH solution, with boron data showing that the degree of alteration of the glass was about 30% after 90 days and nearly 40% after 294 days [105]. In deionised water, dissolution was also relatively fast (the degree of alteration was 8.3% after 90 days rising to ~32% after 294 days) [105]. This was attributed to the fact that, after an initial period, the pH rose to values as high as 11, leading to the development of alkaline conditions similar to those present in other tests. In contrast, in the calcium-containing solutions, the degree of alteration were much lower; only 1.9% and 2.7% after 90 days, rising to 3.2% and 9.4% in the $CaCl_2$ and $Ca(OH)_2$ respectively. In the calcium-containing solutions, dissolution was inhibited by calcium, which was incorporated into alteration products formed on the glass surface [105]. This effect, however, was only observed in the short-term. In the longer-term (90 and 294 days), there was a resumption in the alteration rate similar to that observed in the tests described above [305]. Overall, the dissolution rates observed were much lower than was predicted based on data for other borosilicate glasses leached in calcium-free highly alkaline solutions (see for example [148, 312]).

Borosilicate glass formulations were also studied for the immobilisation of plutonium [306, 307, 308]. Plutonium dissolution rates from a range of compositions were reported to be in the range 10^{-2} to 10^{-4} g m^{-2} d^{-1} at 90 °C over a pH range of 9-12, with little or no effects observed as a result of internal irradiation [308]. These dissolution rates were typically an order of magnitude lower than the rates measured for silicon and boron.

'Non-optimised' clinoptilolite-sand glass (C-S glass), based on a product produced by plasma vitrification in a cold crucible [313] and a PCM/Magnox waste slag (PCM/Mx) produced via the Geomelt® process have also been studied alongside the LBS ILW glass [105,305], using the same experimental methodology[61]. These studies showed that the C-S

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[59] If vitrified ILW was disposed of in cement-backfilled vaults, good resistance to leaching would increase confidence in (but not necessarily be critical to) the safety case by limiting the rate of release of radionuclides from the wasteform and, possibly more importantly, limiting any potential detrimental changes in the properties of the backfill. Disposal of any thermally-treated ILW in vaults not backfilled with cement is also a possibility. In this case, safety of the GDF would place greater emphasis on the leaching properties of the wasteform as a barrier itself to release of radioactivity in the EBS.

[60] Its composition was ~47.5 wt% SiO_2, ~13.5 wt% Na_2O, ~9 wt% B_2O_3, ~4.4 wt% MgO, ~5 wt% Al_2O_3, ~10.2 wt% Fe_2O_3 and ~3.7% LiO_2.

[61] The C-S glass had a composition of ~66 wt% SiO_2, ~14.9 wt% Na_2O, ~5.6 wt%, MgO, ~9.3 wt% Al_2O_3 and ~1.6 wt% CaO. The PCM/Mx slag glass had a composition of ~59 wt% SiO_2, ~6.2 wt% Na_2O, ~12.8 wt%, MgO, ~13.1 wt% Al_2O_3 and ~5.7 wt% CaO. Other minor components were also present in both glasses.

glass and PCM/Mx slag glass were initially (up to 7 days) less durable than the LBS ILW glass in $Ca(OH)_2$, which was attributed to the (transient) precipitation of a calcium borate phase on the glass surface. At longer times, both these glasses showed higher durability than the LBS glass. For these glasses, however, higher dissolution rates were observed in the $Ca(OH)_2$ solution than in deionised water. These results indicate that the dissolution behaviour of glass products is complex and not easy to generalise. Overall, using sodium as a tracer[62], residual rates at pH 12-12.5, were of the order or 4-5 10^{-3} g m^{-2} d^{-1} (C-S glass) and 3-4 10^{-3} g m^{-2} d^{-1} (PCM/Mx slag) at 50°C [305].

Ground Granulated Blast-furnace Slag (GGBS) includes substantial quantities of silica, alumina and lime[63]. It has been recently trialled as an additive for the thermal treatment of four types of PCM using cerium as a surrogate material for plutonium [309]. The wasteforms produced (on a laboratory scale) were heterogeneous and contained a metallic phase and a slag/glass matrix containing crystalline phases. The cerium was found to be in the slag fraction, and mostly in the glass phase compared to the crystalline phases. The slag fraction was ground into a powder and leached using a standard methodology in saturated $Ca(OH)_2$ solution at 50°C. Like previous studies with borosilicate glasses, the tests were characterised by the loss of calcium from solution and precipitation of Ca-bearing secondary phases. Dissolution rates (based on sodium release) were broadly comparable to those obtained with borosilicate glasses, with values of the order of 10^{-3}-10^{-2} g m^{-2} d^{-1} [309].

Potential phosphate glass matrices recently tested for the immobilisation of the UK stocks of separated civil plutonium comprised iron phosphate glasses (P_2O_5-Fe_2O_3), lead-iron-phosphate glasses (P_2O_5-PbO-Fe_2O_3) and sodium aluminium phosphate glasses (P_2O_5-Al_2O_3-Na_2O) [314]. Few residual rate data measurements have been published, but one measurement (4 10^{-3} g m^{-2} d^{-1}) for the lead-iron-phosphate glass after 210-270 days indicated an order of magnitude decrease compared to the forward rate, based on phosphate release data at 90 °C [310].

Overall, these studies indicate residual dissolution rates similar to those evaluated for HLW glasses, suggesting that a release of radioactivity over periods of tens of thousands of years may also be achieved with products of a variety of high-temperature treatments.

7.4.3 Dissolution processes – ceramics and glass-ceramics

Low dissolution rates can be expected for a variety of ceramic and glass-ceramic wasteforms for the immobilisation of ILW and plutonium residues. Dissolution rates depend on the ceramic formulation employed, on the waste to be immobilised, and on the level of heterogeneity of the resulting wasteform.

There is large body of published research on trials for the immobilisation of plutonium and (minor) actinides in ceramic and glass-ceramic wasteforms. Such information is summarised in [302, 303, 304,315]. Relevant ceramics can be grouped into two types:

- single-phase ceramics, such as zircon, monazite, zirconolite, and pyrochlore
- polyphase "SYNROC" ceramics, consisting primarily of mixtures of zirconolite, perovskite, rutile, and/or pyrochlore as crystalline phases.

Stewart et al [53] have used a Hot Isostatic Pressing (HIP) technique to develop four potential products for incorporation of MOX wastes. The products were a zirconolite glass-ceramic with 20 wt % Pu, a zirconolite-rich ceramic single-phase with 20 wt % Pu, a

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[62] These formulations contain very small amounts of boron, so other elements need to be used as tracers for glass dissolution.

[63] The glass composition included 35.7 wt% SiO_2, ~13.2 wt% Al_2O_3 and ~39.7 wt% CaO.

zirconolite-pyrochlore full ceramic with 30 wt % Pu and a pyrochlore-rich full ceramic with 35 wt % Pu. Leach tests were performed with surrogate formulations of each of the four products, containing ThO_2 (as an analogue for PuO_2) and UO_2/U_3O_8.These tests indicated dissolution rates (based on U and Th analyses) of the order of 1-5 10^{-4} g m^{-2} d^{-1} (over 24 hours) falling to 2-5 10^{-5} g m^{-2} d^{-1} over the next 6 days for all four products in deionised water at 90 °C. The same study reported no visible signs of degradation of the matrix of any of the four products after 3-5 years in storage.

Actinide-bearing natural analogues of several of the single-phase ceramics (including mineral phases such as monzanites, zirconolites and zircons) provide further evidence of long-term durability [302, 316]. Ewing [302] reports Soxhlet leaching data in the 120-250 °C range for zircon; the dissolution rate extrapolated to 90°C was 4.6 10^{-5} g m^{-2} d^{-1} and would be "substantially reduced" at lower temperatures. The study concluded that in an open system, in the absence of a solubility-limiting phase, a 100-μm crystal of zircon would require 150,000 years for complete dissolution.

However, internal radiation effects due to alpha decay of radionuclides can lead to lattice defects in some crystalline ceramic matrices. There is a large body of data based on studies of natural and synthetic zircon (summarised in [302]) which show that metamictisation occurs at 0.2 to 0.6 displacements per atom. The extent of radiation damage is a function of dose, temperature and type of radiation. Above certain temperatures, the radiation damage is offset by thermal annealing. For example, zircon with 10 wt % Pu-239 shows no signs of metamictisation above 225°C. Nevertheless, the potential decrease in the durability over longer timescales due to these effects remains an important uncertainty for ceramic and glass-ceramic wasteforms where no analogues exist [303,304].

In general, laboratory studies suggest that ceramic and glass-ceramic wasteforms are the most promising immobilisation matrices for plutonium and actinides, exhibiting low radionuclide release rates of the order of 10^{-5} to 10^{-4} g $m^{-2}d^{-1}$, which is 2-3 orders of magnitude lower than residual rate data measured for glasses. In glass-ceramic systems plutonium tends to be chemically bound in the ceramic phase (whereas other impurities tend to partition in the glass phase), resulting in plutonium leaching rates typically observed in single-phase ceramics [303, 304]. Indicative dissolution rates for a range of potential plutonium wasteforms, including glass, glass ceramics and ceramics, are reported in Table 14, together with the expected dissolution rate for 'storage MOX' (see Section 2.5.2) based on the analysis reported in [303].

Table 14: Indicative dissolution rates for potential plutonium wasteforms [303]

Potential Pu wasteform	Lower bound g $m^{-2}d^{-1}$	Best estimate g $m^{-2}d^{-1}$	Upper bound g $m^{-2}d^{-1}$
Borosilicate glass	$<10^{-4}$	10^{-4} to 10^{-2}	10^{2}
Phosphate glass	$<10^{-5}$	10^{-5} to 10^{-2}	10
Ceramic wasteforms	$<10^{-7}$	10^{-5} to 10^{-4}	5×10^{-1}
'Storage MOX'	$<10^{-7}$	5×10^{-6}	10^{-2}

7.5 Evolution of non-encapsulated wastes (ILW/LLW and DNELU)

A number of ILW/LLW and DNLEU waste streams may not be encapsulated. Upon contact with groundwater they will start leaching radionuclides at a rate that depends on the composition of the materials in question.

This section describes evolution processes of some wastes which may be destined for disposal without encapsulation, including some ILW/LLW as well as DNLEU.

The nature of evolution processes of relevant materials is described at a high level, since such processes will inevitably depend on the waste in question and their upstream processing (for the storage and GDF operational period particularly any drying process). Relevant information is also presented in Section 8.

7.5.1 ILW/LLW

Pre-closure, depending on the waste in question and any processing treatment, non-encapsulated ILW/LLW wasteforms are expected to either undergo minimal degradation or to undergo a variety of degradation processes, depending on their composition. Post-closure, non-encapsulated wasteforms will start leaching radionuclides.

The evolution of non-encapsulated LLW/ILW will largely depend on the waste in question and any treatment process.

During the GDF pre-closure period, depending on the waste in question and any processing (particularly drying) treatment, non-encapsulated ILW/LLW wasteforms are expected to either undergo minimal alteration processes (for example, graphite or corrosion resistant metals) or to undergo a variety of degradation processes, including corrosion (steels and reactive metals), radiolytic degradation (plastics) and gas generation (many waste types). Information relevant to these processes is described below in the context of specific waste types (see Sections 8.2, 8.3).

During the post-closure phase of a GDF's lifecycle, once the waste container is breached, non-encapsulated wasteforms will start leaching radionuclides into the EBS. The rate at which this occurs is likely to depend on the nature of the waste, the extent of any previous degradation, and overall chemical conditions in the vicinity of the waste (dependent on the chemistry of incoming groundwater). Given the broad range of wastes involved, the timescales over which such release processes can occur have not been subjected to detailed R&D and are currently not well underpinned. In some cases (graphite or stainless steels), however, slow degradation processes and slow associated radionuclide release rates can be expected. The release of radionuclides due to some of these processes can be estimated on the basis of information presented in this report (see Section 8.2).

7.5.2 Graphite

Graphite is chemically unreactive in conditions relevant to storage and disposal, although a fraction of its anionic inventory (predominantly ^{14}C and ^{36}Cl) will leach over long timescales once in contact with groundwater. Information about graphite leaching is beyond the scope of this report but relevant information is summarised in [4] and [86], including information on UK graphite from the EC programme CARBOWASTE [317].

7.5.3 DNELU

DNLEU will arise in the form of uranium oxide powders. Pre-closure, evolution processes are likely to be associated with the long-term hydration and agglomeration of the powder. Post-closure, uranium oxide powders will come into contact with groundwater and start dissolving slowly, leading to a slow release of their radioactive inventory.

The evolution of potential wasteforms for DNLEU has been considered in some detail in RWM's technical programme in the content of an integrated project on the disposal of such materials [39] and is not described in detail in this document. Initial considerations of the likely behaviour of uranium oxides in a GDF are included in [318, 319] and further work is planned in the future [10, task 631], depending on the output of ongoing activities aimed at developing disposal concepts and high level disposability assessments for this waste.

For disposal in a GDF, DNLEU arises or will arise in the form of the uranium oxide powders U_3O_8 or UO_3. At the low temperatures of interest (DNELU does not generate heat), uranium oxides are chemically stable. During the GDF pre-closure period, evolution processes are likely to be associated with the long-term hydration and agglomeration of the powder, which is unlikely to result in any detrimental effect in the ability of the wasteform to immobilise radionuclides.

During the post-closure period, after perforation of its disposal container, uranium oxide powders will come into contact with groundwater and, potentially, will start dissolving at a very slow rate [318, 319]. Work discussed in the context of oxide spent fuel (related to uranium dioxide) may be relevant in understanding the long-term behaviour of this material.

8 Evolution of specific ILW wasteforms

This section describes scientific and technical information relevant to the expected evolution processes of specific ILW wasteforms for which detrimental evolution is likely to occur. Wasteforms described include those arising from the encapsulation of metals, organic wastes and mobile wastes (such as sludges and flocculants) in cement, as well as from the packaging of these materials without encapsulation. In these systems, evolution processes may need to be either designed out through the choice of an alternative treatment (such as encapsulation in polymer or high thermal treatment) or accommodated in the design of waste packages (for example, by the design of gas venting systems or internal expansion volumes).

Key sources of information in this area are typically studies produced within the UK nuclear industry[64], although relevant information is likely to include the RILEM workshop series [261], the Scientific Basis for Nuclear Waste Management Proceedings [262], proceedings of the Migration Conference [263] and publications in journals such as Cement and Concrete Research (for example, [264]).

The information presented summarises some of the studies produced in the UK and worldwide in the last 20-30 years. Studies include:

- experimental work on wastes and wasteform simulants
- models of the evolution of the wasteform
- experience with wasteforms and analogues in the nuclear and other industry (for example, the construction industry for concretes)
- monitoring of waste package simulants over a number of years.

8.1 Processes relevant to specific ILW wasteforms

When encapsulated in cement, some ILW may undergo evolution processes likely to lead to volumetric changes which can lead to cracking and, if sufficient in extent, deformation and potential rupture of the waste container. Internal corrosion and gas generation may also occur.

Processes relevant to the evolution of specific wasteforms and encapsulants are described below. These processes are sufficiently understood to allow wasteform formulations to be developed accordingly, thus eliminating or limiting their likely impact. All processes described herein are relative to cemented or non-encapsulated ILW.

Evolution processes and their effects are described in Table 15.

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[64] Many studies in this area have been carried out by waste producers to underpin the disposability of specific waste streams. As a result, relevant information is generally not available in documentation that can be referenced in this document.

Table 15: Processes relevant to specific ILW wasteforms

Waste Type	Period	Evolution Processes	Effect on wasteform	Section
Metallic wastes **(in cement or unencapsulated)**	Pre or post-closure	Corrosion of reactive metals	Formation of expansive phases Gas generation (H_2)	8.2
Organic wastes **(in cement or unencapsulated)**	Pre or post-closure	Radiolytic and thermal degradation Hydration[65]	Formation of expansive phases Change in mechanical strength Container corrosion Gas generation (H_2) Decrease in alkalinity Generation of NAPLs[66]	8.3
Mobile wastes **(in cement)**	Pre-closure	Crystallisation processes Ion exchange Release of bound water Alkali-silica reaction	Formation of expansive or shrinking phases Alteration of cement phases Container corrosion Gas generation (H_2)	8.4

8.1.1 Waste metals (in cement or unencapsulated)

Processes that may need to be considered for metal wastes include corrosion of the metals, cracking of cement encapsulants, deformation of the waste container, and the generation of gas.

There is a significant quantity of various metals in the waste inventory (see Table 1). Some are in relatively good condition, others have been gradually degrading, for example during storage in ponds and silos at Sellafield.

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[65] Some organic ion-exchange resins can hydrate in the presence of cement, degrading the properties of the wasteforms.

[66] The impact of complexants and NAPLs on radionuclide solubility and mobility is considered in [4].

When conditioned using an encapsulant containing a water phase (like cement) or packaged directly in a waste container in the presence of water (unencapsulated wastes, depending on drying processes), these metals may start, or continue, to corrode. Such corrosion could potentially affect the evolution of the wasteform by generating expansive phases or gases inducing mechanical stresses in the encapsulant and the waste container.

For cement-encapsulated wastes (unless resulting in a substantial disintegration of the wasteform and rupture of the waste container) expansive processes are unlikely to affect the ability of waste packages to contain radionuclides in normal conditions, but may result in uncertainty in the performance of the packaged waste under accident conditions [7], particularly during an impact accident. Whilst undesirable, deformation of the waste container may have limited consequence, since the performance of thin-walled, grouted waste packages under impact accident conditions often result in container rupture (but yet relatively small radionuclide release) even in the case of pristine containers, due to the good impact resistance of the wasteform [7].

For both cement-encapsulated and unencapsulated wastes, gas generation, potentially resulting in pressurisation of the wasteform and gas release from waste containers (vented), may also need also to be considered. Corrosion (particularly for reactive metals) can result in the generation of hydrogen gas, which is flammable. Gas generation is discussed in detail in [5].

8.1.2 Organic wastes (in cement or unencapsulated)

In the case of organic wastes, chemical changes leading to internal corrosion of the waste container and gas generation may occur. Expansion processes may also occur but these may be accommodated in the free volume typically present in this type of waste package.

The inventory of ILW contains a relatively large amount of organic wastes. Key waste streams include PCM (typically substantial in volume) and organic ion-exchange resins, less in volume, but generally high in specific radioactive content - including potentially mobile (albeit relatively short-lived) radionuclides such as caesium and strontium isotopes.

PCM typically has a high content of organic material, including PVC. The radiolytic degradation of these wastes may lead to the generation of carbon-containing gases (including CO_2), organic acids and chloride. This can potentially lead to changes in compressive strength and alkalinity of cement-based wasteforms (if CO_2 and/or organic acids are evolved), as well as corroding any metallic components present inside the waste package, including the internal surfaces of the waste container.

PCM is typically supercompacted in carbon steel drums and the resultant ‘pucks’ packaged in cement-lined stainless steel containers. In this configuration, any acid and chloride generated from the degradation of the organic wastes, are likely to corrode the compressible steel cans in which the wastes are loaded and may induce chemical changes in the cement liners (formation of calcium chloride due to chloride attack). These processes, particularly the corrosion of steel pucks, are likely to result in the formation of expansive corrosion products. Organic acids may also decrease the alkalinity of the cement liners typically surrounding the pucks, potentially leading to carbonation of the wasteforms. Together with any chloride released from the degradation of PVC, and in the presence of preferential transport pathways between the pucks and the container envelope (for example, pre-existing cracks), these processes have the potential to result in corrosion of the waste container. Similar processes could take place if these wastes were packaged without encapsulation, particularly in the presence of a liquid phase.

Ion exchange materials can react with cements through hydration and ion-exchange processes, leading to the expansion of the wasteform and potential cracking. Upon irradiation, organic ion-exchange resins may also release sulfate. Sulfates react with calcium hydroxide to form calcium sulfate, and with aluminates to form expansive cement phases such as ettringite and thaumasite.

8.1.3 Mobile wastes (in cement)

Sludges and flocculants can react with cements through hydration and crystallisation processes, potentially leading to expansion or shrinkage.

Sludges, flocculants and raffinates (referred to in this report as ‘mobile’ wastes[67]) also represent a significant fraction of the ILW inventory. These wastes can react with cements through hydration and crystallisation processes. This can lead to the expansion/shrinkage of the wasteform, potentially leading to cracking and deformation of the waste container.

If not encapsulated, these wastes (typically associated with substantial amounts of water), may result in corrosion and associated gas generation from any remaining waste metal contained in the waste and/or of the waste container itself. Relevant studies in this area have not been carried out in our research programme so are not discussed hereafter.

8.2 Evolution of metallic wastes (in cement or unencapsulated)

With the exception of Magnox, aluminium and particularly uranium, most metals are likely to experience very slow corrosion in cement, resulting in low rates of expansion and gas generation. However, in near-neutral pH aqueous conditions, corrosion is expected to proceed at a significant rate for steels and uranium and at a very fast rate for Magnox.

Metals represent a very large volumetric fraction of the inventory of ILW. Stainless steel and other steels are present in very large quantities, followed by substantial amounts of Magnox. Aluminium, lead, nickel alloys and Zircaloy are also present in sizeable quantities, while uranium is likely to be present in relatively small amounts, usually as a contaminant in Magnox-containing waste streams.

The corrosion behavior of waste metals in cement and in near-neutral pH aqueous conditions (relevant to unencapsulated waste) is described in detail below. It is important to note (as discussed in Section 4.3) that reducing or mildly reducing conditions are typically present inside cemented waste packages, particularly those based on BFS/OPC formulations. Comprehensive reviews of the corrosion behavior of many waste metals in cement are available in [320, 321, 322]. Expansion factors due to the corrosion of metallic wastes in cement and associated corrosion rates have also been reviewed more recently by Sellafield [323]. Further work to refine existing analyses of the effects of such processes on the evolution of wasteforms is planned in the future [10, task 572].

A specific consideration is that, for reactive metals, it is also important to consider the potential formation of galvanic couples with more noble metals (such as steels) and graphite. Studies of galvanic coupling between different materials in cements has indicated that corrosion rates could increase significantly in the presence of specific galvanic couples [324].

8.2.1 Stainless steel, nickel alloys and Zircaloy

Stainless steel, nickel alloys and Zircaloy are corrosion resistant. Their degree of corrosion and associated expansion over periods of many centuries is expected to be insufficient to cause substantial cracking of the wasteform and deformation of the waste container.

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[67] Ion exchange resins (both organic and inorganic), typically arising in the form of beads, are also often categorised as ‘mobile’ wastes. In this document, the evolution processes of organic ion exchange resins are described together with that of organic wastes.

Metals such as stainless steel, nickel alloys and Zircaloy are corrosion resistant and do not corrode significantly when in contact with either near-neutral pH solutions [254] or in cement [320]. The good resistance of stainless steels and nickel alloys to corrosion is discussed in detail in Sections 10.9 and 10.10. The corrosion resistance of Zircaloy is discussed in [320, 325] and Section 6.5.

The available information indicates corrosion rates for these metals of the order of 0.01 μm year^{-1} or less at room temperature in both near-neutral and alkaline environments, resulting in a total maximum expansion of a few μm over a century. These materials pose a negligible risk to wasteform durability, since the degree of corrosion and associated expansion over periods of many decades are insufficient to cause substantial cracking of the wasteform and deformation of the waste container. Rates of gas generation are also expected to be insignificant during storage and the operational period of a GDF, although they may become important for the long-term evolution of a GDF [5].

8.2.2 Mild/carbon steel and cast iron

Unless carbonation and relatively high concentrations of chloride are present (only relevant to the post-closure period), steels are expected to corrode very slowly in cement, but will corrode more vigorously in the presence of water at near-neutral pH.

Mild steel, carbon steel and cast iron ('steels'[68]) are generally more reactive than stainless steel, nickel alloys or Zircaloy. In near-neutral pH conditions (relevant to unencapsulated wastes) corrosion rates of the order of 10 μm year^{-1} are expected in relatively dry conditions (see Section 10.7.1). Higher rates could be expected in the case of wet or damp wastes. Corrosion rates tend to decrease with time as corrosion products build up and as the oxygen content of the system decreases (as may be expected inside waste packages). In anoxic conditions, corrosion rates are likely to decrease to values of the order of 1 μm year^{-1} (see Section 10.7.2), but will result in the generation of hydrogen gas.

Unless carbonation and relatively high concentrations of chloride are present (only relevant to the post-closure period), steels are expected to corrode very slowly in cement, at rates similar to, or slightly higher than, those described above for stainless steel and Zircaloy [320]. Chronic corrosion rates of the order of 0.1 μm year^{-1} or less are expected in this case [320], see also Section 10.

The corrosion of cement-encapsulated carbon steel wastes is analogous to the corrosion of steel reinforcing bars in concrete: in the presence of carbonation and chloride ions, there is a potential for corrosion to occur, resulting in the formation of solid corrosion products occupying a greater volume than the parent metal, leading to cracking of the concrete. However, wastes containing large quantities of steel are not generally associated with significant quantities of organic materials, which can generate carbon dioxide within waste packages. Carbonation from external sources of CO_2 (such as the atmosphere) tends to be confined to the outermost parts of cementitious wasteforms, because the carbonation itself causes a reduction in permeability that slows the further movement of CO_2 [283] (see also Section 7.2.3). In addition, steel wastes are not generally associated with significant quantities of chloride, which ensures that the potential for a significant degree of corrosion is also limited[69].

A modelling study was carried out to evaluate the likelihood of cement cracking and container deformation for a cement-based wasteform containing carbon/mild steel [326]. As

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[68] In this section, given that their chemical properties are similar, we refer to carbon steel, mild steel and cast iron as 'steel' to distinguish them from 'stainless steel'.

[69] An exception to this case is represented by plutonium contaminated materials (PCM wastes), which contain chlorinated plastics supercompacted in steel pucks. These are discussed in Section 8.3.1.

expected for the vast majority of the ILW inventory, the study assumed that the levels of chloride in the wasteform were unlikely to result in any localised corrosion. In these conditions, this study indicated that limited volume changes would result in localised cracking of the encapsulant, whilst levels of linear expansion of the order of 0.3% would be required to initiate deformation of the waste container. Much higher values (linear expansion of the order of 10%) would be required to breach the waste container [326]. At the expected corrosion rates of carbon steel in (non-carbonated, non-chlorinated) cement (chronic rate of 0.1 μm year^{-1} at room temperature), the timescales needed to initiate deformation processes would be very long. Higher corrosion rates and resulting rates of expansion would be expected in the presence of chloride and carbonated wasteforms.

8.2.3 Lead

In ILW, lead is typically present in a fairly massive form and the overall rate of any expansive processes associated with corrosion is likely to be limited.

Lead is a relatively noble metal and corrodes slowly in near-neutral pH conditions [254]. In the absence of specific agents (particularly acetate), in oxic conditions lead is likely to corrode at a rate of the order of 1 μm year^{-1}, decreasing to lower values in anoxic conditions [254]. In anoxic conditions, evolution of hydrogen gas occurs.

Lead corrodes at a faster rate in alkaline environments [254]. Data relevant to the likely corrosion rate of lead in cement are somewhat scarce, but upper bound rates of the order of 10-100 µm year^{-1} have been suggested in oxidizing conditions [327]. Recent work at Sellafield, however, indicated very low gas rates of lead when encapsulated in grout, which was interpreted either as the fact that the corrosion rate may not generate hydrogen or as an indication of a low corrosion rate [328]. In ILW packages (either in the waste or as part of inner container furniture), lead is typically present in a fairly massive form (such as lead blocks) and the low surface area to mass ratio may limit the overall rate of any expansive processes associated with corrosion. In some cases, however, wasteforms containing lead in a form with a relatively high surface/volume ratio may be present.

8.2.4 Magnox

Magnox is generally very reactive, experiencing very fast rates of corrosion in the presence of neutral pH water, resulting in the generation of hydrogen gas. Corrosion is substantially slowed down in cement.

Magnesium alloys (including Magnox) are generally reactive, experiencing relatively fast rates of corrosion in the presence of water [254]. Corrosion processes proceed vigorously in both oxic and anoxic conditions, resulting in the generation of hydrogen gas. Corrosion is significantly slowed in alkaline conditions, due to the formation of a partially protective oxy/hydroxide layer. The corrosion of Magnox in cement is expected to be largely driven by the alkalinity of the system and the presence of chloride. Estimates of the durability of cement-based wasteforms containing Magnox are reported in [329], based on data reported in [321]. A subsequent review of the rates of corrosion of Magnox and other metals in cement was also conducted [322], to complement previous work with specific data gathered in the UK nuclear industry, including experience with wasteform simulants.

These studies showed that substantial work on the corrosion behaviour of Magnox has been carried out in alkaline environments simulating cement porewater (and sometimes directly in cements), although data at the high chloride concentrations relevant to the post-closure situation, described in greater detail in the Gas Status Report [5] and in [330], are scarcer. Initial and long-term corrosion rates (often described as ‘acute’ and ‘chronic’ corrosion rates) of the order of 10 μm year^{-1} and 0.78 μm year^{-1} have been reported at 35°C for a low chloride environment (generally expected in waste packages for Magnox-containing waste streams), increasing to values of the order of 35 μm year^{-1} and 4.3 μm year^{-1} at 50°C [321].

The transition between the acute and chronic period is typically expected to occur over periods of several months [321]. The presence of chloride concentrations in excess of 100 ppm will however result in corrosion rates up to 100 times higher [321]. Levels of chloride higher than 100 ppm will almost certainly be present in a UK GDF but are unlikely to be present in many Magnox-containing waste streams.

The reviews were accompanied by experimental work yielding rates of corrosion and resulting wasteform expansion, at different temperatures, of fresh Magnox metal encapsulated in grout formulations (3.44:1 BFS/OPC system, water/solids ratio of 0.35) and Magnox loading (155 kg / 555 litres) typically employed in the industry [331, 332]. The experimental work indicated similar corrosion rates to those previously reported [321], but complemented this information with measurements of expansive forces and the resulting cement cracking. Based on these measurements, it was concluded that, in the system in question and at the low temperatures expected during storage, cracking of the cement due to Magnox expansion would occur over periods between several decades and several millennia, with best estimates of the order of a few hundreds of years. Extrapolation of the low temperature data to long timescales indicated a likelihood of cracking over periods of many decades, but no risk of rupture of the waste container. The results of a modelling study indicated that localised cracking may occur over relatively short periods of time but that substantial amounts of expansion would be required to deform or breach the waste container [326]. Overall, at the expected waste loadings and corrosion rates, rupture of the waste container is unlikely to occur during operations or prior to resaturation of the EBS.

Practical experience arising from the immobilisation of Magnox in cement is available from the UK nuclear industry (see Box 18). This experience confirms that low corrosion and expansion rates can be expected.

Box 18 Observations from monitoring of Magnox swarf waste packages

Magnox swarf is produced at Sellafield as a by-product of fuel reprocessing operations. The resulting waste is predominantly Magnox metal, but also contains relatively small quantities of other materials (such as nickel alloy) and variable quantities of uranium metal. In most cases, the uranium is present as small smears adhered to the Magnox can or as small fragments. Occasionally, larger pieces of uranium are carried into the swarf. The swarf is collected in bins and tipped into 500 litre stainless steel drums. A cementitious grout comprising BFS/OPC is added to the drum. More than 17,000 such waste packages had been manufactured, and placed in storage, by 2008 [333] and processing has progressed considerably since that time.

During 2007, a programme of waste package inspection was carried out by Sellafield Limited. Of the sixteen waste packages inspected, most were found to have undergone no visible changes. However, localised swelling was visible on three waste packages. Further investigation and assessment yielded a high degree of confidence that the ‘bulges’ are attributable to the corrosion of uranium pieces located close to the drum walls or base.

An assessment of the potential safety significance of the observed changes, and the potential future disposability of the affected waste packages, is being carried out through the Disposability Assessment process (periodic review). Further waste packages are being inspected, and Sellafield Limited will need to consider management of affected packages, should it be decided that their remediation is required. Changes have also been made to operational procedures to ensure that most of the relatively large pieces of uranium are removed from the waste prior to encapsulation [334].

8.2.5 Aluminium

Very low rates of corrosion of aluminium are expected at near-neutral pH. In cement, however, relatively fast initial corrosion rates but lower long-term rates are observed.

In near-neutral pH conditions aluminium behaves like a passive metal, due to the formation of a protective layer of aluminium oxide [254]. In these conditions, very low rates of corrosion (<<1 μm year^{-1}) are expected.

Aluminium corrodes rapidly in contact with alkali due to the dissolution of the protective (passive) oxide layer formed in the atmosphere or in near-neutral aqueous conditions [254]. In cement, relatively fast corrosion rates, compatible with experimental studies in simple alkaline solutions, are initially observed [321]. However, after a few hours, far lower long-term corrosion rates are observed [321, 335]. We do not believe that the mechanisms responsible for this behaviour have been fully investigated. It is possible that passivating calcium-silicon-aluminium layers could be forming in these conditions. The layers could be similar to the gel layers formed by the dissolution of calcium-containing borosilicate glasses (see Section 5), in which aluminium is also thought to play a role.

Reference [321] reports rates of acute and chronic corrosion of aluminium in cements of the order of 15,300 μm year^{-1} and 24.5 μm year^{-1} respectively, much higher than those considered for Magnox [321][70]. The timescales for the onset of the chronic rate are typically very short (a few hours). This analysis was based on a variety of tests carried out for grouts employed in the nuclear industry, but was rationalised and discussed in the context of the broader literature, including tests in porewater simulants, cements used in the construction industry and 'long-term' experience (a few decades) of use in contact with construction materials [321]. Recent work at Sellafield confirms that high acute corrosion rates can be expected [328]. The acute corrosion rates are much reduced under less alkaline conditions, so that consideration is being given to the use of cements with lower pH as encapsulants for wastes containing large quantities of aluminium. However, extrapolation of chronic rates indicates that an overall expansion of the order of 100 μm or less is expected over several decades [336], suggesting that long-term corrosion rates may be lower than previously anticipated.

8.2.6 Uranium

The corrosion of uranium is not inhibited by cement and does not tend towards a low chronic rate. The rate is strongly dependent on the availability of oxygen, with higher oxygen concentrations associated with lower corrosion rates.

The corrosion of uranium in cement has been studied less widely than that of Magnox [321], but has been widely studied in the presence of oxygen, water vapour, anoxic water and oxygenated water (see Section 6.4). Available data indicate that, in aqueous conditions, the corrosion of uranium does not tend towards a low chronic rate and is strongly dependent on the availability of oxygen, with higher oxygen concentrations associated, contrary to the case of many other metals, with lower corrosion rates [229].

There are currently limited data to evaluate the likely long-term evolution of uranium metal in alkaline systems. Work by Haschke [232, 233] concentrating on exposure to liquid water or water vapour showed that the reaction is mostly independent of pH, the rate falling by only

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[70] It is worth noticing that one of the largest inventories of aluminium in ILW is the fuel skips at Hunterston A, which these have been paint-dipped prior to grouting so as to provide a barrier between the aluminium and the grout. This is likely to lead to a substantial decrease in acute corrosion rates.

10-15% at pH 13.5, from a constant value between pH 3-7. As a result, the rates of corrosion in reducing conditions reported in Section 6.4 (4-400 μm year^{-1}) may also be applicable to the case of cement.

The corrosion of uranium in cement has recently been reviewed [322], including information not available in previous reviews [321]. A comparison between the two studies (see Section 10.3 of [86]) indicates that the corrosion rate of uranium in cement typically lies between values measured in aerobic and anaerobic aqueous conditions, but typically approaches values similar to that obtained in anaerobic conditions (particularly in reducing cement formulations such as BFS/OPC). Corrosion rates between 20-70 μm year^{-1} are observed at a temperature of 20 °C increasing to values as high as 150-400 μm year^{-1} at 40 °C (Table 47 of [86]). Similar rates (10-14 g m^{-2} day^{-1}, equivalent to 200-280 μm year^{-1}) were found in a recent study at 50°C [337]. With these corrosion rates, lumps of uranium present in ILW would corrode over period of decades or centuries.

The corrosion of uranium in cement has also recently been studied from a mechanistic point of view [338, 339]. The results of this work indicate that corrosion is likely to be associated with the development of uranium hydride underneath a (relatively un-protective) uranium oxide layer (likely to be UO_2). Encapsulation in cement (especially in the case of reducing cements with low permeability, such as BFS:OPC mixtures) may lead to the development of similar conditions to closed systems, leading to the formation of hydride. Hydride pits (<100 μm in depth and up to 500 μm in diameter) develop over short exposure periods [338], and the hydride can be retained for up to a period of ten months after exposure to water in a semi-sealed system [339]. The available data, however, suggest that longer-term general corrosion / pitting rates are likely to be reduced as the corrosion-product layer develops (as for most metals) and due the limited transport of reactive species in an enclosed system such as a cement [339]. Based on the evidence summarised in [86], however, long-term rates may be sufficiently high to lead to relatively fast degradation processes. Further work on the behaviour of uranium in cement is planned in our R&D programme [10, task 574].

Practical experience arising from the immobilisation of uranium in cement is available from the UK nuclear industry (see Box 18). Observations of Magnox-metal waste streams known to contain lumps of uranium (typically in fragments of fuel rods) indicated expansion of the uranium lumps (but not of the bulk Magnox waste) after a few years of encapsulation in cement, confirming that high corrosion rates (accompanied by substantial expansion of the wasteform) can be expected in the case of uranium. After the initially fast period, however, expansion rates dropped substantially. It is currently not clear whether this is due to a decrease in reaction kinetics, limitations associated with the consumption of water in the system, or the reaction proceeding through to completion (complete corrosion of the uranium lumps).

8.3 Evolution of organic wastes (in cement or unencapsulated)

Key waste streams include plutonium-contaminated materials and organic ion-exchange resins. Wastes comprising a significant component of organic materials are expected to undergo chemical changes leading to the release of gases and low-molecular-weight organic compounds, including organic acids and, in the case of PVC, hydrochloric acid.

Organic wastes are relatively abundant in the inventory of ILW. Key waste streams include PCM (typically rich in PVC) and organic ion-exchange resins. It is known that polymeric materials (including those contained in ILW) can undergo radiolytic degradation. These processes require due consideration whether the waste is immobilised in an encapsulant such as cement [340] or remains unencapsulated.

PCM, arising from past operations, has accumulated in large quantities. As discussed in Section 8.1.2, these wastes have typically been supercompacted, packaged and stored in thin-walled stainless steel containers internally lined with cement. Although there is currently no indication of detrimental evolution processes, this type of waste is currently considered a candidate for high temperature treatment due to the expected reduction in volume and reactivity expected after such treatment.

Organic ion-exchange resins, used for the clean-up of spent fuel storage ponds, represent a relatively limited fraction of the ILW inventory (in volume) but can contain relatively high concentrations of radioactivity, including species relatively mobile in groundwater (^{135}Cs being the greatest post-closure concern due to its long half-life). In order to avoid potential detrimental evolution in cement, the use of polymeric encapsulants has been pursued for some ion-exchange resins.

8.3.1 Plutonium contaminated materials (PCM)

Plutonium-contaminated materials may release acidic species within the wasteform. This may lead to the corrosion of internal metallic components of waste packages (potentially leading to expansive processes) as well as damage to the waste container itself. The potential impact is likely to be substantially mitigated through the presence of expansion volumes in waste packages.

Waste packages containing PCM may release acidic species in the wasteform, including carboxylic acids or stronger acids such as hydrochloric acid (HCl, from the degradation of PVC). Since such acids (especially HCl) could have an impact on the potential for internal corrosion of the (mild steel) pucks and of the (typically stainless steel) waste container, waste packages for PCM currently utilise a thick cement annulus, which helps to isolate the waste from the container. Acids and chloride can react with the cement annulus, although the potential for this process to cause, per se, any detrimental effect is relatively limited.

Work to evaluate the likely quantity and rate of acid production has been carried out [341]. This study indicated that cellulose is likely to be the most abundant organic material present in many wastes, but that its radiolytic degradation is unlikely to yield acidic materials in sufficient quantities to be of concern. Conversely, the production of HCl from the radiolysis of chloride-containing polymers such as PVC was identified as the major acid production mechanism. Rates of acid production were estimated to be relatively low and mass balance calculations indicated that the HCl would be expected to react with materials within the waste package itself. In the case of condensation polymers, the process was assessed to be too slow to be of significance. Other work, however, indicated that at high dose rates PVC degradation may induce stress corrosion cracking on stainless steels in direct contact with it [342].

On the basis of evidence from chloride diffusion experiments [343], it is likely that transport of chloride through an intact grout annulus (free from cracks) would be relatively slow, so that a critical build-up of chlorides at the container wall would not be expected over long timescales. The situation may be different if cracks are present or develop in the annulus, particularly if carbonated. In this situation, resulting in the potential for enhanced transport of chloride to the container wall and loss of corrosion inhibition due to a decrease in porewater alkalinity, the potential for internal corrosion of the stainless steel container was highlighted.

Any corrosion of the carbon steel pucks may itself lead to the generation of expansive processes potentially able to affect the integrity of the waste package. However, packaging of supercompacted wastes in waste containers typically leaves some free volume between the pucks and the cement annulus, in which expansion may be accommodated.

Work to investigate the potential for sodium chloride to promote the dissolution of C-S-H gels has also been conducted [344]. This process is unlikely to detrimentally affect the evolution of the wasteform (it is likely to act as a sink for chloride, without resulting in substantial volumetric alteration), but it is important in developing a comprehensive picture of the likely evolution of the system. Although this work was targeted primarily at the conditions and timescales relevant to the EBS under post-closure conditions, it provides a greater understanding of the interactions between chlorides and cement.

8.3.2 Organic ion-exchange resins

When encapsulated in cement, irradiation of organic ion-exchange resins may cause swelling, retardation of cement curing and gas generation reactions that cause cracking of the cement matrix. The potential impact is likely to be substantially mitigated through suitable pretreatment, cement formulation or container design.

Organic ion-exchange resins are composed of flexible random networks of hydrocarbons, which cross-link to make an insoluble resin. Functional groups can be added to produce either cationic (such as sulfonated) or anionic (typically amine-containing) exchange capacity. They can be strongly acidic ($-SO_3H$), weakly acidic (-OH), strongly basic ($=N^+$) or weakly basic ($-NH_2$) [285]. Most resins are in the form of small beads or granules.

The behaviour of organic ion-exchange resins in contact with cement has been studied for over 30 years and relevant considerations are summarised in [268, 345, 346] and more recently in [285, 347]. Research has focussed on increasing waste loadings, improving the compressive strength of the matrix, controlling the heat of hydration during the cementation process, and reducing the leaching rates of radionuclides from the wasteform [347].

The main issues from cement encapsulation of organic ion-exchange resins are:

- the resin may swell or expansive cement phases may form, potentially leading to gross loss of integrity of the cementitious matrix [348, 349]. This could cause deformation of waste packages or cracking/spalling of the cement matrix.
- some resins may release chemical species such as borate ions, which form relatively impermeable solid phases around cement grains and thereby significantly retard hardening of the cement matrix [350, 351]. This may present process throughput issues and may affect wasteform quality.
- breakdown of the resins due to irradiation, leading to gas generation or, in the presence of resins with sulfonic groups, the precipitation of ettringite [352]. These reactions may cause cracking/spalling of the cement matrix.

These effects can be mitigated by some form of pre-treatment (for example, heating to remove trimethylamine [346] or by adding high alumina cement and NaOH to the cement mix to manage organic ion-exchange resins with high borate concentrations [350]), or by selection of a suitable cement formulation (for example, functionalised polystyrene cation and anion exchange resins can be successfully immobilised in 9:1 BFS/OPC grout [345]). However, if these issues cannot be resolved, detrimental evolution processes may need to be designed out either through the choice of a different encapsulant (such as use of a polymer) or by allowing sufficient expansion volume for the waste.

8.4 Evolution of mobile wastes in cement

Sludges, flocculants, and raffinates due to their mobile nature, typically require suitable encapsulation techniques to ensure immobilisation. Encapsulation in cement is typically pursued.

Sludges, flocculants and raffinates represent an important part of the ILW inventory and, due to their mobile nature, typically require suitable encapsulation processes to ensure immobilisation in a solid with the required properties. Encapsulation in cement is typically pursued, requiring the development of suitable formulations.

An in-depth study into the effectiveness of immobilisation of sludges and flocculants by cement encapsulation has been reported in a PhD thesis [286]. The results of this and other relevant studies are summarised below.

8.4.1 Sludges, flocculants and raffinates

Stable wasteforms for various types of sludges can be obtained with cement formulations typically employed in the nuclear industry. Cement products showed good incorporation of sludge simulants in the cement phases and good subsequent chemical stability. Immobilisation of ferritic flocs, raffinates and other colloidal systems in cement is likely to result in some shrinkage/porosity, but good overall immobilisation is likely to be obtained.

Shrinking of cement-based wasteforms due to crystallisation or hydration processes can occur in the presence of a specific type of mobile waste after drying and immobilisation in cement grout. Specific examples of this type of waste include sludges and ferric flocculants. A review of the nature of a variety of 'mobile' wastes present in the UK ILW inventory, together with considerations on their likely ageing processes are available in [353]. Considerations relative to sludges and flocculates based on a recent study [286] are also reported below.

Sludges that arise from the corrosion of spent fuel in pond storage can contain organic and inorganic constituents. The encapsulation of barium, aluminium and magnesium-based waste slurries in cement was recently studied [286]. In this study, a barium carbonate ($BaCO_3$) slurry was used as a simulant to investigate the encapsulation of inorganic constituents of a sludge[71]. The $BaCO_3$ was encapsulated in a BFS:OPC grout and analysed. The data confirmed that the $BaCO_3$ reacted with $CaSO_4$ in the cement, leading to the formation of $BaSO_4$; the resultant CO_3^{2-} ions released then formed new phases within the cement paste, including monocarboaluminate and calcium carbonate. The results of this study showed that the encapsulated product is stable and unlikely to lead to contaminant release, suggesting that a ^{14}C waste stream could be effectively encapsulated by this route. Gamma irradiation at 104 Gy h^{-1} to a cumulative dose of 9 MGy showed that a wasteform of 9:1 BFS/OPS encapsulating $BaCO_3$ was stable under these conditions [354].

Experiments were also carried out on a 15-year old BFS/OPC grout and aluminium-based slurry [286]. Analysis of the encapsulated aluminium slurry showed the formation of cementitious hydrated solid phases such as monosulfoaluminate and monocarboaluminate, alongside C-S-H and a hydrotalcite-like phase. Aluminium was incorporated into the C-S-H structure, resulting in the formation of the phases C-A-S-H, strätlingite and monocarboaluminate. The stability of monocarboaluminate remained unchanged up to 70 ^{o}C, beyond which decomposition to hydrogarnet and calcite phases was observed [355]. Strätlingite is likely to be stable and has been observed at temperatures of 85 $^{\circ}C$.

$Mg(OH)_2$ sludge samples that had been encapsulated in a 3:1 BFS/OPC grout and stored for 15 years were also analysed [286]. Despite the addition of large quantities of simulant waste material, it was found that overall porosity and long term physical durability of the wasteform were good. This may have been associated with the pre-treatment of the $Mg(OH)_2$ with lime during the mixing process [286]. The effective physical encapsulation of $Mg(OH)_2$ within the binding matrix was confirmed, with brucite crystals surrounded by C-S-H being observed. After the period of long term dry storage (15 years), substitution and incorporation of magnesium into the C-S-H phase was not observed [286].

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[71] Radioactive waste in the form of barium carbonate arises in the UK at the Thermal Oxide Reprocessing Plant (THORP) at Sellafield, where $^{14}CO_2$ released during reprocessing of spent uranium oxide fuel is precipitated as $Ba^{14}CO_3$ by the addition of barium nitrate to the nitric acid reprocessing solution.

Ferric flocculants, produced during some effluent treatment processes such as that carried out at the Enhanced Actinide Removal Plant (EARP) at Sellafield, are amorphous, thermodynamically unstable materials in which the solid fraction has a very high surface area (colloids in suspension) [356]. It was initially thought that encapsulation of iron hydroxide flocs with cement could eventually result in crystallisation and cause problems with dimensional stability of the wasteform. However, recent work indicates that, although there is some initial shrinkage, this is unlikely to be sufficient to cause significant issues. Studies indicated no change in crystallinity of a cemented simulant up to 2 years after conditioning, and 12 year old samples showed minimal change (related work can be found in reference [286]).

Rickerby [286] also investigated the encapsulation of three metal hydroxide flocculants, two iron-based and one alumina/ferric-based. Analysis was undertaken after encapsulation of the flocculants in a PFA:OPC matrix, showing successful incorporation; all the resultant microstructures were relatively porous in nature but displayed an acceptable level of physical encapsulation by the C-S-H phase. Analysis of the katoite-like hydrogarnet showed the chemical immobilisation of Fe^{3+} and potentially Al^{3+} within the phase, as well as potential occupation of these ions in the silicate chains.

In February 2013, a routine monthly inspection of the LLW packages in a store near Dessel (Belgium) revealed the formation of a gel-like substance on the cover of one of the drums containing conditioned LLW from evaporator concentrate. Formation of such gels was subsequently observed in other waste packages of this type produced from the same plant. Based on the information available, it is currently believed that an alkali-silica reaction is at the origin of the observed gel formation [283]. The high amounts of sodium hydroxide added to neutralise this waste and the siliceous coarse and fine aggregates used during the production of the matrix are currently considered the root causes of this phenomenon[72].

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[72] Some raffinates arising as acidic solutions from the reprocessing of irradiated fuels from non-commercial reactors (for example DFR), have been processed through neutralisation with alkaline solutions and immobilisation in cement and hence have some similarities with the waste packages produced in Belgium. Information available to date (dimensional stability experiments over prolonged periods of time) suggests that these wasteforms are not susceptible to this process.

9 Waste container materials and their evolution processes

Different container materials have been employed in the UK and worldwide depending on the nature of the wasteform they are designed to package and on the environment in which they are designed to perform. This report discusses separately the cases of ILW/LLW and HLW/spent fuel containers, given that the nature of the waste, the durability requirements and (as a consequence) the package materials and designs are different for the two cases. Other potential wastes (DNLEU and plutonium residues) are likely to be disposed of in similar types of containers so that the discussion presented in this section is likely to be relevant for these materials as well.

This section describes:

- the general characteristics of waste containers and available manufacturing processes
- container designs employed, or being considered, in the UK and worldwide for HLW and spent fuels
- container designs employed, or being considered, in the UK and worldwide for ILW/LLW.

Information on the manufacture of waste containers is presented in Appendix 1, based on studies carried out in other disposal programmes. Initial studies on the manufacture of HLW and spent fuel containers in the UK are planned for the future [10, task 661].

9.1 Container design

The design of radioactive waste containers needs to take account of the type of waste to be packaged in them and of the environments to which the packages will be exposed during storage and eventual disposal.

Waste materials are wide ranging and potential disposal environments diverse. Therefore it is not surprising that a range of container materials and designs are currently being employed or considered for packaged wastes.

9.1.1 Overview of waste container characteristics

Waste containers for HLW and spent fuel are generally designed to provide durability far into the post-closure period. They are typically designed either as single-shell, thick-walled containers or as dual shell containers featuring a thick structural inner component and a thinner external corrosion barrier. Waste containers for ILW/LLW are generally designed to withstand relatively long periods of interim storage and operations of the GDF.

A number of different materials have been considered for thefabrication of waste containers in different countries, however most effort has been focussed on metals. Metals are generally selected on the basis of their mechanical characteristics and corrosion resistance. In some countries (including the UK) some ILW/LLW containers have been made from concrete instead of metal, while in other countries (primarily France) the conceptual design of containers for HLW and spent fuel has considered the use of ceramic materials. Whilst in the UK large volumes of ILW/LLW have been packaged over the last twenty five years in containers considered suitable for storage and disposal, any containerisation of HLW and spent fuel, to date, has largely considered requirements for storage. As their performance requirements are site-specific, the design of disposal containers for HLW and spent fuel is still, in the UK, at a conceptual stage.

Containers for HLW and spent fuel are typically designed either as a single shell container providing both mechanical strength and the required corrosion properties (typically thick-walled carbon steel designs) or as dual shell containers, with one shell providing mechanical strength (typically carbon steel or cast iron inserts) and the other providing the required corrosion properties (typically a copper corrosion barrier). This is not the case for ILW/LLW containers which have, so far, only been designed and manufactured as single shells.

Once emplaced in a GDF, containers will be in contact with either a backfill (ILW/LLW disposal concepts) or a buffer material (HLW/spent fuel disposal concepts). Among other properties, buffers and backfills are typically selected to provide a benign chemical environment for the waste container and, in some case, contribute to the overall mechanical performance of the EBS. Consideration is being given in a number of countries to the manufacture of relatively large disposal assemblies including both the container and its buffer/local backfill in prefabricated emplacement modules (PEMs), or supercontainers. This would facilitate Quality Assurance (QA) operations, thus increasing confidence in the properties of the EBS and the resulting durability of the waste container[73]. Additionally, in some countries, the need for containerisation of spent fuel in systems suitable for dry interim storage and subsequent transport and disposal has led to the development of so called multi-purpose containers (MPCs), in which an inner containment vessel (typically thin-walled stainless steel) is employed in conjunction with different types of interchangeable overpacks (typically thick-walled carbon steel and/or concrete), each designed for either storage, transport or disposal.

From the point of view of corrosion properties (which typically drive the choice of the external containment barrier and its dimensions) there are two basic options for choosing waste container materials, either materials that corrode at an almost negligible rate (known as corrosion-resistant metals) or less resistant metals which corrode slowly but at a predictable rate (the so-called corrosion-allowance metals). In the first case a thin-walled design is used or envisaged. In the second case, a corrosion allowance of sufficient thickness must be designed to preserve functionality for the required period. The advantage of the latter option is that the mechanisms and rate of corrosion are more predictable and possibly more robust to uncertainties in the evolution of the geological environment than for more corrosion-resistant metals. As a result, many waste disposal programmes consider the use of corrosion-allowance designs, particularly for the disposal of HLW and spent fuel.

From the point of view of structural integrity (which influences the choice of material grade and the dimensions of the waste container or structural inserts) suitable designs typically consider the need for providing adequate mechanical strength, stiffness, creep resistance and fracture toughness. Consideration, however, is also given to the potential effects of corrosion processes on material properties (for example, hydrogen embrittlement).

Selection of the container material and design must take into account the required corrosion and mechanical performance, as well as the practicalities of its fabrication. Container design should also consider aspects associated with the processing of different types of wastes (such as in-drum mixing of sludges), radiation-shielding requirements, the potential impact on other GDF barriers and cost/resource usage. The viability of the various materials and associated designs that have been considered internationally for fabrication of waste containers has been reviewed [357].

Containers must include a number of features in their design to allow lifting, identification and, when required (such as for ILW containers), stacking and venting of gases (see Box 19 and Box 20 for examples of typical design features). Degradation processes of these key package features need to be given appropriate consideration.

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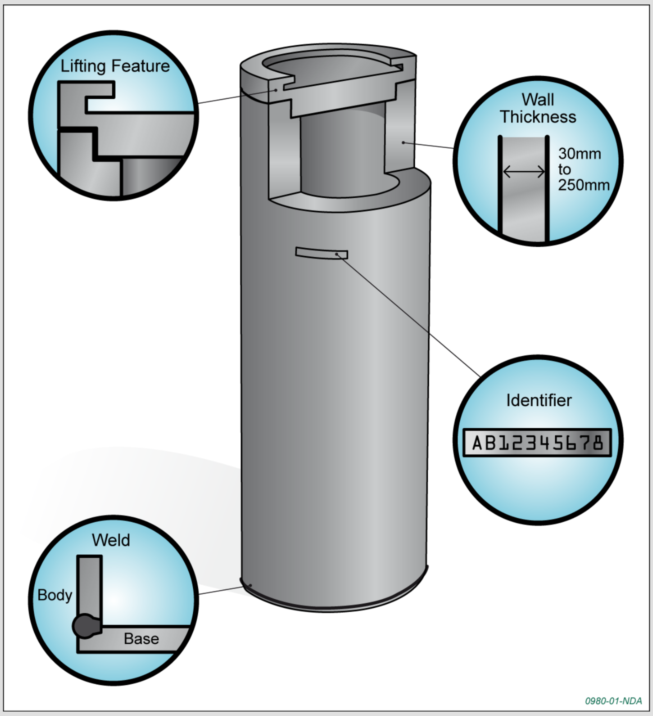
[73] For example, for the disposal of spent fuel, this approach is being considered in Belgium for an EBS envisaging the use of a carbon steel container within a cement buffer.

Box 19 Generic design features of a single shell HLW/spent fuel container[74]

The generic design features of a single shell HLW/spent-fuel waste container are described below and represented in Figure 29.

Figure 29: Generic design features of a single-shell HLW/spent fuel waste container



Wall thickness. In the case of single shell designs, the wall thickness determines the mechanical strength and the radiation shielding characteristics of waste packages, as well as their durability. In the case of dual shell designs, the thickness of any structural inserts determines the mechanical strength and radiation shielding, whilst the thickness of the outer shell determines the container durability.

Welds. High quality closure welds are envisaged for this type of containers (no bolted designs). Welds have to be designed to ensure excellent mechanical and corrosion properties. Suitable inspection techniques are required in order to ensure adequate weld quality.

Lifting features. In most cases, containers are designed with specific features to facilitate lifting and handling. In other cases, lifting operations do not envisage the use of specific lifting features.

Identifier. Unique identifiers are envisaged for HLW/spent fuel packages, similarly to what envisaged for LLW/ILW packages.

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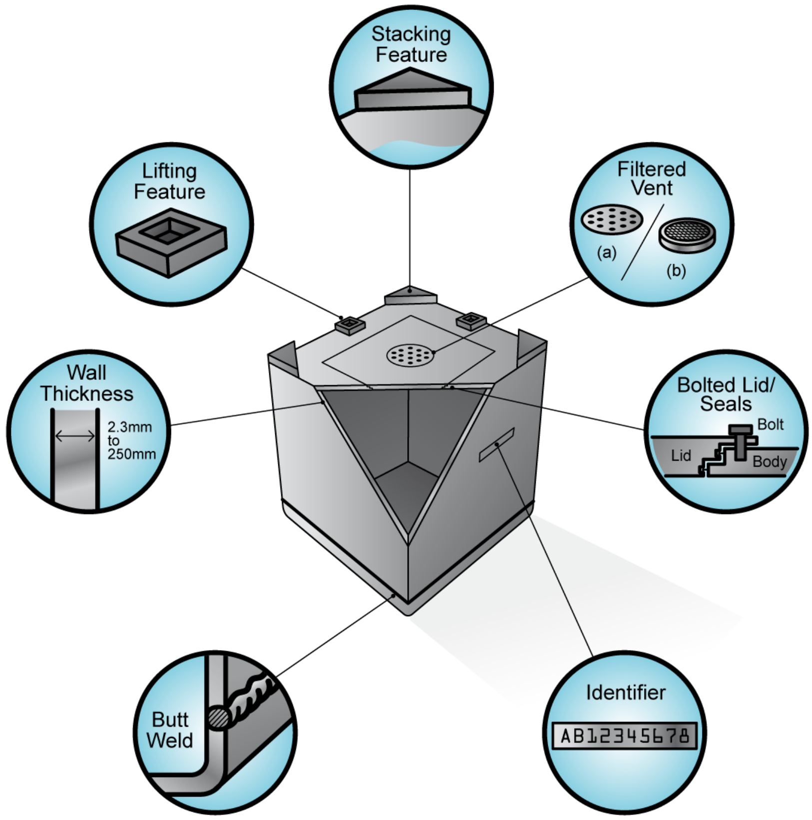
[74] The representation focuses on a single shell container (including the wall thickness). The design of the container would be different in the case of a dual shell container. Additionally, the diagram does not illustrate additional inner furniture (internal vessels) and outer components (such as the buffer) that may be present in the system, particularly in the case of MPCs and/or PEMs.

Box 20 Generic design features of an ILW/LLW waste container[75]

The generic design features of a metallic ILW/LLW waste container are described below and represented in Figure 30.

Figure 30: Generic design features of a metallic ILW/LLW waste container



(a) Container lid with vent holes
(b) Sintered disc

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Wall thickness. The wall thickness determines both the strength and degree of radiation shielding provided. In thin-walled containers, cement liners can provide additional radiation shielding.

Welds and seals. Welds are used in some designs to seal waste packages. In other designs, bolted lids are used to seal waste packages. In this case, elastomeric seals may be used between the lid and the main body.

Handling and stacking features. Containers are designed with specific features to facilitate handling and stacking. In some circumstances, a single feature may be present.

Filtered vent. Metallic LLW/ILW containers are vented by means of a filter in the lid that allows gas to be released while retaining solid particulate. The vent is normally made of fine metallic fibres contained within a coarser metal mesh. Concrete containers are not vented.

Identifier. Each waste package is labelled with a unique identifier on the container walls.

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[75] The representation focuses on a metallic container.

9.2 Waste containers for HLW and spent fuel

Copper, carbon steel, cast iron, stainless steel, titanium, nickel-based alloys and, in a limited number of cases, ceramic materials, have all been considered as candidate waste container materials for HLW and spent fuel.

In a number of geological disposal programmes worldwide, concepts have been developed for the storage and disposal of HLW and spent fuel. Stainless steel, carbon steel, cast iron, copper, titanium, nickel-based alloys and, in a limited number of cases, ceramic materials, have all been proposed or considered as candidate waste container materials.

All container designs featuring a relatively thin external envelope or a thick external envelope made in a material with relatively limited strength (such as copper) include a carbon steel or cast iron internal structural insert. This ensures the corrosion protection afforded by a durable container material is effectively combined with the mechanical strength, ease of fabrication and cost effectiveness of steels.

So far, in the UK, HLW vitrified products have been packaged in thin-walled stainless steel canisters suitable for storage (Section 2.2). Decisions about the suitability of this design for geological disposal have not yet been made, but it is likely that containerisation in a suitable disposal container will be required. Two conceptual designs for disposal containers, based on the use of a dual shell cast iron / copper container (Variant 1, Section 9.2.1) and a single shell carbon steel container (Variant 2, Section 9.2.2), have been developed in the UK [74]. In either design, three HLW interim storage canisters would be loaded into a single disposal container.

Packaging concepts for spent fuel and other nuclear materials are also under development. Similar designs to those developed for HLW have been developed for spent AGR fuel and PWR fuel [74]. Sixteen slotted cans (containing forty-eight fuel assemblies) or four fuel assemblies would be loaded in each disposal container for spent AGR and PWR fuel, respectively.

The use of waste container materials in different countries is summarised below. The current Disposal System Specification for a UK GDF [59] requires HLW waste packages to contain their radioactive content for at least the duration of the ‘thermal period’ (see Section 4.2.1). As a result, in any disposal concept, waste containers would be required to last, as a minimum, for the duration of this period.

9.2.1 Copper containers

Dual shell copper containers are currently considered for the disposal of HLW and/or spent fuel in Sweden, Finland, Canada and, as an alternative option, in Switzerland, Japan and Korea. Copper containers are likely to provide long durability because of the chemical stability of copper in the absence of oxygen and its tendency to undergo slow, uniform corrosion.

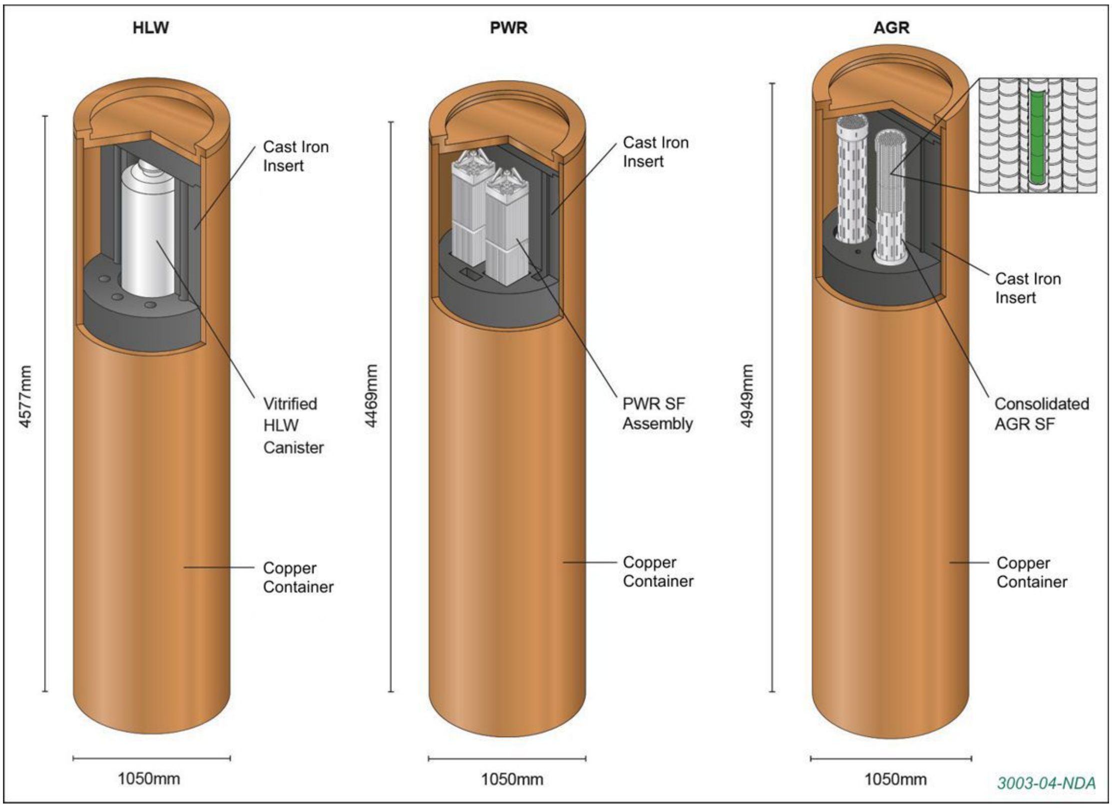
Copper has been proposed as the material for the main corrosion barrier (external shell) of containers for the disposal of spent fuel in Sweden [358], Finland [359] and Canada [360]. Additionally, copper is, or has been, considered as a suitable option for the disposal of HLW and spent fuel in Korea [361], Japan [362] and Switzerland [363]. The bedrock conditions present in some of these countries may provide limited protection from the release of radioactivity to the biosphere and may require the EBS to ensure containment of the radionuclides for long times, of the order of hundreds of thousands of years. In all cases, the use of copper containers has been proposed in conjunction with a bentonite buffer, which plays a key role in protecting the waste container [2].

Copper containers are likely to provide long durability because of the chemical stability of the material in the absence of oxygen and its tendency to undergo slow, uniform corrosion rather than localised corrosion. With a suitable corrosion allowance (a few mm) very long durability can be achieved. These characteristics enable evaluation of the long-term degradation to be made more easily than for some other candidate materials (such as passive metals) and make copper a primary candidate for use in waste containers.

Copper containers have been traditionally designed as dual shell containers, with relatively thick (50 mm) self-standing external shells, combined with a structural insert (typically cast iron). One potential issue with the use of copper is that the manufacture of tubes of the dimensions required for the disposal of HLW and spent fuel is not a standard technology, so it is difficult to provide assurance of the integrity of the resulting containers. This issue, however, has been addressed in countries (such as Sweden and Finland) in which this concept is well developed. As an alternative to the use of a separate cast iron insert, the use of a copper coating (using either a cold spray technique or electrodeposition) applied directly onto a carbon steel load-bearing insert is being evaluated in Canada. Such a design may provide advantages in terms of manufacturability, cost and creep resistance.

Conceptual designs of copper containers for the disposal of HLW and spent fuel have been developed recently in the UK [74] (Figure 31), based on the design developed in Sweden and Finland.

Figure 31: Conceptual design of HLW and spent fuel disposal container developed in the UK (Variant 1)[76] [74]



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[76] In relatively benign conditions, the required corrosion allowance may be small enough to be practically negligible relative to the material thickness required for structural or manufacturing purposes. This is the case for the Variant 1 container design recently developed in the UK based on the Swedish/Finnish KBS-3 design (50 mm thick).

9.2.2 Carbon steel and cast iron containers

Carbon steel has been considered as a container material for HLW and/or spent fuel in Belgium, France, Japan and Switzerland. The primary reason for using carbon steel is the understanding of its corrosion performance in a range of geological environments. This allows waste containers to be designed with a suitable corrosion allowance.

Carbon steel is envisaged as the reference container material or is being considered as a potential option for the disposal of HLW and/or spent fuel in many national waste management programmes, including those in Belgium [364][77], France [162], Japan [362] and Switzerland [82]. In this case, a single shell design providing both the required structural and corrosion performance is employed.

The primary reasons for using carbon steel are the well-developed understanding of its corrosion performance in a range of geological environments (allowing waste containers to be designed with a suitable corrosion allowance) and extensive experience in manufacturing large objects. When employed as a corrosion barrier, carbon steel is generally preferred to cast iron because it is easier to weld. For the same amount of material required, carbon steel and cast iron containers are also likely to have lower costs and resource/usage impact than more expensive and less abundant materials like copper and have the advantage of stimulating the development of reducing chemical conditions in the EBS, which is beneficial in limiting the solubility of some radionuclides.

One issue with the use of carbon steel or cast iron containers for HLW and spent fuel disposal is the potential adverse impact on others barriers in the system. The production of H_2 gas due to anaerobic corrosion of the containers has the potential to disrupt the mechanical integrity of the engineered and geological barriers surrounding the packages after closure. In addition, ferrous ions may have adverse effects on the characteristics of a bentonite buffer, if this were to be used.

Conceptual designs of carbon steel containers for the disposal of HLW and spent fuel have also recently been developed in the UK [74]; these are similar to designs developed in other countries (Variant 2 container, Figure 32). Carbon steels are also considered in MPC systems for the manufacture of overpacks for storage, transport and disposal. For disposal, carbon steel containers are generally designed to work in conjunction with either bentonite/cement buffers or crushed rock.

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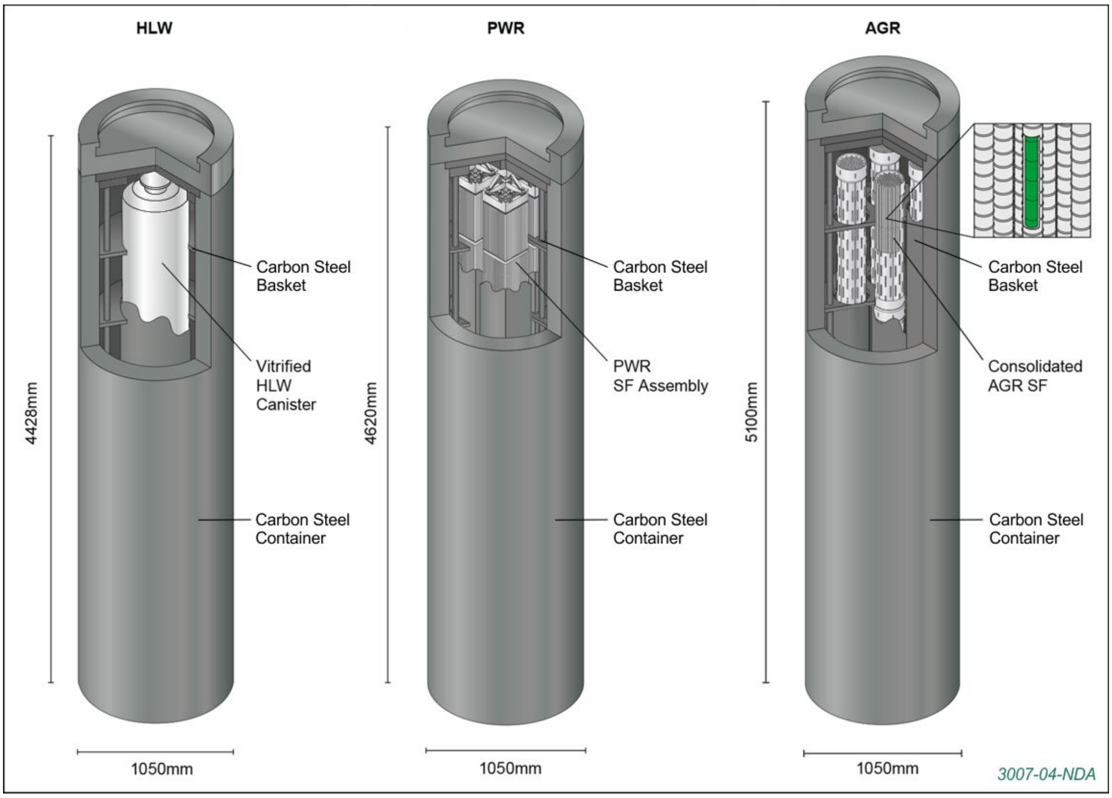
[77] Carbon steel is currently proposed for the ‘overpack’ (in this report ‘waste container’), which is the main corrosion barrier considered in the current PEM (supercontainer) design.

Figure 32: Conceptual design of HLW and spent fuel disposal container developed in the UK (Variant 2) [74]



9.2.3 Titanium containers

Titanium (a very corrosion-resistant material) has been considered as an alternative to copper and carbon steel or cast iron in several national programmes.

Titanium has been considered as a corrosion-resistant container material for disposal of HLW and spent fuel in several national programmes and in Canada it was adopted as the reference material in the 1994 Environmental Impact Statement (EIS) [365]. Titanium was originally selected as the construction material of choice for applications involving warm saline groundwaters (as expected in a Canadian GDF), which are particularly corrosive for a variety of materials. A titanium-carbon steel dual-shell design is considered as an alternative to a carbon steel design for the disposal of HLW in Japan [362]. Titanium was also considered for the manufacture of corrosion-resistant drip shields in the US [366].

Different titanium grades provide different degrees of mechanical and corrosion resistance. More basic grades (grade-2) can be alloyed with aluminium and vanadium to improve the mechanical properties (grade-5), with palladium to increase the corrosion resistance (grade 7), or both (grade-24).

There is a significant amount of information regarding the corrosion behaviour of titanium in conditions likely to arise in a GDF from Canadian, US, Japanese and other European programmes. There is also some experience with fabrication and manufacture of prototypes. However, some development to evaluate suitable container designs and manufacturing technologies and to demonstrate its behaviour in a geological environment may need to be undertaken.

9.2.4 Stainless steel containers

For HLW and spent fuel, there may be potential to employ stainless steel to provide a durable waste container using grades with suitable corrosion resistance with a cementitious backfill.

In the past, stainless steel has been considered in some countries (such as Belgium [143]) as a potential container material for the disposal of HLW and spent fuel. However, the high temperature reached in heat-generating HLW/spent fuel packages, the high salinity present in host geological environments typically considered in waste disposal, and potential presence of reduced sulphur species in underground environments may be corrosive towards the metal. For this reason, stainless steel has to be considered carefully as a container material if significant durability is required.

Stainless steel (austenitic grade 309) is currently employed in the UK in the manufacture of canisters for the interim storage of HLW vitrified products (WVP cans) before decisions on container materials suitable for disposal are made. This grade has been selected due to its good high temperature corrosion/oxidation resistance, which is required during both the manufacture (exposure to molten glass) and subsequent storage (dry, hot conditions) of HLW. Disposal options for HLW in the UK currently consider a range of options, including direct disposal in stainless steel canisters[78].

In general, for both HLW and spent fuel, there may be potential to employ stainless steel to provide a durable waste container using grades with suitable corrosion resistance with a cementitious backfill, depending on the salinity, the potential presence of sulphur species, and the likely redox evolution of the system.

9.2.5 Nickel-alloy containers

Nickel can be alloyed with other elements to achieve very high corrosion resistance, providing a more corrosion-resistant alternative to stainless steel. Highly resistant grades have been considered for the manufacture of HLW/spent fuel containers in a permanently aerobic (and therefore corrosive) disposal system.

Nickel alloys may offer an alternative to stainless steel or titanium if a corrosion-resistant container material for HLW and spent fuel is specified. There is a wide range of possible compositions of nickel alloys. The alloys that have been considered as candidate waste container materials can be divided into two broad categories, namely the Ni-Cr-Mo group (Inconel 625 and Hatelloy C-22, and Hastelloy C-4 and C-276) and the Ni-Fe-Cr-Mo group (Incoloy 825).

Like iron in stainless steel, nickel can be alloyed with other elements (such as chromium or molybdenum) to achieve very high corrosion resistance. The most corrosion-resistant grades can withstand very aggressive environments. For example, Inconel 625 and Hastelloy C276 have been studied in the Canadian programme [365] and Hastelloy C-4 has been studied in various European programmes [367], while Hastelloy C-22 had been proposed in the USA for the Yucca Mountain programme, in a permanently aerobic (and therefore corrosive) disposal system [366]. Hastelloy C22 was selected for the Yucca Mountain repository since, in contrast to all other GDF concepts proposed worldwide, in this disposal concept waste packages are exposed to a permanently oxidising environment (the disposal system would lie above the water table).

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[78] As any other disposal concept, a concept envisaging direct disposal in the current vitrification canisters would need to demonstrate adequate containment over the thermal period, which may not be possible in some disposal scenarios.

As for titanium alloys, there is some experience with the manufacture of large components, as well waste container prototypes. Further R&D may however be required to increase confidence in the use of this material for waste disposal.

9.2.6 Ceramic containers

Advantages for the use of ceramics containers are their high chemical stability. However, fabrication and mechanical behaviour present substantial challenges.

Ceramics have been considered as container materials for HLW and spent fuel for some time, either in the form of a massive ceramic vessel [83, 368, 369, 370] or in the form of a corrosion-resistant coating for a metallic container [371, 370].

Various types of ceramic materials have been considered over the years, including: alumina (Al_2O_3), with or without silicon oxide (SiO_2); silicon carbide (SiC); silicon nitride (Si_3N_4); partially stabilised zirconia (PSZ); or titanium oxide (TiO_2). Thermally sprayed ceramic coatings considered include Al_2O_3, Al_2O_3/TiO_2, and spinel ($MgAl_2O_4$) [371].

The two main advantages for the use of ceramics as HLW/SF container materials are their high chemical stability, resulting in potentially long container lifetimes, and the lack of adverse effects on other barriers, especially the absence of gas generation under anaerobic conditions (an issue for carbon steel or cast iron containers). However, there have traditionally been a number of concerns about the use of ceramics for this purpose, including the low fracture toughness, the challenge of fabricating and sealing large ceramic structures and, for ceramic coatings, the difficulty of predicting the lifetime of the coating and what happens to the underlying metal in the case of coating failure.

Some of these issues have been resolved, in particular the fabrication of large ceramic components of complex shape [372]. However, currently available sealing technology involves the use of high temperatures that may result in damage to the wasteform. In addition, there are still challenges to overcome in terms of fracture properties.

Currently, only Andra (France) have an active R&D programme investigating the possible use of ceramics for disposal containers. Nagra (Switzerland) have maintained a watching brief over such work, but at this time have no plans to further investigate the use of ceramics [83].

Information on the likely evolution of ceramic containers is not presented in detail in this report, since these materials are not currently considered in RWM's programme beyond this watching brief.

9.3 Waste containers for ILW and LLW

Stainless steel, carbon steel, cast iron and concrete have all been used or proposed as suitable materials for ILW and LLW containers.

In a number of waste management programmes worldwide, stainless steel, carbon steel, cast iron and concrete have been used or proposed as suitable materials for ILW and LLW containers. In the UK, containers manufactured in stainless steel have typically been used. These are generally thin-walled and are used in conjunction with suitably immobilised wasteforms. Thick-walled cast iron containers have recently been considered for the packaging of some ILW, often without previous immobilisation. In this case, a robust container is required.

In specific cases, concrete has also been used. Concrete containers of a design similar to that currently employed in France may also be used in the UK for ILW/LLW generated by future nuclear power plants.

In order to manage gas generation processes occurring in a variety of wasteforms (particularly when cement is employed as an encapsulant), waste containers for ILW/LLW are generally vented. The presence of the vent result in a design which is not hermetically sealed and in which the ability of the waste package to contain radionuclides for long periods of time after disposal in a GDF needs to take into account any (slow) release of radionuclides through the vent (see Box 21).

These types of containers are generally designed to withstand long periods of storage and, potentially, operations of a GDF. Containers able to withstand long periods of exposure to the groundwater, however, increase confidence in the safety case.

Box 21 Containment and the need of venting for cement-based ILW/LLW wasteforms

The disposal concept for ILW and LLW historically developed in the UK typically considers the use of waste packages made with a cement-based encapsulant and a thin-walled stainless steel waste container. Encapsulation of the wastes with cement offers a number of advantages but carries the disadvantage of the cement porewater reacting with some types of waste to produce gas[79] (see Sections 7-8). As a consequence, packages produced with cement need to be fitted with engineered vents to ensure that any gas generated by the wasteform is released through the vent, preventing any risk of pressurisation.

The presence of the vent in this type of package makes it unlikely for them to provide complete containment of the radionuclides during the post-closure phase, even if the package functionality was preserved for long times: after backfilling, the GDF will be resaturated with groundwater and transport of radionuclides through the vent is likely to occur slowly. This is unlikely to be a problem since, we think that, in a suitable host geological environment, a safety case for this type of waste can be made even if the containment provided by the waste package were to be limited. This is consistent with the approach generally considered internationally for these types of wastes [373].

However, the vents are tortuous and, while the overall container is intact, it is unlikely that a direct flow path through the waste package would be established. As a result, there would effectively be no water flow through the package. Solute transport would be by diffusion and the radionuclides would be effectively contained within the waste package until the waste container fails, for example through corrosion. As a consequence, if the container remains in good condition, it will provide a good degree of containment or at least significantly limit the movement of groundwater to and around the wasteform, adding strength to the arguments for the safety of the GDF. Initial modelling work considering the representation of physical containment in our performance assessment is discussed in [374].

The potential for gas generation and the need for venting can be reduced by using alternative encapsulants (e.g. polymers, glasses). Additionally, if required, it may be possible to engineer a GDF with systems aimed at limiting the access of groundwater to the packages [373].

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[79] Gas generation does not occur exclusively in cement-based wasteforms but may also occur in other wasteforms, for example in non encapsulated wastes containing residual water or, to a lower degree, in 'dry' polymeric wasteforms (due to radiolysis).

9.3.1 Stainless steel containers

Thin-walled stainless steel containers have been extensively used in the UK to package ILW. Austenitic grades have been typically employed. More recently, duplex grades have also been considered.

In the UK, stainless steel containers have been used to package most ILW. Austenitic grades 316L and 304L[80] have been used to date [38]. More recently some duplex grades (2101, 2205 and 2507) and other, more corrosion-resistant, austenitic grades (904L) have also been considered when required[81]. Waste producers have developed a variety of designs of containers, from large boxes (for solid items), to drums (for sludges), to containers pre-installed with additional shielding (for example the Mosaik and TRU-shield packages). Examples of austenitic stainless steel waste containers are shown in Figure 33. Lower grades of stainless steel (Cromweld 3CR12, with a composition similar to ferritic grade 409[82]) have also been employed in the UK for the manufacture of stillages to handle and stack waste containers.

Apart from the UK, stainless steel is used as a container material in some other countries (for example, in the US, in some instances [375]).

The selection of stainless steel is mainly based on its corrosion resistance during above-ground storage. There is also a wealth of experience in fabricating items from stainless steel. Despite being resistant to corrosion in a variety of chemical environments, stainless steel is not totally immune to degradation processes. The nature of the degradation processes (specifically, localised corrosion) can make it difficult to predict the durability of waste packages in conditions in which corrosion is possible. This represents a potential difficulty with the use of stainless steel for waste containers.

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[80] Most container parts have been made in 316L. 304L has been generally used for sections thicker than 10 mm (such as some lid flanges).

[81] Grades 2101, 2205 and 2507 are duplex grades providing increasingly high corrosion resistance. The superaustenitic grade 904L also provides superior corrosion resistance to 316L.

[82] Cromweld 3CR12 has a chromium and nickel content of 12 wt% and 1.5 wt% respectively, compared with 18wt% and 12wt% for 316L.

Figure 33: Examples of austenitic stainless steel ILW containers: (left) the 500 litre drum; (right) the 3 cubic metre box

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9.3.2 Carbon steel and cast iron containers

Carbon steel and cast iron are common ILW/LLW container materials in a number of national nuclear waste programmes. Carbon steel and cast iron are less corrosion resistant than stainless steel. The use of painted, thick-walled containers with a suitable corrosion allowance balances the decrease in corrosion resistance against an increase in mechanical strength and radiation shielding.

The use of thick-walled cast iron containers to manufacture disposable waste packages for ILW has been recently considered in the UK. Examples of proposed packages are shown in Figure 34 [38]. Carbon steel has been employed in the past to manufacture some ILW containers, although in relatively thin-walled designs (such as the Miscellaneous Beta Gamma Waste Boxes at Sellafield). In the UK, thin-walled carbon steel containers are also currently used to package DNLEU, although their disposability has not yet been fully assessed.

Carbon steel and cast iron are also common ILW/LLW container materials in a number of other national nuclear waste programmes. For example, painted 200-litre steel drums are used for some ILW in Switzerland [562]. These drums, however, will only be used for storage and will be emplaced in concrete vessels for disposal. Ontario Power Generation (OPG) in Canada are also using a number of different designs of steel-based ILW/LLW containers, including galvanized steel ash bins, painted and unpainted mild steel boxes and drums, painted steel drum racks, and coated steel and stainless steel containers [376]. Ductile cast iron (DCI) is also widely used as an ILW storage container in Germany.

Carbon steel and cast iron are less corrosion resistant than stainless steel. The use of thick-walled containers with a suitable corrosion allowance, however, would balance the decrease in corrosion resistance and at the same time offer increased mechanical strength and radiation shielding. The increase in size and weight of these packages, however, could make handling and transport operations more complex. Additionally, particularly for cast iron, some concerns exist relative to its potential brittleness.

From the point of view of evolution processes, one of the advantages of using carbon steel and cast iron is that we have a good understanding of their corrosion behaviour and a good basis for predicting their durability. Once the corrosion rate has been determined, containers can be designed with a suitable corrosion allowance to ensure that the container functionality is retained for the required time. Widespread experience of manufacturing large and complex objects is also a potential advantage.

Figure 34: Examples of Ductile Cast Iron Containers (DCIC)

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9.3.3 Concrete containers/overpacks

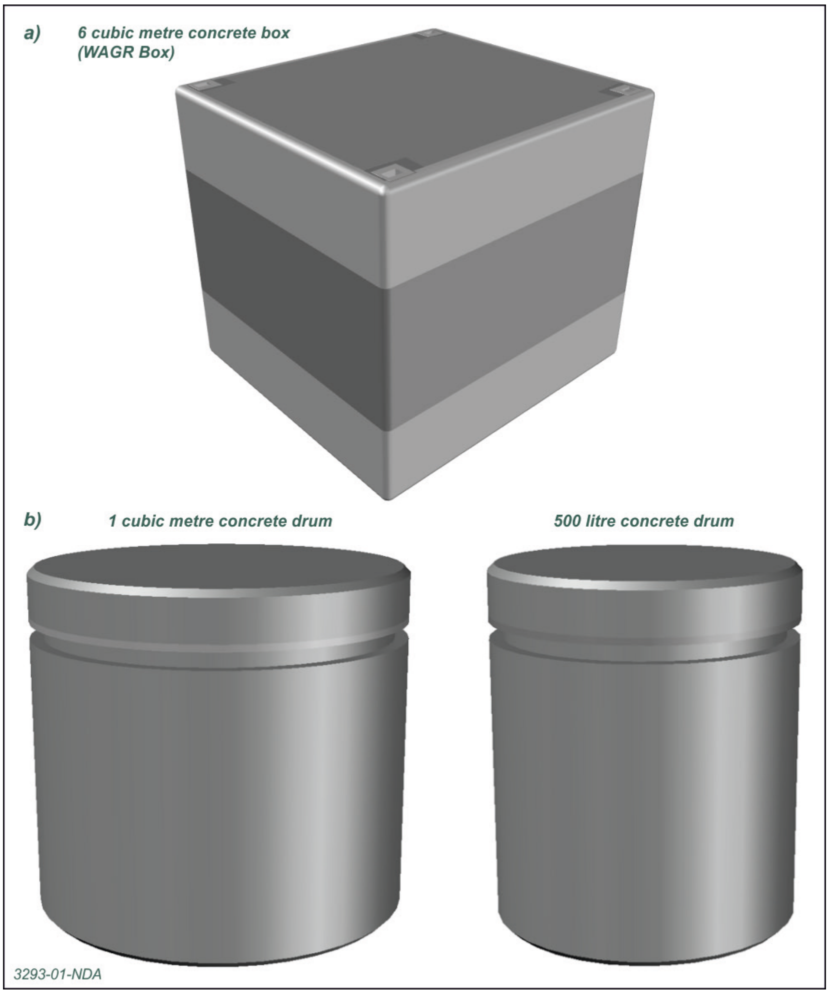
Thick-walled concrete containers for ILW/LLW have been considered in a number of national waste management programmes. Concrete is a very versatile and readily available material. Large containers with good mechanical properties and good durability can be manufactured. A thick-walled concrete container will also provide radiation shielding.

Concrete in relatively thick-walled designs has been selected as a container material for ILW/LLW in a number of national waste management programmes, for example in France [162], Switzerland [562] and Sweden [377]. In these countries, concrete is generally used as an overpack to contain ‘primary’ containers made in carbon steel. In the UK, concrete has been employed for the manufacture of a limited number of waste packages (for ILW arising from the dismantling of the Windscale AGR) and is currently being considered for the storage and disposal of future ILW that may arise from new power stations. Concrete designs employed in the past and/or currently being considered in the UK for the disposal of future ILW streams are shown in Figure 35.

Concrete possess a good combination of properties as a material for waste packages. It is a very versatile and readily available material. It has been used extensively in the construction industry and its properties are well known. Large containers with good mechanical properties (particularly under compression) and good durability can be manufactured. Similarly to other thick-walled container designs, a thick-walled concrete container will also provide radiation shielding. These advantages, however, need to be balanced against the substantial size and weight of the resultant waste packages, which may complicate handling operations, and the potential for corrosion of the rebars during prolonged exposure to atmospheric environments, leading to the spallation of the external surfaces. Concrete is also more susceptible to mechanical damage than metallic containers (particularly in tension and upon impact).

After closure of a GDF, in contrast to metallic containers, concrete containers may also contribute to the chemical conditioning of the EBS pore water, limiting radionuclide solubility. They may also provide small rates of gas generation (when compared with carbon steel or cast iron containers) and affect the overall mineralogy of the EBS (particularly in the case of a non-cementitious backfill).

Figure 35: Concrete containers currently considered in the UK. a) the 6 m^3 Box (or WAGR box), used in the past for encapsulation of some ILW streams. b) C1-C4 containers, planned for the disposal of ILW from new power stations



10 Evolution of waste containers

This section describes scientific and technical information relevant to the expected evolution of waste containers, particularly corrosion processes and, to some extent, mechanical processes. Key sources of information include the proceedings of a series of workshops on the prediction of corrosion damage in nuclear waste systems [378, 379, 380, 381, 382] and studies carried out by other waste management organisations, particularly for the disposal of HLW and spent fuel. A summary of UK studies is also available [383].

The information presented summarises some of the evidence produced on this topic in the UK and worldwide in the last 20-30 years. It considers evidence from research performed on relevant materials, as well as relevant analogues.

This evidence has come from a number of sources:

- laboratory studies of the behaviour of different materials in simplified conditions
- in-situ tests and demonstration experiments that studied the behaviour of relevant materials in underground environments and in contact with relevant EBS components, both small scale (corrosion coupons), and large scale (full-scale containers)
- natural and anthropogenic analogues, particularly for materials like copper and carbon steels
- various types of models (mechanistic, semi-empirical or parametric, etc.) that have been used to evaluate the likely development and effect of degradation processes and how the predicted behaviour compares with other sources of information.

The information presented considers a variety of materials employed, or being considered, for ILW/LLW, HLW and spent fuel. These materials, however, may be used in the future for the disposal of other materials requiring disposal, including any plutonium residues and DNLEU. Greater emphasis is given to container types that have either been employed, or are considered prominent candidates for use in the future. In particular, more limited information is presented relative to titanium and nickel alloys, which are currently considered as alternative options for the disposal of HLW and spent fuel.

An overview of evolution processes is presented, followed by a more detailed description of specific ones. The overall impact of such processes on the evolution of waste containers is described in Sections 11 and 12.

10.1 Overview of container evolution processes

10.1.1 Initial state and pre-closure period

During dry storage, the main degradation process affecting waste containers is likely to be atmospheric corrosion. The length of interim storage, the environmental conditions during storage, and the resulting importance of this process, are likely to be dependent on the type of waste.

Important characteristics of the initial state of waste containers include their mechanical properties, the extent of any residual stresses, the metallurgical state of the metal, its surface finish and the frequency, nature and typical size of post-manufacture defects. Depending on the material under consideration these characteristics may affect the mechanical, corrosion and environmentally-assisted cracking behaviour. Manufacturing defects could lead to premature degradation of a waste container (below the design life) and require specific consideration.

During periods of storage preceding transport of the waste to a GDF, and during the operational period of a GDF, waste containers will be exposed to indoor atmospheric conditions, generally in facilities able to provide a degree of environmental control. Atmospheric corrosion processes are likely to occur on metallic containers, as well as concrete containers. These processes can lead to structural damage (resulting from general corrosion) or perforation of the container walls (localised corrosion), potentially affecting the ability of the waste package to contain radioactivity (particularly during accidents). The importance/relevance of atmospheric corrosion depends on the timing of containerisation and the length of any subsequent period of exposure to atmospheric conditions.

In the case of ILW/LLW, these periods are likely to be long and atmospheric corrosion processes require detailed consideration.

In the case of HLW and spent fuels, waste containers may not be employed until the time of transport to the GDF. For this reason, atmospheric corrosion may be less relevant than for ILW/LLW containers. However, prolonged periods of exposure to atmospheric conditions could occur in scenarios of prolonged dry storage, or GDF operations envisaging prolonged periods with unsealed tunnels. Beyond any impact on pre-closure operations, this may introduce some uncertainty in HLW and spent fuel containers' post-closure behaviour.

Overall, the likelihood of substantial atmospheric corrosion depends on the potential for the occurrence of deliquescence (that is, the absorption of moisture at a relative humidity below the nominal dew point), which depends in turn on the temperature difference between waste packages and their environment, the relative humidity, and the presence of hygroscopic particles (such as salts). In the case of HLW and spent fuel disposal packages (particularly MPCs), temperatures may be too high for deliquescence to occur for long periods of time.

Evolution processes and their effects are described in Table 16.

10.1.2 Post-closure period

After disposal in a GDF, the main degradation process is likely to be aqueous corrosion of the waste container. Slow mechanical evolution (creep) may also be important for specific container designs. In some cases cracking and embrittlement processes may need to be considered.

During the post-closure period, particularly after resaturation, waste containers are likely to undergo chemical evolution processes, including corrosion (for metallic containers) or mineralogical alteration (for concrete containers). These processes can lead to structural damage or perforation of the container walls, eventually resulting in the waste container losing its ability to contain radionuclides and chemotoxic species.

Mechanical degradation processes are also possible. This is particularly the case for copper and, possibly, titanium, which could potentially undergo creep at relatively low temperatures.

For some materials, coupled mechanical/chemical degradation processes may also occur. These processes tend to occur when corrosion processes, beyond resulting in mass loss, result in degradation of the intrinsic mechanical properties of a material, for example its compressive strength or fracture toughness. Examples of this type of process include stress corrosion and hydrogen embrittlement of metallic materials, as well as carbonation of concrete containers.

Evolution processes and their effects are described in Table 16.

Table 16: Processes of general relevance to waste containers

Period	Evolution process	Effect	Section
Initial state	Container manufacture	Mechanical properties and residual stresses Metallurgy and surface finish Size of initial defects	10.2
Pre-closure	Corrosion (air)	Change in structural integrity	10.4-10.10
	Environmentally-assisted cracking (air)	Change in structural integrity	10.4-10.10
Post-closure	Plastic deformation (static and creep) Brittle fracture	Change in structural integrity	10.3
	Corrosion (groundwater)	Change in structural integrity	10.4-10.10
	Environmentally-assisted cracking (groundwater)	Change in structural integrity	10.4-10.10
	Carbonation, chloride and sulfate attack	Change in structural integrity	10.10

10.2 Initial state

Mechanical properties, the level of stresses (particularly residual stresses), the presence of defects, the metallurgical state (particularly in welds), and the surface finish, are important characteristics of the initial state of waste containers.

A number of characteristics of the initial state of waste containers may be important in assessing their evolution. Mechanical properties, level of stresses (particularly residual stresses) and the presence of defects are particularly important when considering the mechanical behaviour, whilst the metallurgical state (particularly in welds) and the surface finish are particularly important when considering the corrosion behaviour.

Mechanical properties are particularly important for HLW and spent fuel containers, since they are required to provide high integrity for long periods of time after closure of the GDF, during which they may be exposed to high mechanical loads associated with evolution of both the container and its host geological environment.

10.2.1 Mechanical properties and residual stresses

Structural steels envisaged for the manufacture of LLW/ILW containers have typical yield strengths of 200-500 MPa. Steels for HLW and spent fuel containers would have strengths towards the lower end of this range. Given the nature of manufacturing processes currently envisaged, residual stresses of yield strength magnitude are expected on final closure welds unless post-weld heat treatment is carried out.

The bulk mechanical properties of waste containers (yield strength, ductility, etc.) depend largely on the materials employed, their grade and any manufacture and post-manufacture treatment. For all waste container types, steels or cast iron are used as structural materials.

Structural steels envisaged for the manufacture of LLW/ILW containers have typical yield strengths of 200-500 MPa [384, 385]. Steels for HLW and spent fuel containers would have yield strengths towards the lower end of this range since the thick wall required as a corrosion allowance would provide sufficient mechanical strength without the need to use a higher-strength alloy [82]. The lower-strength materials also have the advantage of being less-susceptible to hydrogen-related degradation (see section 10.7.2). Given the nature of manufacturing processes currently envisaged, residual stresses of yield strength magnitude are expected on final closure welds unless post-weld heat treatment is carried out For carbon steels, using lower strength grades generally reduces the potential for hydrogen embrittlement [82].

Residual stresses of high magnitude are expected in many, but not all (see for example [386]), container designs. Residual stresses are particularly important for materials which, in specific chemical conditions, are subject to forms of environmentally-assisted cracking (such as stainless steels) but are less important for materials, like copper, that are not. Studies of the likely nature and level of residual stresses present in spent fuel containers are available in [386, 82], while studies on ILW stainless steel containers are available in [387, 388].

In general, there is sufficient experience with manufacturing of relevant materials to ensure that detrimental effects associated with welding and residual stresses can be minimised if suitable manufacturing or post-manufacturing procedures are employed, at least before the wasteform is emplaced inside the waste container. For example, solution annealing of Alloy 22 was specified in order to relieve residual stresses of spent-fuel containers in the Yucca Mountain project [389].

10.2.2 Metallurgical state and surface finish

Metallurgical state and surface finish can be tailored to the required mechanical and corrosion properties.

The metallurgical state of a metal depends on the thermo-mechanical treatments to which it has been subjected during its lifetime. Waste containers will undergo manufacturing processes (such as forming and welding) likely to locally affect the metallurgical state of the metal and its resulting corrosion behaviour. Testing of waste container materials (in both lab-based and demonstration experiments) generally includes specific design features (particularly welds) as well as parent material. Examples of metallurgical analysis of container materials after relevant manufacturing processes and their effect on the corrosion behaviour can be found in [388, 390].

Surface finish can also affect the corrosion behaviour of some metals. This parameter is particularly important for passive materials such as stainless steels. Stainless steel containers for ILW have been manufactured with either a wet bead blasted (WBB) or a cold-rolled, heat treated, pickled and lightly cold-rolled (2B) surface finish. Examples of studies including a characterisation of the surface finish are [388, 391].

Guidance on surface finish has been developed for stainless steel ILW containers [392].

10.2.3 Initial defects

Information to evaluate the nature and size of initial defects is available from studies carried out in other disposal programmes, although their applicability to the UK context will largely depend on the materials and manufacturing processes selected.

Defects are likely to be present in any large population of engineering components. The nature, size and location of such defects depend on the material and manufacturing technology in question. Consideration of manufacturing defects is important in evaluating the likelihood and impact of radioactivity released at early times in the post-closure period of a GDF, as well as the potential evolution of defective containers over time. Work on manufacturing defects in waste containers has not yet been carried out in our research programme, since container design and manufacturing technologies are not yet defined. Safety assessments are currently based on information available from more advanced disposal programmes, particularly the Swedish programme.

In tests supporting the manufacturing of the cast iron insert and copper shell minor defects were found, and none was considered to pose a threat to container integrity [393]. For example, clusters of pores were found in a cast BWR insert, but these only amounted to a total defect volume of approximately 10 cm^3 for the entire insert. In a similar insert designed for PWR fuel, two defects with dimensions of approximately 10 mm were identified (see also Appendix 1). For the copper shell the greatest concern is flaws in the closure weld. Using optimised welding techniques, only joint line hooking (a type of crack-like discontinuity that can occur at the base of friction stir welds because of bending of the joint between the lid and container body during welding) with a maximum extent of 0.4-1.5 mm was observed [393]. These defect sizes are less than the critical defect size that would lead to container failure under the expected loading, and SKB (Sweden) is confident that available inspection techniques are capable of identifying injurious defects [358].

10.3 Mechanical evolution processes

Predictability of the loading conditions expected during periods preceding and following disposal (static or slowly evolving) makes it relatively straightforward to design components to withstand the expected loads.

The durability of waste containers may be affected by mechanical processes. In the absence of defects or flaws the container may undergo plastic yielding if exposed to excessive mechanical forces, for example generated by the expansion of the wasteform or, in a GDF, by geological movements. If flaws or defects are present within a container, at sufficient stress levels the outer shell and/or any inner vessel could also be subject to fracture.

Beyond the susceptibility of materials to specific processes, it is important to consider mechanical processes in the context of container design. Not all degradation processes of a potentially susceptible material are relevant to all possible designs, so the relevant processes must be identified on a case-by-case basis. For example, creep processes may need to be considered in the case of a dual-shell copper-cast iron or titanium-cast iron container in which a physical gap between the copper/titanium corrosion barrier and the cast iron structural insert exists, but not in the case of a single shell copper-coated carbon steel container in which there is no void space into which the copper can creep.

10.3.1 Plastic deformation

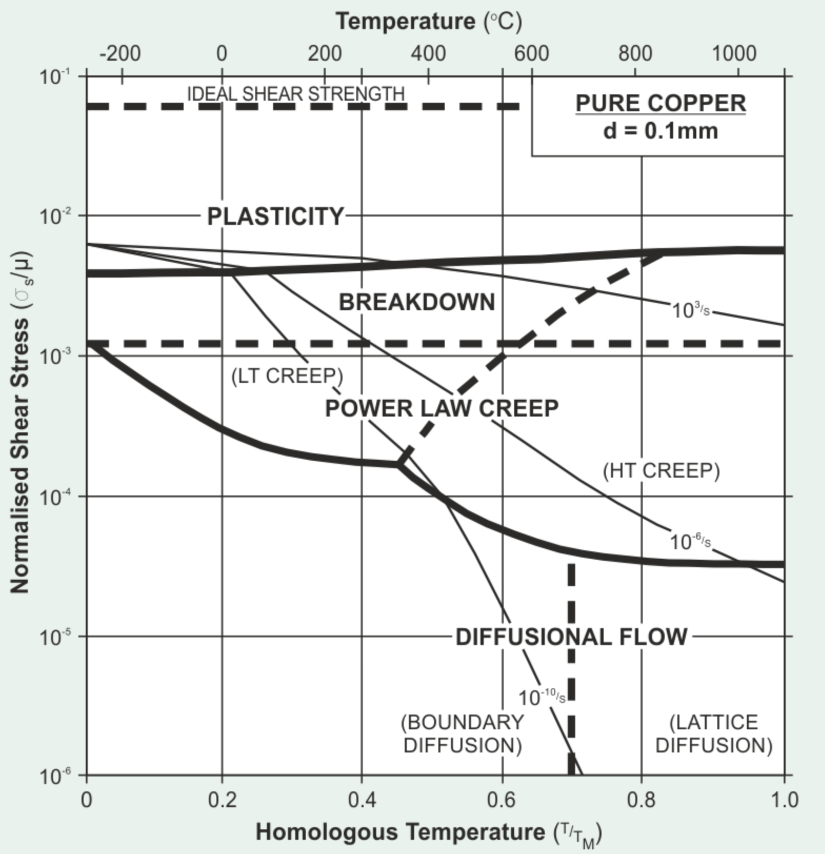
Slow deformation processes at stresses below yield (creep) can potentially occur in some materials, particularly copper. If load-bearing components are fabricated from materials resistant to creep (at the temperatures of interest), these processes can be effectively neglected.

Information on the stress-strain characteristics of many engineering materials (particularly steels) is widely available in the technical literature [394]. This information (particularly yield strength, ultimate strength and ductility) can be used to evaluate the likely plastic behaviour of container designs under assumed loading conditions. Confirmatory tests on specific batches of materials employed for the manufacture of high integrity components such as HLW and spent fuel containers will be required at a more advanced stage of the disposal programme. For materials which are not commonly employed for the manufacture of high-integrity components (such as copper), any desk-based analysis will need to be supported by suitable mechanical testing.

The slow plastic deformation of a material at loads lower than its yield stress (that is, creep) must also be considered in the design of the container. Among candidate container materials for waste disposal, copper (and possibly titanium) are the only ones which, at the temperatures of interest, are thought to be potentially affected, especially if the external load is not fully supported by an inner structural member.

For a given material, different creep regimes are conveniently represented by a Frost-Ashby deformation-mechanism map, as shown in Figure 36 [395]. As illustrated in the map for pure copper, the regions of creep behaviour are shown in terms of the homologous temperature (the ratio between the operating and the melting temperature) and the normalised shear stress (the ratio between the shear stress σ_S and the shear modulus μ). Diffusional creep mechanisms dominate at low stress levels and high temperatures, while dislocational (power law) creep dominates at higher stress levels. Additional information about creep of metals is reported in Box 22.

Figure 36: Illustration of Frost Ashby deformation-mechanism map for pure copper [395]



3307-01-Based on Frost/Ashby/Pergamon Press

The exact nature of the deformation-mechanism map will depend on the alloy type, grain size, and metallurgical condition. For instance, the map for copper illustrated here exhibits a broad transition from power-law creep to plasticity, referred to as power-law breakdown [395]. Ferrous alloys (not shown) tend to exhibit more-limited ranges of low-temperature creep (referred to as L.T. creep in the figure) and would not be susceptible to creep at the temperatures expected in the GDF.

In early studies of the creep of oxygen-free high-conductivity (OFHC) copper, the creep ductility was found to be less than 1% [396]. Trace amounts of sulphur in the alloy were found to be detrimental, whilst phosphorous additions improved the creep ductility. This resulted in the development of oxygen-free copper with added phosphorus (OFP) in the Swedish programme, with specified limits of <12 ppm S and 30-100 ppm P. These specifications improved the creep ductility to approximately 40% at 175 °C, with a grain size of 100 µm. The creep strain decreases with increasing grain size [397,Table 3-1].

Box 22 Creep

Creep is defined as the time-dependent plastic deformation of a material at stress levels lower than the yield stress. With increasing time, materials are typically found to exhibit different stages of creep consisting of ([398], Sections 8.1.3, 8.1.4):

- *primary creep,* during which the rate of deformation (or strain rate $d\varepsilon/dt$) decreases with time as the material undergoes strain hardening
- *secondary* or *steady-state creep,* in which the rate of deformation is constant
- *tertiary creep,* characterised by an increasing rate of deformation which culminates in rupture.

The duration of the primary and tertiary creep stages are typically relatively short and structures spend most of their service life in the secondary creep regime. The secondary or steady-state creep rate increases with increasing temperature (T) and level of stress (σ), with a corresponding decrease in the creep rupture time. Rupture results from microstructural and/or metallurgical changes in the material due to grain boundary separation or the formation of internal cracks, cavities, or voids.

As an engineering rule, creep is generally not considered at temperatures less than 30-40% of the melting point T_M (expressed on the absolute scale) - a fraction of 0.3-0.4 of the so-called homologous temperature T/T_M ([398], Section 8.1.4). However, some materials exhibit measurable creep rates at lower temperatures. Examples of the melting points of alloys considered for HLW/SF containers include 1355 K for copper, 1788 K for carbon steel, 1422 K for ductile cast iron, 1700 K for Type 304 stainless steel, 1561 K for Hastelloy C, and 2089 K for titanium [399, page D-190]. At a temperature of 100°C (373 K), the homologues temperatures are about 0.25-0.3 for copper and ductile cast iron and lower than 0.23 for the other materials.

The stress-dependence of the steady-state creep rate can be expressed as $d\varepsilon/dt = A\sigma^n$. The stress exponent (n) can be used to characterise the microscopic mechanism of the creep. Generally, two different mechanisms can be found:

- *dislocational flow (also referred to as power-law) creep at high stress levels ($n \approx 3\text{-}10$) is the result of the motion of dislocations*
- *diffusional flow (sometimes referred to as linear or viscous) creep at low stress levels ($n \approx 1$) is the result of the diffusion of atoms.*

Within each regime there are subsidiary creep mechanisms, such as Nabarro-Herring and Coble diffusional creep [395], involving the diffusion of atoms though the lattice and at grain boundaries respectively.

The creep ductility of electron-beam and friction stir welded copper samples has also been determined at temperatures between 75 °C and 175 °C, with the latter welds exhibiting at least 30% creep ductility [400, Table 3-1]. The formation of creep cracks has also been investigated using notched OFP copper compact tension specimens, with no cracks observed at temperatures of 22 °C and 75 °C but cracking observed at 175 °C and 215 °C [401]. Models have been developed for making long-term predictions of the creep behaviour of copper containers [402,403],but it has been suggested that further study of the mechanism of the creep behaviour of OFP copper is needed in order to justify long-term predictions [404]. Creep deformation of the container insert will be insignificant [405].

Titanium alloys also exhibit creep at low temperatures [389,406]. This behaviour is the result of thermally-activated dislocation motion, as opposed to the high-temperature self-diffusion mechanism commonly associated with creep at elevated temperatures. As for other alloys, it is the rate of secondary creep (see Box 20) that would determine the lifetime of a titanium container (on the assumption that the wall is not structurally supported, such as in the case of a design featuring an excessive gap between the shell and the insert). The secondary creep rate increases with increasing stress, with rates for titanium Grades 2 and 7 of approximately 4×10^{-6} hr^{-1} and 10^{-4} hr^{-1} at room temperature and at 100-150 °C, respectively, for an applied load of 100% of the yield strength. At these rates, relatively rapid perforation of the waste container would occur if the ductility of the system is insufficient to tolerate the expected displacement. Higher strength titanium alloys exhibit lower secondary creep rates at the same applied stress, with the rate for Grade 5 titanium (similar to that for the Grade 24 alloy considered for the struts for the drip shields in the Yucca Mountain Project), some five orders of magnitude lower than for the Grade 2 alloy [389].

10.3.2 Brittle fracture

Brittle fracture needs to be considered in the presence of defects. However, the levels of neutron irradiation for all wastes are expected to be insufficient to cause embrittlement.

Brittle fracture can occur in the presence of mechanical stresses and defects in the microstructure of a material.

Information on the resistance to fracture of many engineering materials (particularly steels) is widely available in the technical literature [394]. This information (specifically the fracture toughness) can be used to evaluate the likely mechanical behaviour of a variety of container designs under assumed defect sizes and loading conditions. The presence of radiation is not expected to affect the fracture toughness of the container. In particular, the fluence[83] of any fast neutrons (from spent fuel) is unlikely to be sufficient to cause radiation embrittlement, which is different from the case of other nuclear applications with far higher fluence (for example, reactor pressure vessels [407]). Confirmatory mechanical tests on specific batches of materials employed for the manufacture of high integrity components such as HLW and spent fuel containers will be required at a more advanced stage of the disposal programme. Any desk-based analysis will need to be supported by suitable mechanical testing.

A comparison of the resistance of various materials to brittle and plastic failure, represented as ‘failure curves’ as a function of the stress intensity factor (K_I) and tensile strength (σ_{ref}), is illustrated in Figure 37. Such information was used in a recent study to evaluate the likely behaviour of a variety of materials applied as a coating or cladding onto a carbon steel structural member [408]. Under the same loadings and defect types/sizes, this comparison shows that: most steels and nickel alloys present good strength and fracture toughness; copper presents good fracture toughness but poor strength; cast iron, some titanium alloys and ceramic materials present good strength but poor or very poor fracture toughness.

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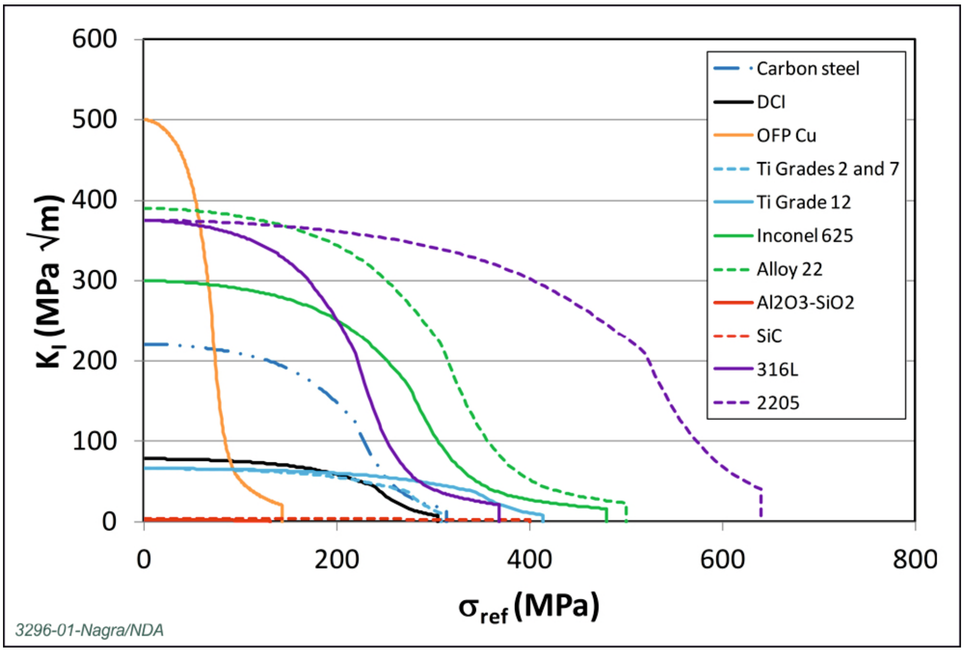
[83] The fluence is the number of particles that intersect a unit area.

Figure 37: Comparison of the resistance of candidate waste container materials to plastic collapse (based on their yield strength) and brittle fracture (based on their fracture toughness) [408]; σ_{ref} is the tensile strength, K_I the stress intensity factor. Reproduced from information presented in [83]



10.4 Chemical evolution processes

The main processes which will affect the durability of waste containers are corrosion and, in some cases, environmentally-assisted cracking. After disposal in a GDF, the main factors affecting the corrosivity of the environment will be the redox potential, the temperature, and the chemistry of the water in contact with the containers.

Provided they are properly designed and fabricated, the main processes which will affect the durability of waste containers are corrosion and, in some cases, environmentally-assisted cracking (EAC)[84]. These processes can affect both the container body and characteristic features of waste containers (such as welds and lifting features). In the case of concrete containers, mineralogical alteration processes are expected to occur, followed by corrosion of the re-bars.

An illustration of corrosion and EAC mechanisms can be found in Box 23 and Box 24. The effects of environmental factors on these processes are described in Box 25. Further details can be found in textbooks dedicated to the subject (for example, [409]).

During any interim storage and GDF operational period, the main factors affecting corrosion of waste containers will be the temperature, the relative humidity (RH) and the presence of specific surface contaminants, particularly chloride-containing aerosols (which are both hygroscopic and chemically reactive). Lighting and the presence of organic contaminants (such as those arising from marine aerosols) may also be important to minimise the potential for microbiological degradation.

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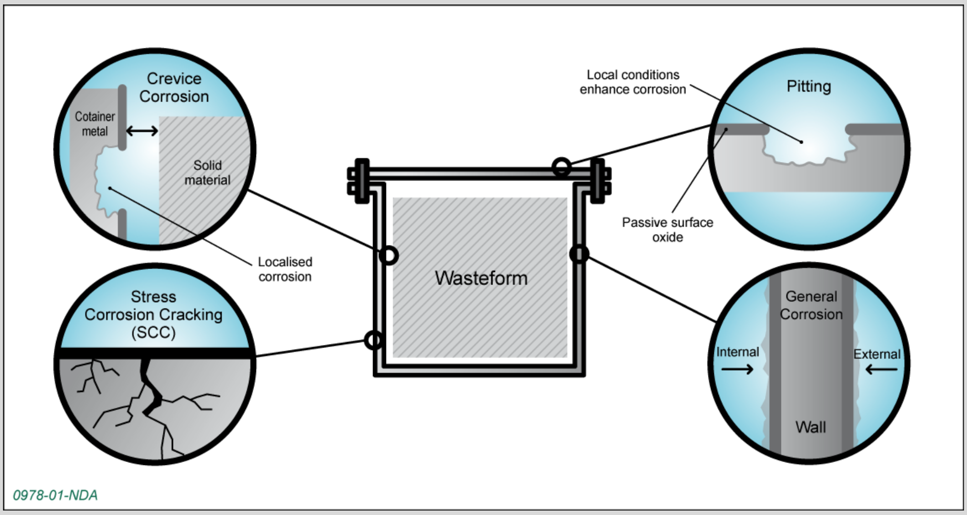
[84] In this document, we refer to corrosion and EAC separately, since some the latter process involves a mechanical as well as chemical component. Some authors, however, refer to some EAC processes as to corrosion processes (for example stress corrosion cracking is often described as a form of localised corrosion).

Box 23 Corrosion and environmentally-assisted cracking processes

Figure 38: Illustration of various corrosion and EAC mechanisms on a generic metallic waste container (see also [410])



General corrosion

General corrosion occurs evenly on the whole surface of a metal or alloy. The corrosion rate of materials that do not form protective films of corrosion products (active metals) tends to be much higher than those that form a protective film of corrosion products (passive metals).

Active materials include carbon steel and copper in near-neutral pH aerobic environments. Even if not as protective as in the case of passive materials, corrosion products tend to reduce the rate of further degradation of the underlying metal, ensuring that long term predictions based on short-term corrosion rates are conservative.

Passive materials include stainless steel and titanium. In these systems, general corrosion tends to be so slow it is practically negligible in the pre-closure period and low enough to ensure long durability in the post-closure period, even with a thin-walled design.

Localised corrosion

Localised corrosion (pitting or crevice corrosion) tends to occur on passive materials or on otherwise active materials if they become passivated by the environment (for example, carbon steel in alkali). In passive materials, this form of corrosion is generally observed in near-neutral pH in the presence of chloride, but is inhibited by high pH and by other anions (sulfate and nitrate).

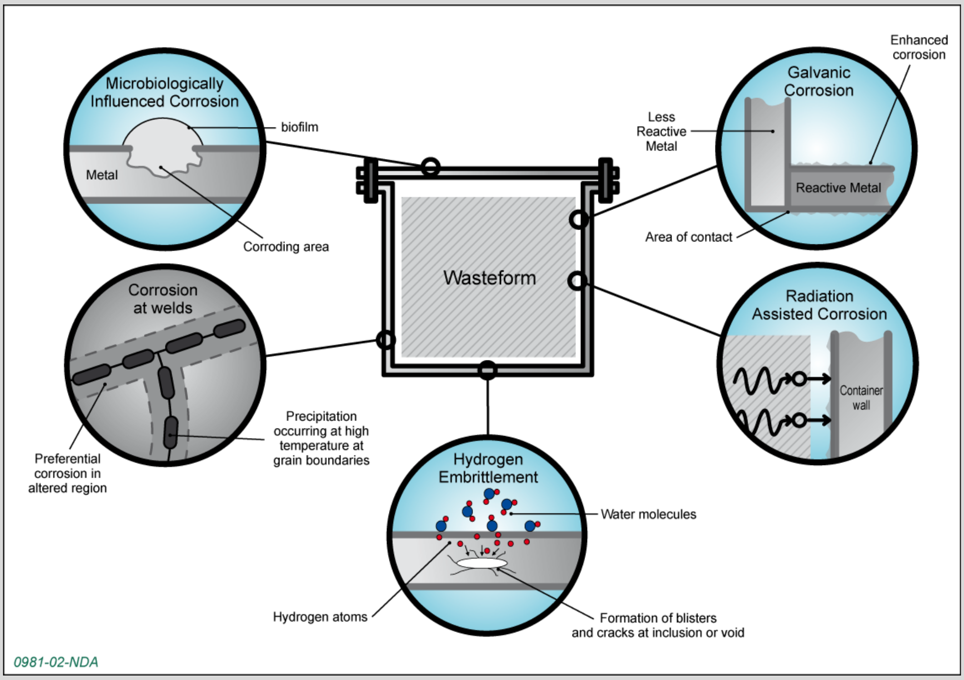
The conditions in which localised corrosion occurs are generally well understood. However the rate of corrosion is difficult to predict. For this reason, the choice of materials in potentially susceptible systems is often aimed at ensuring that localised corrosion cannot occur. In many systems, the propagation of localised corrosion tends to slow down as its progresses through the material (it ‘stifles’). Stifling may result from the inherent properties of the alloy or due to other environmental factors (for example, a decrease in temperature or a lack of O_2).

Stress corrosion cracking (SCC)

Stress corrosion is due to the combined effects of a corrosive environment and (tensile) stress. It generally results in cracking at relatively low tensile stresses. In some metals (particularly stainless steels), stress corrosion cracks are most likely to initiate at surface defects and sites of pitting or crevice corrosion.

Box 24 Corrosion and environmentally-assisted cracking processes (cont.)

Figure 39: Illustration of various degradation mechanisms on a generic metallic waste container (see also [410])



Microbial corrosion or microbiologically-influenced corrosion (MIC)

MIC may occur as the result of the ability of micro-organisms to change the nature of the local environment, leading for example to the formation of occluded conditions (biofilms) and generation of aggressive by-products of microbial metabolism (such as sulphide). MIC can also occur in the absence of a biofilm due to the transport of microbial by-products from remote locations. In this case, much lower corrosion rates may be observed. There are three basic requirements for MIC: a source of viable organisms, liquid water, and nutrients.

Galvanic corrosion

Galvanic corrosion occurs when different metals are in contact with each other, allowing the free flow of electric current between the two. The corrosion rate of the most reactive metal is enhanced due to the formation of a macroscopic electrochemical (‘galvanic’) cell with the less reactive material supporting the cathodic reaction.

Radiation-assisted corrosion

The ionising radiation generated by radioactive waste may interact with the materials inside and potentially surrounding the waste package to produce chemically-excited species. Some of these species tend to promote metal corrosion (they are oxidants).

Hydrogen Induced Cracking (HIC)

For redox potentials favouring corrosion due to the electrochemical reduction of water on the material surface of a metal, or in the presence of a hydrogen-rich gas phase, hydrogen atoms can enter the metal lattice, decreasing its fracture toughness (but not its strength). This tends to occur in specific metals (particularly high-strength grades) in conditions of high overpressure of hydrogen gas (H_2) and low redox potentials and can lead to the formation of blisters and cracks (in carbon steels) or the precipitation of hydrides (in titanium alloys) . In waste disposal, hydrogen embrittlement is a potential degradation mechanism for carbon steel/cast iron and titanium alloys.

After disposal in a GDF, the main factors affecting the corrosivity of the environment will be the redox potential, the temperature, and the chemistry of the water in contact with the containers (which will be determined by the chemistry of the groundwater and how it is modified by the buffer/backfill employed). In clay buffers, the mass transport properties of the environment are likely to be an important factor. In the case of cement buffers/backfills the high alkalinity of the environment will be important. In either circumstance, microbial activity will be predominantly limited by high swelling pressures / low water activities (in the case of clays), hyper-alkalinity (in the case of cements), or possibly hyper-salinity of the groundwater (in both cases), rather than by the lack of nutrients.

The presence of radiation and its intensity mainly affect the corrosivity of the environment by generating reactive chemical species able to affect its redox potential. For wastes with limited radioactivity (LLW and most ILW), radiation levels are unlikely to have a significant impact on the corrosion behaviour of waste containers, even with relatively limited shielding. In the case of wastes with higher radioactivity (such as HLW), in disposal concepts relying on long periods of containment in the EBS and in which groundwater is likely to come into contact with waste packages, waste containers will be designed with sufficient shielding (wall thickness) to substantially decrease external dose rates to levels below those expected to affect the corrosion of metals (1-10 Gy h^{-1} [413]).

The effects of different environmental factors for different candidate container materials in the context of disposal studies on HLW and spent fuel were also considered in specific detail and reproduced in Table 17 [411, 412].

Table 17: Summary of 'critical' and 'marginal' conditions for durability of candidate HLW/SF container materials [411, 412]

Parameter	Copper	Carbon steel	Titanium alloys	Nickel alloys	Stainless steels
Host rock	High sulphide mineral content	High sulphide mineral content	None	High sulphide mineral content	**High sulphide mineral content**
Redox conditions	**Permanently aerobic**	**Permanently aerobic**	None	None	None
Temperature	>150 °C	>200 °C	>200 °C	>150 °C	<100 °C (in the absence of cementitious backfill)
Gamma radiation	>1-10 Gy/h	>1-10 Gy/h	>1000 Gy/h	>1-10 Gy/h	>1-10 Gy/h
Backfill material and near-field mass transport	**No backfill**	None	Cementitious backfill	None	**Requires the use of a cementitious backfill**
Chloride concentration	No upper limit, lower limit 0.01-0.1 mol/L	>400 mg/L with cementitious backfill	Alloy dependent	Alloy dependent	Dependent on nature of backfill and alloy
Other ground water species	$([SO_4^{2-}] + [HCO_3^-]):[Cl^-] > 0.1\text{-}1.0$, ammonium ions	None	Fluoride	None (sensitivity to lead)	None
Sulphur species	Uncertain	Uncertain	None	H_2S, elemental S	**Thiosulfate,** sulphide
Microbial activity	**Microbial activity at the container surface**	**Microbial activity at the container surface**	None	Minimal	**Microbial activity at the container surface**
Residual stress and external load	None	None	Dynamic loading	None	Dependent on nature of backfill and alloy
GDF saturation time	None	None	None	None	None

Note: 'Critical' conditions are those for which the durability of candidate container materials may be questionable. 'Marginal' conditions are those in which the durability of a candidate container material may prove to be acceptable, but for which a more detailed analysis is warranted. 'Critical' conditions are shown in bold font, 'marginal' conditions in regular font.

10.4.1 Corrosion processes

During periods preceding closure of the GDF, particularly for waste containerised and subjected to long periods of dry storage, atmospheric corrosion processes are expected to occur. Following closure of the GDF, aqueous corrosion processes are expected to occur.

The likelihood/rate of these processes will be mitigated effectively by controlling the storage conditions and by the use of suitable buffer and backfill materials.

Corrosion processes are relatively varied and diverse in nature. They tend to be classified according to their morphology or to the main factors responsible for their occurrence. Forms of corrosion relevant to the degradation of radioactive waste containers include:

- general corrosion, which is associated with all metals and alloys, but is particularly important for ‘active’ materials (such as copper, carbon steel and cast iron in non-passivating environments)[85]
- localised corrosion, which is generally associated with ‘passive’ metals (titanium, stainless steel and nickel alloys) but can occur on active metals passivated by the environment (such as carbon steel or cast iron in alkali)
- microbiologically-influenced corrosion (MIC), which is generally associated with the presence of certain micro-organisms and can lead to severe degradation of most engineering materials, with the possible exception of some very corrosion resistant metals (titanium alloys)
- galvanic corrosion, which is associated with the electrochemical coupling of metals with different electrochemical reactivity and can be important for containers made with different materials (for example, dual shell containers)
- radiation-assisted corrosion, which is generally associated with the reactive radicals and stable chemical species generated by ionising radiation[86]. If not mitigated through adequate shielding, it can induce or accelerate corrosion processes on most metals, although it can also enhance the corrosion resistance on passive materials.

Weld regions tend often to display enhanced susceptibility to corrosion processes, due to metallurgical changes induced in the microstructure and, in some circumstances, the presence of microstructural defects (such as enhanced porosity) potentially leading to the accumulation of environmental stressors (for example, water). These effects can be mitigated or eliminated through correct material selection and welding processes and appropriate quality assurance.

During periods preceding closure of a GDF, the main corrosion processes requiring consideration are, depending on the systems of interest, either general corrosion or localised corrosion. Galvanic corrosion, radiation-induced corrosion and MIC are strongly inhibited by the lack of a bulk water phase in contact with the metal. Galvanic corrosion is also inherently inhibited by the design of the waste container, which typically employs a single type of material for the corrosion barrier.

After closure of a GDF, disposal systems are generally designed to prevent all forms of corrosion beyond, depending on the system, general corrosion and, in specific cases, localised corrosion. The potential for galvanic corrosion in waste containers is mitigated through designs employing a single material for the corrosion barrier. With some exceptions, the potential for radiation-assisted corrosion is mitigated by the design of sufficiently thick containers to ensure that dose rates are below the values expected to result in significant effects [413].

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[85] A degree of localisation leading to surface roughening is generally observed in most systems undergoing general corrosion. In this document this is referred to as ‘general corrosion’ or ‘surface roughening’ to distinguish it from fundamentally different corrosion mechanisms (‘localised corrosion’).

[86] In some cases, radiation can also induce metallurgical modifications in the metal, leading to a ‘sensitisation’ to some forms of corrosion. In other cases, however, it is not unknown for γ-irradiation to improve corrosion properties.

The potential for MIC during the post-closure period of a GDF requires specific consideration and is the subject of ongoing research. In a GDF, the potential for MIC is mitigated either through the use of hyperalkaline systems or compacted clays [414, 415]. All cases of severe MIC (for example, water-treatment plants and sewage systems) are associated with the presence of biofilms on the surfaces of interest. In a GDF, the development of biofilms on container surfaces will be inhibited by the environmental stressors (high temperatures and radiation). Perhaps more importantly, the design of the GDF will employ buffer/backfill materials either creating an environment in which water activity is too low (compacted clays), or in which chemical stressors are too strong (for example, the high pH in cements) to support microbial metabolism. The suppression of microbial activity in compacted bentonite is well established [2]. The suppression of microbial activity in hyperalkaline systems is also relatively well established, although questions remain about the potential development of microbial activity in lower-pH niches, which may developed in large scale backfilling operations (typically, microbial activity is observed at pH as high as 10 but nor at a pH greaten than 12, see for example [416]). Over very long timescales, however, microbial activity remote from the container surface may still result in corrosion if aggressive metabolic by-products (for example sulphide) can diffuse to the container surface. Any such corrosion would be expected to be uniform in nature and to occur at a slow rate due to the restrictive mass-transport properties of the buffer.

10.4.2 Environmentally-assisted cracking

Some metals exhibit environmentally-assisted cracking (EAC) - that is, cracking in conditions in which they would normally not crack. Weld regions often tend to display a lower resistance to environmentally-assisted cracking than the base metal.

In the presence of environmental factors and mechanical stresses (see Box 23), some metals (often ductile) exhibit environmentally-assisted cracking (EAC) – that is, cracking in conditions in which they would normally not crack. Depending on materials and environmental conditions, these processes are generally referred to as:

- stress corrosion cracking (SCC), which typically affects a variety of metals in the presence of specific chemical species such as chloride
- hydrogen-induced cracking (HIC)[87], which typically affects some steels and titanium alloys in the presence of relatively vigorous electrochemical reactions (water reduction) and/or substantial hydrogen overpressures.

Similarly to the case of corrosion processes, weld regions often tend to display a lower resistance to EAC than the base metal. Beyond the effects highlighted in Section 10.4.1, typically higher levels of mechanical (residual) stress are found in welded regions, enhancing their susceptibility to EAC.

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[87] Also referred to as hydrogen embrittlement.

Box 25 Main environmental factors affecting corrosion and EAC processes

Water

In the absence of liquid water, corrosion processes will be limited to oxidation in dry air, the rate of which is generally very slow at the temperatures of interest.

Oxygen and redox potential

High redox potentials generally result in more corrosive conditions for a metal. The nature of the buffer or backfill material affects the initial inventory of atmospheric O_2 when the facility is closed. Once oxygen is consumed and fully anoxic conditions are established, some metals (such as copper) may become chemically (thermodynamically) stable and remain virtually unattacked. For other metals (such as stainless steel) low redox potentials ensure that some corrosion mechanisms (localised corrosion) become unlikely.

pH

Acidic conditions can increase the likelihood of metal corrosion and the rate at which it occurs. In contrast, alkaline conditions are particularly benign for a number of metals (including carbon steel, cast iron and stainless steel) as corrosion processes are inhibited or significantly slowed. Low and high pH also tend to inhibit microbial activity and, hence, decrease the potential for microbiologically influenced corrosion.

Temperature

Corrosion reactions are generally favoured by higher temperatures. The difference in temperature between different waste types (for example, between spent fuel and ILW) may drive the choice of different container materials. On the other hand, if the temperature of a metal surface is high enough to prevent the presence of liquid water (such as during dry atmospheric storage) corrosion processes will be inhibited.

Salinity and sulfur species

The corrosivity of an aqueous environment can depend on the nature and concentration of ionic species in solution. Chloride and reduced sulfur ions (such as sulfide and thiosulfate) are particularly corrosive towards the majority of metals of relevance to waste management. Sulfate is generally not corrosive towards metals, but can attack concrete. Deep UK groundwaters are generally saline (see Section 4).

Microbiological activity

In some circumstances, the products of microbial metabolism can lead to corrosion damage in environments which would otherwise not be corrosive. In particular, sulfate reducing bacteria (SRB) are well known to be able to enhance the degradation of a variety of metals due to the production of sulfide [414, 415].

Mass transport properties of the environment

The transport properties of buffer/backfill materials, or of the host geological environment, can determine the steady-state flux of corrosive species (for example, the concentration of sulfide produced by remote microbial activity) and oxygen entrapped in the EBS. Mass transport can also determine the rate at which inhibitive species leave the metal, for example hydrogen gas.

Radiation dose rate

Ionising radiation (especially gamma and neutron radiation) can affect the corrosion behaviour of a metal directly and indirectly. The effect of radiation on the solution chemistry (specifically water radiolysis) is particularly important. A threshold absorbed dose rate (~ 1-10 Gy hr^{-1}) below which radiation effects on materials relevant to waste management are likely to be marginal has been suggested [413].

10.4.3 Chemical degradation of concrete

During periods preceding closure of the GDF, the main evolution process able to affect the durability of concrete containers is carbonation of the cement and the resulting potential for corrosion of carbon steel re-bars and inner containers. During the post-closure period hydration/leaching and sulfate attack also become important.

Concretes are subjected to specific degradation processes, generally associated with alteration of the cement mineralogy and corrosion of internal steel re-bars. These processes have been described in Section 7.2 and are further discussed in Section 10.10. This section provides additional details on carbonation processes which are considered particularly important for concrete containers.

During periods preceding closure of the GDF the main evolution process able to affect the durability of this type of concrete containers is carbonation of the cement (also discussed in Section 7.2.3) and the resulting potential for corrosion of the carbon steel re-bars and, where employed (for example in France), inner ('primary') containers [162, 283]. The loss of portlandite to buffer the pH leads to a decrease in the concrete pore-water pH, which in turn leads to an increase in the rate of corrosion of the steel re-bars or inner containers and the formation of expansive corrosion products. Thus, spalling and cracking of the concrete is accelerated and the durability of the container could be compromised. The other evolution processes that occur in atmospheric conditions, also discussed in Section 7.2 (hydration and radiolytic degradation), are unlikely to negatively affect the mechanical properties or chemical state of the concrete.

Beyond a dependence on the atmospheric concentration of CO_2, the rate of carbonation depends on the cement properties (in particular its permeability) and the relative humidity. Cements with low permeability present good resistance to atmospheric carbonation. The dependence on RH is somewhat complex. On the one hand, the depth of carbonation will increase with decreasing humidity, as gaseous CO_2 can penetrate further through the unsaturated pores in the concrete. On the other hand, an aqueous phase is required for the carbonation process, so decreasing the relative humidity to too low values will hinder the process. Consequently, the rate of carbonation is found to be highest at intermediate values of relative humidity, typically in the range 55-65% RH [162].

During the post-closure period key degradation processes will include chloride and sulphate attack, leaching and further carbonation. These processes are described in more detail in Sections 7.2.5 and 10.11.2.

10.5 Integration of mechanical and corrosion processes

In the case of materials susceptible to hydrogen-induced cracking (HIC), particularly carbon steels and titanium, consideration of the mechanical performance of waste containers needs to take into account the potential reduction in fracture toughness expected as a result of anaerobic corrosion processes and the development of hydrogen overpressures in the EBS. Consideration of the integration of mechanical and corrosion processes may also need to be given to materials susceptible to stress corrosion cracking (SCC).

For some container materials there may be a significant interaction between corrosion and mechanical processes. The importance of accounting for this interaction when evaluating the evolution of waste containers is being increasingly recognised in waste disposal programmes.

The interactions between corrosion and mechanical processes can be complex. They tend to occur when the simultaneous presence of corrosion processes and mechanical stress leads to enhanced crack-propagation rates, resulting from ether an increase in stress intensity factor and/or a decrease in fracture toughness. In the case of HIC, for example, the absorption of hydrogen in the microstructure can lower the fracture toughness.

Examples of studies considering the potential interaction of mechanical and corrosion processes are reported in [82] and [417, 418]. In both cases, the effect of corrosion-mechanical interactions has been considered for a single-shell carbon steel container with a bentonite-buffer, which is perhaps the design most sensitive to complex corrosion-mechanical interactions. This is largely because the HIC susceptibility of carbon steel is likely to be accentuated in a clay-based EBS, where corrosion is likely to occur, at least initially, at an appreciable rate and where the rate of hydrogen dispersion from the EBS to the far field is low. A more recent study extended the analysis presented in [417, 418] to other disposal scenarios and to the case of a carbon steel container coated or cladded with a variety of materials, demonstrating how the analysis can be generalised to other container designs and potential disposal conditions [408].

An effective way to assess and illustrate the evolution of the integrity of a waste container is the use of a Failure Assessment Diagram (FAD). In this approach, the proximity of a component (for example a weld) to either brittle failure or plastic failure is assessed over time and represented as a trajectory on a suitably constructed diagram. The effect of corrosion in affecting the proximity of a waste container to plastic failure (typically due to the gradual decrease in wall thickness) or affecting its resistance to brittle failure (typically due an increase in stress intensity factor and/or decrease in fracture toughness) can be explicitly represented and assessed over time. Further details on FADs are provided in Box 26.

Alternative approaches have also been developed:

- In Japan, a method for integrating the effects of various mechanical, material, and corrosion degradation modes to estimate the durability of carbon steel HLW containers has been developed [419, 420, 421]. The basic approach is to determine the maximum allowable flaw size, taking into account the reduction in wall thickness due to corrosion, growth of a defect, possible embrittlement of the steel due to neutron irradiation (found to be insignificant), and a suitable safety factor. This procedure permits the specification of suitable welding and inspection procedures to ensure only maximum flaw sizes below the critical value are present.
- In the US (Yucca Mountain Project [366]), the consequences of physical impacts on the corrosion behaviour of Hastelloy C-22 and titanium Grade-7 were considered. Detailed structural analyses were conducted and the consequences for breach of the waste package or the introduction of elevated residual stress were estimated [366].
- Consideration is also being given to the possibility of over-pressurisation due to H_2 formation for the carbon steel-concrete supercontainer design in the Belgian programme [422]. In this case, the concern is that H_2 generated by the corrosion of the carbon steel container and the stainless steel liner could lead to over-pressurisation of the ‘supercontainer’ shell.

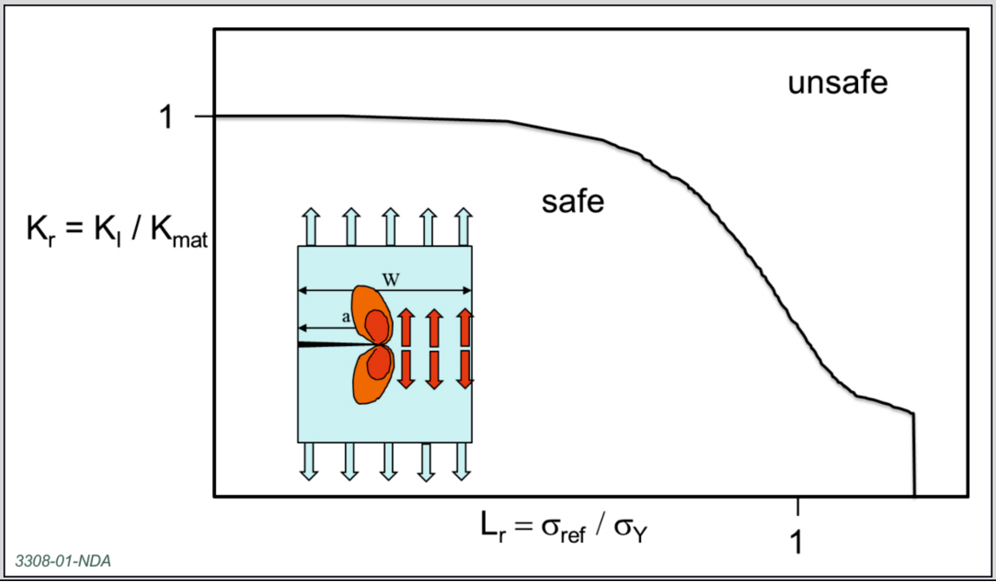
Box 26 Time-dependent assessment of mechanical integrity through Failure Assessment Diagrams (FAD)

When high integrity is required, it is important to carry out robust assessments of the resistance of critical components to both plastic deformation and fracture propagation. The basic method used in many industrial applications to address this effect is an elastic-plastic stress analysis, generally performed using one of a number of commercially available finite-element (FE) codes. The required inputs for the analysis are the container design, the material properties and the external (and internal) loads. In the case of waste management and disposal, with the exception of accident conditions [7], loads can be treated as static.

This type of analysis is typically performed as part of the container design process [74, 82]. For mechanical degradation modes involving plastic deformation, the results of the FE simulations can be directly compared with the associated failure criteria. For mechanical failure modes involving a fracture mechanism, the stresses predicted by the FE code are combined with a suitable fracture mechanics expression to estimate the corresponding stress intensity factor for the assumed geometry of defect(s).

A suitable means of presenting the results of mechanical integrity assessments for components containing defects is the use of a Failure Assessment Diagram (FAD). The approach, developed by the UK nuclear industry, has been adopted as part of various national codes [423, 424] and has been used to assess the integrity of a wide range of structures, including primary and secondary systems in nuclear power plants, off-shore structures, turbine blades, aircraft landing gear, and oil and gas transmission pipelines, among others. A diagram illustrating the use of a FAD is reproduced in Figure 40 [417]. In this approach, the proximity of a component (such as a disposal container) to failure is evaluated comparing simultaneously its tensile stress (σ_{ref}) and stress intensity factor (K_I) to its yield strength (σ_Y) and fracture toughness (K_{mat}), noting that at high tensile stresses and stress intensity factors there is typically a negative synergy between plasticity and brittle fracture, leading to failure in conditions in which evaluation of these effects separately would still indicate a safety margin (the 'safe' region in the top right corner of Figure 40 is smaller than the rectangle generated by $K_r = 1$ and $L_r = 1$).

Figure 40: The use of Failure Assessment Diagrams (FAD) to evaluate the proximity to failure of engineering components [417]. Kr is the ratio between the stress intensity factor (K_I) and the material fracture toughness (K_{mat}). Lr is the ratio between the tensile stress (σ_{ref}) and the material yield strength (σ_Y).



10.6 Copper containers

Copper containers for the disposal of HLW and spent fuel are typically designed for emplacement within a bentonite buffer. Extensive information relative to their corrosion resistance in atmospheric and aqueous conditions is available.

Copper (in a relatively pure form) is currently a primary candidate material for the corrosion barrier of containers for HLW and spent fuel in the UK, particularly if a higher strength host rock GDF site be identified during the Government's siting process. For disposal, copper containers would most likely be employed with a bentonite buffer.

Copper containers are usually designed either with a dual shell employing a copper external shell and a cast iron structural insert, or in a single shell design employing a copper coated carbon steel shell. In either case, copper is designed with a 'corrosion-allowance' that is less than the overall thickness of the shell/coating. The corrosion allowance (of the order of a few mm) is based on the maximum amount of corrosion that can occur during the early post-closure period (aerobic conditions) and subsequently as a consequence of the transport of sulfide to the container surfaces. However, it is possible that after an initial period of slow uniform degradation, corrosion will cease.

The corrosion resistance of copper containers is discussed in detail in [425] and is briefly summarised below. Further detail can be found in [67, 89, 358, 426, 427, 428]. In the presence of water and oxygen, can copper undergo general corrosion at an appreciable rate (depending on the temperature and the chemistry of the water). However, in anoxic conditions and if specific compounds (sulphides) are largely excluded, the rate of general corrosion can be drastically reduced.

Since copper is generally considered for disposal containers for HLW and spent fuel, technical work (and the text below) has mainly focused on corrosion during the disposal period. Work has also focused on creep which, as discussed in Section 10.3.1 (for a low-melting point material like copper), is considered a potential degradation mechanism.

10.6.1 Corrosion during interim storage and GDF operations

Copper corrosion processes in benign atmospheric conditions are expected to be slow ($<<1\ \mu m\ year^{-1}$).

Under normal atmospheric corrosion conditions, if the RH of the environment is sufficient to allow deliquescence of moisture, copper undergoes relatively slow corrosion. A duplex corrosion product film typically develops in these conditions, with an inner layer of Cu_2O and an outer layer of Cu(II) salts. The identity of the salt depends upon the contaminants present in the environment, which depends on the geographic location of the exposure. Paratacamite ($CuCl_2.3Cu(OH)_2$) is observed at coastal locations, brochantite ($CuSO_4 \cdot 3Cu(OH)_2$) in urban locations. This film leads to the familiar green patina associated with copper roofs and other architectural components exposed to the atmosphere. Outdoors, the associated corrosion rates are of the order of 1-2 $\mu m\ year^{-1}$ [429].

The atmospheric corrosion rate of copper in relatively dry conditions is expected to be very low ($<< 0.1\ \mu m\ year^{-1}$) [427]. The results of in situ tests and analogue studies of specific relevance to waste disposal suggest that the rate of corrosion of copper containers during the GDF operational phase will be minimal. For example, Taxén [430] exposed copper coupons to air (or to bentonite) at ambient temperature and at 75 °C for a period of 3 years at the underground Äspö Hard Rock Laboratory in Sweden and observed a mean corrosion rate of $<0.1\ \mu m\ year^{-1}$.

10.6.2 Corrosion after sealing and closure of the GDF

In anoxic conditions, upon exposure to groundwater and in the presence of a bentonite buffer, copper is expected to corrode at the rate at which any sulphide present diffuses through the bentonite, such that copper containers would be expected to last more than 100,000 years. Other degradation processes are not expected, as long as sufficient swelling of the buffer occurs and is maintained.

Current disposal concepts considering the use of copper containers envisage them to be emplaced in a GDF surrounded by a bentonite buffer. Once in the GDF, general corrosion will initially proceed until any residual oxidant is consumed and the redox potential of the system becomes sufficiently low. This process is likely to corrode a very limited thickness of metal (a few 100s of μm).

Depending on the composition of the (bentonite-pore) water in contact with the container, localised corrosion of copper may be possible as long as an oxidant (dissolved O_2 or Cu(II) species) is present. Pitting is most likely to occur in the period immediately following emplacement and prior to equilibration of the bentonite pore water with the groundwater. During this period, the environment is relatively oxidising, but the pore water is relatively dilute. Pitting of copper can be induced by low levels of Cl^- or SO_4^{2-} ions but, in contrast to the behaviour of many other alloys, high levels of Cl^- promote general rather than localised corrosion.

The manner in which the potential damage from localised corrosion of copper containers has been assessed has changed over time [431]. At first, estimates of the maximum pit depth were based on the use of pitting factors (the ratio of the maximum depth of penetration to the depth of general corrosion) based on the analysis of buried objects and Bronze Age artefacts. The maximum pitting factor derived from this analysis was a value of 25, although a value of 2-5 was considered to be more realistic. Subsequently, extreme-value analysis (EVA) of the same data was used to predict the probability that a pit of a certain size would grow on any of the containers in the GDF in a given time [431]. An example of relatively old work using EVA for copper containers is reported in [432]. This work estimated that the probability of a pit depth greater than 9 mm on any of the containers after a period of 1,000,000 years was less than 1 in 10^9.

Both of these approaches are based on the assumption that conditions involving a permanently separated anodes and cathodes will persist indefinitely on the container surface. However, the results of short-term laboratory tests under simulated GDF conditions and of large-scale *in situ* studies indicate that, rather than discrete pits, the copper surface exhibits non-uniform general corrosion. This form of attack (surface roughening) is now considered more appropriate to account for corrosion damage [431]. For example, a surface roughening allowance of ± 50 μm was recently used [67,89].

Assessment of the potential for coupling of mechanical and corrosion degradation mechanisms has concentrated on the potential for stress corrosion cracking, which is considered the form of EAC with the greatest potential to affect the integrity of copper containers. Copper is only susceptible to SCC in the presence of a limited number of substances (such as ammonia, acetates or nitrite) and only under oxidising conditions. The literature on this subject has been reviewed [433], and indicates that the concentration of aggressive agents during the early closure period (oxic) is expected to be too low to cause SCC. Japanese work has suggested the possibility of intergranular attack or SCC of copper in the presence of relatively high concentrations of sulphide (>5 mM) [434] but such observations could not be reproduced with later tests [435]. In general, these values are much higher than expected in a GDF. However, this an area of some uncertainty.

Once oxygen is consumed, further corrosion will depend on the possibility that sulphide will come into contact with the waste packages. This depends on the amount of sulphide present in the buffer and in the groundwater, and the amount produced by microbial activity in the buffer (but remote from the container), whose transport to the container will depend on the buffer thickness and level of compaction. To give an indication of likely corrosion rates due to the sulphide present in the groundwater, for an intact buffer, a sulphide concentration of the order of 0.01 mM and groundwater flow rates expected in a hard rock environment, corrosion rates lower than 0.001 μm year^{-1} (1 nm year^{-1}) have been estimated [67].

At higher sulphide concentrations (0.005-0.01 M, much higher than those expected in many underground environments), corrosion rates as high as 0.6 μm year^{-1} to 10-15 μm year^{-1} have been reported [434]. There have been studies reporting that copper could also corrode in anoxic conditions in the absence of sulphide; that is, in the presence of pure water. Further details about these studies are provided in Box 27.

Due to the compacted bentonite buffer currently envisaged for a copper-based disposal concept, it is expected that microbial activity will be very low because of the limited availability of water to support microbial growth. Hence, a long-term corrosion rate and a relative corrosion allowance can be determined based on the rate of diffusion of sulphide (produced outside the bentonite-filled region) through the bentonite barrier. Based on an analysis of the expected corrosion behaviour in a GDF, lifetime predictions for copper containers in excess of 100,000-1,000,000 years have been reported in typical GDF conditions [67, 428].

Observation of natural analogues (Figure 41) supports the idea that, in suitable geological conditions, copper can remain stable for very long timescales [130,436,437]. There are many cases of native copper deposits around the world [438], including extensive deposits in Michigan, USA and in the UK [436, 437]. Anthropogenic analogues date from the Bronze Age (as early as 3000 BC):

- Bresle et al. [439] used a collection of Bronze Age artifacts to estimate pitting factors for the localised corrosion of copper containers.
- Hallberg et al. [440] used more modern lightning conductor plates that had been buried in soil for periods of up to 100 years for the same purpose.
- A bronze cannon from the Swedish warship *Kronan* have been used to both provide estimates of corrosion rates [440] and to lend support to proposed copper corrosion mechanisms [441].
- Crossland [442] has collated corrosion rates from a number of analogue sites that are in general agreement with measured corrosion rates under aerobic conditions.

A number of in situ tests have been carried out to increase confidence in the performance of a copper-bentonite EBS. Key tests include the Prototype Repository experiment [443] (Figure 42), the Miniature Canister (Mini-Can) experiment [444, 445, 446, 447], the Long Term Test of Buffer Material (LOT) [448], the Canister Retrieval Test (CRT) [449], and the Buffer Coupon Long-term Test (BCLT) [450]. In the Mini-Can experiment, even in the presence of active sulfate-reducing bacteria and in the absence of compacted bentonite, the corrosion rate of copper was only 0.15 µm year^{-1} [444]. With this rate, a corrosion allowance of 10 mm would last about 70,000 years. The other in situ tests were conducted in compacted bentonite but under aerobic conditions, thus were not representative of the long-term evolution of a GDF. Such tests produced corrosion rates of 1 µm year^{-1} or lower[88]. A summary of some key experiments is reported in Box 28.

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[88] It should be noted that none of these experiments had corrosion studies (particularly anaerobic studies) as their main goal, so results from these tests should be interpreted with care.

Box 27 The corrosion behaviour of copper in pure water

The understanding of the corrosion behaviour of copper in anoxic environments has been challenged by studies performed by Swedish researchers [451, 452, 453, 454]. Such studies suggest that copper may continue corroding in oxygen-free water. An equilibrium pressure of hydrogen (~ 1 mbar) has been reported. The researchers' proposed mechanism is that, in the absence of oxygen, copper will react with water to form an oxy-hydride compound, resulting in the evolution of hydrogen. The evidence presented by the researchers includes:

- measurements of hydrogen generation in anoxic water (using pressure gauge and ion-pump measurements)
- the detection of hydrogen absorbed into the copper after exposure to anoxic water
- analysis of copper samples exposed in conditions in which hydrogen gas was allowed to accumulate or not, thus determining whether equilibrium conditions are achieved (exposure in a flask with membranes permeable/impermeable to H_2).

A review of the available evidence up to 2010 is available in [455]. Recent evidence from studies carried out in the Swedish disposal programme suggests that whether H_2 is generated or not depends on the source of material, the condition of the surface and the pre-treatment of the sample [456, 457]. Very pure copper does not produce H_2, except when the surface is scratched after careful cleaning, but then only for a very limited period of time (at a maximum a few days).

The material grade currently specified in Sweden (Cu-OFP), conversely, did produce H_2 in the experiments. However, if the material was previously heated no H_2 was observed, suggesting that the source of H_2 is hydrogen entrapped in the microstructure (presumably absorbed during the fabrication process) rather than generated by corrosion processes [456].

Even if the proposed mechanism was valid, the consequences for the durability of the container would be minimal, since the rate of corrosion would be limited by the diffusion of dissolved H_2 away from the container surface (limiting the corrosion rate to the order of 1 nm year^{-1}) [67,455].

Figure 41: Top and centre: example of native copper sample embedded in clay (Littleham Mudstone Formation, Devon, UK, >176 million years old), showing the presence of thin metallic plates (typically <0.2-2 mm thick). The exposure to groundwater (largely reducing conditions), accompanied by the formation of nickel arsenide, resulted in limited corrosion over very long times (reproduced from [436, 437]). Bottom: example of copper exposed to oxic conditions, leading to the development of cuprite (reproduced from [130])

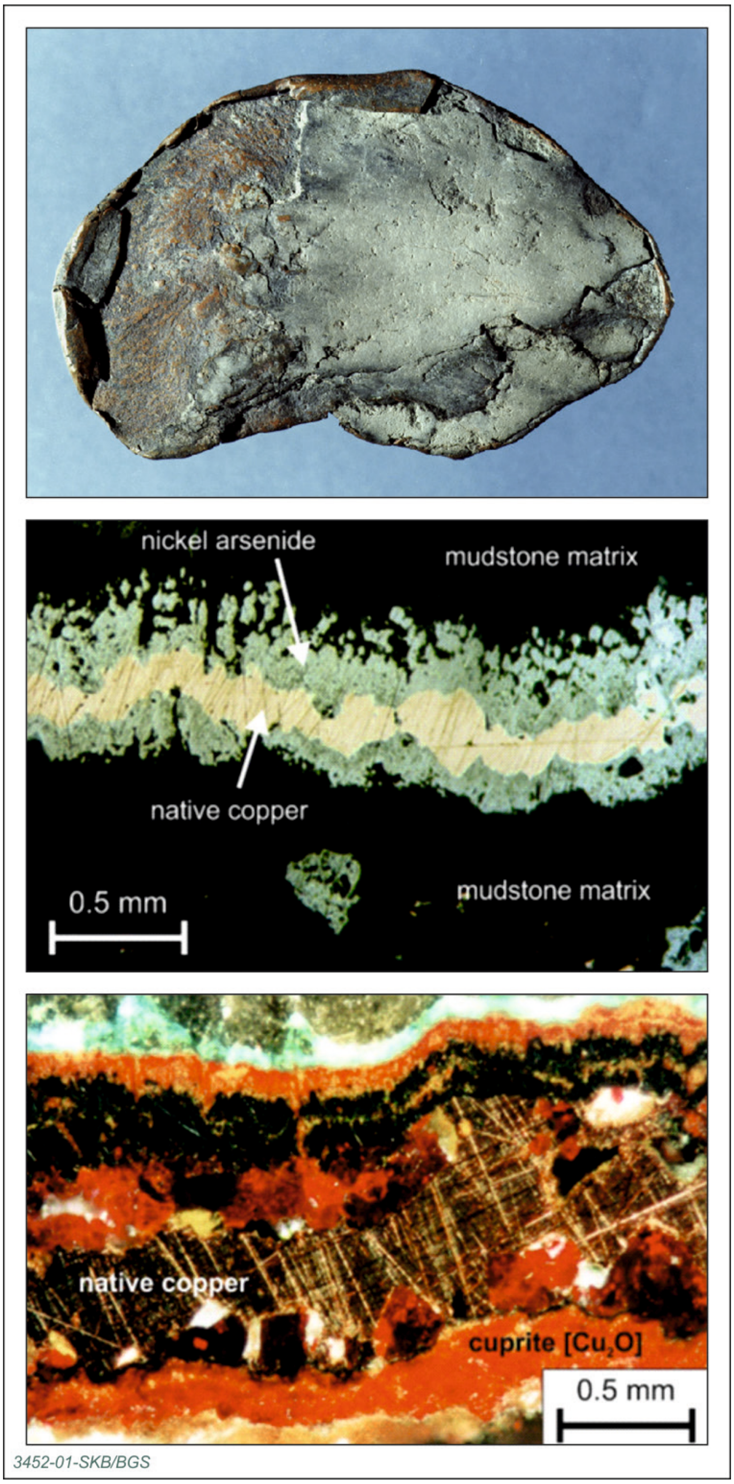

Figure 42: Image from the Prototype Repository project, showing a full scale copper container retrieved after about seven years of emplacement in contact with compacted bentonite in the Aspo URL [443]

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Box 28 Results of in-situ tests for copper spent fuel containers

Prototype Repository experiment

In the Prototype Repository experiment [443], six full-scale, dual-shell, copper containers have been emplaced in vertical deposition tunnels in contact with compacted bentonite disks in a configuration similar to that expected in the Swedish/Finnish disposal concept. Heaters and a variety of monitoring sensors have been used to simulate radiogenic heat and to monitor the temperature, humidity (level of resaturation) and pressure in the buffer and backfill. Examination upon retrieval of two of the six containers after a period of about seven years (the other four have been left in fully sealed conditions for retrieval in the future), and of corrosion coupons, indicated very little corrosion of the copper. Over the exposure period the sensors indicated the gradual development of anoxic conditions and the partial, uneven, resaturation of the bentonite buffer expected in the early post-closure period of a GDF. Microbial activity was observed in a portion of the backfill (a relatively low-density bentonite/sand mixture), but not in the buffer.

Mini-Can experiment

In the Mini-Can experiment, small-scale containers reproducing the main features of a dual-shell copper and cast iron container, but including a small hole in the copper shell deliberately introduced to study the likely evolution of a defective container, were studied, with the aim of evaluating whether any corrosion of the cast iron would result in expansion and deformation of the external copper shell [446]. Five such miniature canisters were installed in five near-horizontal boreholes at a depth of 450 m along with corrosion coupons and electrochemical probes. The boreholes were then flushed with anaerobic ground water. In three of the five tests, an annulus of bentonite was placed around the Mini-Can in order to chemically condition the groundwater before it reached the container. In a fourth test, the Mini-Can was embedded in compacted bentonite and in the fifth test no bentonite was used. Monitoring of the corrosion process was carried out using electrochemical and electrical resistance methods. Groundwater samples were routinely taken for chemical and microbial analyses via stainless steel tubing passing through gas-tight flanges sealing the boreholes.

In 2011, after nearly 5 years exposure, one of the Mini-Cans exposed to an annulus of bentonite (Experiment 3) was examined [444, 447]. Prior to decommissioning, the on-line measurements had given indications of high corrosion rates (from electrochemical measurements) and indications of microbial activity (from water sampling). Upon disassembly, the inside of the Mini-Can was found to be extensively covered by a black precipitate, thought to be iron sulphide. Consistent with indications from the prior on-line electrochemical measurements, cast iron corrosion coupons were found to have completely graphitised (a process in which the iron phase corrodes and leaves the carbon phase un-attacked), indicating a corrosion rate of cast iron of at least 500 μm year^{-1}. Despite the evidence for widespread microbial activity inside the autoclave involving the reduction of sulfate to sulfide ions by SRB, the corrosion rate determined from the copper weight-loss coupons was only 0.15 μm year^{-1}. There was no evidence for the formation of expansive cast iron corrosion products causing the deformation of the copper shell in the vicinity of the drilled defect[89].

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[89] It should be emphasised that the microbiologically active environment that developed in Experiment 3 is not representative of the conditions expected around a container in a GDF. The

10.7 Carbon steel and cast iron containers

Carbon steel and cast iron containers are typically considered for the disposal of ILW/LLW as well as HLW and spent fuel. In the case of HLW and spent fuel, they will be employed together with a bentonite, cement or crushed rock buffer. Extensive information relative to their corrosion resistance in atmospheric and aqueous conditions is available.

In the UK, carbon steel is currently a primary candidate container material for the disposal of HLW and spent fuel in lower strength sedimentary rock or evaporite. Carbon steel and cast iron are also being considered for ILW/LLW containers. In the case of HLW/spent fuel containers, they would be employed in single-shell designs in combination with a bentonite, cement or crushed rock buffer[90]. In the case of ILW/LLW containers, they would be employed with a cement or crushed rock backfill.

In dry environments (such as that expected in an evaporite) corrosion processes would not occur. In an aqueous, near-neutral pH environment (such as in a lower strength sedimentary rock employing a bentonite buffer), carbon steel and cast iron would undergo general corrosion. In an anaerobic environment, however, the corrosion rate is slow enough to ensure high durability, with an appropriate corrosion allowance (typically 10s of mm thick). In highly alkaline (cementitious) environments these metals become passivated, displaying a very low rate of general corrosion but becoming, particularly at pH values around 10-11[91], susceptible to localised corrosion.

The properties of carbon steel and cast iron in relation to disposal of HLW and spent fuel are discussed in [458, 459]. Further detail can be found in [162, 562, 364, 460, 362, 461, 462]. Although largely produced in the context of HLW and spent fuel containers, this information is expected to be relevant to ILW/LLW containers as well. Since this material is generally considered for waste containers suitable for either/both interim storage and disposal, technical work (and the text below) has considered corrosion during both the pre-disposal and the post-disposal period.

10.7.1 Corrosion during interim storage and GDF operations

Corrosion rates of carbon steel and cast iron containers in benign atmospheric conditions are expected to be relatively slow (about 10 μm year^{-1}).

The atmospheric corrosion resistance of carbon steel and cast iron has often been evaluated in relation to ILW/LLW packages, but similar considerations apply to HLW/spent fuel packages and overpacks. Carbon steel and cast iron are, and have been, employed in industry for a number of applications for many years, including structures exposed to the atmosphere (for example, bridges). The corrosion behaviour of these materials is well understood and experience from industry confirms that they can be used successfully if

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annulus of bentonite in Experiment 3 chemically conditioned the incoming groundwater but did not suppress microbial activity as the highly compacted bentonite in contact with the container in the repository is expected to do. A more realistic representation of the environment in the GDF is provided by the Mini-Can surrounded by compacted bentonite (experiment 4). Current plans are to decommission this experiment in 2015.

[90] For all types of containers, crushed rock is mainly being considered in the case of an evaporite host rock.

[91] Higher values of pH result in a higher degree of passivation (that is, less susceptibility to general corrosion) and provide, at the same time, a higher degree of inhibition to localised corrosion. As a result, the highest susceptibility to localised corrosion for carbon steel and cast iron is generally in the pH range 10-11 (at lower levels, general corrosion, is generally predominant).

appropriately deployed [384]. In particular, the atmospheric corrosion resistance of cast iron containers has been extensively studied in Germany [463].

During above-ground storage and the GDF operational period, any deliquescence of moisture on any exposed (un-painted) surface of waste containers would lead to general corrosion, with the formation of a layer of 'rust' consisting of various types of iron oxides, iron hydroxides and other minerals [464]. At relatively low temperatures a rate of general corrosion of several tens of microns per year (10-30 μm year^{-1}) is generally estimated in indoor atmospheric conditions [384, 409, 465]. Recent work carried out in the UK [384] indicates that atmospheric corrosion rates of the order of 10 μm year^{-1} can be expected for cast iron containers in conditions of relatively low corrosivity (such as a surface store or a well ventilated underground facility). In conditions of higher corrosivity, much higher corrosion rates can be expected. For example, corrosion rates of the order of 600 μm year^{-1} were reported for cast iron coupons stored in a non-ventilated gallery at a relative humidity of 80% and temperature of 42 °C, see [384, Figure 4.3, reproduced from 463]. With a corrosion rate of 10 μm year^{-1}, 10 mm of cast iron (compared to the typical wall thickness of 120-160 mm currently considered for containers in the UK) would last 1,000 years. With a corrosion rate of 600 μm year^{-1}, the same thickness would only last 16-17 years. The latter case, whilst quite extreme for a ventilated facility, emphasises the needs of a good environmental control and use of protective coatings to ensure a good durability of carbon steel and cast iron containers.

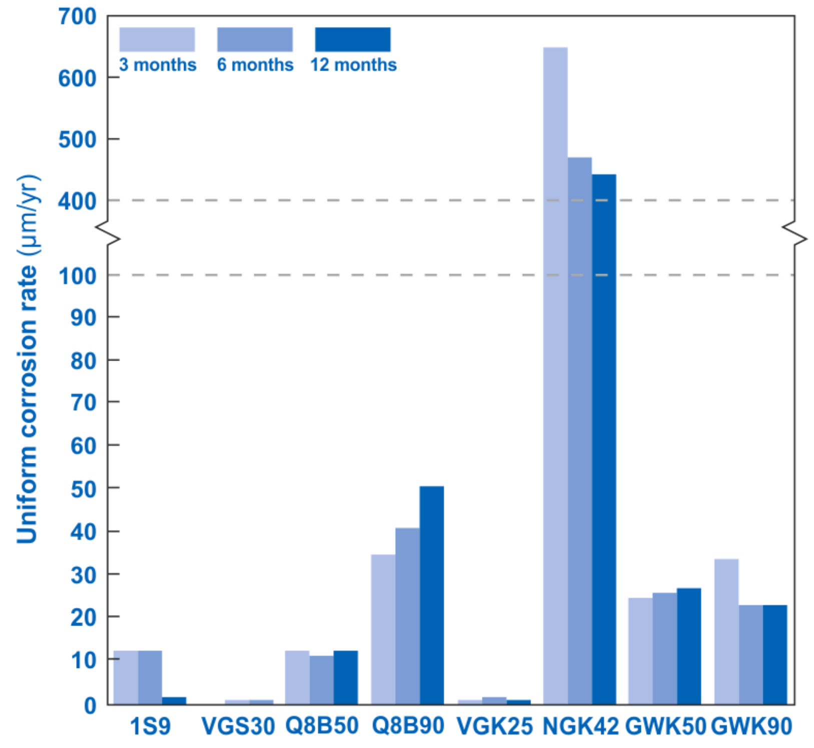
Whilst, in conditions of limited corrosivity, rusting is unlikely to affect the integrity of waste containers, it could affect some other functionality of the container and increase uncertainty in its evolution after closure of a GDF. For this reason, if long periods of storage are expected (as for ILW/LLW), it is necessary to use a corrosion-resistant paint system, which should significantly hinder rusting. An initial review of the degree of protection offered by epoxy paint systems currently envisaged for cast iron containers is available in [466].

In the absence of protective coatings (such as paints), under atmospheric conditions neither cast iron nor carbon steel suffer from localised corrosion. In the presence of protective coatings, however, localisation of corrosion is possible. In these conditions, any form of 'localised' attack would be associated with 'defects' present or developed in the coating system. There may be some acceleration of corrosion at crevice sites, mainly because they can act as traps for water from condensation. However, due to the protective nature of the scale formed on cast iron, the corrosion rate will fall with time as the corrosion product on the surface of waste containers thickens [409].

Studies of archaeological artefacts to evaluate the long-term corrosion behaviour of steels in atmospheric conditions include [464, 467, 468].The best known analogue for the long-term atmospheric corrosion of carbon steel is the 1600-year-old iron pillar in Delhi [467]. The corrosion product on the pillar comprises various forms of iron(III) oxide-hydroxide (goethite, α-FeOOH), magnetite (Fe_3O_4) and hydrated iron hydrogen phosphate. The latter species, which formed as a result of the relatively high phosphorous content of the underlying steel, developed a highly protective layer at the metal-oxide interface, thus conferring a superior corrosion resistance to those anticipated for grades typically employed industrially. Other analogues from historical buildings and artefacts (for example from the middle ages) are also available to support understanding of atmospheric corrosion processes over long timescales. Given differences in composition and exposure conditions, the use of these materials to fully underpin corrosion rates of relevant materials may be inappropriate. However, these analogues provide some additional confidence that very long durability can be achieved.

Work to further underpin estimates of the durability of carbon steel and cast iron containers after prolonged periods of atmospheric exposure and to identify suitable storage conditions are planned in the future [10, tasks 682 and 683].

Figure 43: Corrosion rates measured on cast iron up to 1 year in an interim store, in unbackfilled underground facilities (a salt dome and an iron mine) and in groundwaters from such facilities [384, reproduced from 463]



Storage Conditions	Label on X axis	Test Conditions		Corrosion Media
		Temp.	Relative Humidity	
Interim storage above ground (roof-covered in air)	IS9	~9°C, averaged over one year	~80%	*In-situ* test at KfK site
Disposal in a salt dome:				
Ventilated gallery	VGS30	30°C	~30%	*In-situ* test at -775m level of Asse salt mine, samples covered with crushed rock salt
Quinary salt brine	QSB50 QSB90	50°C 90°C	n/a	Saturated salt brine[1], pH ~5, O_2 content ~3 mg/l
Disposal at Konrad iron ore mine:				
Ventilated gallery	VGK25	25°C	~35%	*In-situ* test at -1250m level of Konrad mine, samples in contact with crushed iron ore
Non-ventilated gallery	NGK42	42°C	~80%	As above
Deep groundwater from Konrad mine	GWK50 GWK90	50°C 90°C	n/a	Deep groundwater, pH ~6, O_2 content ~5 mg/l

[1] Composition of Type Q quinary (five-component) salt brine: Mg^{2+} 87 g/l, Na^{+}7.6 g/l, K^{+}24.3 g/l, Cl^{-}270.2 g/l, SO_4^{2-} 23.7 g/l

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10.7.2 Corrosion after sealing and closure of the GDF

In anoxic conditions, upon exposure to groundwater and in the presence of a bentonite buffer, carbon steel and cast iron are expected to corrode relatively slowly (at a rate of the order of 1 μm year^{-1}). In the presence of a cement buffer, general corrosion is expected to occur more slowly (less than 0.1 μm year^{-1}). In these conditions, however, the evolution of the system will strongly depend on the evolution of the pH of the buffer.

In neutral pH, carbon steel and cast iron behave as ‘active’ materials in that they are subject to general corrosion, even in the presence of agents typically promoting localised corrosion (such as chloride). In oxic conditions, corrosion rates can be relatively high (10-100 μm year^{-1}), depending on the temperature and salinity of the environment (both typically increasing the corrosion rate) [469]. However, maximum depths of corrosion of the order of 100s of μm can be estimated on the basis of expected oxygen inventories, similar to the case of copper containers [68].

In anoxic conditions, however, the rate of corrosion decreases substantially, due to a reduced driving force. Corrosion rates reported in anoxic, neutral pH environments are of the order of 1-10 μm year^{-1} [158, 462, 470]. With such a corrosion rate, a corrosion allowance of 10 mm would last 1,000-10,000 years. Higher corrosion rates may be expected in the case of very saline systems, for example in the case of chloride-rich brines (potentially relevant to evaporite systems).

The presence and nature of the backfill material has a significant effect on the corrosion rate of carbon steel and cast iron. A number of long-term tests have been carried out to evaluate the general corrosion rates of carbon steels in contact with bentonite, including tests at high temperature. These tests show initial rates somewhat higher than those expected in simulated bentonite porewater but similar longer term rates (generally of the order of 1-2 μm year^{-1}). The short-term effects of bentonite on the corrosion rate may be related to the ion-exchange properties of the clay, which appear to hinder the formation of a protective layer of magnetite as is observed in near-neutral pH solutions. Instead, less-protective carbonate-based corrosion products are observed in short-term tests in the presence of bentonite. In bulk solution, a protective magnetite corrosion product film is observed to form under anaerobic conditions, whereas a less-protective carbonate-containing film is observed to form in the presence of compacted bentonite under the same redox conditions [462]. A recent study (based on a simulation of the effect of the build-up of corrosion products in the EBS) indicated that corrosion rates as low 0.1-1 μm year^{-1} as should be expected [471].

Similar to the case of copper-based containers, the use of compacted bentonite may have the additional advantage of eliminating the potential for MIC to occur on the container surface. Tests at low bentonite compaction/density are currently being carried out in the Swiss disposal programme (under the Materials Corrosion Testing experiment, see Box 29) to evaluate the effect of different levels of compaction on the potential for MIC to occur. The potential for microbiological processes to affect the durability of waste containers is also being considered explicitly in the French disposal programme, in which emplacement of waste containers without a bentonite buffer (the host rock itself being a clay) is being considered. A recent analysis [472] indicates that, beyond short-term effects associated with the reduction of sulfate minerals (formed by the oxidation of pyrite during the GDF’s operational period) and the presence of the initial oxic period (in which heterogeneous microbial colonies may lead to accelerated corrosion), the effect of microbiological activity in a clay host rock is likely to be an increase in the long-term rate of general corrosion by a factor of two.

There is extensive experience with the use of carbon steel and cast iron in a variety of geological environments, although often at shallow depth (for example, for pipelines [473]). This, and other types of information (from anthropogenic analogues), have been used to account for the potential localisation of general corrosion in waste containers. In particular, the empirical correlation between the ratio of the typical depth of pits to the depth of general corrosion (the so called 'pitting factor'[92]) and the mean depth of general corrosion has been proposed on the basis of a very large amount of data, including relatively short-term tests and studies on archaeological analogues [461, 562]. Given the widespread instances of MIC in soils, data from analogues are likely to take into account any microbiological effects [472].

In other concepts (particularly for ILW/LLW), the use of carbon steel packages is envisaged in conjunction with cement-based materials. In this case, the high pH 'passivates' the steel, making it more resistant to general corrosion. An effective passive film is retained at pH levels above 10 [474]. At high pH (>12), it has been reported [475] that the anaerobic corrosion rate of the steel falls to very low values (less than 0.1 μm year^{-1}) due to the build-up of a layer of iron hydroxide on the surface. This situation is analogous to the use of re-bars in concrete structures, where the corrosion rates of the reinforcement bars are very low unless specific circumstances arise (such as high chloride concentrations or carbonation). In general, if environmental stressors are present (particularly chloride), passivated metals can be susceptible to localised corrosion, with a propagation rate and potential to impact on the durability provided by a waste container being more difficult to predict than for general corrosion. In the case of cement buffers, inhibition of MIC is expected due to the high alkalinity and salinity of the environment.

SCC and HIC are generally considered unlikely under disposal conditions for carbon steel in the GDF. The form of SCC potentially relevant (SCC in the presence of carbonates) requires cyclic loading (which will not occur), while HIC of carbon steel only occurs in high strength grades and can be excluded if suitable grades are selected [362].

In package designs with thick walls (≥100 mm) radiation-effects tend to be negligible due to the significant shielding effect [475]. In designs with less wall thickness (for example, 30 mm in the Belgian supercontainer design) work is ongoing to determine whether significant radiation effects should be anticipated [476, 477]. In either case, packages can be suitably dimensioned, with a corrosion allowance based on lifetime predictions estimated on the basis of a long-term, conservative general corrosion rate.

In the case of disposal in an evaporite (carbon steel is currently considered as one of the primary candidates in this type of environment), a range of corrosion rates have been reported, from about 0.1 μm year^{-1} to more than 100 μm year^{-1} [367]. The corrosion rate is highly dependent on the amount of brine likely to form (likely to be limited by the supply of water from the surface) and on the chemical composition of the brine (NaCl brines tend to be less corrosive than $MgCl_2$ brines) [367]. The highest corrosion rates have been reported in laboratory experiments; in reality, due to the low water content in these systems, it is likely that very low amounts of corrosion and high durability could be achieved.

The capability of carbon steel to withstand exposure to the geological environment for long times is supported by a number of studies on relevant archaeological artefacts, which show that the corrosion rates observed over centuries or millennia are consistent with those evaluated experimentally after short-term exposures. The French and Japanese programmes have made extensive use of these analogues to provide confidence in long-term predictions of corrosion processes [460, 478]). Examples of specific studies on buried

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[92] The pitting factor is the ratio between the depth of the deepest pit and the average depth of general corrosion. In the case of actively corroding systems (such as carbon steel in bentonite) this refers to a localisation of the general corrosion process which, like any natural process in a real environment, is associated with a degree of heterogeneity and spatial variability. As general corrosion proceeds, the degree of localisation decreases, the corrosion damage becoming more evenly distributed across the surface, resulting in surface roughening and in a substantial decrease of the pitting factor. This process is inherently different from the pitting of passive systems (stainless steels or carbon steel in hyper-alkaline environments) in which the pitting factor may increase as localised corrosion occurs.

steel archaeological artefacts include [442, 460, 479, 480, 481, 482, 483, 484]. These studies have been used to support the prediction of general corrosion, pitting and MIC. However, no natural or archaeological analogues exist to support predictions of SCC or HIC.

A number of long-term in situ tests with full-scale containers or small coupons manufactured in carbon steel are currently either under way or planned, particularly in the Swiss program. Examples include the Full-scale Engineered Barriers Experiment (FEBEX, Figure 44) and the Materials Corrosion Test (MaCoTe, Figure 45) at the Grimsel URL in Switzerland, and the Full-Scale Emplacement (FE) experiment at the Mont Terri URL in Switzerland[93]. These tests generally indicate that carbon steel has evolved according to corrosion processes and rates compatible with those evaluated on the basis of lab-based experiments. Additional details about the findings of selected In-situ experiments are described in Box 29.

Figure 44: Extraction of heater no. 1 from the FEBEX experiment [485]

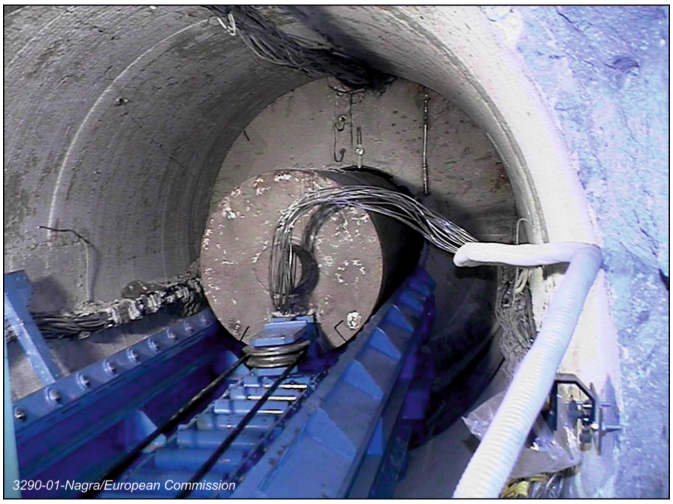

Figure 45: Illustration of the setup of the Materials Corrosion Test (MaCoTe)

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[93] The URLs at Grimsel is located in a granitic host rock. The URL at Mont Terri is located in a clay host rock.

Box 29 Results of in-situ tests for carbon steel waste containers

FEBEX and FE experiment

In the FEBEX experiment a large-scale carbon steel heater resembling a disposal container has been emplaced, together with a bentonite buffer and a perforated steel ‘liner’, in a granitic host rock. In this test, heaters have been employed to simulate heat generated inside waste containers. Compacted bentonite blocks and granular bentonite have been deployed. The bentonite has been extensively instrumented in order to determine the temporal and spatial dependence of the temperature, moisture content, and oxygen concentration. In addition to the container, corrosion coupons have been placed in the system. A very similar experiment, the FE experiment, is being setup in a clay host rock.

Following five years of heating, the FEBEX test was partially dismantled and various metallic components removed for corrosion analysis [485, 486, 487]. Less corrosion was observed in hotter/drier zones than in the cooler/wetter zones. The carbon steel heater exhibited general corrosion only, with no evidence of localised attack. The estimated corrosion product layer thickness was less than 20 μm, from which one would infer a corrosion rate of <2 μm year^{-1}. The perforated carbon steel liner located around the heaters exhibited uneven general corrosion to a depth of between 130 μm and 200 μm. Carbon steel corrosion coupons embedded in the bentonite exhibited a general corrosion rate of only 0.1 μm year^{-1}.

Stainless steel (Type 316L) and grades 2, 7, and 12 titanium coupons exhibited no general or localised corrosion, whereas copper coupons exhibited a time-averaged corrosion rate of 0.7 μm year^{-1}, as a result of initially trapped atmospheric oxygen. In contrast, Type 316L stainless steel sensor components located in the wetter regions of the bentonite suffered extensive corrosion, with evidence for MIC [485, 486, 487]. The stainless steel sensor sheath was penetrated by SCC, likely to be due either to Cl^- present in the buffer or, possibly, thiosulfate produced by SRB. Both aerobic bacteria and SRB could be cultivated from the bentonite surrounding the sensors but not from the bentonite surrounding the corrosion coupons, for which there was no evidence of MIC. In general, this test was not set up with the aim of studying corrosion processes and there is some uncertainty about the environmental conditions within the experiment, including the redox potential.The remaining sections of the FEBEX experiment have recently been dismantled and plans are underway for their examination in the near future, providing further insight into the behaviour of the EBS over a period of about eighteen years [10, task 651].

MaCoTe experiment

In the MaCoTe experiment [10, task 648], the corrosion behaviour of a variety of candidate container materials (copper, carbon steel and stainless steel) in contact with a bentonite buffer are being investigated. This experiment, making use of corrosion coupons and large scale samples, uses bentonite at different levels of compaction to provide confidence, when sufficiently compacted, in bentonite’s ability to provide a low corrosivity environment for embedded metallic materials (by reducing water transport and excluding microbial activity). A key objective of this experiment is to evaluate the likelihood of MIC developing on the corrosion coupons at different levels of compaction of the bentonite.

The results of a comprehensive study evaluating the corrosion rates of buried steels are shown in Figure 46. The large majority of observations indicate corrosion rates below 10 mm in 1,000 years (<10 μm year^{-1}). An example of well-preserved iron artefacts from the Roman era includes a large hoard of iron nails buried in clay soil almost 2,000 years ago (Figure 47) [488]. Another example from the medieval period is shown in Figure 48; this helmet was found in very good condition after burial for longer than 1200 years in conditions of limited access of oxygen and limited microbial activity [489].

Figure 46: Compilation of corrosion rates from steel archaeological artefacts [460] (based on information initially published in [479])

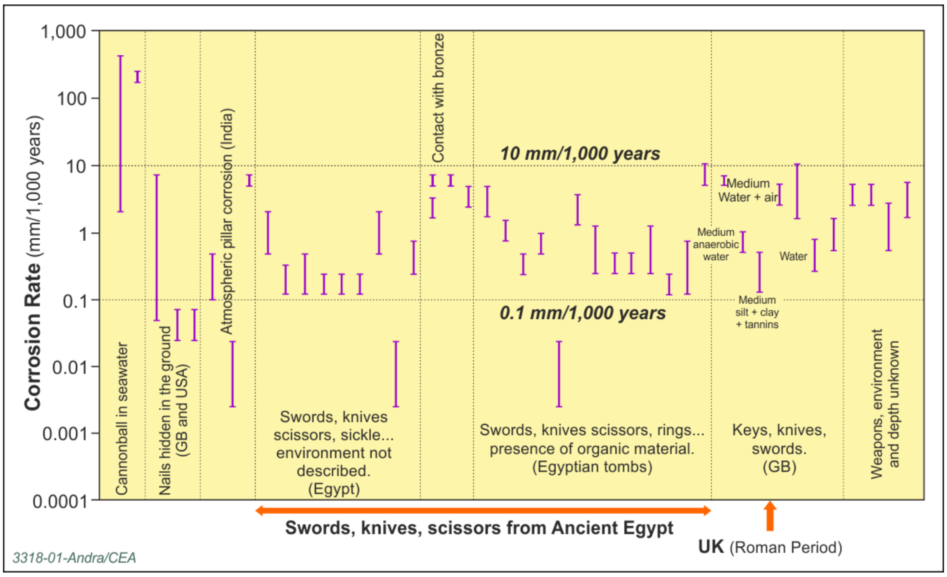

Figure 47: Photograph of a 30-centimetre-long Roman nail from the central part of the Inchtuthil hoard (~ 2,000 years old) [488], reproduced from [490]

Figure 48: The Coppergate Helmet [489]. The helmet, made of iron, brass, bronze and silver, was found in Coppergate (near York, UK) in a waterlogged pit after being buried for more than 1200 years[94]

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[94] The conditions of the burial site included a low oxygen concentration and a lack of microbial activity.

10.8 Titanium containers

Titanium has been considered for the manufacture of containers for HLW and spent fuel. Relevant information relative to their corrosion resistance in atmospheric and aqueous conditions is available.

In the UK, titanium is currently considered as a candidate material for the corrosion barrier of containers for HLW and spent fuel. For disposal, it would be employed in combination with a bentonite, cement or crushed rock buffer.

Titanium is a corrosion-resistant material, its general corrosion rate being practically negligible for most industrial applications. To ensure adequate durability, specific grades are selected to ensure that the environmental conditions to which they will be exposed are not conducive to other forms of corrosion, particularly crevice corrosion [493]. If other corrosion mechanisms can be excluded or proven unlikely to affect their durability, titanium-based containers could provide extremely high durability.

Some grades of titanium alloys exhibit excellent static strength and good creep resistance (much greater than pure copper, for example). Like copper they would most likely be employed as a corrosion barrier in conjunction with other materials (carbon steel or cast iron) to provide structural stability. A review of the knowledge base related to the potential application of titanium as a container material for HLW/spent fuel can be found in [491]. Further details can be found in [83, 362, 365, 390, 492, 493].

Since this material is generally considered for disposal containers for HLW and spent fuel, technical work (and the text below) has mainly focused on corrosion during the disposal period.

10.8.1 Corrosion during interim storage and GDF operations

Titanium is very corrosion resistant in atmospheric conditions. Very low general corrosion rates are expected.

In contact with water or oxygen, titanium forms a highly protective surface film consisting predominantly of titanium dioxide (TiO_2), which substantially slows any corrosion of the underlying metal [362, 494].

Titanium alloys are very resistant to atmospheric corrosion in the presence of a wide range of pollutants, including at high temperatures. HLW/SF containers fabricated from titanium would not degrade noticeably due to corrosion during surface storage or after emplacement in a repository, prior to backfilling.

If crevices were present in the container, if deliquescence and accumulation of moisture inside them was possible, if chloride was present in the environment, and if the temperature was sufficiently high, crevice corrosion could initiate in specific locations. The amount of corrosion generated in these conditions is likely to be limited by the scarcity of.

Titanium Grade-7 samples exposed to humid Boom Clay atmospheres during in situ experiments at temperatures up to 90 °C exhibited a maximum corrosion rate of 0.008 μm year^{-1} [367, Table 4-35]. Furthermore, the titanium cladding on the Guggenheim museum in Bilbao has provided excellent corrosion resistance over the past 20 years [495].

10.8.2 Corrosion after sealing and closure of the GDF

Titanium is very corrosion resistant in aqueous conditions. In a GDF, corrosion rates of the order of 0.01 μm year^{-1} have been estimated. With this corrosion rate, 1 mm of material is likely to last 100,000 years. Unless very corrosion resistant grades are selected, however, titanium alloys are susceptible to crevice corrosion in the presence of oxic, chloride containing solutions at relatively high temperatures.

The general corrosion rate of titanium in aqueous conditions is typically of the order of 0.01 μm year^{-1} [390, 493]. With a corrosion rate of 0.01 μm year^{-1}, a wall thickness of 1 mm would last 100,000 years. At temperatures greater than 70 °C some titanium alloys are however susceptible to crevice corrosion at relatively low chloride concentrations. Alloying with appropriate elements (molybdenum or palladium) can however significantly increase the resistance to crevice corrosion and in most circumstances an alloy with suitable corrosion resistance can be selected [367]. Most research in waste disposal has focussed on the use of alloys that are resistant to this form of corrosion (for example, Grade 7, which contains 0.2 wt.% palladium). However, recent work has been carried out in the UK to evaluate the corrosion resistance of a lower grade (Grade 2) [496]. In all grades, even when corrosion initiates, a stifling of the propagation rate is generally observed, suggesting that the amount of damage likely to be produced may be limited by other factors.

Titanium is generally resistant to pitting, stress corrosion cracking, sulphur-assisted corrosion and MIC, thus allowing potential application in environments containing corrosive sulphur species or in which the potential for microbial activity cannot be ruled out [362].

One of the main potential issues with the use of titanium alloys is the potential for HIC caused by the absorption of hydrogen in the metal lattice, leading to the formation of brittle hydride phases. Hydrogen can be absorbed in the metal during corrosion [362], especially in certain pH ranges and if the titanium is galvanically-coupled to a more electrochemically active metal.

There are no natural analogues for titanium and the relatively recent development of titanium and its alloys means that there are few anthropogenic analogues to help support long-term corrosion predictions. However, a number of in situ studies (such as FEBEX and MACOTE) have employed, or plan to employ, titanium corrosion coupons together with coupons of other materials. In the Belgian programme, Grade-7 titanium was exposed directly to Boom Clay at temperatures of 16 to 170 °C with, and without, gamma radiation at an absorbed dose rate of 400 Gy/hr. Both weight gain (due to the formation of an adherent oxide film) and weight loss was observed, with estimated corrosion rates varying from 0.005 μm/year at 16 °C to 0.155 μm/year at 170 °C [367]. Irradiation did not appear to accelerate the corrosion rate.

10.9 Stainless steel containers

Stainless steels are currently employed for the manufacture of containers for ILW/LLW. They have also been considered for the manufacture of containers for HLW and spent fuel, although, in this case, they are generally considered unsuitable for the manufacture of high durability containers. Extensive information relative to their corrosion resistance in atmospheric and aqueous conditions is available.

In the UK, stainless steel is currently considered as a primary material for the manufacture of ILW/LLW containers and as a candidate material for the corrosion barrier of containers for HLW and spent fuel. In the case of ILW/LLW containers, they will only be employed with a cement or crushed rock backfill[95]. In the case of HLW/spent fuel containers, they would probably be employed in combination with a clay or crushed rock buffer.

Stainless steel is a corrosion resistant material, its general corrosion rate being practically negligible for most industrial applications. To ensure adequate durability, specific grades are selected to ensure that the environmental conditions are not conducive to other forms of corrosion, particularly localised corrosion and SCC. If other corrosion mechanisms can be

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[95] For all types of containers, crushed rock has mainly been considered in the case of an evaporite host rock.

excluded, stainless steel containers would be able to provide extremely high durability. In this case, a corrosion allowance may be identified for the purpose of lifetime assessments.

Although they present excellent static strength and creep resistance, if structural strength under potentially high stresses was required, stainless steels would be, most likely, employed as a corrosion barrier in conjunction with other materials providing structural stability (such as carbon steel or cast iron).

A review of the knowledge related to the potential application of stainless steel as a container material for HLW/spent fuel can be found in [497]; further detail can be found in [367]. A description of its properties in the context of containers for ILW/LLW can also be found in [498] and [385].

Since this material has been considered for waste containers potentially suitable for both interim storage and disposal, technical work (and the text below) has considered corrosion during both the pre-disposal and the disposal period. Consideration is also provided for the stainless steel stillages used to handle some ILW/LLW containers (Box 30).

Box 30 The corrosion resistance of Cromweld 3CR12 stillages

A lower grade of stainless steel (Cromweld 3CR12, a ferritic-martensitic steel with 10.5-12 wt.% chromium) has been employed in the UK to manufacture ‘stillages’ to handle and stack a specific design of ILW packages (‘500 litre drums’). The stillages are currently employed for interim storage but consideration is being given to whether they would be suitable for disposal in a GDF. Their corrosion resistance in atmospheric conditions is hence important to evaluate their ability to provide a durable means to handle some ILW packages.

The corrosion resistance of Cromweld 3CR12 has been reviewed in [498]. Although still a stainless steel, its relatively low content of chromium (and some other elements) makes it much more susceptible to general and localised corrosion than 304L or 316L. As an example, an average rate of weight loss of the order of 1-2 μm year^{-1} has been reported in a marine environment, compared to values < 0.1 μm year^{-1} for 304L/316L [499]. However, like many low-nickel ferritic stainless steels, Cromweld 3CR12 is more resistant to SCC than austenitic grades. There have been no specific experimental studies on Cromweld 3CR12 in conditions relevant to interim storage and the operational period of a GDF. Overall, based on available information, it is likely that pitting corrosion will develop over long storage periods. Given the inherent resistance of this grade to SCC, however, the structural integrity of the stillages may remain sound for long periods of time.

10.9.1 Corrosion during interim storage and GDF operations

Stainless steel is very corrosion resistant, with very low general corrosion rates in atmospheric conditions. Stainless steels are sensitive to localised corrosion in oxic conditions and in the presence of chloride. This introduces the potential for pitting and SCC to occur during interim storage.

Stainless steel is commonly used in industrial or architectural applications in which good corrosion resistance is required [164, 500]. The addition of significant amounts of chromium confers the required corrosion resistance by creating a thin protective oxide which is impermeable to the external environment and protects the underlying metal from any significant degradation [164]. The chromium oxide is very stable and is able to immediately re-form if damaged.

In atmospheric conditions typical general corrosion rates are less than 0.1 μm year^{-1} [498], meaning that a wall thickness of 1 mm would take more than 10,000 years to be perforated.

Some authors report an atmospheric corrosion rate of the order of 0.1-0.5 mg·m^{-2}·yr^{-1}, equivalent to a penetration rate of <0.1 nm year^{-1} [429].

An example of the good resistance of stainless steel to atmospheric conditions is illustrated in Figure 49, which shows two buildings with stainless steel cladding exposed for several decades to an urban environment. After this time the cladding showed little sign of degradation [500]. Decades of practical experience with the use of stainless steel for the manufacture and storage of waste packages has so far shown very little degradation of waste containers during storage in surface facilities. Results from in-situ tests in underground facilities are also available. For example, types 309 and 316Ti stainless steel were exposed to humid clay atmospheres during in situ tests in the Belgian programme and exhibited a corrosion rate of 0.1 μm year^{-1} at temperatures up to 90 °C [367, Table 4-34].

Figure 49: The Socony-Mobil building, after cleaning 40 years of grime from its stainless steel panels. The stainless steel clad peak of the Chrysler building is shown in the background

General corrosion does not pose a significant problem for stainless steel in many applications, but localised corrosion and SCC can occur in the presence of chloride-containing aerosols if the relative humidity of the environment is such that chloride-rich droplets or moisture layers can form on the metal. The potential for localised corrosion and SCC increases significantly as the temperature increases [164]. Duplex grades, however, are known be particularly resistant, although not immune, to SCC [385, 501].

An initial review of the technical literature to identify conditions in which localised corrosion and particularly SCC are unlikely to occur was carried out in 2010 [502]. This included consideration of a monitoring programme on a prototype container [503]. Subsequent experimental testing in the presence of pure chlorides ($MgCl_2$) [388, 504] and additional practical experience in a real ILW store [64] broadly confirmed the initial findings. The latest work has focussed on identifying likely environmental conditions in real ILW stores in the UK [65], on the potential effect of fungi and algae on the risk of MIC [505], and on testing the behaviour of materials in realistic storage conditions [506, 507]. The results of lab-based studies and field experience with the use of stainless steels in conditions relevant to storage of ILW have been summarised and analysed in detail in [508, 509].

It is also possible that, even if corrosive conditions are established, corrosion may only develop to a limited extent, since any propagation deep into the metal is likely to be inhibited by the lack of sufficient aqueous phase. Mechanistic studies [510, 511, 512] and associated models of pitting corrosion [513], for example, indicate that propagation is likely to be limited by mechanistic factors, resulting in severe constraints on the size of any pit that may develop in the metal (at least for a single propagation event). Examples of other modelling studies and practical experience leading to similar conclusions can be found in [514] and [515].

On the other hand, studies of atmospheric corrosion of stainless steel indicate that irradiation is unlikely to enhance corrosion processes at the dose rates typically expected outside ILW packages [516]. An analysis of stainless steel tubes exposed to high gamma dose rates for about forty years [342] also indicated that the presence of radiation did not lead to corrosion per se but may have resulted in SCC in the presence of high chloride contents (SCC was observed in contact with a PVC tape surrounding the steel).

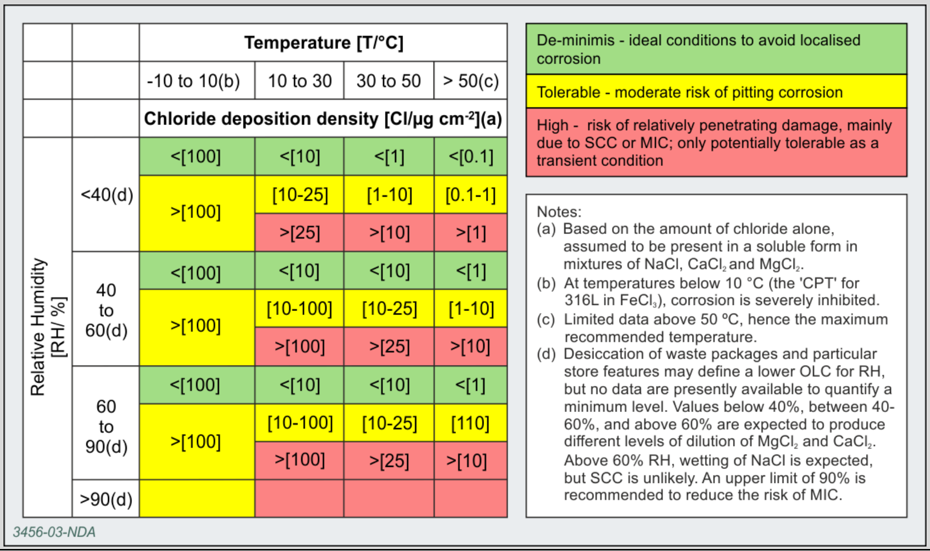
The overall understanding gained from the studies and experiences described in this section is being used to develop a parametric model, the Atmospheric Corrosion of Stainless Steel in Stores model (ACSIS), intended to support current and future operators of interim stores and of the GDF to identify environmental conditions able to limit the degradation of waste containers and to help estimating, in given environmental conditions, their likely durability [517]. Work to further develop the model and better underpin estimates of the durability of stainless steel containers after prolonged periods of atmospheric exposure and to refine the identification of suitable storage conditions (Box 31) is planned in the future [10, tasks 699 and 682].

Box 31 Environmental conditions to minimise corrosion of stainless steel

Guidance on environmental conditions (operational limits and conditions, OLCs) to mitigate the potential degradation of 316L stainless steel containers have been developed based on the R&D recently summarised in [508] (Table 18 refined from the information presented in [63]). The underpinning concept is that localised corrosion and SCC are severely inhibited at low temperatures (particularly below the 'critical pitting temperature' (CPT), which for 316L is ~20°C in NaCl [385]), and that SCC is only observed at RH values 'close' to the deliquescence point of divalent chloride salts [518, 519] above a minimum surface deposition density [508]. An important observation is that divalent chlorides ($CaCl_2$ and $MgCl_2$) are much more corrosive than NaCl [508], but also much less abundant [65]. As a result, during initial storage periods NaCl is likely to be the dominant chloride species, resulting in relatively benign conditions. In particular, the low risk of SCC at RH values above 40% is based on the dilution of solution containing divalent chlorides (their deliquescence point is around 20-30% at room temperature) and the fact that no SCC is typically observed in NaCl solutions [506]. Thresholds for SCC are based on the work carried out in [508] and the analysis described in [508, 509] but conservatively assume that all soluble chloride would arise from divalent chloride sources[96].

Although the result of substantial R&D, the values presented in Table 18 have been identified using extrapolation and expert judgement and should be interpreted with care, since they are based on testing over much shorter periods than those envisaged for interim storage (from a few years up to about 10 years), and cover only a relatively limited range of conditions (temperatures between 20 and 50 °C). Materials with superior corrosion resistance, such as duplex grade 2205, will provide tolerance to a wider range of OLCs due to their greater resistance to chloride-induced SCC and localised corrosion [385].

Table 18: Risk-based operational limits and conditions (OLCs) for 316L stainless steel waste packages (refined from [63])



		Temperature [T/°C]			
		-10 to 10(b)	10 to 30	30 to 50	> 50(c)
		Chloride deposition density [Cl/μg cm^{-2}](a)			
Relative Humidity [RH/ %]	<40(d)	🟩 <[100]	🟩 <[10]	🟩 <[1]	🟩 <[0.1]
		🟨 >[100]	🟨 [10-25]	🟨 [1-10]	🟨 [0.1-1]
			🟥 >[25]	🟥 >[10]	🟥 >[1]
	40 to 60(d)	🟩 <[100]	🟩 <[10]	🟩 <[10]	🟩 <[1]
		🟨 >[100]	🟨 [10-100]	🟨 [10-25]	🟨 [1-10]
			🟥 >[100]	🟥 >[25]	🟥 >[10]
	60 to 90(d)	🟩 <[100]	🟩 <[10]	🟩 <[10]	🟩 <[1]
		🟨 >[100]	🟨 [10-100]	🟨 [10-25]	🟨 [110]
			🟥 >[100]	🟥 >[25]	🟥 >[10]
	>90(d)	🟨	🟥	🟥	🟥

🟩 De-minimis - ideal conditions to avoid localised corrosion

🟨 Tolerable - moderate risk of pitting corrosion

🟥 High - risk of relatively penetrating damage, mainly due to SCC or MIC; only potentially tolerable as a transient condition

Notes:
(a) Based on the amount of chloride alone, assumed to be present in a soluble form in mixtures of NaCl, $CaCl_2$ and $MgCl_2$.
(b) At temperatures below 10 °C (the 'CPT' for 316L in $FeCl_3$), corrosion is severely inhibited.
(c) Limited data above 50 ºC, hence the maximum recommended temperature.
(d) Desiccation of waste packages and particular store features may define a lower OLC for RH, but no data are presently available to quantify a minimum level. Values below 40%, between 40-60%, and above 60% are expected to produce different levels of dilution of $MgCl_2$ and $CaCl_2$. Above 60% RH, wetting of NaCl is expected, but SCC is unlikely. An upper limit of 90% is recommended to reduce the risk of MIC.

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[96] Soluble chloride is likely to arise from a variety of salts, including NaCl. In a marine environment, for example, soluble chloride salts may arise in proportions reflecting the composition of seawater (typical ratio Na/Mg ~ 10/1, and Na/Ca ~ 25/1). In these conditions, a simplistic assessment would suggest that only 10% of the chloride content is available in a form which can led to the development of SCC and hence evaluate the risk of SCC assuming that only such fraction of the deposited chloride is compared with reported threshold values.

10.9.2 Corrosion after sealing and closure of the GDF

Stainless steel is very corrosion resistant, with very low general corrosion rates in aqueous conditions. For conditions anticipated in a GDF, rates of the order of 0.01 μm $year^{-1}$ have been estimated. To mitigate the risk of localised corrosion, the use of cement buffer/backfills is required. Stainless steels are sensitive to MIC, requiring (as in the case of copper and other steels) the use of a buffer (cement or bentonite) able to exclude this process.

Based on experimental observations in relevant electrochemical conditions, a very low general corrosion rate is expected for stainless steel in a geological environment, depending on the temperature and pH. In near-neutral and alkaline pH, up to relatively high temperatures (80 °C), corrosion rates measured over a period of at least a few months or longer are of the order of 0.01-0.1 μm $year^{-1}$ (rates can be inferred on the basis of information in [498]). Higher corrosion rates have been reported in short-term electrochemical measurements (0.1-1 μm $year^{-1}$) [497]. More recent gas generation measurements in alkaline environments (NaOH solutions, pH 12.5) indicated that corrosion rates of the order of 0.01 μm $year^{-1}$ can be expected at high temperatures (80 °C), but that rates as low as 0.001 μm $year^{-1}$ are observed at room temperature [252, 253][97].

Overall, a general corrosion rate of the order of 0.001-0.1 μm $year^{-1}$ can be expected based on these measurements. With a general corrosion rate of 0.01 μm $year^{-1}$, waste containers with a wall thickness of few millimetres would be able to retain their functionality for over 100,000 years if general corrosion was the only active corrosion mechanism.

Although the general corrosion rate of stainless steel is likely to be low enough to ensure good containment, even for thin-walled designs, the potential for localised corrosion has to be considered with care. Pitting, crevice corrosion and SCC could develop if chloride-rich groundwater were to come into contact with the container whilst oxygen is still present in the GDF (especially if the temperature of the packages is high), or if any thiosulfate (that may be produced by the redox transformation of sulphur species by microbiological activity) were present [498]. The potential for chloride-induced corrosion becomes significantly reduced once oxygen is consumed and anaerobic conditions are established [498]. However, there is some uncertainty about whether thiosulfate corrosion [367] and MIC [414] may occur in anoxic conditions, particularly in a near-neutral pH environment.

It may be possible to manage these risks through the use of highly corrosion-resistant grades (even more corrosion resistant than those currently used for ILW packages) and cement-based buffer/backfills (as for ILW). The high alkalinity of cements is well known to inhibit chloride-induced corrosion [498] and it may also inhibit the potential effect of corrosive sulphur species [520]. High alkalinity is also known to create an environment in which microbial metabolism is significantly suppressed, thus reducing the potential for MIC [521].

Stainless steel in contact with cement porewater is analogous to the situation of stainless steel re-bars in concrete, which are employed when corrosion resistance superior to that offered by the normally employed carbon steel rebars is required [500]. The use of stainless steel rebar in aggressive (e.g. marine) conditions is known to provide a substantially higher durability than provided by carbon steel rebar, typically indicating minimal damage over the lifetime of existing structures [522]. Additional information about the expected behaviour of

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[97] Electrochemical measurements may overestimate corrosion rates by inherently accelerating corrosion (under anodic polarisation). Measurements based on H_2 evolution, conversely, may underestimate corrosion rates due to the incorporation of hydrogen in the metal microstructure. On balance, a corrosion rate of the order of 0.01 μm $year^{-1}$ is considered appropriate for stainless steel in disposal conditions.

stainless steel in a cement-backfilled GDF can be found in the extensive literature produced by Nirex [523, 524, 525, 526] and other subsequent studies [527].

In situ tests with stainless steel at high temperatures under simulated disposal conditions were conducted as part of the early Belgian programme in the context of HLW and spent fuel disposal [367]. The maximum reported corrosion rate for 309 and 316Ti stainless steels in contact with wet Boom Clay at temperatures up to 170 °C was 0.013 µm $year^{-1}$ [367, Table 4-34]. The corrosion rate generally increased with temperature, but γ-irradiation at an absorbed dose rate of 400 Gy h^{-1} had no apparent effect on the corrosion rate.

Legacy (Nirex) information about the corrosion behaviour of stainless steel in contact with cements is provided in Box 32.

Box 32 Summary of Nirex work on the corrosion behaviour of stainless steels in contact with a cementitious wasteform or backfill (from the 1990s)

General corrosion

Stainless steel is passive in alkaline environments and exhibits a very low general corrosion rate (0.01-0.1 µm year^{-1}) [523, 524, 528, 529, 530]. The chromium oxide is thermodynamically stable and reforms in contact with water/oxygen [525, 530].

Chloride-induced localised corrosion

The amount of chloride required to induce pitting corrosion of stainless steels in alkaline environments has been characterised [525, 527]. A conservative value of the Cl/OH ratio of the order of 10 (specifically 14) has been suggested up to about 70 ˚C (corresponding to about 10,000 ppm Cl in a porewater of pH 12.5) [527]. The amount of chloride necessary to induce crevice corrosion of stainless steel in an alkaline environment has also been characterised [525, 531]. Tests using NRVB (pH 13) at temperatures up to 80 ˚C [531, 532] confirmed that, in order to initiate crevice corrosion, chloride levels in the porewater exceeding 2,000-20,000 ppm are required. In stainless steels, localised corrosion is a prerequisite for Cl-induced SCC - so SCC cannot occur if pitting and crevice corrosion are not viable.

Sulphur-assisted localised corrosion

The presence of some sulphur species (particularly thiosulfate $S_2O_3^{2-}$) in contact with stainless steels may significantly reduce the quantity of chloride necessary to sustain localised corrosion, but this effect occurs only in specific concentrations and potential ranges and is likely to be inhibited at pH above 12-13 [520, 533]. At 80 ˚C and a pH of 12, evidence of crevice corrosion was observed in aerated solution in the presence of both chloride and thiosulfate [534, 535]. SCC was observed only on dynamically strained material [534, 535].

Experience gained through corrosion monitoring of sulphur-containing grouts (such as BFS) suggests that sulphur-assisted localised corrosion does not occur inside waste packages. Experiments to test crevice corrosion in the presence of graphite in aerated BFS:OPC grouts indicated that corrosion did not occur with up to 1,000 ppm Cl at 80 ˚C [536].

Galvanic corrosion

Galvanic corrosion due to coupling with other metals is unlikely to affect waste containers as stainless steel is nobler than the metals present in the waste, with the exception of graphite [324]. At 80 ˚C, galvanic corrosion rates of the order of 1-10 µm year^{-1} were measured in BFS-containing grouts containing up to 10,000 ppm Cl [324, 532] and up to a graphite:metal area ratio of 5. Observations suggested that general corrosion, rather than localised corrosion, occurs in this condition [324]. Crevices formed between stainless steel and graphite are not worse than those created by contact between two stainless steel surfaces [532].

Effect of radiation on corrosion

The effect of the presence of radiation may increase the oxidising potential of the environment of an aerobic system. For an aerobic alkaline system, tests carried out at 16 Gy h^{-1} [537] indicated a free corrosion potential for 316L similar to that obtained in the absence of radiation [324], suggesting that the presence of radiation does not increase the oxidising potential of an alkaline system at radiation dose rates of interest to ILW containers. The addition of up to 1,000 ppm Cl at room temperature did not initiate pitting [20]. A more recent review of the literature and field experience suggests that the effect of radiation on corrosion may be marginal at dose rates expected on most ILW packages [516].

10.10 Nickel-alloy containers

Nickel alloys have been considered for the manufacture of containers for HLW and spent fuel. Relevant information relative to their corrosion resistance in atmospheric and aqueous conditions is available.

In the UK, nickel alloys are currently considered as a candidate material for the manufacture of containers for HLW and spent fuel. For disposal, they would be employed with a bentonite, cement or crushed rock backfill. A review of the knowledge related to the potential application of nickel alloys as a container material for HLW/spent fuel can be found in [538]. Further details can be found in [365, 390, 539, 540].

Nickel alloys are very corrosion-resistant materials. In many ways, nickel alloys and stainless steels can be considered part of the same continuum of materials. In these materials the addition of chromium leads to the formation of a highly insoluble chromium rich oxide or hydroxide film, which confers a high degree of corrosion resistance [541]. The gradual increase in content of nickel and of other alloying elements leads at some point to alloys in which the nickel content is high enough that they become defined as nickel alloys. In particular, higher amounts of molybdenum and nickel greatly increase resistance towards localised corrosion and SCC relative to stainless steel.

Although they present excellent static strength and creep resistance, if structural strength under potentially high stresses was required, nickel alloys would be, most likely, employed as a corrosion barrier in conjunction with other materials providing structural stability (such as carbon steel or cast iron).

10.10.1 Corrosion during interim storage and GDF operations

Nickel alloys are very corrosion resistant in atmospheric conditions. Very low general corrosion rates are expected.

The atmospheric corrosion resistance of nickel alloys is likely to be similar to that of austenitic stainless steels. General corrosion is likely to occur very slowly. At very high temperatures, localised corrosion and stress corrosion cracking could hypothetically occur in the presence of the aggressive aqueous solutions (containing chloride [542]) which may form in the proximity of corrosive hygroscopic salts.

Localised corrosion of nickel alloys in these conditions was studied extensively as part of the Yucca Mountain project [366]. In order to form a corrosive aqueous phase at temperatures in excess of the ambient boiling point of water, specific binary, ternary and quaternary salt mixtures must be present. These salt mixtures tend to include nitrate salts (highly deliquescent) and chloride-based salts (corrosive) [366].

10.10.2 Corrosion after sealing and closure of the GDF

Nickel alloys are very corrosion resistant in aqueous conditions. In a GDF, corrosion rates of the order of 0.01 μm year^{-1} have been estimated. With this corrosion rate, 1 mm of material is likely to last 100,000 years. Nickel alloys are similar to stainless steel, but are generally more resistant to localised corrosion.

The general corrosion rate of nickel alloys in a backfilled geological disposal facility is likely to be very low. As an example, the general corrosion rate of Hastelloy C-22 (an extremely corrosion-resistant grade) has been measured as lower than 0.01 μm year^{-1} in concentrated brines at 60 °C (such as those anticipated in the Yucca Mountain repository), [539, Figure 19], increasing to 0.9 μm year^{-1} at higher temperature (200 °C) in magnesium-rich Q-brines (tested in the German programme) [367, Table 4-14]. A general corrosion rate of 0.01 μm year^{-1} would result in a wall thickness of 1 mm lasting 100,000 years.

The variables controlling the susceptibility of nickel alloys to localised corrosion in a geological environment are similar to those relevant to stainless steels (redox potential, chloride concentration and temperature). In light of these factors, the potential for corrosion of nickel alloys in the context of waste disposal has been reviewed [389, 543]. Temperature is particularly important, with SCC and localised corrosion susceptibility increasing at temperatures over 150-200 °C. However, the propagation of localised corrosion of certain nickel alloys (including Hastelloy C 22) tends to slow down with time (due to 'stifling') [544]. Stifling may result from the inherent properties of the alloy or, because of limitations in the supply of O_2 to support pit or crevice propagation, or because of the decrease in temperature with time as the containers cool.

Similarly to copper, stainless steel and other ferrous alloys, the potential for localised corrosion and SCC in nickel alloys can be affected by the presence of reduced sulphur species, such as those generated by microbial activity. However, the most corrosion-resistant grades of nickel alloys (such as Hastelloy C 22) are expected to be largely unaffected by sulphur-assisted corrosion [366, 542]. Nickel alloys are also likely to show good resistance to MIC [366, 542].

Overall, if the temperature is not too high, and if the presence of reduced sulphur species can be excluded through appropriate siting of the GDF and engineering of the buffer/backfill, it is expected that a lifetime of 100,000 years is achievable for waste containers manufactured with nickel alloys.

As in the case of titanium alloys, there are no natural or man-made analogues for nickel alloys, but there are a number of in situ experiments that have employed corrosion coupons made from nickel alloys. For example, Inconel 625 and Hastelloy C-4, were exposed to Boom Clay as part of in situ testing in the Belgian programme. Samples were exposed at temperatures of 16 to 170°C, with and without a γ-radiation field of 400 Gy h^{-1}. With one exception, the coupons exhibited a mass gain during exposure, making it difficult to estimate a corrosion rate without knowledge of the nature of the composition of the corrosion product. The one sample that exhibited a mass loss was an as-received Hastelloy C-4 coupon exposed to Boom Clay with a radiation field of 400 Gy h^{-1} at 80 °C for a period of 5 years, resulting in an estimated corrosion rate of about 0.01 µm $year^{-1}$ [367, Table 4-35].

10.11 Concrete containers

Concrete containers are typically designed to package ILW/LLW. Relevant information on their corrosion resistance in atmospheric and aqueous conditions is available.

A limited number of concrete containers have been produced in the past in the UK to contain ILW (WAGR boxes). In the future, concrete containers may be used for ILW arising from new power stations. Concrete containers are also employed for similar wastes in other countries. These are often employed to overpack internal steel containers. Extensive information about the likely evolution of these types of packages exists from other national programmes (for example, France [545]).

Concrete containers/overpacks are massive, with wall thicknesses of 200-300 mm for the designs employed or being considered in the UK. Containers already manufactured feature carbon steel re-bars inside the cement structure and are fitted with metallic lifting features, metal cladding on the edges to protect them from impact, and with a metallic plaque labelled with a unique identifier. All external metallic components are made with carbon steel treated with a zinc-based coating to enhance their corrosion resistance.

Large volumes of concrete containers have only been considered recently in the UK disposal programme and have not yet been considered in detail in our research programme. As a result the text below provides an initial consideration. Further work is planned for the near future [10, task 711].

10.11.1 Corrosion during interim storage and GDF operations

Degradation of concrete containers is expected to be associated with carbonation of the cement and subsequent corrosion of the steel re-bars or inner containers and associated expansion and cracking. These processes are typically slow in benign atmospheric conditions (provided that the relative humidity, level of carbon dioxide and the chloride content of the environment are controlled).

The main ageing processes potentially able to affect the functionality of concrete containers are those which may have a significant impact on the mechanical properties of the cement and those potentially generating significant changes in their metallic components, including reinforcing re-bars, inner containers, and external cladding and plaques. Key processes include carbonation and corrosion of the steel re-bars and/or internal containers.

There is a wealth of research, practical experience and evidence from analogues demonstrating the durability of cement structures in atmospheric conditions, as discussed in Section 7.2.

Given the significant thickness of the cement layer considered in the design of concrete containers/overpacks it is likely that the carbonation front will reach the carbon steel re-bars only after relatively long periods [545], especially if the relative humidity is higher or lower than critical levels (Section 10.4.3).

Reinforcing re-bars and inner containers employed in concrete waste packages existing or planned in the UK are made of carbon steel, the material commonly used in most concrete structures. The corrosion behaviour of carbon steel in contact with cement has been discussed in Section 10.7.2. There is extensive experience from concrete structures made with carbon steel re-bars. Carbon steel is likely to corrode very slowly in cement, due to the formation of a protective layer of iron hydroxide. Significant corrosion can occur only if carbonation or significant ingress of chlorides occurs [254]. At the pH of a carbonated cement ($pH<10$) the formation of corrosion pits is generally observed, at sufficiently high chloride concentration. L'Hostis et al [545] characterised the corroded interface between rebar and concrete. They found a range of Fe(III) corrosion products and reported an expression for the pitting factor as a function of the depth of general corrosion [545]. In common with other systems, the degree of localisation decreases with increasing depth of general corrosion. Thus, as the concrete becomes progressively carbonated, the degree of localisation of corrosion decreases. If appropriate storage and handling procedures are followed, it is unlikely that significant amounts of chloride will reach the rebars. Problems with chloride-induced corrosion of re-bars are generally observed in outdoor environments and in proximity to the seashore, where marine aerosols are abundant [162, 283].

Any external metallic parts made with zinc-coated carbon steel are likely to withstand atmospheric corrosion for long times. Treatment of carbon steel surfaces with a zinc-based coating is widely used in the construction industry to increase the corrosion resistance of the steel. The zinc treatment offers the advantage of reducing the corrosion rate of the surface, as well as protecting the underlying metal from corrosion if the coating were to be mechanically damaged (galvanic protection). A few hundred microns of zinc (typical thickness of the coating) can offer protection for a number of decades, depending on the nature of the environment to which the coating is exposed. For example, for a coating of about 200 μm in thickness, lifetimes of 50-150 years are reported for rural environments [409]. Given that concrete containers are self-shielding, it is likely that any repair or maintenance of the coating can be applied prior to transport to the GDF in a relatively straightforward manner, if required.

10.11.2 Corrosion after sealing and closure of the GDF

Once in a GDF concrete containers/overpacks will continue to undergo carbonation (and corrosion of steel re-bars and any inner container) but will also be subjected to sulphate and chloride attack in the groundwater.

Despite their relatively wide use as container materials for ILW/LLW, there has been little work published internationally on the post-closure evolution of concrete containers, presumably because no credit is typically taken for their containment properties following disposal. Relevant work, however, has been carried out in the French programme [162]. In their programme, the main degradation processes considered for concrete containers following saturation of a GDF are leaching (referred to as hydrolysis in [162]), carbonation, sulfate attack and corrosion of the steel internal components (re-bars). The first processes are effectively precursors of the latter processes. The third and fourth processes are likely to lead to the formation of expansive phases and substantial cracking of the containers.

Leaching of the different mineral phases in concrete in contact with groundwater occurs sequentially and results in a slow evolution of the pore-water pH [162]. This process is also described in [2] in the context of the evolution of cement-based buffers/backfills. Initially, the alkaline and alkaline-earth oxides (hydroxides) maintain alkaline conditions with a high pH (with OPC-rich formulations, typically greater than pH 12.5). As the oxides are leached out, the pH is controlled by the presence of portlandite. Following the leaching of the portlandite, the hydrated calcium silicate (CSH) phases are transformed to silicates and a reduction in pH is observed. As the pore-water pH decreases from 12.5 to 10.5, brucite ($Mg(OH)_2$) and other phases dominate the concrete mineralogy. Finally, once all of the alkaline mineral phases have been leached from the concrete, the pore water pH will be near neutral. This process and the timescales over which it is expected to occur have been studied extensively in the UK in the context of the evolution of cement backfills [2]. Depending on the initial alkalinity and groundwater flow rates, the reduction of pH to values below 12.5[98] is expected to occur over very long periods [2].

Closure of the GDF will seal the disposal rooms from further ingress of atmospheric O_2 and CO_2. In contrast to the case of some metallic container materials, the availability of O_2 has a comparatively minor impact on the durability of a concrete container. Closure of a GDF, will limit (although not completely eliminate) further carbonation of the concrete, but will introduce the potential for chloride and, more importantly, sulfate attack (a reaction accompanied by an increase in volume, leading to cracking). Under saturated conditions, the rate of carbonation and sulfate attack will depend on the supply of carbonate and sulfate to the concrete.

The corrosion rate and the nature of the corrosion products of carbon steel re-bar under post-closure conditions have been studied in the French programme [546, 547]. Polished or pre-corroded steel coupons embedded in concrete have been exposed to aerated and de-aerated groundwater at temperatures of 25 °C and 50 °C for periods of up to 3 years. Corrosion rates were observed to decrease with time under all conditions. Interestingly, pre-corroded samples exhibited higher corrosion rates than initially polished samples and there was relatively little difference (within a factor of two) between the rates measured under aerated and de-aerated conditions. Under de-aerated conditions, an evolution in the nature of the corrosion products was observed. Corrosion products composed entirely of Fe(III) species were present after 12 months exposure (ferrihydrite/goethite), whilst some Fe(II) species were observed after 2 years exposure (magnetite). This suggests that, in a GDF, the

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[98] For scoping purposes, a pH level of 12.5 can be considered a value below which, in the case of oxic, chloride-rich groundwaters, localised corrosion can occur.

corrosion behaviour of the re-bar in concrete containers will evolve during the transition from the oxic to anoxic period (as well as with any subsequent changes in pH).

As well as evolution of the corrosion behaviour of carbon steel re-bar for ILW containers, the post-closure evolution of the corrosion behaviour of carbon steel in concrete overpacks is also of interest for the disposal of HLW and spent fuel. Kursten et al. [548] describe preliminary results of the monitoring of the corrosion rate of carbon steel within a half-scale mock-up of the Belgian ‘supercontainer’. Embedded corrosion sensors have been used to monitor the evolution of the corrosion rate under air-saturated conditions for periods of up to 160 days, with more measurements planned.

Overall, post-closure ageing of concrete containers will depend on the nature of the disposal environment. Various concrete pore-water evolution models have been developed, for example that of Berner [549]. The time required to degrade the containers is uncertain but could, in principle, be estimated. The rate at which these processes occur has not yet been evaluated in the context of typical UK groundwaters [10, task 711] so current durability estimates will require refinement and underpinning.

11 Evolution of HLW and spent fuel waste packages

This section integrates information presented in other sections in order to provide a description of the expected evolution of HLW and spent fuel waste packages during periods preceding and following closure of the GDF. The discussion focuses on periods following closure of the GDF since, for most HLW and spent fuel, packaging in a disposal container is expected to occur close to the time of disposal and evolution processes of the wasteform during periods preceding disposal are expected to be minimal.

The durability of containers manufactured from copper and carbon steel are discussed in greater detail, but alternative container materials (titanium, stainless steel and nickel alloys) are also discussed. The discussion on radionuclide release from the wasteforms considers UK-specific materials but also, for comparative purposes, materials studied in other programmes.

The description focuses on host rocks which will be subjected to resaturation and water flow (for example a higher strength host rock or a lower strength sedimentary rock). The evolution of waste packages in an evaporite environment would differ quite considerably from that presented in this section as there would be effectively no groundwater flow to either promote corrosion or to transport radionuclides from the GDF.

11.1 Degradation of HLW and spent fuel waste packages during the pre-closure period

The extent of degradation of HLW and spent fuel waste packages prior to closure of the GDF is expected to be modest.

The extent of degradation of HLW and spent fuel waste packages during periods preceding closure of the GDF will depend on the nature of the wasteform, the timing of containerisation, the design of the container and the environmental conditions inside and outside the waste container. Overall, for most waste types, evolution processes over these periods are expected to be modest.

11.1.1 Degradation of the wasteform before transfer to a disposal container

For HLW, corrosion of the vitrification canister is expected to occur relatively slowly in atmospheric storage conditions. For spent fuels, any evolution of the wasteform will depend on the type of fuel and waste management strategies.

It is informative to consider potential evolution processes of the wasteform during periods preceding transfer to a disposal container.

For HLW, corrosion of the vitrification canister is expected to occur relatively slowly in atmospheric storage conditions. Atmospheric corrosion rates of stainless steel at high temperature have not been evaluated in detail in our R&D programme, but are expected to be very low ($<0.1\ \mu m\ year^{-1}$). With this rate, the canister (5 mm thick) is likely to last for a very long time. As long as the vitrification canister remains in good condition, evolution processes of the HLW glass are not expected to occur, although the potential for long-term microstructural alteration has not yet been reviewed in detail in our programme [10, task 541].

For spent fuels, any evolution will depend on the type of fuel and the specific waste management strategy. For oxide fuels, it is likely that minimal degradation processes will occur on the cladding and underlying fuel during wet/dry storage. Any damage to the cladding during pond storage is likely to result in fuel with a lower IRF but a potentially higher matrix dissolution rate (Box 33). For metallic fuels (currently stored in water ponds), corrosion of the cladding and underlying fuel that started during pond storage periods may or may not continue, depending on the future waste management strategies. Evolution of the wasteform as currently assumed (disposal without further treatments beyond drying) is however unlikely to detrimentally affect the evolution of the waste package in the GDF (if anything, conditioning would result in fuel with a lower radionuclide inventory).

Box 33 Spent fuel with breached cladding ('failed' or 'damaged' fuel)

During the operation of nuclear reactors and the ensuing storage operations the cladding of spent fuels may breach. In general, cladding breach during reactor operations is very infrequent and is managed by the operators of reactors and storage facilities through appropriate means. A small amount of AGR fuel has however been subjected to corrosion and subsequent perforation of the fuel cladding during storage at Sellafield, due to contamination of pond water by chloride aerosols.

The impact of cladding breach during spent fuel management and disposal operations needs to be considered. In terms of dissolution behaviour after closure of the GDF, breaching of the cladding of wet-stored fuel may result in exposure of the fuel pellets to pond water, with the subsequent release of small amounts of radioactivity to the pond and, potentially, oxidation of the fuel matrix [75]. Following containerisation in a disposal container, reaction of the fuel with any available oxygen (dry oxidation) could also occur. Any release of radioactivity in cooling ponds is likely to lead to disposal in a GDF of a fuel with lower IRF_{GAP} than un-breached fuel. Any wet/dry oxidation of the fuel in ponds, or within a (dry) storage/disposal container, may however lead to some alteration of the fuel matrix and associated effects on its long-term behaviour. The limited data available (measurements of the release of elements such as ^{90}Sr and ^{144}Ce [550]) suggests that, beyond a loss of easily accessible radionuclides, the rate of fuel alteration in pond water is very slow. This indicates that any process of this type is likely to have a marginal effect on its leaching behaviour in the GDF. Conversely, the results of a study employing pre-oxidised fuel to evaluate the possibility of cracking affecting the surface area and the resultant leaching behaviour of the fuel indicated that these effects may be important [551]. Work to explore the likely evolution of failed fuel in pond water is planned for the future [10, task 549].

Beyond any effects on the fuel dissolution behaviour, an important consideration for this type of fuel is the likelihood of drying operations fully removing any entrained water. The water inventory assumed in [553, 554] takes into account the possibility that one or two fuel elements will be substantially waterlogged by water being present within the cladding.

11.1.2 External degradation of the disposal container

As waste is expected to be placed in containers shortly prior to disposal and disposal tunnels are expected to be promptly sealed after waste emplacement, external corrosion due to exposure to atmospheric or aerated conditions is expected to be modest. However, a good durability is expected in other scenarios.

Currently, containerisation of most of the HLW and spent fuel in disposal containers is expected to occur at the time of transport to the GDF and disposal operations are assumed to be carried out in such a way that disposal containers will be emplaced in deposition holes in contact with the buffer after relatively short periods of time. As a result, external corrosion due to exposure to atmospheric or aerated conditions is expected to be minimal.

It is however informative to consider the likely evolution of waste containers in alternative waste management and disposal scenarios. A specific study considered the potential effects of long periods of (dry) interim storage, or periods of emplacement in un-backfilled or improperly sealed tunnels (allowing ongoing access of oxygen to the disposal containers), on the evolution of the waste containers during the pre-closure and post-closure period

[552]. This study concluded that most container materials would be able to withstand scenarios of prolonged dry storage or exposure to un-backfilled or improperly sealed tunnels, provided that the environmental conditions and important QA aspects are adequately controlled.

Specific consideration needs to be given to existing PWR fuel, for which current plans are for packaging in multi-purpose containers and storage in atmospheric conditions. This approach may also be employed for HLW or other spent fuels. Multi-purpose containers will be designed with specific overpacks for the storage, transport and disposal period so that any degradation of the storage overpack will be not result in a degraded disposal container (that is, the disposal overpack will be fitted at the time of disposal). However, understanding the durability of the storage overpack is important to provide confidence in this approach. Work to evaluate the likely durability of storage overpacks and to identify suitable storage conditions is planned for the future [10, task 653].

11.1.3 Internal degradation of the disposal container

Internal corrosion in HLW containers is expected to be minimal, given the dry nature of the wasteform. Consideration of the realistic volume of water carry-over into a spent fuel container, together with consideration of helium generation and the temperature profile, does not challenge the structural integrity of the container.

Internal corrosion in HLW containers is expected to be minimal, given the dry nature of the wasteform.

The degree of internal corrosion of spent fuel containers will largely depend on the presence of any bulk water that, upon containerisation, may remain from previous pond storage operations. Our current expectation is that, before containerisation for dry storage and/or disposal, any spent fuel will be dried. However, it is possible that some spent fuels may be more difficult to dry (especially if waterlogged, see Box 33), or that it may be difficult to evaluate with confidence residual levels of water/moisture likely to be present after drying.

Specific studies of the potential effects of residual water associated with waterlogged fuel (a bounding case for dry fuel) have been carried out [553, 554]. According to such studies, the heat generated by radioactive decay inside waste containers is likely to lead to natural convection fluxes, resulting in a well-mixed vapour phase uniformly corroding all exposed internal steel surfaces. In the presence of amounts of water considered representative of waterlogged fuel, such processes would be responsible for a depth of general corrosion of the order of 10s of μm for internal 'steel' components [554] or, in the case of a carbon steel single shell [553], of the container shell itself. Some localisation of corrosion is likely to occur at the base of waste containers where, if the water content of the system was sufficient to cause condensation, a pool of liquid water may develop. In this case, corrosion could lead to a loss of a few 100s of μm of metal. In all cases, the amount of damage is likely to be trivial compared with corrosion allowances or the thickness of internal components [553, 554].

Given the nature of the environment inside waste containers, degradation mechanisms other than general corrosion (such as localised corrosion, SCC, or MIC) are not expected to occur, either on steel or on copper [553, 554]. The presence of high radiation fields is expected to generate oxidising conditions (possibly yielding high corrosion rates), but not to lead to the development of specific radiation-assisted corrosion mechanisms [553, 554]. Some HIC is expected to occur on steel surfaces due to the development of a hydrogen overpressure, but this is expected to be very modest [553, 554].

Whilst unlikely to lead to any structural concern, internal corrosion (and radiolysis) may result in pressurisation of the waste container. For BWR fuel, up to 600 g of water has been previously considered in the Swedish disposal programme as a pessimistic upper bound of the water inventory that may be associated with the fuel upon containerisation. In the case of spent AGR fuel, a water inventory of 1,400 g inside a disposal container is currently used as an estimate [553, 554]. Studies of the extent of pressurisation associated with a water inventory of the order of 1,400 g indicated that, over a period of years or decades, levels of H_2 pressurisation of the order of 0.2-0.5 MPa could develop, compared with levels of vapour pressurisation of the order of 0.1-0.2 MPa associated, over shorter timescales, with evaporation [553, 554]. Further work on the potential pressurisation of spent fuel containers, including considerations of accident conditions, is planned for the future [10, task 654].

Levels of internal pressurisation due to helium generated by alpha decay are expected to be low and to arise only over a very long period of time [258,259].

11.2 External degradation of HLW and spent fuel containers during the post-closure period

The durability of different container designs for the disposal of HLW and spent fuels has been evaluated in many international disposal programmes, based on expected degradation mechanisms and rates. Initial work has also been carried out in the UK to evaluate the likely suitability of different materials and to estimate the durability of specific designs in generic UK conditions.

This section presents estimates of the durability of container designs for HLW and spent fuel in geological conditions that might be expected in the UK, largely based on studies carried out in other countries. Additional information can be found in [411, 412] and, to a lower extent, in earlier desk-based studies [555, 556, 557]. Work to refine this analysis and to develop models for the evolution of the EBS is planned for the future [10, task 652].

The section focuses primarily on copper and carbon steel containers, which are currently primary candidates for the manufacture of waste packages. One of the main factors driving the choice of copper and carbon steel is the predictability of their corrosion behaviour in the long term. Direct measurements of corrosion rates over relatively short periods (years to decades) are supported by evidence available from man-made and, in the case of copper, natural analogues. For these materials ensuring a good durability and, even more importantly, a relatively high degree of confidence in durability estimates, relies on the absence (or suitable engineering mitigation) of environmental stressors known to result in specific corrosion or EAC processes. In the case of copper in benign conditions (low sulphide concentrations), typical corrosion allowances are sufficiently small to allow designers to consider it effectively a corrosion-resistant material[99].

In the UK the geochemical conditions arising in potential disposal site(s) are currently not known. However, if similar buffers and container designs to those being developed elsewhere are used, the durability of waste containers may be similar to that reported in other countries. In particular, for designs based on copper and carbon steel, it is important to note that:

- the latest assessments of the durability of copper-based designs suggest that the main factor controlling the rate/depth of corrosion is the rate of transport of sulphide present in the groundwater through the buffer [67, 89, 428]. Such analyses suggest

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[99] In environmental conditions relevant to waste disposal, copper is not protected by a passive film and behaves like an active material, which would require it to be designed with a suitable corrosion allowance. At this stage of the disposal programme, in the absence of information about the geochemical conditions at a disposal site, in the design of the Variant 1 disposal container, we assumed that any corrosion allowance would be sufficiently small to not require specific consideration in the design process. From a scientific prospective, however, copper is better consider as a corrosion-allowance material, more similar to carbon steel than to inherently corrosion-resistant materials such as stainless steel or titanium.

that the durability of copper containers is largely dependent on the properties of the buffer, and in particular its transport properties.

- the corrosion behaviour of carbon steel in reducing, near-neutral pH conditions (for example, in the presence of a bentonite buffer) is likely to be only slightly dependent on the specific groundwater chemistry [460]. This suggests that, in a number of plausible scenarios, the durability of carbon steel containers is unlikely to depend strongly on the specific geochemical conditions at the site(s).

11.2.1 Copper containers

Durability greater than 100,000 years can be obtained with a copper-based design provided that a clay buffer is used, so that microbiological effects can be excluded due to sufficient swelling of the buffer.

The durability of copper containers for HLW and spent fuel has been evaluated by a number of waste management organisations. Table 19 summarises evaluations of their likely durability from studies carried out in Sweden, Finland, Canada, Switzerland and Japan. In geochemical conditions in which the use of copper containers has been proposed, their durability in a bentonite buffer is generally predicted to be greater than 100,000-1,000,000 years [89, 363, 428]. The information is taken from the latest published sources. The reported values do not necessarily represent definitive estimates since, in most countries, R&D is still ongoing.

The durability estimates presented are based on a corrosion-allowance considered in the design of the waste packages, on a long-term general corrosion rate, and on a maximum amount of damage associated with the inventory of specific species in the EBS (oxygen and sulphide). The possibility for corrosion to produce localised damage is considered in the design of the corrosion allowance through the use of estimates of a maximum pit depth or surface roughening, while the potential for MIC at the surface of the waste container is excluded due to the use of compacted bentonite. Durability estimates have been purely based on corrosion processes and assume that creep deformation is unlikely to lead to rupture of the waste container and that coupling between mechanical and corrosion processes (specifically, SCC) is expected to be insignificant.

The general corrosion rate in anaerobic conditions depends on the rate of transport of the main corrosive species (sulphide) to the container surface. The durability estimates described above generally consider groundwater sulphide concentrations of less than 1 ppm (that is, <1 mg L^{-1}) and the presence of an intact bentonite buffer providing diffusion control over the transport of sulphide. Higher corrosion rates and lower resulting durability is expected in the case of high sulphide groundwater concentrations and in the absence of effective diffusive control provided by the bentonite. Studies from the Japanese programme indicate that, in a compacted bentonite-sand mixture, after one year of exposure, general corrosion rates as high as 0.6 μm $year^{-1}$ and 10-15 μm $year^{-1}$ could be obtained at high temperature (80 °C) with sulphide concentrations of 0.001 M, 0.005 M and 0.1 M respectively (about 30, 150 and 3,000 ppm), resulting in a maximum durability of the order of 50,000 years (with 30 ppm sulphide) [434][100]. The sulphide concentrations employed in these tests are not however representative of typical groundwaters expected in disposal systems (typically less than 1 ppm). Additionally, results from the Mini-Can experiment [444, 447] (see also Box 28) indicated that corrosion rates are expected to be low even in the

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[100] The thickness of bentonite used in these experiments (and hence the diffusional length of sulphide) is not clear from the reference but, if the same as that reported in previous work, would have been about 6 mm, which is much smaller than currently envisaged in relevant disposal concepts (about 70 mm).

presence of relatively high sulphide concentrations and in the absence of any mass-transport limitation by compacted bentonite in the system. In particular, a corrosion rate as low as 0.15 μm $year^{-1}$ was found in the presence of sulphate reducing bacteria and without compacted bentonite [444, 447]. With this corrosion rate, 10 mm of copper would last more than 60,000 years.

Detailed analysis of the durability of the Variant 1 container (copper-based) has not yet been carried out in the UK programme. However, based on the type of analysis performed by SKB [67, 89] it is possible to develop a simplified assessment of the potential lifetime of a copper container in a UK GDF. For current purposes, it is assumed that the Variant 1 container is disposed of in a GDF with highly compacted bentonite backfill, similar to that envisaged in Sweden and Finland.

Based on the exclusion of all corrosion mechanisms other than general corrosion driven by the flux of sulphide through the buffer, and assuming that any microbial activity remote from the container surface is such that the concentration of sulphide at the container surface is limited, and that pyrite in the rock does not constitute a substantial source of additional sulphide, a simple calculation can be used to estimate the likely durability. With a sulphide concentration in the groundwater of less than 0.1 mg L^{-1} (0.1 ppm, equivalent to 3.0×10^{-6} mol dm^{-3}), considered representative of the UK [70, 71], a diffusion path length (equivalent to the minimum thickness of bentonite) of 25 cm, and an effective HS^- diffusivity in saturated bentonite of 10^{-7} cm^2 s^{-1}, the steady-state flux of HS^- is 1.2×10^{-17} mol cm^{-2} s^{-1}, equivalent to a corrosion rate of less than 0.0001 μm $year^{-1}$ (0.1 nm $year^{-1}$) based on the expected stoichiometry of the sulphide film (Cu_2S). Based on this corrosion rate, in all scenarios, the lifetime of a 50-mm-thick copper container will be greater than 1,000,000 years. Scenarios involving the loss of buffer mass due to chemical erosion of the bentonite by dilute glacial meltwater could however lead to significantly shorter lifetimes.

At higher sulphide concentrations, for example 20 or 200 ppm, the same calculation would lead to a corrosion rate of 0.01 μm $year^{-1}$ and 0.1 μm $year^{-1}$ respectively (that is, 10 mm of copper would be lost over 1,000,000 and 100,000 years respectively). The results reported in [434] would indicate a substantially shorter lifetime. However, in these experiments, a bentonite thickness much lower than that typically envisaged for the EBS may have been used.

11.2.2 Carbon steel containers

A durability of at least 10,000 years has been estimated for carbon steel containers in many international programmes and is based on specific studies carried out in the UK. Such durability can be achieved with both bentonite and cement buffers.

The durability of carbon steel containers emplaced with a bentonite buffer (Table 20) is generally predicted to be lower than that of copper containers. For carbon steel (and cast iron) containers, in anoxic, near-neutral pH conditions (bentonite) general corrosion processes are expected to be dominated by the development of corrosion products on the metal, rather than by the presence of specific aggressive ions. In these conditions, the corrosion rate is expected to depend only moderately on the chemical composition of the groundwater, with corrosion rates generally of the order of 1-10 μm $year^{-1}$.

Considering typical corrosion allowances (>10 mm), and including estimates of the degree of localisation of corrosion (pitting factor), containers are expected to last at least 1,000 years (Japanese programme[101]) and possibly much longer (generally more than 10,000 years).

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[101] Estimates carried out in the Japanese programme are likely to be particularly conservative, since they assume both a high corrosion rate (10 μm $year^{-1}$) and a small corrosion allowance. The corrosion allowance is based on the requirement to ensure dose rates at the surface of waste containers (at the

These estimates are either based on the ability to exclude MIC through the use of sufficiently compacted bentonite or on the assumption that its overall effect is likely to be small or bounded by the underpinning data (such as from corrosion in soils).

If passivating layers are formed (at pH>10 [474], such as those expected in the presence of a cement buffer/backfill) corrosion processes are expected to be substantially slower. In relatively long-term experiments (up to 5 years exposure), the corrosion rate of carbon steel in solutions simulating fresh cementitious pore water (pH 13.4) at 80 °C is reported to be in the range 0.2-0.8 μm year^{-1} [476], with lower rates measured for longer exposure periods. For a cement-buffered EBS, estimates of container ('overpack') durability in the Belgian programme indicated that the container is likely to remain intact at least for the period over which alkaline conditions are likely to prevail in the EBS. Modelling calculations suggest that the cement porewater will maintain a high pH (>12.5), and hence the overpack will be in a passive state for a period of at least 80,000 years [364]. However, in the Belgian disposal concept chloride concentrations in the groundwater (controlling its corrosivity) and the water flow through the GDF (controlling the timescales over which high pH is expected) are expected to be low.

In the case of disposal in bentonite, the coupling between corrosion and mechanical properties may become important and the potential for HIC needs to be taken into account. Studies were carried out in Switzerland [82] and in the UK [417, 418] to evaluate the effect of mechanical and embrittlement processes on container durability. The UK study [417, 418] focused on the durability of the Variant 2 design (minimal wall thickness 75 mm at the closure weld) and considered an illustrative baseline scenario, as well as sensitivity to key parameters. The study indicated that, assuming a corrosion rate of 1 μm year^{-1},a corrosion allowance based on mechanical considerations (rather than radiation-effects), and mechanical stresses typically expected in a GDF not subjected to rock creep (a high strength host) the durability of the waste container in a variety of scenarios was generally dictated by the loss of wall thickness associated with general corrosion, leading to durability of the order of 50,000 years. This is illustrated in the FAD diagram in Figure 50, which shows the evolution of the ratio of the stress to the yield strength (L_r) and the ratio of the stress intensity factor to the fracture toughness (K_r) as a function of time (see Box 26 for further details about the methodology). With the corrosion rate, corrosion allowance and mechanical stresses assumed, failure due to plastic deformation (L_r>1) is likely to occur at times greater than 55,000 years even in the presence of 10 mm deep defects in a number of locations. Failure through brittle fracture (K_r>1) or mixed brittle/plastic failure was only found in the presence of defects located in locations subjected to high tensile stresses (in the load scenario assumed, the container base) and in the presence of high additional external loads associated with glaciation (in the illustrative calculations shown in Figure 50 assumed to occur around 50,000 years, which is considered unrealistic for the UK [8]). Qualitative considerations on the sensitivity of the time and mode of failure to key parameters (corrosion rate, defect size and external loads, including lithostatic loads that may be associated with host rocks subjected to creep) indicated that high durability (greater than 10,000 years) is likely to be achieved in all but few particularly challenging scenario (deep and/or extended embedded defects).

Corrosion of carbon steel or cast iron containers will result in the generation of hydrogen gas. The impact of such gas on the GDF is discussed in [5]. One way of potentially mitigating the potential for corrosion and resulting gas generation of carbon steel containers is to employ a metallic coating (for example made of copper or titanium). Beyond increasing

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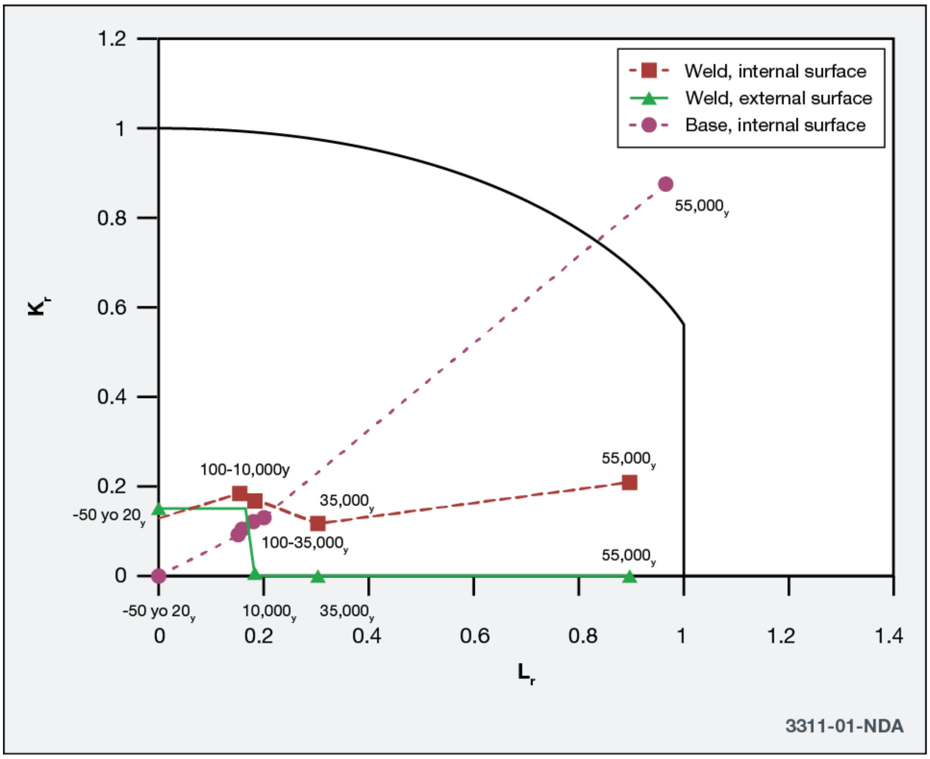
time of disposal) below thresholds expected to be associated with the onset of radiation effects on corrosion (1 Gy h^{-1}). By the time the corrosion allowance is lost (1,000 years), however, dose rates would have decreased to values for which any effect on corrosion rates are expected to be negligible.

its corrosion resistance, depending on material and manufacturing route, such coating (particularly if made with a ductile material like copper) may also present good resistance to mechanical failure [408], thus resulting in a very durable waste container.

Figure 50: Use of FAD to illustrate the proximity of a Variant 2 carbon steel container to plastic collapse or brittle failure at different times during the post-closure period in an illustrative scenario for a UK GDF [418][102].



11.2.3 Containers manufactured from passive materials

It may be possible to obtain a very high durability with a variety of passive materials (titanium, stainless steel and nickel alloys), provided that specific corrosion mechanisms can be ruled out through the selection of optimised alloy and buffer material.

Estimates of the durability of HLW and spent fuel containers based, on the use of corrosion-resistant materials (typically titanium or nickel alloys) in a variety of international programmes, are reported in Table 21 and Table 22. In contrast to the behaviour of the active container materials, beyond (very slow) general corrosion, relevant forms of corrosion for these materials include localised corrosion and EAC. All classes of passive materials under consideration are generally susceptible to some form of localised corrosion (particularly crevice corrosion) and EAC (both SCC and HIC), although the material grade can be selected so that the most relevant degradation mechanisms under GDF conditions

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[102] The scenario assumes the presence of defects (10-30 mm deep) in regions of high tensile stress (the weld and the base in the assumed loading scenario) and the onset of glacial loading at 55,000 years after closure. The latter assumption is unrealistic for the UK but was used to develop the methodology. In the baseline scenario considered (higher strength host rock with relatively low lithostatic loads up to the glaciation event) container breach is likely to occur due to general corrosion and eventual plastic collapse at the time of load increase due to the glaciation. In this case, the durability is largely dominated by the general corrosion rate, assumed to be 1 μm year^{-1}.

are not viable. This is the case for highly corrosion resistant titanium alloys (such as grade 7) and nickel alloys (such as ‘Hastelloy C-22’).

In contrast to the case of active materials, analogues are not available to support estimates of durability over long time periods. For these materials, ensuring a good durability and confidence in durability estimates relies on the absence, or engineering mitigation, of environmental stressors known to result in specific corrosion or EAC processes. In this case a (small) corrosion allowance and a (very slow) general corrosion rate may be identified for the purposes of lifetime assessments, even if, in the absence of suitable analogues, confidence in the estimates is likely to be more limited than in the case of active materials (such as copper and carbon steel).

The estimates presented in Table 21 and Table 22 show that, even with relatively low grade alloys (for example, titanium grade 2), a substantial durability may be achieved. However, in some cases early failure is possible if specific processes cannot be ruled out, particularly crevice corrosion and HIC. With the most resistant alloys (for example the nickel alloy ‘Hastelloy C-22’ and titanium grade 7) very high durability has been estimated in conditions that would otherwise be corrosive for active materials (such as permanently aerobic conditions). Whilst not directly relevant to disposal in a GDF, this illustrates that if specific degradation mechanisms can be excluded through alloy selection very high durability could be achieved.

Additional work on the use of corrosion-resistance materials (particularly titanium) for the disposal of HLW and spent fuels is planned in the UK programme [10, task 667].

Table 19: Summary of published corrosion assessments for copper HLW and spent fuel containers

Country	Host formation	Uniform Corrosion	Localised Corrosion	SCC	MIC	Predicted Lifetime
Sweden/Finland [89] (50 mm shell)	Granite	<1 μm due to air oxidation during storage. Maximum of 500 μm due to initially trapped O_2. Maximum 114 μm due to pyrite in deposition hole. Maximum 0.6 mm in 10^6 years due to sulfide in groundwater for the case of intact buffer.	±50 μm due to surface roughening.	SCC not included because of limited tensile stress, absence of SCC agents, insufficiently positive E_{CORR}, and inhibitive effects of Cl^-.	Maximum of 3 mm in 10^6 years due to SRB activity in the buffer and backfill.	$>10^6$ years
Canada [428] (3-5 mm layer)	Granite	0.17 mm due to trapped O_2.	0.1 mm due to surface roughening.	SCC not included because of limited period of stress, absence of SCC agents, E_{CORR} below threshold value, and inhibitive effects of Cl^-.	1 mm in 10^6 years due to diffusion of sulphide across the bentonite buffer.	$>10^6$ years
Japan [362] (none given)	Generic	9-13 mm in 10^3 years, depending on repository design.	18-26 mm in 10^3 years based on pitting factor of 3, 2 mm in 10^3 years based on extreme-value analysis.	Maximum concentrations of ammonia, nitrite and acetate less than threshold concentration.	SRB assumed to reduce all sulfate to HS^-.	None given
Switzerland [363] (50 mm shell)	Crystalline rock, Opalinus Clay	<100 μm due to O_2. 0.9 mm in 10^5 years due to sulfide.	<100 μm best estimate due to surface roughening but 5 mm based on conservative pitting factor of 5.	SCC not included because of limited period of stress, absence of SCC agents, general lack of oxidant and inhibitive effects of Cl^-.	Not included due to absence of microbial activity in compacted bentonite.	$>10^5$ years

Table 20: Summary of published corrosion assessments for carbon steel HLW and spent fuel containers

Country	Host formation	Uniform corrosion	Localised corrosion	Environmentally assisted cracking (SCC/HIC)	MIC	Corrosion prediction
Japan [362] (190 mm shell, 40 mm corrosion allowance)	Generic	Aerobic period 0.3-1.8 mm, based on O_2 mass balance. 10 μm·year^{-1} during the anoxic period.	Additional pit depth 4.1-10.0 mm during aerobic period. Pitting factor of 2, corresponding to 10 mm pit in anoxic period.	No H embrittlement, sulphide stress cracking, or HIC based on threshold [H] arguments.	MIC taken into account during anoxic period based on conversion of SO_4^{2-} to HS^-.	24.6 mm, 30.7 mm, and 31.8 mm in 1000 years for in-room, in-borehole (higher strength rock) and in-borehole (lower strength rock), respectively.
Switzerland [363, 558] (150 mm wall thickness)	Opalinus Clay	<1 mm during the aerobic phase. Corrosion rate 1 μm·year^{-1} during the anoxic period. 0.02 μm·year^{-1} due to HS^- diffusion, including an allowance for localised corrosion based on an assumed pitting factor of 5	Pitting corrosion during aerobic phase = 10 mm based on empirical pitting factor.	No SCC based on absence of cyclic loading and aggressive species. No H-related failures due to absorbed [H] below threshold concentration	No MIC based on the absence of microbial activity in compacted bentonite.	~12 mm in 1000 years. ~21 mm in 10,000 year.
Canada [68] (100 mm corrosion allowance)	Sedimentary rock	0.087 mm due to O_2 during aerobic phase. Corrosion rate of 0.1-1.0 μm·year^{-1} during the anoxic period.	Depth-dependent pitting factor.	No SCC based on absence of cyclic loading and aggressive species. No H-related failures due to absorbed [H] below threshold concentration.	MIC not included because of use of 100% bentonite in repository and assumption of no microbial activity in the host rock.	9-34 mm in 10,000 years 34-175 mm in 10^5 years depending on anoxic uniform corrosion rate.
France [559] (55-110 mm wall thickness)	Sedimentary rock	Aerobic period <1 mm Anaerobic corrosion rate 2-5 μm year^{-1}.	Not considered.	Not considered.	Not considered, although recent studies suggest the effect would be limited.	55 mm in 15,000 years (HLW containers). 110 mm in 30,000 years (SF containers).

Table 21: Summary of published corrosion assessments for HLW and spent fuel containers manufactured in titanium

Container material	Host formation	Uniform corrosion	Localised corrosion	Environmentally assisted cracking (SCC/HIC)	MIC	Corrosion prediction
Canada [365] Titanium Grade-2 disposal container (6.35 mm shell, 4.2 mm corrosion allowance)	Granite	Not included in lifetime assessment model.	Temperature-dependent crevice corrosion rates based on empirical data.	Containers that do not fail by crevice corrosion fail instantly by HIC at T ≤30°C.	Not considered	0.23% of containers fail in first 1000 years due to initial defects and HIC. Majority (>97%) of containers fail by crevice corrosion between 1200 and 7000 years.
Japan [362] Titanium disposal container	Generic	2.8 µm after 1000 yr based on empirical data.	Assumed not to occur because of suitable choice of alloy.	No HIC as estimate of absorbed H (11-16 ppmw) is less than the critical concentration of 500 ppmw.	Not considered	>1000 years.
USA [366] Titanium Grade-7 drip shield (permanently aerobic)	Tuff	Temperature-dependent rate derived from experimental data.	Ti-7 considered to be immune to localised corrosion.	SCC prediction based on the periodic rupture of a passive film at the crack tip (‘slip dissolution model’) HIC not considered, as assumes that no H forms under aerobic conditions.	Ti-7 assumed to be immune to MIC	Failure between 270,000 and 340,000 years for nominal scenario.
USA [560] Titanium Grade-7 drip shield (permanently aerobic)	Tuff	Weibull distribution of general corrosion rates based on empirical data.	Not considered.	HIC due to absorbed H, critical [H] in range 100-600 ppmw.	Not considered	First failure after approximately 10,000 years due to HIC.
USA [561] Titanium Grade-7 drip shield (permanently aerobic)	Tuff	Temperature-dependent rate derived from experimental data.	Ti-7 considered to be immune to localised corrosion.	HIC due to absorbed H, critical [H] of 1000 ppmw. Assumed to be immune to SCC.	Ti-7 assumed to be immune to MIC.	Assessment based on general corrosion. Apart from ‘juvenile failure’, first failure after 40,000 years. Incidence of failure after 10^6 years was 66%.

Table 22: Summary of published corrosion assessments for HLW and spent fuel containers manufactured in nickel alloys

Container material	Host formation	Uniform corrosion	Localised corrosion	Environmentally assisted cracking	MIC	Corrosion prediction
USA [366] Hastelloy 22 disposal container (permanently aerobic)	Tuff	Temperature-dependent rate derived from experimental data.	Initiation based on critical crevice repassivation potential criterion. If initiation occurs, crevice propagates at constant rate.	SCC prediction based on the periodic rupture of a passive film at the crack tip (‘slip dissolution model’), followed by crack propagation with stress-intensity dependent crack growth.	Enhancement factor for general corrosion of between 1 and 2 for RH above a threshold value between 75% and 90%.	Minimum container lifetime 300,000 years.
USA [561] Hastelloy 22 disposal container (permanently aerobic)	Tuff	Temperature-dependent rate derived from experimental data.	Initiation of crevice corrosion based on multiple criteria: (i) presence of aqueous phase, (ii) specific water chemistry, (iii) prior drip-shield failure, (iv) temperature greater than threshold value. If initiation occurs, propagation assumed to decrease with time (‘stifling’).	Initiation of SCC based on multiple criteria: (i) presence of suitable aqueous phase, (ii) $E_{CORR} > E_{SCC, crit}$, (iii) surface tensile stress must exceed threshold value. If SCC initiates, crack growth assumed to be fast.	Enhancement factor for general corrosion of between 1 and 2 if T is below threshold for microbiological activity (corresponding to water activity of 0.96).	Assessment based on (microbiologically-enhanced) general corrosion. Apart from ‘juvenile failure’, first failure after 336,000 yrs. Incidence of containers failed after 10^6 years was 15%.

11.3 Degradation of metallic components of the wasteform

Upon exposure to groundwater, the stainless steel canister containing the HLW and the cladding of oxide spent fuel are likely to undergo relatively rapid localised corrosion processes. Even after perforation, these components may provide a transport barrier to the release of radionuclides. In the case of metallic fuel, degradation of the cladding will be particularly fast and it will not provide a transport barrier. Corrosion of structural steels inside the waste container will result in generation of hydrogen gas.

Once the waste container has been breached, groundwater will access the internal furniture of the waste container, interacting with the HLW vitrification canister or spent fuel cladding and other assembly components.

Corrosion of structural steel components or internal furniture of the disposal container (carbon steel or cast iron) will result in the generation of hydrogen gas. The impact of such gas on the GDF is discussed in [5]. Amongst other effects, hydrogen accumulating in the EBS will have a beneficial effect on the stability of oxide spent fuels (see below).

Localised corrosion of the stainless steel HLW vitrification canister and of the stainless steel cladding of oxide spent fuels is likely to occur once these components come into contact with the groundwater. Conversely, localised corrosion of Zircaloy or failure by another mechanism (for example, HIC) may or may not occur over relatively long times. If degradation occurs, it may lead to a relatively rapid perforation of such components. For both stainless steel and Zircaloy cladding, the nature of degradation processes is such that, even when perforated, the component is likely to provide a transport barrier. This may be particularly important in determining the leaching behaviour of the wasteform since its long-term dissolution behaviour will depend on the chemistry generated in close contact with it.

The very small quantity of activation products present in the HLW vitrification canister and the low rates of general corrosion are such that any radionuclide release associated with this process is likely to be negligible. However, in the case of oxide spent fuels, corrosion of the cladding and other fuel assembly components is likely to lead to the release of specific activation products (for example, ^{63}Ni). Typically, general corrosion rates estimated for stainless steel and Zircaloy in reducing conditions are of the order of 0.01 μm year^{-1} or less. Based on such a corrosion rate, the release of radionuclides from fuel cladding (typically about 0.3-0.5 mm thick) would take place over periods of the order of tens of thousands of years [184].

In the case of fuel clad with Magnox metal (such as some metallic fuel), corrosion of the cladding is expected to proceed rapidly in a GDF, leading to a rapid exposure of the underlying fuel (we estimate within a few decades). Cement-based buffers could be used to reduce the corrosion rate of the cladding (see Section 8.2.4). However, given its initial state (in many cases substantially corroded) and the likelihood in a UK GDF of chloride-rich groundwaters (substantially increasing the corrosion rate), it is likely that any cladding left on the fuel would still degrade rapidly in the context of long-term safety assessments.

11.4 Radionuclide release from vitrified HLW

Upon exposure to groundwater, vitrified HLW will start leaching radionuclides at a rate dependent on the amount of cracking, the glass formulation and presence of other EBS components.

Once groundwater has perforated the waste container and the vitrification canister, the vitrified HLW product will come into contact with the groundwater and will start leaching radionuclides. Whilst the residual rate is likely to be responsible for the release of the vast majority of the radioactive inventory over time, the initial (forward) rate is likely to result in a relatively small (but significant) release of radioactivity over a relatively short period (decades or centuries). For some HLW, micro-segregation of soluble phases may lead to the release of relatively enhanced levels of specific radionuclides.

In many international programmes the glass surface area (dependent on the cracking factor) and the dissolution rate have been used to estimate the likely release over time for radionuclides contained in HLW, either through simple calculations (for example, assuming constant dissolution rates and accompanying congruent release of radionuclides), or through more complex models (generally focusing on the likely evolution of the dissolution rate with time). However, even more complex models may present a simplification of the actual behaviour of the systems. In reality, the rate of release of radionuclides will depend on whether they are likely to behave similarly to soluble components (such as boron) or are strongly retained in the altered gel layer and secondary phase products that will form on the surface of the glass (such as aluminium and magnesium).

A substantial amount of information is available for glass compositions containing calcium (relevant to the French and Belgian disposal programmes). This information is important in providing a good mechanistic understanding of the likely dissolution behaviour of HLW and the main factors affecting it, but may only be partially relevant to the behaviour of UK HLW compositions. Work is currently ongoing to evaluate the behaviour of UK-specific glass compositions (containing magnesium) and to compare it with that of other, well-researched glasses.

11.4.1 Glass dissolution: Calcium-rich compositions (non-UK)

The release of radionuclides from the dissolution of glass formulations rich in calcium is expected to occur over hundreds of thousands of years. Up to about 1% of the inventory may be released during shorter periods.

Similar approaches to the evaluation of glass durability are used in a variety of international programmes (the Belgian, Japanese and Swiss programmes). Estimates are based on constant long-term release rates (in relevant temperature and geochemical conditions) and surface areas estimated on the basis of the amount of cracking developed upon solidification. A more refined approach is employed in the French programme (see Box 34).

A summary of glass package durability data from international programmes has been collated in [566] and is summarised in Table 23. Glass durability of the order of hundreds of thousands of years was estimated in the French [162] and Swiss [562] programmes. Conversely, lower durability has been estimated in the Belgian programme [563] and, in the past, in the Japanese programme [564]. The differences between the R7T7 data used in the Swiss/French and Belgian safety cases are due to the fact that the Belgian data have been obtained from experiments of glass in contact with Boom Clay, which acts as a sink for silica and accelerates the residual rate. In the absence of clay in direct contact with the glass, the glass durability is in the range of hundreds of thousands to a million years (fractional releases of 10^{-6} to 10^{-5} year^{-1}) for R7T7-type glasses.

Short-term releases of the radioactivity associated with the initial rate have been considered explicitly in some programmes. A release of about 1% of the radioactive inventory was estimated for French glasses, based on the maximum sorption capacity of ferrous corrosion products likely to be present in a disposal container (Box 34). Recent studies of glass dissolution in the presence of metallic iron [565] (see also Section 5.3) indicated that the formation of iron-silicate secondary phases may also contribute to prolonging the dissolution of HLW glasses at faster rates. If this is the case, then a larger proportion of the radioactive inventory could be releasable at a faster rate. However, in this case, the rate of glass dissolution and the extent of short-term radionuclide release may be linked to the corrosion rate of the container steels. The slow rates of steel corrosion under

GDF conditions (see Sections10.7 and 10.9) may limit both the sorption capacity of ferrous corrosion products available and the extent of secondary phase formation in the short-term.

Table 23: Summary of HLW glass durability for (non-UK) calcium-rich compositions (based on data collated in [566])

Glass Type	Durability (Years)	Comments[1]
R7T7 (France [162])[2]	>300,000	Based on data from a range of leaching experiments in water and buffer solutions covering the full compositional range of R7T7-type glasses with variations in temperature (50 to 180 °C) and pH (7.0 to 10.5) [534]. The dissolution rate, on a mass-loss basis, is temperature dependent and accounts for the expected cooling from 50 °C at 4,000 years (on container breach) to 25 °C at 10,000 years post-closure. A cracking factor of 40 was assumed for the reference case (constant surface area of 68 m^2).
R7T7 (Switzerland [562])	530,000	Based on a constant linear corrosion rate, with a cracking factor of 15. Leaching data in deionised water at 90 °C.
R7T7 (Switzerland [562])	215,000	Based on a constant rate of mass loss, with a cracking factor of 15 (constant surface area of 25.5 m^2). Leaching data in deionised water at 90 °C.
R7T7 and PAMELA (Belgium [563])	20,000 - 1,000,000	Based on in situ experiments in Boom clay at 16 °C, with a cracking factor of 5-27, assuming a constant linear corrosion rate.
P0798 (similar to R7T7) (Japan [564])	66,000	Based on constant rate of mass loss using data from a number of international programmes prior to 1991, extrapolated to 60°C, and assuming a cracking factor of 10 (constant surface area of 17 m^2).

Notes:

(1) Similar sizes of vitrification canister are used in the UK and overseas. These assessments are based on dissolution of a cylindrical glass block of radius 0.215 m with a glass density of 2.7 g cm^{-3} and an external geometric surface area of 1.7 m^2. Two methods have been used to estimate glass wasteform lifetimes: (i) constant mass loss (which assumes a constant surface area and cracking factor); (ii) a constant linear corrosion rate along the radius of the cylinder. The latter method gives a greater lifetime by a factor of about 2.5.

(2) Note that, in the model, about 1% of the glass is estimated to dissolve in the first decades to a few a hundred years (duration depending on the pH and temperature) during an initial fast dissolution (V_0) phase. This is equivalent to an IRF of 1%. The residual dissolution rate (V_r phase) is temperature dependent, but independent of pH in the range 7.0 to 10.

Box 34 The French V_0-V_r model for the long-term behaviour of R7T7 waste packages

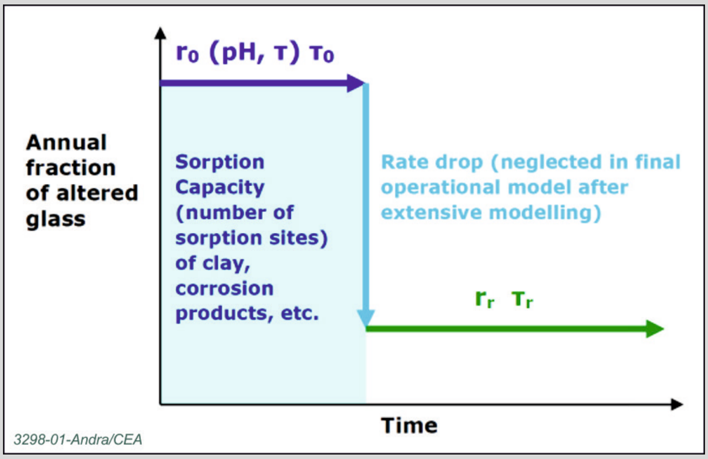
For their 2005 assessment [162], ANDRA adopted a simple, but conservative, source-term model for radionuclide release from HLW that reflects the phenomenological dissolution behaviour of R7T7-type glasses. The approach was considered to be more realistic than a simple constant source term-model adopted in earlier international assessments.

The V_0-V_r operational model (shown schematically in Figure 51) takes a two-stage approach, assuming that the glass will dissolve first at a relatively high initial rate (V_0), until the surrounding EBS medium becomes saturated with silicon released from the glass, and thereafter at a slower, residual rate (V_r) [93, 162]. The transient rate-drop regime is not represented in the model. The initial rate is dependent on pH and temperature, the residual rate on temperature only. The surface area of the glass is represented by the geometric surface area of the glass wasteform (*S*) multiplied by an effective fracture ratio / cracking factor (τ_0, τ_r), which accounts for the higher surface area of the glass available for dissolution due to cracking of the glass wasteform and the extent to which cracks contribute significantly to glass dissolution (it has been found that only the most accessible cracks contribute to glass dissolution during the initial rate regime, whereas even fine cracks contribute during the residual regime). The glass is assumed to be homogeneous and both glass dissolution and the release of radionuclides to be congruent at all times.

In this model, the extent of glass dissolution during the V_0 phase is controlled by the sorption capacity of the EBS, whilst the duration of this phase is determined by pH and temperature. For the 2005 assessment [162], only the sorption capacity of the corrosion products arising from the degradation of the packaging container was taken into account. This was determined to account for about 1% of glass dissolution within a few decades and assumed to occur within a few hundred years of glass exposure to groundwater.

In the reference calculations, failure of the packaging was assumed to occur about 4000 years after disposal, at which time the near-field temperature had dropped to ~50 °C; the temperature was expected to continue to decrease, stabilising at 25 °C after 10,000 years. The resulting glass package lifetime was estimated to be at least 300,000 years.

Figure 51: Schematic of the French model for HLW dissolution [93, 162]. The notation r_0, r_r has been used instead of V_0, V_r for the dissolution rates



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11.4.2 Glass dissolution: Magnesium-rich compositions (UK)

The release of radionuclides from the dissolution of glass formulations rich in magnesium is expected to occur over tens of thousands of years. Up to about 1% of the inventory may be released during shorter periods of time.

A study [566] was carried out to critically assess the appropriateness of durability estimates initially employed in the 2010 DSSC (based on laboratory-based and in-situ studies on Belgian glass compositions [563, 567]) and to suggest refined estimates for the main UK HLW products (Magnox and Blend glass). Based on extrapolation of data produced for a 25% incorporation Magnox glass simulant after a 12 year leaching test in deionised water at 90 °C [106] to temperatures closer to those expected at the time of container perforation (30 °C), this study [566] estimated[103]:

- a maximum durability of the order of 1,000,000 years based on a long-term dissolution rate of 4 10^{-5} g m^{-2} day^{-1} at 30 °C and a cracking factor of the order of 40 (used in the French programme to include fine cracks); a durability of 1,000,000 years is equivalent to a normalised dissolution rate of 10^{-6} $year^{-1}$.
- best estimate values of the durability of about 50,000 years (for a cracking factor of 40) and about 150,000 years (for a cracking factor of 12, based on [20]), considering the enhancement of dissolution rates (that is, resumption of alteration) associated with sorption of silica on clays and iron corrosion products likely to be present in proximity to HLW in a GDF (based on [90]); a durability of 100,000 years is equivalent to a normalised dissolution rate of 10^{-5} $year^{-1}$.
- a very pessimistic lower bound value of 4,000 years, based on a forward rate of 1.7 10^{-2} g m^{-2} day^{-1} at 30 °C and a cracking factor of 27 (used in the Belgian programme for glasses subjected to mechanical stresses)[104]; a durability of 4,000 years is equivalent to a normalised dissolution rate of 2.5 10^{-4} $year^{-1}$.

The best estimate calculation presented in [566] may be cautious, since it assumes an indefinite removal, at a relatively fast (not kinetically-limited) rate, of silicon from solution due to sorption on clays, based on in situ experiments in which direct exposure of HLW simulants to clays and magnetite was carried out for a finite duration of time [90]. In reality, the presence of the stainless steel vitrification canister, acting as a transport barrier, is likely to hinder ionic transport between the glass and any clay buffer [568]. The available sorption sites in the silica may also saturate. The interaction with iron corrosion products from the corrosion of the waste container and from the vitrification canister may also be important in determining the long-term dissolution rate, but considerations of the effect of a transport barrier between the glass and the waste container may also apply. In the future, tests on UK HLW compositions in the presence of radiation and iron-based materials, as well as in situ tests, are planned to explore these effects [10, tasks 539 and 540].

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[103] For a cylindrical block of glass with a 0.215 m radius, geometric external surface area of 1.7 m^2 and glass density of about 2.7 g cm^{-3}.

[104] Fine cracks are considered particularly important if the glass experiences a low long-term dissolution rate since, in these conditions, fine cracks are expected to produce a substantial contribution to the overall corrosion process. Values of 40 have been used to account for fine cracks in the case of long-term dissolution rates, based on estimates from the French programme. At higher rates (at the forward rate), fine cracks are expected to easily saturate with silicon and will become blocked, thus not contributing to the dissolution process. Values of 5 have been evaluated for the forward rate regime in the French programme. Values of about 12 have been calculated for typical HLW in the UK programme and as high as 27 for glasses subjected to mechanical stresses.

So far, there has been comparatively little consideration of the likely effect of the forward rate on the initial release of radioactivity upon perforation of the disposal container. Notwithstanding possible differences in forward dissolution rates between magnesium and calcium-rich formulations, it is possible that the overall initial release of radioactivity to the environment will be dominated by the total sorption capacity of the surrounding materials (such as ferrous corrosion products of the disposal container) rather than by differences (if any) in initial dissolution kinetics, as currently assumed in the French model (see Box 34). In this case, the IRF would be the same as, or very similar to, that of other glass compositions, currently estimated to be of the order of 1%.

The likely rate of release of radionuclides from glasses other than Magnox and Blend glasses has not yet been considered in our research programme [10, task 538]. It is however possible that some of these products may display micro-segregated phases (yellow phase) leading to the initial release of a higher inventory of specific radionuclides.

There is limited information available to evaluate the effect of any microstructural alteration on the long-term behaviour of UK glass compositions. Relevant work is planned for the next stages of the technical programme [10, task 541].

11.5 Radionuclide release from spent fuel

Based on information from micro-structural (i.e. segregation), leaching, and fission gas release studies, Instant Release Fractions (IRFs) and matrix dissolution rates for different types of spent fuel have been estimated in disposal programmes worldwide, particularly for LWR fuels.

Once groundwater has perforated the waste container and the cladding, the spent fuel will come into contact with the groundwater and start leaching radionuclides. In the case of oxide fuel, an initial fast release of a fraction of specific radionuclides (i.e. the IRF) is expected, followed by a slower release of the rest of the radionuclide inventory congruently with the dissolution of the fuel matrix. Given the very long timescales over which radionuclides may be released from the fuel matrix, the IRF is likely to be important in evaluating the radiological risk of a GDF containing spent fuel, particularly in the initial period following container perforation. In the case of metallic fuel, corrosion is likely to proceed rapidly and result in a relatively fast release of the radioactive inventory of the fuel.

Comprehensive assessments of IRF values have been performed for LWR fuel in several national programmes. Broadly speaking, these data are expected to be applicable to the case of UK LWR fuels. These studies show that the IRF of ‘volatile’ radionuclides (for example, ^{135}Cs and ^{129}I) tend to significantly increase with burn-up and power rating, so that conservative estimates can be made on the basis of high FGR data obtained at the highest levels of burn-up and power ratings. The IRF of other radionuclides (particularly ^{14}C and ^{36}Cl) is currently more uncertain.

An initial study [569] was completed in 2011 to estimate specific values of the IRF of a variety of important radionuclides for UK-specific spent fuels types, including AGR, Magnox and some ‘exotic’ fuels. Values of the IRF have been estimated based on direct measurements (when available), correlation with other fuels (where appropriate) and/or evaluation of the likely chemical form and extent of segregation. Beyond recommending suitable values of the IRF for UK spent fuels, this study employed available data (largely from PWR fuels) to identify correlations between the IRFs and fuel burn-up.

Specific considerations for the case of fuel whose cladding was breached during reactor irradiation or following storage operations (‘failed fuel’) are reported in Box 33.

11.5.1 LWR fuels

For LWR fuels, typical IRFs for ^{135}Cs and ^{129}I of the order of 4-12% are expected at relatively high burn-up and power rating. Values of 1% or less have been estimated for other key radionuclides. In the conditions expected in a GDF, the release of the remaining inventory is expected to occur over periods of millions of years.

Example IRF values for PWR fuel are given in Table 24, based on studies performed in Sweden, Switzerland and France [195]. The ranges of FGR and IRF values given in Table 24 relate specifically to the differences in power rating and burn-up of the fuel from the various reactors considered (see the FGR distributions in [184] and [192]). It should be noted that these are examples for specific cases and that the linear power rating and end-of-life burn-up values should be examined in order to make estimates for any given reactor.

Fuel matrix dissolution rates have been estimated in several national programmes. Shoesmith [179] proposes a best estimate dissolution rate of UO_2 for hydrogen-dominated conditions of ~2×10^{-6} mol m^{-2} year^{-1} (Figure 52). Consistent with this, recent reviews by SKB [89, 570] and Nagra [184] have proposed a best estimate fractional dissolution rate of spent fuel of 10^{-7} year^{-1} in hydrogen-dominated environments, meaning that, in groundwater, the whole radioactive inventory of the fuel would be released over a period of approximately ten million years. Long-term microstructural evolution processes are currently expected to have a limited impact on the IRF and long-term release rates, with the exception of some radionuclides for which larger uncertainties exist (particularly ^{36}Cl).

The results of these studies and the overall analysis are expected to be directly applicable to the case of UK PWR fuel, and likely, fuel from new LWR power stations. Confirmatory work is planned for the future [10, task 556].

Table 24: IRF values of LWR fuel for radionuclides based on assessments in the Swiss, Swedish and French repository programmes

	Swiss programme [184] (~60 GWd/tHM)[105] (Mean values, %)	Swedish programme [570] (~45 GWd/tHM) (Mean values, %)	French programme [195] (60 GWd/tHM) (Best estimate, %)
FGR	1.8	4.3	4
Cs-135	5.8	4.3	4
I-129	5.8	4.3	4
Cl-36	5.4	13	16
C-14	10	11	10
Se-79	0.2	0.65	-
Sr-90	1	1	1
Tc-99	1	0.2	0.1

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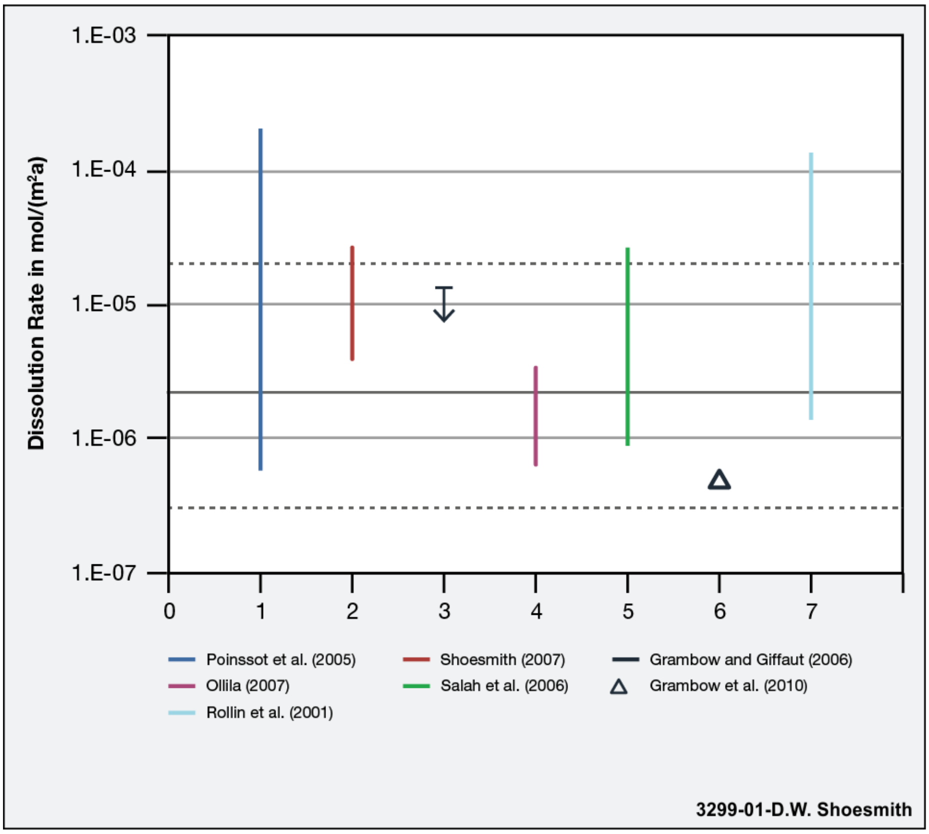
[105] Data from Beznau power station.

Figure 52: UO_2 corrosion rates from various literature sources. The solid line is the best estimate chemical (non-oxidative) dissolution rate and the dashed lines are the selected upper and lower bounds [179]



11.5.2 AGR fuel

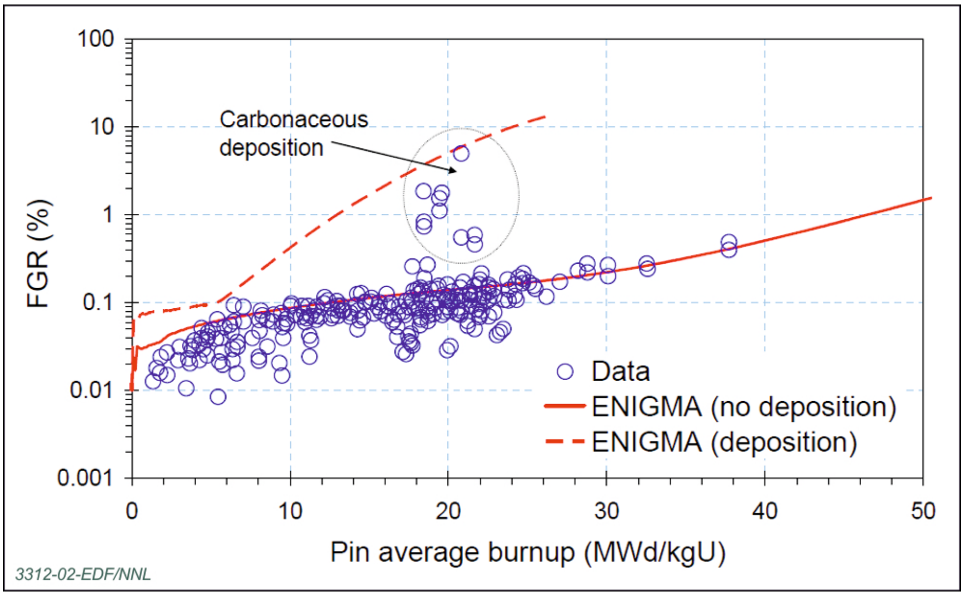
For AGR fuels, typical IRFs for ^{135}Cs and ^{129}I of the order of 0.1-10% are expected, depending on burn-up, power rating and other factors. Values of 1% or less have been estimated for the IRF of other radionuclides. In the conditions expected in a GDF, the release of the remaining inventory is expected to occur over periods of millions of years.

Initial considerations of the IRF of AGR fuel suggested that, given the similarity between AGR and LWR fuels and their irradiation conditions (see Box 2), there is a relatively good basis to estimate the IRF of AGR fuel based on information produced in other countries (largely for LWR fuels) [569]. The analysis presented in [569] indicated that the IRF of key radionuclides such as ^{135}Cs and ^{129}I measured on LWR fuels could be used, in the absence of specific AGR data, to identify likely IRF values for AGR fuel. A fractional release rate of the order of 10^{-7} year^{-1} was also recommended for AGR fuels in hydrogen-dominated environments, similar to that estimated for LWR fuels [186].

A subsequent desk-based study focused on estimating values of the IRF at lower burn-up than that modelled in [569] (lower than 36 GWd/teU), considered more representative of the majority of AGR fuel irradiated to date and expected to arise in the future [75]. Whilst low values of the IRF/FGR are likely to arise on a large proportion of the AGR fleet, due to the higher temperatures experienced locally, higher values of the FGR (and presumably the IRF) are likely to be associated with the development of carbonaceous deposits on some AGR fuel elements, with values of FGR of the order of 5% for fuel irradiated up to 20 GWd/teU [75]. Release of specific radionuclides that may be contained in the actual deposits (for example ^{14}C) may also occur. Both the well-researched FGR data for 'un-deposited' elements and the high excursions observed on deposited elements can be modelled with the ENIGMA code by providing higher input temperatures for the cladding (induced by the thermal insulation provided by the deposit) into calculations, as shown in Figure 53.

A detailed analysis of the matrix dissolution rate, discussing the effect of α-radiolysis and reducing species (H_2) on the solubility and kinetics of dissolution of AGR fuel was also carried out [75]. Expected dissolution rates for AGR are similar or lower than that of LWR fuels due to the lower levels of α-radiation (a factor of about 0.5 less after 1,000 years for AGR fuel).

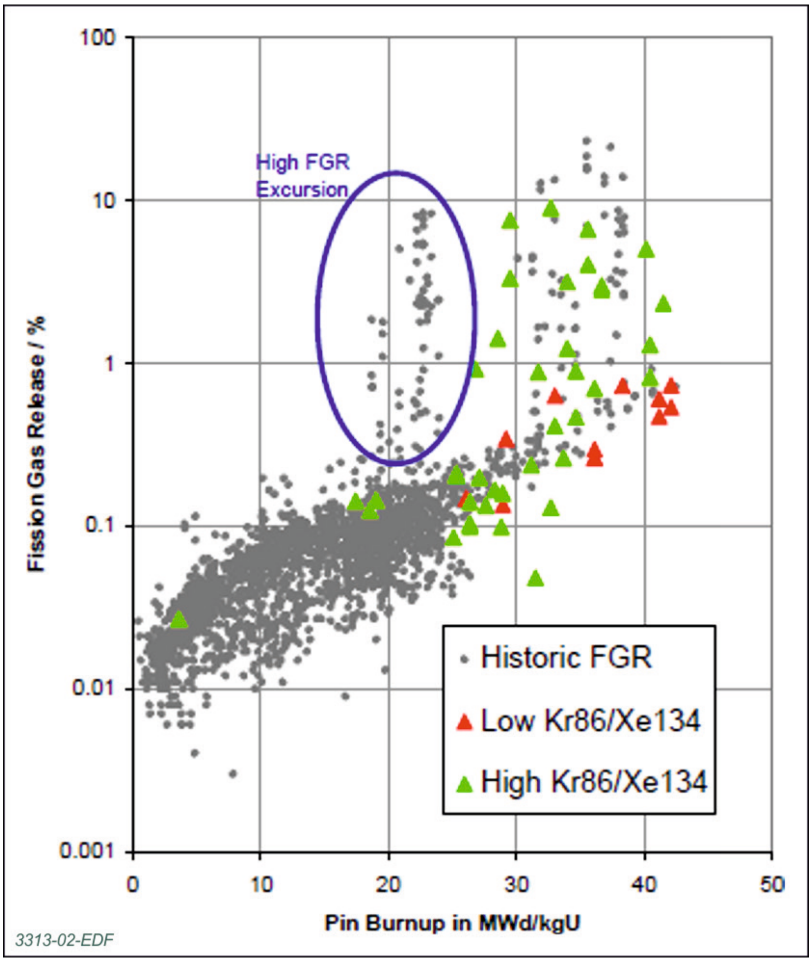
Figure 53: Measured and predicted AGR fission gas release (%) for element 6 as a function of pin average burn-up. Data are based on [571], while modelling calculations are based on the code ENIGMA (see [75,186]). The 'deposition' curve refers to a simulation considering higher temperatures than nominal values



Recent experimental work on AGR fuel [187] in naturally aerated conditions largely confirmed the conclusion of desk-based studies. The cumulative release of caesium and iodine isotopes from samples extracted from the hotter regions of a reactor after two years leaching was found to generally correlate with the measured FGR, with values broadly similar to those generally observed on LWR fuels. Values of the matrix dissolution rates were also relatively similar to those reported for LWR fuels in similar conditions. Work is planned to evaluate the leaching behaviour of AGR fuel in a hydrogen-dominated environment and to confirm this analysis [10, task 551].

Based on this analysis, the values of IRFs and matrix dissolution rate currently expected from LWR fuels are likely to be broadly applicable to AGR fuels. For volatile isotopes like ^{135}Cs and ^{129}I, values of the IRF are expected to be well-represented by values of the FGR. An analysis of FGR values for AGR fuels is reported in [572] and reproduced in Figure 54.

Figure 54: Typical fission gas release values measured on spent AGR fuel as a function of burn-up [572]. The 'high FGR excursion' refers to fuel elements which may have been affected by carbonaceous deposition



11.5.3 Metallic fuel

Metallic fuel is expected to degrade rapidly in a GDF, leading to a release of its radioactive inventory over relatively short periods of time.

Existing information on the dissolution behaviour of metallic spent fuel has not yet been reviewed in our research programme and is planned in the future [10, task 554]. As a result, the information presented herein should be considered as an initial, scoping analysis.

As discussed in Section 6.4, we have not yet reviewed any experimental studies of the dissolution behaviour of metallic spent fuel in conditions representative of a GDF. However, given the nature of corrosion on an active metal and the limited changes expected in chemistry and microstructure of metallic fuel during reactor irradiation (Magnox fuel was subjected to relatively low burn-up), the fuel may be sufficiently similar to that of uranium metal to allow a meaningful scoping evaluation.

In the anoxic, high chloride and near-neutral (or alkaline) environments expected in a GDF a high fuel corrosion rate can be expected. With a corrosion rate of the order of 100 μm year^{-1} (considered representative of fuel rods at a temperature of about 40°C), a uranium bar of the diameter of 3 cm would release its entire inventory over periods of the order of a hundred years.

Overall, compared to the rate of radionuclide transport processes expected in a GDF, the rates of release of radioactivity from spent metallic fuel are likely to be very fast and can be modelled in safety assessments assuming an ‘instantaneous’ release of the whole radioactive inventory of a container (IRF =1).

A specific consideration associated with the management of metallic fuels is the potential for exothermic reactions of the fuel upon exposure to air, associated with the formation of pyrophoric corrosion products (uranium hydride) from previous contact with water.

11.5.4 Exotic and plutonium-bearing fuels

Exotic and plutonium-bearing (for example, MOX) spent fuels are expected to behave similarly to metallic or oxide fuels, depending on their chemical form. Very high burn-up fuels will require specific consideration.

Existing information on the dissolution behaviour of exotic and plutonium-bearing (for example, MOX) spent fuels has not yet been reviewed in our research programme and is planned in the future [10, task 550]. As a result, the information presented herein should be considered as an initial, scoping analysis.

It is likely that exotic fuels will have a range of characteristics, any metallic and carbide fuel behaving in a way similar to that described in Section 11.5.3 and any oxide fuel behaving in a way similar to that described in Sections 11.5.1 and 11.5.2. However, the behaviour of oxide fuel irradiated at very high burn-up (>70 GWd teU^{-1}) would require specific consideration.

It is likely that plutonium-bearing fuels will display either similar characteristics to oxide fuels (in the case of MOX fuel) or metallic fuels (in the case of uranium-plutonium alloys). Some work on the behaviour of MOX fuel has already been carried out in some international programmes [177, 218] and further studies are expected to be completed in the future.

12 Evolution of ILW/LLW, DNLEU and plutonium residues waste packages

This section integrates information presented in other Sections in order to provide a description of the expected evolution of ILW/LLW, plutonium residues and DNLEU waste packages. It considers both periods of interim storage and the operation of the GDF as well as periods following closure of the GDF.

Estimates of the durability of containers manufactured from stainless steel, carbon steel and concrete are presented. General consideration of the expected evolution of the wasteform is also provided, recognising that the evolution of the wasteform will largely depend on the nature of the waste and any pre-treatment processes, as well as the host geological environment.

The description focuses on host rocks which will be subjected to resaturation and water flow (for example a higher strength host rock or a lower strength sedimentary rock). The evolution of waste packages in an evaporite environment would differ quite considerably from that presented in this section as there would be effectively no groundwater flow to either promote corrosion or to transport radionuclides from the GDF.

12.1 Degradation of waste containers during periods preceding closure of a GDF

The durability of ILW/LLW containers has been evaluated for both periods preceding and following disposal, based on expected degradation mechanisms and rates of relevant processes. The durability of stainless steel containers has been estimated on the basis of extensive research carried out in the UK, whilst estimates provided for other designs are based on comparatively less information and/or information produced in other programmes.

This section presents estimates of the durability of container designs for ILW/LLW containers based on the use of different materials currently employed or being considered in the UK. The information is based on studies generated in the UK or other disposal programmes (particularly France).

A key difference between HLW/spent fuel and ILW containers is that, due to the nature of the wastes they contain, the potential for significant heat generation in ILW and LLW packages is very limited and the surface temperature of most waste packages is likely to follow that of the external environment. This makes the environmental conditions to which the waste containers are exposed less corrosive during the post-closure period, but potentially more corrosive during the pre-closure period (due to the higher likelihood of deliquescence or condensation).

12.1.1 External corrosion of stainless steel containers

In well-controlled atmospheric conditions thin-walled stainless steel containers are likely to provide a very high durability (many centuries or millennia). However, a lower durability could result, especially in coastal locations, if environmental conditions in storage and disposal facilities were not sufficiently well managed (such that the waste is exposed to relatively high temperatures and indoor chloride deposition rates).

The general corrosion rate of stainless steel in atmospheric conditions is far too low to generate substantial wall thinning over very long periods of time [498]. In the presence of chloride deposits, however, pitting and SCC can occur. In this case the durability can be evaluated on the basis of the risk of SCC leading to concerns over structural integrity. This is currently considered the only credible mechanism potentially able to affect the functionality of waste containers containing a solid, immobilised wasteform. Any pit, even if penetrating deep into the metal, is unlikely to affect its functionality since this type of container is generally vented and does not contain radioactive fluids (because wasteforms are immobilised).

Practical experience with stainless steel components exposed for many decades to outdoor conditions [515], as well as experience with ILW container prototypes exposed for up to about a decade in indoor conditions [503], indicates that micro-pits (up to a few 100 μm deep) are likely to develop over sufficiently long periods. This phenomenology is also expected based on the results of mechanistic modelling studies [513, 514]. Pits, however, are likely to remain small in size since pit depths (or overall sizes) are likely to be limited by the maximum cathodic current available in conditions of limited electrolyte (atmospheric) conditions [513, 514].

Conversely, in specific environmental conditions, SCC has been found to penetrate deeply and in relatively short timescales in stainless steel components [508]. This is typically observed in the presence of divalent chlorides (for example, $MgCl_2$ and $CaCl_2$) in conditions of relative humidity 'close' to the deliquescence point of the salt (typically below 50% RH), at relatively high temperatures (>30 °C), and if the deposited concentration of chloride salts on a surface is high enough (>10-25 μg cm^{-2}) [508][106]. Considering available information on typical environmental conditions found in real ILW storage facilities [65, 64] or other indoor facilities [503], the durability of thin-walled stainless steel components can be estimated on the basis of the timescales over which the deposition of chloride is likely to be high enough to reach critical levels for SCC to occur.

Based on this criterion, a preliminary analysis of the likely durability of stainless steel ILW containers during long periods of interim storage in surface facilities in the UK is presented in [509, Appendix A], based on the potential propagation of SCC to depths of some concern (>100 μm). This work concluded that:

- for facilities operating at room temperature (and up to 30 °C) SCC may not develop for timescales ranging from twenty years to greater than 1,000 years
- for facilities operating at higher temperatures (30-50 °C), there is a potential risk of SCC over periods ranging from about ten years up to many centuries.

12.1.2 External corrosion of carbon steel and cast iron containers

A very high durability (many centuries or millennia) is expected with thick-walled carbon steel and cast iron containers in well-controlled conditions (controlled relative humidity).

In atmospheric conditions, carbon steel and cast iron undergo rapid rusting processes. General corrosion rates of the order of 10 μm year^{-1} have been estimated for cast iron in conditions expected in surface stores with a relatively well-controlled relative humidity [384]. Corrosion rates of the same order of magnitude are expected for carbon steels. With these corrosion rates, thick-walled containers (>100 mm) are likely to retain their radioactive content for long periods of time. In these conditions, a corrosion allowance of 10 mm would last about 1,000 years.

Depending on the specific environmental conditions expected during the operational period of a UK GDF, faster degradation may occur on carbon steel and cast iron. Due to the higher RH expected in some underground environments, corrosion rates of the order of 100 μm year^{-1} may be possible if control of the temperature and relative humidity proves difficult (for example, see Figure 4.3 in [384], reproduced from [463]). In these conditions, a corrosion allowance of 10 mm would last about 100 years.

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[106] At low temperature (about 22 °C) and higher relative humidity (about 60%) much higher levels of chloride (deposition density greater than 1,000 μg cm^{-2}) were required to initiate SCC.

Even if the environmental conditions in surface stores and a GDF were controlled in a way that reduced general corrosion rates to values beyond levels of concern for structural integrity, over time these processes may degrade other functionalities of the waste container (lifting features, sealing systems, etc.). As a result, the use of protective coating systems and their periodic maintenance may be required to maintain waste containers in good conditions.

12.1.3 External corrosion of concrete containers/overpacks

A good durability (many decades or centuries) is expected of thick-walled concrete containers/overpacks in well-controlled conditions.

The extent of degradation of concrete containers/overpacks will depend on the RH of the environment and the duration of the pre-closure period. In the UK, inside buildings designed to maintain the air above the dew point (such as many ILW stores), the RH undergoes substantial daily and seasonal variations, with values typically between 20-90% and average values typically of the order of 60-70% (see Section 4.1.2). Around the average values, the rate of carbonation will be relatively high (see Section 10.11.1). Conversely, the RH in a UK GDF will depend on a number of factors (including the GDF design, the efficiency of ventilation, and the nature of the host rock) and it is not yet possible to identify likely operational ranges.

In France, a systematic approach to the assessment of the corrosion behaviour of reinforcement bars under storage conditions is being developed, based on a combination of (i) short-term laboratory experiments, (ii) the study of archaeological analogues, and (iii) predictive modelling [545]. Under atmospheric conditions the corrosion rate of the steel re-bars and inner containers depends on the level of carbonation and the resulting pH of the cement, the rate of O_2 supply through the concrete cover, and the concentration of chloride. A model taking into account these processes (CORDOBA) has been developed to predict the time-dependent cracking of the concrete due to the formation of corrosion products, although quantitative validation of the model is still required [545].

Similar processes are likely to occur or continue once concrete containers/overpacks are transported to a GDF. Andra have estimated that the RH within their Type B ILW disposal cells in a sedimentary Callovo-Oxfordian argillite GDF will be approximately 50%, resulting in 20-30% saturation of the concrete [162]. Thus, although gaseous CO_2 will be able to penetrate into the concrete, the extent of carbonation will be limited by the availability of water. In this case, the maximum depth of carbonation is predicted to be approximately 1 cm after 100 years [162]. The higher RH in the air inlet shafts (~90% RH) and the correspondingly higher degree of saturation of the concrete (40-50% saturated) will also limit the depth of carbonation, in this case due to the reduced rate of transport of CO_2 in saturated concrete. A maximum depth of carbonation of ~1 cm in 100 years was also predicted in this case [162]. In general, the maximum depth of carbonation is predicted to occur within disposal drifts where the RH is in the range of 50-90%. In this case, the maximum depth of carbonation is predicted to be ~10 cm in 100 years [162].

Estimates of the durability of concrete containers based on designs and environmental conditions expected in the UK have not yet been carried out and are the subject of future work [10, task 711]. However, based on the estimates from the French programme [162], using as a criterion the timescale over which the carbonation front reaches the internal steel components (re-bars), it seems likely that the depth of carbonation will be in the range 1-10 cm for a pre-closure period of 100 years, meaning that containers/overpacks in which the distance between the external concrete surface and the inner steel components is greater than 10 cm should maintain their integrity over a period of at least 100 years.

12.1.4 Internal corrosion of the waste container

The potential for internal corrosion is low for dry wasteforms. In the case of cement-based wasteforms, cement containers, or wet unencapsulated wastes the porewater or bulk water can provide a medium in which corrosion can occur but, based on expected water inventories in the waste, any damage is expected to be modest.

ILW/LLW is generally dry. This minimises the potential for internal corrosion. In the case of cement-based wasteforms or cement containers, however, the cement porewater can provide a medium in which corrosion can occur. In specific circumstances, associated with the accelerated clean-up of a small number of high-hazard legacy facilities, the UK nuclear industry is considering the containerisation of wet, unencapsulated wastes. In this case, the potential for corrosion is more significant and requires specific consideration.

In the case of cement-based wasteforms, the alkalinity of the cement inhibits the corrosion of any stainless steel in contact with it (including the waste container), even if the waste were to contain a significant amount of corrosive species (such as chloride). Relevant information is provided in Section 8.2. Levels of chloride which are likely to pose a corrosion risk for stainless steel have been evaluated in conservative conditions (up to 70 °C, [527]), indicating that, at the temperature of interest, a Cl:OH ratio greater than 10 would be needed to initiate pitting corrosion on 316L stainless steel. For a cement with a pH of 12.5, this is equivalent to a chloride concentration in the cement porewater of at least 10,000 ppm (assuming that all chloride is freely available in the porewater), and possibly substantially higher, taking into account the likely formation of chloride minerals (see [573] and the analysis of this effect presented in [527]). The limited potential for internal corrosion in this type of package is confirmed by monitoring and destructive examination of dummy packages and coupons in contact with a variety of inactive wasteform simulants [574]. However, specific waste streams may present some risk of internal corrosion, particularly if they contain, or able to release, a substantial quantity of acids and/or chloride (see Section 8.3.1).

In cementitious wasteforms the level of chloride expected to lead to corrosion of carbon steel or cast iron containers, or of carbon steel re-bars in the case of concrete containers, is likely to be lower than for stainless steel. In particular, a Cl:OH ratio of about 1 can be inferred from [527, Section 2.3], suggesting that chloride concentrations of the order of approximately 1,000 ppm would be required in a wasteform with a pH of 12.5 to initiate localised corrosion. In all cases these values are much higher than those expected inside the great majority of ILW and LLW packages.

Polymeric wasteforms are expected to contain minimal amounts of water. However, if a water phase was present, this could result in the release of corrosive species in contact with waste containers. Studies of three candidate encapsulants [296] indicated the release of chloride and organic species in sufficient quantities to generate a risk of localised corrosion in stainless steel containers if the water was not conditioned by the use of cement liners. For glassy wasteforms, due to their dry nature, the potential for internal corrosion of waste containers is very low.

Wastes packaged without encapsulation generally require the use of thick-walled containers, typically carbon steel, cast iron or concrete. The potential for internal corrosion depends on the presence and quantity of residual water in the waste. For carbon steel or cast iron containers, any water present is likely to react relatively rapidly with the metal (rates of the order of 10 μm year^{-1} or higher, see Section 10.7.1), leading to internal damage and, potentially, hydrogen pressurisation (generally mitigated through the use of vents). However, considering typical inventories of water that may be expected inside waste packages (no more than a few litres) it is easy to show that the risk of substantial structural damage will be minimal, even if all water was to react with the waste container [466]. For example, assuming a container with a base surface of 1 m^2, a water inventory of

10 litres would generate an average depth of corrosion of 2 mm if distributed evenly across the base[107]. In the case of stainless steel containers, the potential for any corrosion to occur will depend on the concentration of chloride expected in the system, the radiation levels (potentially affecting the redox potential of the environment) and the material grade. For the austenitic grades that have conventionally been used, chloride concentrations as low as 200-300 ppm are known to be sufficient to initiate crevice corrosion in naturally aerated conditions [164, 575]. Higher concentrations could be tolerated with more resistant grades, such as 2205 or 2507 [385, 576]

12.2 External degradation of waste containers during periods following closure of a GDF

The durability of different container designs for the disposal of ILW/LLW has been evaluated based on expected degradation mechanisms and corrosion rates. Relevant work has been carried out in the UK, as well as other international programmes.

In a number of circumstances, depending on their condition at the time of disposal, the disposal concept and site-specific considerations, ILW and LLW containers may last for substantial periods of time following closure of the GDF.

This section presents estimates of the durability of container designs for ILW/LLW containers based on the use of different materials currently employed or considered in the UK. The information is based on studies generated in the UK and other countries' disposal programmes (particularly France). Initial estimates of the durability of stainless steel ILW containers during the post-closure period of a GDF backfilled with cement are based on work done by Nirex in the 1990s. Although estimates of container durability during the post-closure period are subjected to substantial uncertainty (the durability is expected to be dependent on the groundwater chemistry of the disposal site), the technical work underpinning such estimates is relatively mature. As a result, recent R&D in the UK has focused on periods of interim storage, previously assumed to be substantially shorter than currently estimated.

12.2.1 Stainless steel containers

In the presence of a cement backfill thin-walled stainless steel containers are either expected to provide a relatively low durability (a few years or decades) or a very high durability (>1,000 years), depending on site-specific conditions. Low durability can be expected in the absence of a cement backfill. Confidence in their expected durability, however, is affected by a number of uncertainties and the absence of any natural analogues.

Similar to the case of HLW and spent fuel containers, estimates of the durability of ILW/LLW containers can be based on a corrosion allowance and a general corrosion rate. For typical stainless steel designs (wall thickness ~2-6 mm) and expected corrosion rates in relatively high pH cement (0.01 μm year^{-1} or less, see [498] and [252, 253]), containers could last as long as 100,000 years if a high alkalinity was retained in the system over similar periods.

However, it is important to understand that this type of assessment relies on the ability to exclude, with confidence, the potential occurrence of other corrosion mechanisms, particularly localised corrosion and MIC. If these mechanisms were possible, even for relatively short periods of time (years), containers could be perforated over much shorter

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[107] Based on a conservative stoichiometry of one atom of iron generated for two molecules of water reacting.

timescales. For example, in sea water, propagation rates for crevice corrosion can be as high as 1 mm year^{-1} [164][108].

Given that deep groundwaters (and in particular UK groundwaters) are likely to be rich in chloride, the potential for localised corrosion, particularly in the early post-closure (oxic) period, cannot be currently ruled out. The potential for localised corrosion of stainless steel in a GDF (particularly during the early post-closure period) can be mitigated through the use of a high pH cement. In particular, experimental studies indicate that, at low temperature (<70 °C), a chloride to hydroxide concentration ratio of the order of 10 is required to initiate localised corrosion [527], indicating that a chloride concentration of the order of 0.3-3 M (10,000-100,000 ppm) would be required at a pH values of 12.5-13.5 respectively. However, even in the case of large scale inhibition due to the use of alkaline cements, the risk of localised corrosion may still exist if niches of low pH are possible, depending on the groundwater chloride content, the temperature, and the redox potential of the environment at the time of groundwater resaturation. At least some of these factors (particularly the salinity and timescale for groundwater resaturation) are site-specific and their likely effect on the risk of localised corrosion has not yet been evaluated in the UK disposal programme.

Once anoxic conditions are established (for example, in the case of a site in which the rate of oxygen ingress from groundwater resaturation is lower than the rate of oxygen consumption), chloride-induced localised corrosion may not occur, even at low pH or high chloride concentrations. However, other corrosion mechanisms (particularly MIC or corrosion induced by sulphur species) may remain viable. The long-term inhibition of MIC (and possibly sulphur-assisted corrosion) in a cement-backfilled GDF will rely on the ability of the backfill to maintain a high pH (>12.5), which in turn depends on the groundwater flow. Models for the pH evolution of the backfill are currently being refined, but it is likely that high pH conditions will last many tens of thousands of years, depending on the groundwater flow [2]. Future, more precise, estimates of the durability of stainless steel containers will need to take into account the likely rates of resaturation and oxygen consumption as well as the evolution of the cement pH with time, which is also site-dependent.

Overall, if the chemistry and redox potential of the groundwater are not conducive to localised corrosion during the oxic period (for example, if the rate of resaturation with chloride-rich groundwater is slower than the rate of oxygen consumption), and if alkaline conditioning is expected to be retained for long periods of time, thin walled stainless steel containers could last for very long periods of time (>>1,000 years). However, due to the lack of suitable analogues, the relatively long pre-closure periods (at least several decades), the fact that ILW containers cannot be considered sealed systems, and that it may not be possible to rule out the potential for MIC, our level of confidence in their ability to contain radionuclides for very long periods is currently more limited than for HLW and spent fuel containers. Moreover, short durability (a few decades) would be expected in some particularly challenging scenarios.

12.2.2 Carbon steel and cast iron containers

Thick-walled carbon steel and cast iron containers are expected to provide substantial durability (>1,000 years) during the post-closure period of a GDF. However, confidence in their expected durability is affected by a number of uncertainties.

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[108] Although not necessarily relevant to the case of a cement-backfilled GDF, this rate gives an indication of how rapidly these processes can occur in corrosive conditions.

Similarly to the case of HLW and spent fuel containers, relatively high corrosion rates of carbon steel and cast iron are expected during the initial oxic period, depending on the corrosivity of the groundwater. Rates of the order of 10-100 μm year^{-1} can be expected [469], suggesting that an oxic period of the order of 10 years would only result in the loss of several 100s of microns of exposed material. Estimates of the likely amount of corrosion during the oxic period were provided for the case of HLW and spent fuel containers (see Table 20). Given their higher emplacement density, a lower inventory of oxygen per container and less resulting damage can be expected on average in the case of ILW/LLW containers.

Once anoxic conditions have been established general corrosion rates will depend on the nature of the backfill employed and the chemistry and redox potential of the groundwater. In the case of a near-neutral pH (crushed rock backfill), a long-term (anoxic) corrosion rate of the order of 1 μm year^{-1} is likely to be observed [158, 462, 470] (on the lower end of the rate expected in the case of HLW and spent fuel containers, given the lower temperatures expected in ILW vaults). In the case of cement-backfilled vaults, long-term (anoxic) corrosion rates of the order of 0.1 μm year^{-1} or less can be expected [475]. In this case, estimates of the likely durability are coupled with estimates of the period over which alkaline conditions (pH >12.5) are likely to be retained in the EBS. Existing studies indicate a gradual loss of passivity of these materials at pH levels below 10 [474]. In these conditions, rates of corrosion similar to, or lower than, those expected in near-neutral conditions can be expected.

Overall, thick-walled steel containers are likely to provide very long periods of containment of radionuclides during the post-closure period of a GDF. With a long-term general corrosion rate of 0.1-1 μm year^{-1} (relevant to a near-neutral and an alkaline system respectively), 10 mm of steel is likely to last for periods of 10,000-100,000 years. Substantial confidence in the expected durability is provided in this case by archaeological analogues, particularly in the case of a GDF backfilled with crushed rock.

However, similar to the case of thin-walled stainless steel containers, prolonged periods of interim storage before disposal, the fact that containers are not fully sealed systems, and the fact that the potential for MIC to occur is somewhat higher than for HLW and spent fuel containers, currently limit our confidence in estimating their durability.

12.2.3 Concrete Containers/overpacks

Thick-walled concrete containers and overpacks are expected to provide a substantial durability during the post-closure period of a GDF (>1,000 years). However, confidence in their expected durability is affected by a number of uncertainties.

Degradation of the concrete containers during the post-closure period will result from the continuation of carbonation started during periods preceding closure, as well as from the onset of other processes, particularly leaching and sulfate attack. These processes will result in either a change in permeability of the concrete (due to changes in porosity or the onset of cracking) or a change in the pore-water chemistry, in particular the pH. However, most of these processes can only occur in an aqueous phase, requiring a substantial degree of saturation. Slow saturation of a GDF following closure would delay the onset of chemical alteration, so that the degradation of concrete containers is likely to take longer in a host rock with low hydraulic conductivity than in rock with a higher hydraulic conductivity.

A model has been developed to predict the evolution of the corrosion behaviour of rebar and metallic wastes in ILW containers [577]. Although the predictions from the model have yet to be validated, either against experimental data or the results of large-scale *in situ* experiments, it is apparent that there is sufficient mechanistic understanding of the various processes involved that such modelling efforts are well founded.

Andra [162] estimated the timescales over which the degradation mechanisms described above are likely to produce substantial alteration of cement in Callovo-Oxfordian argillite. For this type of host rock (a lower strength sedimentary rock), the rate of advective-water transport is expected to be so low that the rate of concrete degradation is determined by diffusive processes. The estimated depths of concrete alteration for the three main alteration processes are:

- leaching (referred to as hydrolysis in [162]) – 7 cm in 10,000 years and 30 cm in 100,000 years. These estimates do not take into account any effects of the decrease in porosity due to carbonation.
- carbonation plus hydrolysis – if the effect of the decrease in porosity due to carbonation is taken into account, the combined effects of hydrolysis and carbonation are estimated to result in a depth of attack of 4 cm in 7,500 years.
- sulfate attack – an estimated depth of 10 cm in 10,000 years, for the sulfate pore-water concentration in Callovo-Oxfordian argillite.

As a result of these processes, Andra [162] concluded that the degradation of concrete containers will proceed progressively over periods of hundreds of thousands of years.

The rates of concrete degradation processes in the UK GDF will depend on a number of design- and site-specific parameters, such as the nature of the concrete used for containers, the thickness of cover over the re-bar, the sulfate concentration in the groundwater and the extent, if any, of advective-water transport. In the absence of more specific information, estimates available from the French programme can be used but further work is planned to refine this analysis [10, task 711].

Whilst, unlike metallic containers, concrete containers do not represent an impermeable barrier to the release of radionuclides, it is very likely that, as long as a relatively high pH and the structural integrity of the concrete are maintained, the rates of release of radionuclides from waste packages will be slow. The estimates of durability described above assume that a container will eventually lose its functionality, either as the result of a substantial loss in pH (assumed to result in subsequent cracking due to corrosive expansion of internal steels) and/or as a result of cracking due to mineralogical changes of the cement. These conditions will eventually result in the release of radionuclides to the EBS through lower-alkalinity, advective paths in which the solubility and mobility of many radionuclides will be higher.

12.3 Evolution of the wasteform during periods preceding and following closure of a GDF

The evolution of ILW/LLW, plutonium residues and DNLEU wasteforms depends both on the waste and any encapsulation or embedding process.

The evolution of ILW/LLW, plutonium residues and DNLEU wasteforms depends on the waste and encapsulation or embedding process employed to immobilise it (if any). This section provides a high level summary of the expected evolution of such wasteforms during periods preceding and following closure of a GDF on the basis of the immobilisation process employed. Further details about the expected evolution processes of specific waste streams are reported in Section 8.

It is important to understand that, even for the same type of wasteform (for example, cement or glass) the ILW/LLW disposed of in a GDF will be quite variable in nature. The wasteforms will, therefore, corrode or degrade by a range of processes and over a range of timescales. Overall, given the broad range of wasteforms and dissolution processes involved, with the possible exception of ILW glass and glass ceramic wasteforms, dissolution processes of ILW/LLW wasteforms have not been the subject of detailed R&D

under our research programme. For ILW/LLW disposal concepts consideration of the chemical state and transport of radionuclides in the EBS (based on solubility and sorption) are typically used to estimate the fate of radionuclides in a GDF (described in [4]).

Conversely, wasteforms for DNLEU and plutonium residues are less diverse in nature and, as a result, their dissolution behaviour can be described in a simpler manner. However, R&D on these wasteforms is not particularly mature, given that they have been considered only relatively recently in the disposal programme and given that, at least for DNLEU, other processes are likely to control their overall impact on the GDF [318].

12.3.1 Cementitious wasteforms (ILW)

Cement-based wasteforms are expected to undergo long-term hydration and carbonation processes during periods preceding closure of the GDF. After closure, once the waste container has been breached, cementitious wasteforms will start leaching radionuclides at a rate dependent on the type of waste in question.

Cement-based wasteform are expected to undergo long-term hydration and carbonation processes during periods preceding closure of the GDF, leading to some changes in the mineralogy and strength of the wasteform (typically increasing the strength). Radiolysis processes are expected to result in gas generation, but no detrimental effect on cement strength. In the case of wasteforms containing reactive metals (Magnox, aluminium and particularly uranium), organic materials (such as PCM or ion-exchange resins), and mobile wastes (sludges and flocculants) processes leading to dimensional changes (typically expansion) are likely to lead to cracking of the cement. However, with suitable cement formulations and design of the waste container these processes are unlikely to result in rupture of the waste container.

During the post-closure period of a GDF, once the waste container is breached, cement-based wasteforms will start leaching radionuclides into the EBS. The rate at which this occurs is likely to depend on the nature of the waste, the extent of any previous degradation of the cement and the waste, and the chemical conditions in the vicinity of the waste (governed by the chemistry of incoming groundwater). Given the broad range of wastes involved, the timescales over which such release processes can occur have not been subjected to detailed R&D. However, in some cases (for example, steel and other corrosion-resistant metals) slow degradation processes and slow associated radionuclide release rates can be expected. The release of radionuclides due to some of these processes can be estimated on the basis of information presented in this report (see, for example, Section 8.2).

12.3.2 Polymeric wasteforms (ILW)

Polymeric wasteforms are expected to be subject to radiolysis processes during periods preceding closure of the GDF. After closure, once the waste container has been breached, polymeric wasteforms will start leaching radionuclides at a rate dependent on the type of waste in question.

Polymeric wasteforms are expected to undergo radiolysis during periods preceding closure of the GDF, leading to some changes in the strength and stiffness of the wasteform (typically reducing them) as well as leading to gas generation. Given the relatively dry nature of the wasteform and the type of wastes considered for polymer-encapsulation (typically metals), other evolution processes are not expected, but R&D considering specific polymer/waste interactions has not been carried out.

During the post-closure period of a GDF, once the waste container has been breached, polymeric wasteforms will start leaching radionuclides into the EBS. Given the limited amount of waste already encapsulated or planned for encapsulation in polymer, and the likely complexity and diversity of the behaviour associated with different waste streams, only a limited amount of R&D has been carried out to understand their likely evolution and the resulting radionuclide release in a GDF. However, information on the radiolytic and thermal degradation (for example, TOC values, Section 7.3.2) could be used to allow an initial evaluation of the likely rate of degradation of the encapsulant.

12.3.3 Glass, glass-ceramic and ceramic wasteforms (ILW and plutonium)

Glass, glass-ceramic and ceramic wasteforms are not expected to undergo significant degradation during periods preceding closure of the GDF. After closure, wasteforms will start leaching radionuclides. Radionuclide release processes are likely to occur over relatively long timescales.

Glass, glass-ceramic and ceramic wasteforms are not expected to undergo significant degradation during periods preceding closure of the GDF.

During the post-closure period of the GDF, once the waste container has been breached, glass, glass-ceramic and ceramic wasteforms will start leaching radionuclides into the EBS. A limited amount of R&D has been carried out to understand their likely evolution and the resulting radionuclide releases in a GDF, but available information indicates that radionuclide release processes are likely to occur over relatively long timescales. A range of wasteforms have been studied, including Synroc-type mineral phases (zirconolite) for plutonium, and borosilicate and other types of glasses (such as phosphate glasses) for ILW and plutonium. The release of radionuclides from these potential wasteforms has not been studied extensively, but there is sufficient information to estimate release rates based on the rate of dissolution of the glass or glass/ceramic matrix. With the dissolution rates described in Section 7.4, the release of radioactivity is expected to occur over periods of tens or hundreds of thousands of years.

12.3.4 Non encapsulated wastes (ILW/LLW and DNLEU)

Non-encapsulated ILW/LLW wastes may undergo a variety of degradation processes during periods preceding closure of the GDF, including corrosion of metals, radiolytic degradation of polymeric materials, and gas generation. After closure, once the waste container has been breached, non-encapsulated wasteforms will start leaching radionuclides at a rate dependent on the type of waste in question.

During the GDF pre-closure period, depending on the waste in question and any processing (particularly drying) treatment, non-encapsulated ILW/LLW wasteforms are expected to either undergo minimal alteration (graphite or corrosion resistant metals) or to undergo a variety of degradation processes, including corrosion (steels and reactive metals), radiolytic degradation (plastics) and gas generation (many waste types). Information relevant to these processes is described in the context of specific waste types (see Sections 8.2 and 8.3).

During the post-closure period of a GDF, once the waste container is breached, non-encapsulated wasteforms will start leaching radionuclides into the EBS. The rate at which this occurs is likely to depend on the nature of the waste, the extent of any previous degradation, and overall chemical conditions in the vicinity of the waste (governed by the chemistry of incoming groundwater). Given the broad range of wastes involved, the timescales over which such release processes can occur have not been subjected to detailed R&D and are currently not well underpinned. However, in some cases (graphite or stainless steels) slow degradation and slow associated radionuclides release rates can be expected. The release of radionuclides due to some of these processes can be estimated on the basis of information presented in this report (see Section 8.2).

There has been very little R&D on the likely evolution of DNLEU wasteforms, since these materials have only recently been included in the inventory for disposal. However, evolution processes are expected to be very slow during periods preceding closure of the GDF (largely limited to the slow hydration and aggregation of powders). Dissolution of the wasteform in the GDF has not yet been evaluated in our R&D programme, but relevant understanding is likely to exist (for example, based on information on uranium oxides presented in Section 6).

13 Concluding remarks

The science and technology underpinning geological disposal of the materials currently considered in the UK radioactive waste inventory is well established. The knowledge base includes information from laboratory studies, demonstration experiments, models and studies from archaeological and natural analogues that can be used to support the implementation of geological disposal.

The key message emerging from the analysis presented in this status report is that durable waste packages, able to withstand their storage and disposal environments for very long periods of time, have been produced and can be produced in the future for the wastes considered in the disposal inventory. Specifically:

- existing information relevant to the likely evolution of HLW and oxide spent fuels from international programmes indicates that these wasteforms should be able to retain their radioactive inventory for very long periods of time. Scoping research on waste specific to the UK disposal inventory (UK HLW, spent AGR fuel, spent Magnox fuel) suggests that the behaviour of these materials present similarities and differences from the behaviour observed in well-researched HLW compositions or spent LWR fuels. With the exception of spent Magnox fuel, however, these wasteforms are also expected to retain their radioactive inventory for very long periods of time
- cement-grouted wasteforms so far produced to immobilise ILW/LLW in the UK are generally expected to undergo very modest and slow evolution processes. Evolution processes of some waste types may require specific consideration, including the use of a different immobilisation process
- a variety of container designs has been considered internationally for the disposal of HLW and spent fuels (mainly focusing on copper, carbon steel, cast iron, titanium, stainless steel and nickel alloys as the external corrosion barrier). Desk based studies indicate that different materials are likely to provide a high durability in a variety of disposal conditions that may be expected in the UK. In particular, designs based on the use of copper with compacted bentonite or on the use of carbon steels with a variety of buffer materials indicate that a durability greater than 10,000 years and, in some cases, greater than 100,000 years can be expected
- a variety of container designs is currently being considered for the storage and disposal of ILW/LLW in the UK and abroad (typically using stainless steel, carbon steel, cast iron or concrete). Studies carried out in the UK and internationally indicate that, if suitably designed and stored, these designs should be able to withstand long periods of surface storage before disposal as well as, in a suitably designed GDF, periods of underground operations. Depending on their initial state at the time of disposal and on the nature of the geochemical conditions expected at a disposal site, these containers may also provide a substantial durability after closure of the GDF.

Information contained in the suite of Research Status Reports has been used to underpin the development of the 2016 gDSSC. In particular, information from this status report has been used to provide technical underpinning to the expected evolution of waste packages before and after emplacement in the GDF.

Appendix A : Manufacture and monitoring of waste containers

This appendix complements information presented in other sections (particularly Section 9) with information on the manufacturing and monitoring technologies currently employed or planned for waste containers. The availability of suitable manufacturing and monitoring techniques is important to provide confidence in the feasibility of obtaining containers with the required properties. In particular, information on the size of defects initially present in the waste containers (or developed as a result of pre-disposal operations) is important to underpin estimates of their durability.

The discussion focuses on HLW and spent fuel disposal containers, which may be required to provide containment of radionuclides for long periods after disposal and for which, at least in the UK, limited experience with manufacturing and monitoring, currently exists.

A1 Manufacture of HLW and spent fuel containers

Containers for HLW and spent fuel have not yet been manufactured in the UK. Evaluating the feasibility of manufacture and the type of technologies likely to be employed is important to underpin existing disposal concepts and the likely impact of manufacturing on the evolution of waste containers.

In the UK there is no experience in the manufacture of HLW and spent fuel waste containers, since emplacement of the wastes in such containers is unlikely to occur in the near future. However, for most materials there is substantial experience from either other industrial applications (for example, steels and cast iron), or through development from other international radioactive waste management and disposal programmes. Sealing with a high-integrity final closure weld is of critical importance to containers for HLW and spent fuel so substantial work has been carried out internationally to develop and validate suitable techniques.

A1.1 Manufacture, QA and stress relief of container components

Many techniques (such as casting, forging and rolling) are available for the manufacture of container components. Full scale prototypes for designs employing copper, carbon steel and cast iron, but also nickel alloys, have been manufactured in several countries.

Manufacturing technology for HLW and spent fuel containers is most mature in Sweden and Finland, where the use of a 50-mm-thick outer copper shell, supported by a cast iron load-bearing insert, is proposed [393, 578]. As of 2010, SKB had manufactured 27 extruded copper tubes and a total of 55 cast iron inserts [393]. In the United States, a single prototype Alloy 22 waste package has been fabricated [579] and several titanium Grade-2 containers were manufactured and tested in the early Canadian programme [365]. Methods for manufacturing, sealing and inspecting carbon steel HLW/SF containers have been investigated by Nagra [82, 580], although no actual containers have yet been fabricated. In Canada, an alternative procedure for manufacturing a copper-coated container is under development and a full-scale prototype has been manufactured [581].

Large cylindrical vessels, sometimes with a substantial wall thickness, are routinely manufactured for a number of industries. In this sense the manufacture of HLW/SF containers does not represent a significant technological challenge, although some specific developments will undoubtedly be required. For example, various technologies exist for the manufacture of the container body, including [82]:

- casting
- forging (of a single piece or of multiple pieces, with or without an integral base)

- pierce and draw (with or without an integral base)
- rolled plate.

Because of the possibility of preferential corrosion, as well as the potential decrease in mechanical properties and increase in the likelihood of defects, welds are always critical components in systems requiring high integrity. For waste containers, manufacturing methods able to reduce the number of welds are generally preferred. For example, methods capable of producing a single long tube are considered desirable over methods where welding would be required to join several shorter tubes (short forging) or two or more rolled plates. Fabrication of a container body with an integral base would also reduce the number of welds required, although control of the metallurgical properties of the material may be challenging because of different rates of cooling of the body and base.

Patel et al. [82] concluded that all of the above methods were suitable for the fabrication of a thick-walled carbon steel container of the design specified by Nagra, although a long-forged (single piece) body with a welded base was identified as perhaps the most favoured method at this time because of the high quality possible with hollow forgings. The reference method selected by SKB for manufacturing the outer copper shell of their container design is to extrude a tube (Figure 55) from a copper ingot and to weld on forged bottom and top lids [393]. In the U.S. Yucca Mountain Project, the 'Hastelloy C-22' corrosion barrier was to be fabricated from rolled plate material, with longitudinal welds to join the components for the body and circumferential welds to join the lids. A single prototype waste package was fabricated prior to the winding down of the programme [579].

Virtually all HLW/SF container designs include some sort of internal structure to allow positioning of the wasteform and, in some cases, to provide structural support to the outer corrosion barrier. As for the outer shell, existing manufacturing technologies can be either used or adapted for the fabrication of the internal furniture. For example, a system of welded box sections with welded top and bottom plates was proposed by Patel et al. [82] as a simple and cost effective method to position PWR or BWR fuel assemblies inside a thick-walled carbon steel container. A more substantial structure is needed when the internal furniture is required to support the external load that develops in the GDF.

In the Canadian programme a different approach is being taken for the fabrication of a copper corrosion barrier supported by an inner iron-based structural component. Instead of the massive copper-cast-iron dual-wall KBS-3 design, NWMO are developing a copper-coated carbon steel container design [581]. Sufficient copper (of the order of a 3-5 mm thick layer) would be coated onto a carbon steel inner vessel that would provide the structural support against external loads. Both electrodeposition and a cold spray technique are being investigated for applying the coating and a combination of the two methods (electrodeposition for the head and main vessel, and cold spray for the final closure weld) could be used. Although a wide range of carbon steel structures could be coated, NWMO are investigating the use of commercially-available thick-walled carbon steel pipe as a cost-effective option for the inner vessel.[109]

Figure 56 shows a full-scale copper-coated container recently fabricated by NWMO. In this case, both the hemispherical head and the body assembly (comprising a hemispherical bottom head welded to a 1.95 m length of NPS 22 Schedule 120 carbon steel pipe) were pre-coated using a high-pressure cold-spray technique. The hemispherical head was then welded to the body assembly and the closure weld coated using cold spray. The entire container was then machined to produce the required surface finish. The manufacturing

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[109] NWMO have considerable flexibility in the size of the container because the small size of a CANDU® spent fuel bundle (approximately 50 cm long by 10 cm diameter) lends itself to a number of packaging configurations.

technology for a copper-coated container is still under development, but the prospects for the manufacture of cost-effective containers at the required rate and to the required quality look promising.

Prior to loading the wasteform, all of the pre-fabricated container components can be inspected, repaired (if necessary), machined, and stress relieved to assure the desired quality and initial condition. For example, thermal treatments can be applied to either relieve residual stress or to produce the desired microstructural features without concern for violating any thermal constraints on the wasteform. Figure 57 shows the transfer of an annealed 'Hastelloy C-22' prototype waste package to a quench tank in order to provide the desired annealed and quenched treatment to optimise the corrosion properties of the outer corrosion barrier [579].

Figure 55: Extrusion of a copper tube [393]

Figure 56: A full-scale copper-coated steel spent fuel container for CANDU® fuel [581]

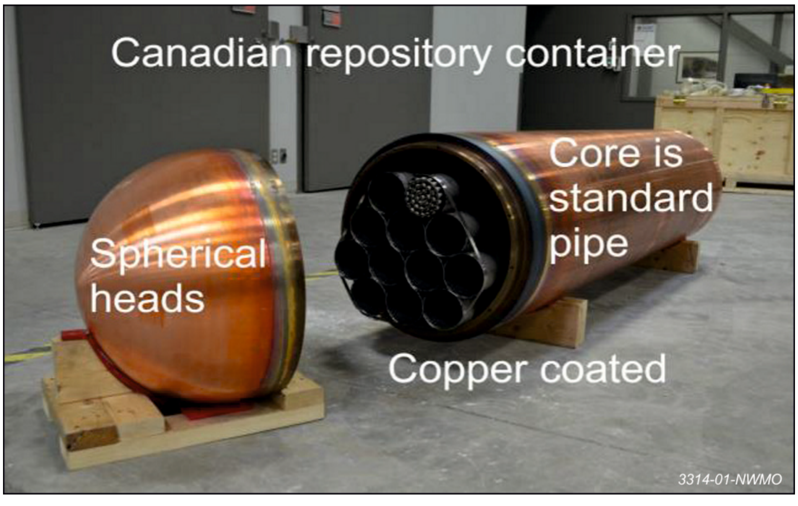

Figure 57: A heat-treated nickel alloy (Hastelloy C-22) outer corrosion barrier being lowered into a quench tank [579]

A1.2 Manufacture, QA and stress relief of the final closure weld of HLW/spent fuel containers

Specific techniques (for example, friction stir welding or electron beam welding) are available for the final sealing of waste containers. Full scale prototypes for designs employing copper, carbon steel and cast iron, but also nickel alloys, have been manufactured in many countries. Post-manufacturing techniques are also available to reduce residual stresses.

Containers for HLW and spent fuel will require sealing with a high integrity final closure weld after being loaded with radioactive waste. Even with the substantial shielding provided by the robustness of the waste container, sealing will need to be carried out remotely and with very reliable techniques.

A range of welding methods have been investigated for the remote sealing of HLW/SF containers [421, 580, 365, 393, 582]. Both SKB and Posiva have selected friction stir welding (FSW) for the final closure weld of their copper corrosion barrier [393], although the use of electron beam (EB) welding was also considered [582]. Trials have shown that both techniques can produce high quality welds in 5-cm-thick copper, even though copper is challenging to weld because of its high thermal conductivity. Because it does not involve melting, FSW has the advantage over EB welding that there is limited grain growth and lower levels of residual stress.

Asano and co-workers investigated the use of EB, gas-tungsten arc welding (GTAW, also referred to as tungsten inert gas TIG), and gas metal arc welding (GMAW, also referred to as metal active gas MAG) for the welding of carbon steel up to 190 mm thick [421]. All three methods were found to be feasible in mock-up tests. For a similar application, Pike et al. [580] concluded that narrow-gap GTAW and EB welding were the most suitable methods for welding thick-section carbon steel in the Nagra programme.

After sealing, the final closure weld must be inspected remotely in a hot cell environment. The aim of the inspection step is to determine whether there are flaws present that exceed a specified size or population. Weld flaws could be in the form of various types of inclusion, lack of fusion, solidification cracking, or excess porosity [82]. Suitable techniques for the detection of sub-surface flaws include ultrasonic testing (UT) and radiographic techniques. Eddy current testing can be used for the detection of surface-breaking flaws.

It is likely that a population of sealed containers will contain flaws that may be too small to be detected by the inspection methods employed. Whether these flaws are large enough to cause a decrease in durability of the container (that is, whether they should be classified as defects[110]) depends on the properties of the container material and the loads to which the container will be exposed during storage, handling and disposal.

The nature of the flaws in the closure weld will depend on the welding procedure, weld design and the material properties. For example, FSW of copper leads to two types of defect: joint line hooking and wormholes [393]. Under non-optimised welding conditions joint-line cracks with a radial extension of 1.4-5.4 mm and wormholes with a radial extent of up to 10 mm have been observed. The circumferential extent of these flaws (that is, in the direction parallel to the side of the container) could be several tens of cm in length. However, under optimised welding conditions, only joint-line hooking with a maximum extent of 0.4-1.5 mm was found by destructive examination. Electron-beam (EB) welds in copper lids were also examined. Welds obtained with EB were reported to be “almost defect-free” [582]. Further testing of lid welds indicated that all the flaws met the acceptance criteria [583], which range from 3 mm for cracks to 8-10 mm for porosity, joint-line hooking, lack of fusion, and inclusions (all dimensions in the radial direction) [584].

Sandia [579] summarised the results of UT and destructive examination of sixteen test welds on nickel alloy (Hastelloy C-22) mock-ups. The dimensions of the weld flaws found by UT inspection varied from 1.6-14 mm in depth, 1.6-3.2 mm in width and 3-35 mm in (circumferential) length [579]. Destructive examination did not locate any larger flaws and the only flaws found that were not detected by UT were minor gas pores less than 0.08 mm in diameter [584]. Although the weld procedure was not fully developed an acceptable flaw size of 1.6 mm (1/16 inch) was proposed, above which weld repair would be necessary.

Apart from the possible introduction of flaws, sealing the container may introduce a high level of residual stress into the closure weld. Post-weld stress relief may then be necessary to reduce the probability of EAC. The usual practice of post-weld heat treatment (PWHT) may not be possible because, in the case of HLW and spent fuel, there are thermal constraints for the wasteform which may limit the PWHT soaking temperature (the temperature at which the container is maintained to relieve the stresses) and exposure time. Preliminary simulations for a Nagra carbon steel container with a PWHT soak temperature of 550-600 °C indicated that a thermal limit of 450 °C for HLW would be exceeded [82]. However, the results of the analysis suggested that optimisation of the heat treatment process or changes to the container design (for example, by increasing the distance between the heated band and the wasteform) should result in suitable stress relief without exceeding the thermal limits.

In the US Yucca Mountain Project, two non-thermal post-weld stress relief methods were investigated, laser peening and plasticity burnishing [585]. In laser peening the application of a laser to the surface of the test piece creates a high pressure plasma which imparts a shock wave into the material and creates a compressive layer [585]. Plasticity burnishing

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[110] The conventional non-destructive testing (NDT) terminology is used here, in which the term “flaw” or “discontinuity” is used to refer to a feature that may or may not be detectable, but which may be acceptable. The term “defect” is used to refer to one or more flaws whose aggregate size, shape, location, or orientation do not meet specified acceptance criteria.

involves plastically deforming the surface of the test piece using a hydraulically loaded ball. As the load is removed after the ball has passed over the surface, the surface relaxes into a compressive state [585]. Both methods are capable of imparting a surface layer of compressive residual stress with a minimum depth of 1.9 mm in Hastelloy C-22 [585]. For a passive material such as Hastelloy C-22, with a correspondingly low rate of general corrosion, such a relatively thin compressive zone may be sufficient to suppress the initiation of EAC for a considerable length of time. However, for a material that corrodes at a higher rate, such as carbon steel, it is likely that the layer of surface compressive residual stress would be lost by corrosion in a relatively short period of time.

A2 Manufacture of ILW/LLW containers

Containers for ILW/LLW are routinely manufactured in the UK and in other countries. The manufacture of metallic containers employs standard technologies including casting, rolling, forming, welding and bolting. The manufacture of concrete containers involves standard concrete casting techniques.

The status of the technology for the manufacture of ILW/LLW containers is more advanced than that for HLW/SF containers. Various types of ILW/LLW container have been manufactured for use in the UK for the past several decades. Tens of thousands of containers have been manufactured and employed. In general, given the somewhat limited durability requirements of ILW/LLW containers, sealing is usually carried out through the use of (relatively complex) lid systems employing bolts and elastomeric seals. Welding is not usually used to provide a final closure to ILW/LLW containers.

Manufacture of stainless steel containers for ILW/LLW packaging has been carried out successfully for many years in the UK with standard technology. Manufacture of a 500 litre drum by a specific manufacturer, for example [387], involves the rolling of plate materials to develop body and neck parts, followed by an initial longitudinal seam-weld to allow ‘swages’ to be added to give flexural rigidity. Other body parts (the base and lid) are then hydraulically formed and plasma-welded to the body before final machining and fitting of internal components (such as mixing paddles). As part of the welding operations, washing and non-destructive examination of welds is carried out with dye penetrants on all waste containers to look for evidence of cracks and defects. Lids are manufactured with similar technologies. Containers and lids are then leak tested. Finally, a wet bead blasting operation is carried out to give the surface a homogenous surface finish, which removes any external heat tint and provides a surface with good corrosion resistance which is easy to decontaminate. A unique identifier is also added by laser etching. Guidance on welding of stainless steel containers for the UK radioactive waste industry has been developed by The Welding Institute [586].

Manufacture of other types of ILW/LLW containers has also been carried out successfully in the UK and abroad.

A3 Monitoring of waste packages during periods preceding closure of a GDF

Monitoring techniques deployable during interim storage are used or are being developed for waste (ILW) that has already been packaged. These techniques may also be deployable to other wastes (including HLW and spent fuel) when required, particularly after waste containerisation.

A summary of many of the available techniques to monitor ILW packages during interim storage was described in [587] and more recently in [63]. These techniques may be applicable to other wastes, especially after containerisation.

Relevant techniques are described below. Most of the techniques described (with the exception of the non-destructive techniques and direct measurements of the wasteform) were applied in an experimental programme to monitor the potential degradation of a prototype (inactive) waste container [503, 509]. Some non-destructive techniques were employed in another programme on a number of prototype containers [588, 589] and wasteforms [574]. Such work indicates that the monitoring techniques can be used successfully to detect signs of package evolution and helps to identify the most suitable monitoring strategies for waste packages. Initial considerations of monitoring of a GDF after closure have been developed internationally as part of a European project and will continue to be developed as part of a follow-up project [590].

A3.1 Visual examination

The simplest monitoring technique for the waste containers is visual examination. This technique is currently employed in a number of storage facilities. External damage or staining on the surface (indicative of corrosion), and container deformation (indicative of dimensional changes of the wasteform or internal pressurisation) may all be detected visually. Remote viewing of packages can be implemented using colour CCTV.

A3.2 Techniques for monitoring dimensional changes

Evolution of the wasteform may lead to volume expansion which in turn may lead to deformation of the container. The dimensions of the container can be measured using mechanical, optical and laser techniques. Strain gauges can also monitor such changes in the geometry of the container.

A3.3 Non-destructive testing (NDT) techniques to monitor changes in the wasteform

Reference [587] lists a number of NDT techniques that may be capable of development to provide information on the state of the wasteform through the container wall.

Radiography, similar to medical radiography but with the option to use neutron sources as well as X-rays, has the potential to identify cracks and voids in the wasteform. Recent developments in digital detectors and in tomography have improved the application of these techniques. In a report on the characterisation of radioactive sources in waste, the IAEA describes radiographic imaging techniques and provides examples of the images that can be obtained [591].

Ultrasonics, the use of high frequency sound in a manner analogous to sonar, can be used to identify changes at the interface between the inner wall of the containers and the waste, highlighting areas where corrosion is occurring or can potentially occur. It also has the potential for identifying cracks and voids in the wasteform but the practicalities of transmission across the container/wasteform interface may prevent a reliable inspection from being achieved.

Thermal imaging cameras (thermography) can identify variations in temperature within the wasteform, highlighting heat-generating physico-chemical changes, whilst acoustic emission may be able to detect any acoustic signals generated by cracking or dimensional changes in the waste.

Measurements of gas generated within a package may also provide information on the evolution processes occurring within a wasteform and their rates.

A3.4 Non-destructive testing (NDT) techniques to monitor changes in the container

NDT can also be applied to detect corrosion and mechanical damage to the surface of waste containers. Reference [592] describes the use of various NDT techniques on copper waste containers developed in Sweden.

Dye penetrant inspection is a sensitive technique which can be applied to all materials. The position and extent of corrosion damage (mainly cracks) are highlighted by the application of a dye and a developer to the surface under examination. This requires close access by an operator and cleaning of the containers following the inspection, which may preclude its use on waste packages requiring remote handling.

Eddy current inspection is an electrical technique that monitors the flow of induced currents in the surface of a component. Defects are identified by the changes they cause in the flow of the eddy currents. The eddy current technique can be applied remotely, but it requires special procedures for application on magnetic materials (such as carbon steel).

A3.5 Direct measurements of the wasteform

Removal of the lids (for containers featuring them, see Section 7) would allow internal visual inspection, hardness testing of the waste and the removal of samples for physical and chemical analysis which would allow identification of any deterioration in the waste. This would need to be performed remotely in a cell.

A3.6 Dummy packages and materials

Dummy packages are packages of the same composition as real ones but without any radioactive waste incorporated in them. Materials with a chemical nature similar to that of real wasteforms, but which are not radioactive, can be employed in this case. Their examination can provide reassurance over the evolution of waste packages. For waste packages whose likely degradation mechanisms may be significantly affected by the presence of radiation (such as polymers), dummy packages would need to be kept in the waste store so that the contents would be exposed to a representative level of radioactivity.

Dummy packages can be subjected to both destructive and non-destructive examination. Apart from the techniques described above, additional techniques relying on the use of sensors within the waste package can also be employed. For example, electrochemical measurements to monitor the corrosion rate of metals present in the waste or of the waste containers can be performed, such as those employed in [574].

Corrosion coupons and corrosion probes can also be employed to monitor the corrosivity of the environment in which the waste containers are stored. Corrosion coupons can be designed to contain important features of real waste containers (for example, welds), can be moved, subjected to examination and then replaced in a store [593]. Dummy packages can also be employed to monitor the performance of container seals and filters.

A3.7 Monitoring of environmental conditions

By maintaining suitable storage conditions the degradation of the waste packages can be minimised. Monitoring helps to ensure that the required conditions are maintained. Monitoring of storage conditions includes temperature, humidity and the nature and amount of the contaminants present in the store atmosphere and on the surface of waste packages (primarily chloride). Examples of suitable methodologies to carry out monitoring of such parameters can be found in [503, 509].

A3.8 Reworking techniques

Potential approaches to reworking of ILW packages whose evolution may challenge their functionality have been analysed by the EA [594]. A wide range of reworking methods is available, but there is little experience of using them. This is due to the fact that, so far, reworking of waste packages has not been required. It is likely that experience with reworking will increase if some waste packages were to show detrimental evolution.

Four generic types of reworking options were identified, including: repair of the waste container; use of an overpack; stabilisation of the wasteform; and retrieval and reconstitution of the wasteform. A demonstration of some reworking techniques is reported in [595].

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