

Geological Disposal

Behaviour of Radionuclides and Non-radiological Species in Groundwater Status Report

December 2016



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ISBN 978-1-84029-569-6

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RWM Feedback
Radioactive Waste Management Limited
Building 587
Curie Avenue
Harwell Campus
Didcot
OX11 0RH
UK

email rwmfeedback@nda.gov.uk

Abstract

The Behaviour of Radionuclides and Non-radiological Species in Groundwater 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 Behaviour of Radionuclides and Non-radiological Species in Groundwater status report is to provide an introduction to the scientific literature relating to how radionuclides and non-radiological species derived from the wastes may behave in the geological disposal facility (GDF) and migrate in groundwater during the post-closure period. There is a good understanding of the processes that are likely to control the behaviour and transport of radionuclides and non-radiological species in groundwater, and considerable research has been conducted into their behaviour and transport in the more common engineered barrier materials. There are, however, several areas where understanding is incomplete and further research may be necessary. Our Science and Technology Plan sets out the range of generic research that is being conducted and planned, as well as an approach for moving to site-specific research. Given the site-specific nature of groundwater species behaviour and transport in the geosphere, there will need to be a significant programme of work at any potential site for the GDF to characterise the hydrogeochemical system, understand which processes may be of significance and assess the overall safety of waste disposal.

Executive Summary

The Behaviour of Radionuclides and Non-radiological Species in Groundwater status report is part of a suite of research status reports that provide an introduction to the scientific literature underpinning geological disposal of higher-activity wastes.

The report considers all wastes and potential wastes in the disposal inventory, including intermediate level waste (ILW), low level waste (LLW), high level waste (HLW), spent fuel, depleted, natural and low enriched uranium (DNLEU), and plutonium. The report covers a range of disposal concepts, engineered barrier system (EBS) materials and host rocks that are being considered for the disposal of higher-activity radioactive wastes.

The report describes key processes that may influence the behaviour and transport of radionuclides and non-radiological species in groundwater. These processes include radioactive decay and ingrowth, chemical speciation, organic complexation, radiolysis, sorption, solubility, precipitation and co-precipitation, mineral surface ageing, colloids, microbial activity, non-aqueous phase liquids, advection, diffusion, dispersion, rock-matrix diffusion, filtration and ion exclusion.

The report notes key regulatory requirements relating to non-radiological hazardous and non-hazardous species, identifies knowledge gaps in this area (such as a detailed knowledge of the content of these substances in higher activity radioactive wastes) and refers to plans for further work to address these gaps and extend assessments of potential impacts.

The report summarises how radionuclides will be released from the main wasteforms (vitrified HLW, spent fuel, plutonium and uranium, and ILW/LLW), once contacted by water:

- Radionuclide release from vitrified HLW will be controlled by glass dissolution processes. Initial, relatively fast, dissolution processes are expected to release up to about 1% of the radionuclide inventory over a period on the order of decades. Subsequently, slower, long-term rates of glass dissolution are expected to release of the rest of the radionuclides over tens to hundreds of thousands of years.
- In the presence of water, radionuclides may be released from LWR and AGR spent fuels in stages. A small proportion (up to ~10%) of certain radionuclides (such as ^{135}Cs and ^{129}I) will be released in the Instant Release Fraction (IRF). The IRF comprises radionuclides on the surface of the fuel, in pellet-cladding gaps, on fracture surfaces, at grain boundaries and in other accessible segregated phases, and it is expected to be released over a period of days to a few hundred years. Corrosion of fuel cladding and other fuel assembly components will influence the release of certain activation products (for example, ^{14}C , ^{36}Cl , ^{59}Ni , ^{93}Zr and ^{94}Nb). The release of the rest of the radionuclide inventory from the fuel matrix will occur much more slowly, at a rate controlled by oxidative dissolution of uranium dioxide. In the conditions expected in a GDF, the release of radionuclides from the fuel matrix is expected to occur over millions of years. Radionuclide releases from the relatively small amount of metallic spent fuel are expected to be much faster than for uranium oxide spent fuels, with release of the entire inventory from these wastes over ~100 years. Exotic and plutonium-bearing spent fuels (for example, MOX) are expected to behave similarly to metallic or oxide fuels, depending on their chemical form. Very high burn-up fuels will require specific consideration.
- Plutonium and uranium materials are included in the waste inventory, but have not yet been formally declared as wastes. Therefore, wasteforms for these materials have yet to be decided. It is currently assumed that almost all of the plutonium will be converted into Mixed Oxide (MOX) fuel. The small proportion of plutonium that is unsuitable for conversion to MOX fuel and the highly-enriched uranium (HEU) in the inventory will be converted into a titanium-based ceramic wasteform. The majority of DNLEU is either in the form of ceramic oxides (UO_2 , UO_3 or U_3O_8) or gaseous (UF_6).

UF₆ will have to be converted to a more stable form before disposal (current plans are to convert UF₆ into U₃O₈). A range of disposal options for DNLEU is being evaluated, including overpacking of the current mild steel storage containers containing powdered DNLEU in more robust and durable waste packages. The use of cement grouts to intimately immobilise the DNLEU waste followed by packaging in stainless steel containers is also being evaluated. Another alternative being considered is the entombment of the existing waste storage containers containing the uranium oxide powders in cement. The release of radionuclides from these potential wasteforms has not been studied extensively, but there is sufficient information (for example, from studies of UO₂ spent fuel dissolution) to estimate broad ranges of indicative release rates for use in generic safety assessments.

- The majority of ILW/LLW is packaged as cementitious wasteforms, but some unconditioned wastes may be disposed of within robust shielded containers, and some ILW/LLW may be disposed of in vitrified form or with other waste encapsulants, such as polymers. Consequently, radionuclides will be released from ILW/LLW over a wide range of timescales. The release of radionuclides from ILW/LLW will depend on the particular waste, the encapsulant and conditions in the geological disposal facility (GDF). Relatively fast releases are expected from un-encapsulated wastes and those containing reactive metals or organics. Slower releases are expected from less reactive wastes (such as corrosion-resistant metals, graphite and uranium oxides), encapsulated wastes and thermally-treated wastes.

Corrosion of large quantities of iron and steel wastes and waste containers in the GDF will cause conditions to become generally reducing. Under reducing conditions, redox-sensitive radionuclides tend to occur in their lower redox states and are only sparingly soluble. Iron and steel corrosion products may sorb many radionuclides quite strongly.

Where GDF conditions are buffered to high pH values by cement-based materials, the solubilities of many radionuclides are very low. Cement-based materials also sorb many radionuclides quite strongly. Organic complexants, particularly those derived from cellulosic ILW/LLW, may enhance radionuclide solubilities and reduce radionuclide sorption in the EBS if present at or above millimolar concentrations. However, sorption of organic complexants may reduce their effect in enhancing concentrations of mobile radionuclides. Organic complexation effects are expected to decrease over time due to radiolytic and microbial degradation of the organics and the effects are not expected to occur in the far-field where the concentrations of waste-derived organics are expected to be below millimolar concentrations.

Chemical alteration may occur at the interface between the EBS and the host rock, particularly at the contact between the host rock and cementitious materials. This may result in some dissolution of the rocks and the precipitation of secondary minerals such as calcium-silicate-hydrate (CSH), carbonates and oxides. Colloid formation may occur. Precipitation of secondary minerals, such as calcite, may effectively seal fractures around the GDF. Transport in the altered region may be further retarded by sorption and co-precipitation.

Bentonite-based materials are being considered for use as buffers and backfills in HLW/spent fuel disposal concepts. As long as the bentonite is emplaced in the GDF at a suitable density, it will swell on resaturation to form a very low permeability barrier, such that radionuclides and other species could only be transported by diffusion. Bentonite has a high sorption capacity for some radionuclides. Transport and retardation in bentonite barriers can be quantified using approaches based on apparent diffusion coefficients, but there are open questions relating to the fundamental understanding of porosity and the precise mechanisms of transport and retardation in compacted clays. The small pores in compacted bentonite are expected to preclude the movement of colloids and to limit the

growth and mobility of microbes. If dilute groundwaters interact with bentonite, erosion may cause some loss of buffer function and lead to the generation of colloids. RWM is conducting research into bentonite stability, erosion and colloid formation, and colloid-enhanced radionuclide transport.

Cement-based barriers are proposed for backfilling caverns, tunnels and shafts in ILW/LLW disposal concepts. Transport in cement-based backfills may occur by advection and diffusion in the pores of the materials and in any open cracks and fractures (such as those within the backfill or along the interfaces between the backfill and the waste packages or host rock). The initial permeability to water of the Nirex Reference Vault Backfill (NRVB) is of the order 6×10^{-17} to $3 \times 10^{-16} \text{ m}^2$ and this may tend to decrease with time as a result of groundwater interactions and calcite precipitation.

Salt-based or magnesium oxide materials may be used as engineered barriers in GDFs in evaporite host rocks. Once compacted as a result of rock creep, salt-based barriers are assumed to attain very low permeabilities, such that there would be no groundwater flow - solute transport is, therefore, not expected. Radionuclide retardation in barrier materials in evaporite host rocks would only be relevant for unlikely scenarios. Safety assessment studies generally assume no radionuclide sorption on salt materials.

The pattern of groundwater flow at a site is determined by the forces driving the flow (such as hydraulic head gradients), and the properties of the rocks (particularly permeabilities and porosities) and the groundwaters (salinity and viscosity). Thermal gradients near to disposed high-heat generating wastes may also drive groundwater flow.

Many factors can affect the behaviour and transport of radionuclides and other species in groundwater in dual porosity rocks:

- transport of dissolved and colloidal radionuclides and non-radiological species can occur by advection and diffusion
- transport may occur primarily by advection in fractures
- some transport may also occur by advection and diffusion in the rock matrix
- sorption and rock matrix diffusion may retard the transport of some species
- colloidal interactions and complexation by naturally occurring organic matter have the potential to enhance transport in some circumstances
- minor mineral phases, particularly those in fractures, may dominate sorption behaviour
- some species may be retarded by processes such as isotopic exchange and mineral (co)precipitation.

In the absence of a significant hydraulic gradient and/or in rocks with very low permeabilities or connected porosities, transport may occur primarily by diffusion. Diffusion rates in clay rocks may be affected by electrostatic effects. Sorption in clay rocks is likely to be dominated by minerals such as illite, smectite, illite/smectite mixed-layer clays and kaolinite; the pores in these rocks may not be connected and/or may be too small to allow colloidal transport. In some potential GDF host rocks such as halite, radionuclides and non-radiological species would only be transported in groundwater following the occurrence of an event that caused unexpected groundwater movement in these systems (such as human intrusion). The potential for a groundwater pathway to develop following an unlikely event such as human intrusion would be assessed at the site-specific stage should an evaporite host rock be selected.

In conclusion, there is a good understanding of the processes that are likely to control the behaviour and transport of radionuclides and non-radiological species in groundwater, and considerable research has been conducted into the more common engineered barrier

materials. There are, however, several areas where understanding is incomplete and further research may be necessary (for example, relating to the content of non-radiological species in the wastes, to the dissolution of UK-specific spent fuels and HLW glasses, to wasteforms for plutonium and to transport in and erosion of bentonite). We use an expert elicitation process to develop probability distribution functions (PDFs) of solubility and sorption values for use in safety assessments, based on available experimental data and taking account of uncertainties - there is a need to update the information input to this process to take account of the most recent research results. Our Science and Technology Plan sets out the range of generic research that is being conducted and planned, as well as an approach for moving to site-specific research. Given the site-specific nature of groundwater species behaviour and transport in the geosphere, there will need to be a significant programme of work at any potential GDF site in order to characterise the hydrogeochemical system, understand which processes may be of significance and assess the overall safety of waste disposal.

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List of Acronyms

AGR	Advanced Gas-cooled Reactor
APS	Advanced Polymer System
CANDU	CANada Deuterium Uranium
CCC	Critical Coagulation Concentration
CDP	Cellulose Degradation Products
CDZ	Chemically Disturbed Zone
CFM	Colloid Formation and Migration
CSH	Calcium-Silicon-Hydrate
CRA	Compliance Recertification Application
DNLEU	Depleted, Natural and Low-Enriched Uranium
DSSC	Disposal System Safety Case
DTPA	Diethylenetriaminepentacetic Acid
EBS	Engineered Barrier System
EC	European Commission
EDTA	Ethylenediaminetetraacetic Acid
EDZ	Excavation Disturbed Zone
EPR10	Environmental Permitting (England and Wales) Regulations 2010
FEPs	Features, Events and Processes
GDD	Groundwater Daughter Directive (2006/118/EC)
GDF	Geological Disposal Facility
GRA	Guidance on Requirements for Authorisation
HEU	High-Enriched Uranium
HLW	High-Level Waste
HHGW	High Heat Generating Waste
ILW	Intermediate-Level Waste
IRF	Instant Release Fraction
ISA	Isosaccharinic Acid
LHGW	Low Heat Generating Waste
LLW	Low-Level Waste
LLWR	Low-Level Waste Repository Limited
LoD	Limit of Detection
LWR	Light Water Reactor
Magnox	Magnesium-Aluminium Alloy
MOX	Mixed Oxide Fuel
MRV	Minimum Reporting Value

NAPL	Non-Aqueous Phase Liquid
NOM	Natural Organic Matter
NRVB	Nirex Reference Vault Backfill
PCE	Polycarboxylate Ethers
PDF	Probability Distribution Function
PWR	Pressurised Water Reactor
S&T	Science and Technology
TDB	Thermodynamic Database
URL	Underground Rock Laboratory
VES	Vinyl Ester Styrene
WFD	Water Framework Directive (2000/60/EC)
WIPP	Waste Isolation Pilot Plant
XAS	X-ray Absorption Spectroscopy

1 Introduction

1.1 Background

In order to build confidence in the safety of a future geological disposal facility (GDF)¹, and 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 can be found in the Technical Background Document [1].

The documents comprising the 2016 generic DSSC are shown in Figure 1 and include a number of research status reports, representing the 'knowledge base'. The purpose of the research status reports is to describe the science and technology underpinning geological disposal of higher-activity wastes by providing a structured review and summary of relevant published scientific literature and discussing its relevance. 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 the different safety cases that comprise the DSSC. The research status reports include:

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

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

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

1.2 Objectives and scope

The objective of the Behaviour of Radionuclides and Non-radiological Species in Groundwater status report is to provide an introduction to the scientific literature relating to how radionuclides and non-radiological species derived from the wastes may behave in the GDF and migrate in groundwater during the post-closure period. Available information is

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 and that these facilities should be located as near to the sites where the waste is produced as possible.

discussed with the aim of providing a sufficiently-detailed description of key processes that can be used in the development of safety cases. Safety-related considerations are excluded from the scope of this document and are provided solely in the safety cases. For example, illustrative post-closure safety assessment calculations are presented in a separate report [11].

The scope of this status report 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. The report considers various processes that may affect the behaviour of radionuclides and non-radiological species in groundwater under the conditions that may be expected in a geological disposal system comprising appropriate combinations of candidate engineered barrier materials and possible host rock types.

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

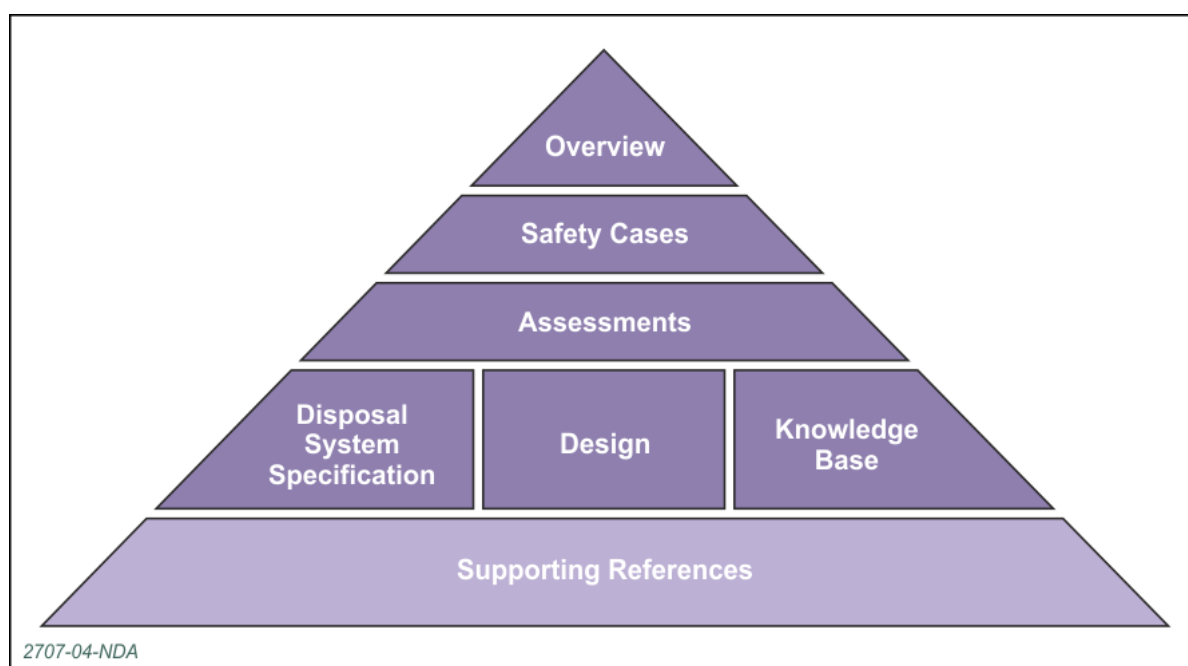
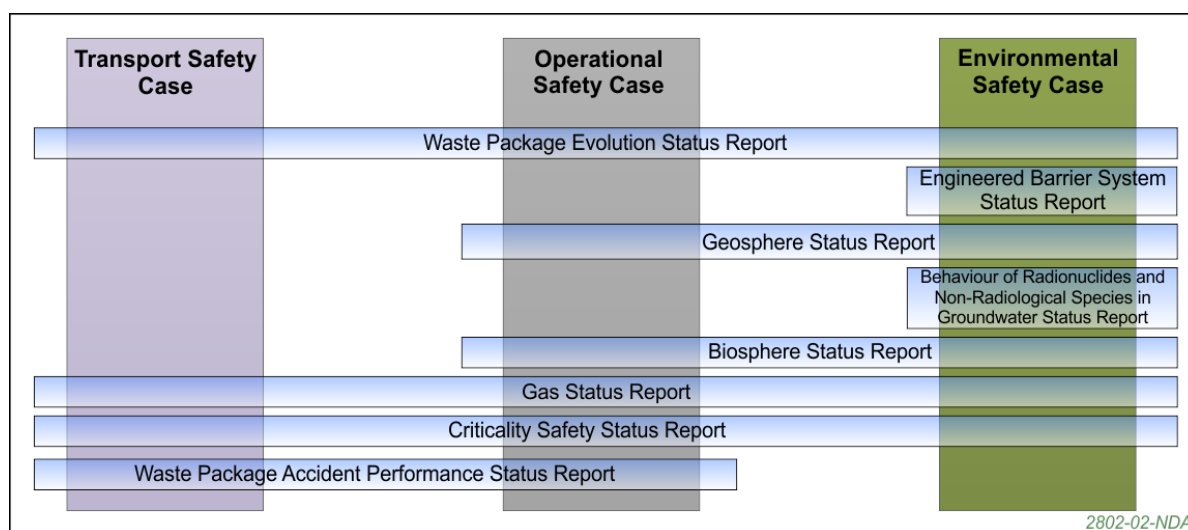


Figure 2. Safety cases and status reports in which underpinning information can be found.



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 this status report include:

- information on the potential disposal concepts and GDF designs (described in [1] and [12])
- information on the composition and inventory of the wastes and on their packaging (described in [2] and [13])
- information on the evolution of waste packages, potentially leading to the release of radionuclides and non-radiological species (described in [2])²
- information on the materials and evolution of EBS beyond the waste packages, including the buffer/backfill (described in [3])
- information on the possible nature and evolution of the geosphere, in particular the nature of groundwater and its flow, and the timescales of GDF resaturation (described in [4]).

Information from this status report that underpins other reports includes:

- understanding of processes leading to release and transport in groundwater that informs the development of safety assessment and biosphere models (described in [11] and [8]) and the selection of data for use in safety assessments (described in [9]).

1.5 Changes from the previous issue

This document updates and replaces the 2010 Radionuclide Behaviour Status Report [14], which was published as part of the 2010 generic DSSC. This issue includes the following developments:

- a broader and updated discussion of processes that may influence the transport and retardation of radionuclides in groundwater
- consideration of non-radiological species
- inclusion of recent research results on many topics, including: chemical speciation, organic complexation, sorption, solubility, precipitation and co-precipitation, mineral surface ageing, colloids, microbial activity, non-aqueous phase liquids, and rock-matrix diffusion.

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.

² For organisational reasons the Waste Package Evolution status report [2] also contains the primary source of information on waste dissolution and is the basis for the parameter values on wasteform dissolution used in the 2016 generic Post-Closure Safety Assessment.

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 introduces and describes key processes that may affect the behaviour of radionuclides and non-radiological species during and following their release from the wasteforms, during interactions with other engineered barrier materials and during transport in groundwater
- section 3 describes the behaviour of radionuclides and non-radiological species in engineered barrier systems
- section 4 describes the behaviour of radionuclides and non-radiological species in the geosphere
- section 5 provides concluding remarks
- appendix A provides a table based on the information discussed in the report that summarises the locations in a geological disposal system where certain key processes may be relevant in controlling the behaviour and transport in groundwater of radionuclides and other species.

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 Key processes affecting behaviour and transport in groundwater

Transport in groundwater may provide a route by which radionuclides and non-radiological species derived from the wastes in the GDF could migrate towards the biosphere. A number of well-known physical and chemical processes may occur and control the behaviour and transport of such species in groundwater. This section describes and discusses the possible occurrence of these processes.

Processes relating to the formation, behaviour and transport of radionuclides in the form of gas and in the biosphere are discussed elsewhere in [5] and [8]. Similarly, other routes by which radionuclides and non-radiological species could reach the biosphere (for example, as a result of human intrusion into the GDF or as a result of uplift and erosion) are discussed in [11] and [4] respectively.

The wastes to be disposed of in the GDF will be conditioned into stable solid wasteforms and packaged in ways that are designed to facilitate waste handling and limit radionuclide releases to groundwater in the post-closure phase. The relevant wasteforms are as summarised below; more detail is provided in Section 3.1 and in reference [2]:

- some of the ILW/LLW has already been packaged. Most of the ILW that has been packaged has been conditioned using cement-based grout.
- A significant quantity of HLW has already been vitrified into a durable borosilicate glass wasteform.
- Most of the spent fuel being considered for disposal in the GDF comprises uranium dioxide, UO_2 , but there is also some mixed oxide (MOX) fuel that requires disposal. It is currently assumed that both UO_2 and MOX spent fuel will be disposed of in the same way, although the amounts to be placed in each waste container are yet to be determined. The inventory also includes a smaller amount of legacy metallic uranium spent fuel and some 'exotic' spent fuels from experimental reactors.
- For planning purposes, it is currently assumed that almost all of the plutonium will be converted into MOX fuel. It is further assumed that the small proportion of plutonium that is unsuitable for conversion to MOX fuel (and the highly-enriched uranium (HEU) in the inventory) will be converted into a titanium-based ceramic wasteform. The majority of depleted, natural and low enriched uranium (DNLEU) is either in the form of ceramic oxides (UO_2 , UO_3 or U_3O_8) or gaseous (UF_6) which will have to be converted to a more stable form before disposal (current plans are to convert UF_6 into U_3O_8). A range of disposal options for DNLEU is being evaluated [15], including overpacking of the current mild steel storage containers containing powdered DNLEU in more robust and durable waste packages. The use of cement grouts to intimately immobilise the DNLEU waste followed by packaging in stainless steel containers is also being evaluated. Another alternative being considered is the entombment of the existing waste storage containers containing the uranium oxide powders in cement.

HLW and spent fuel containers are designed to contain the waste by preventing groundwater from reaching the wasteform for a long period. In contrast, many ILW/LLW containers have vents because the wastes have the potential to generate gas and it is important to avoid pressure build-up within the container during interim storage and underground operations. Long-term corrosion studies in chemical conditions representative of a GDF show that the rate of uniform corrosion of the materials typically used for ILW/LLW containers is very low [2]. As waste containers corrode they are expected to establish chemically reducing conditions in the GDF porewaters. Under such conditions the solubility of many radionuclides is very low. Reference [2] provides more detailed information on the waste containers and the evolution of the waste packages.

The GDF will be located in a stable geosphere. Section 4 and reference [4] provide more detailed information on the geosphere and its potential evolution. The majority of the degradation reactions that could affect the engineered barrier systems are water mediated. The geosphere will be a significant control on the rate of water flow through the GDF and will thereby influence EBS degradation and the release of radionuclides and other non-radiological species from the waste. Various physical and chemical processes in the geosphere will retard the transport towards the biosphere of radionuclides and other non-radiological species released from the waste.

The discussion that follows focusses on processes that are considered likely to be the most important to safety and environmental impact. Many other, less important, processes (for example, electrochemical processes) could occur in a disposal system, but it is not the purpose of this report to document the consideration of the many less significant Features, Events and Processes (FEPs).

Processes affecting the concentrations of radionuclides and other species in groundwater will include:

- Radioactive decay and ingrowth (Section 2.1)
- Chemical speciation, as influenced by factors such as pH, redox and temperature (Section 2.2)
- Organic complexation (Section 2.3)
- Radiolysis (Section 2.4)
- Sorption (Section 2.5)
- Solubility, mineral precipitation and co-precipitation and mineral surface ageing (Section 2.6)
- Colloids (Section 2.7)
- Microbial activity (Section 2.8)
- Non-aqueous phase liquids (NAPLs) (Section 2.9).

Processes affecting radionuclide transport include:

- Advection, dispersion and diffusion (Section 2.10)
- Rock-matrix diffusion (Section 2.11)
- Filtration and ion exclusion (Section 2.12).

All of these processes have been the subject of research over a number of years and are well-known. Their specific relevance to geological disposal of radioactive waste has been studied in detail through many safety assessments, for example, [16, 17, 18, 19, 20, 21, 22] and in many national and international research projects, for example:

- The European Commission (EC) NF-PRO³ project examined key processes affecting the long-term barrier performance of near-field systems [23, 24].
- The EC FUNMIG⁴ project considered radionuclide migration in three rock types (clay, crystalline rocks and salt) [25, 26, 27, 28, 29].

³ **Near Field PRO**cesses: 'Understanding and Physical and Numerical Modelling of the Key Processes in the Near Field and their Coupling for Different Host Rocks and Repository Strategies' commenced in 2004 and finished in 2008 and was co-funded by the EC under the Euratom research and training programme on nuclear energy within the Sixth Framework Programme.

⁴ **Fundamental Processes of Radionuclide Migration** (FUNMIG) commenced in 2005 and finished in 2008 and was co-funded by the EC under the Euratom research and training programme on nuclear energy within the Sixth Framework Programme.

- The EC BELBaR⁵ project aimed to increase knowledge of the processes that control the generation, stability and transport of radionuclides with bentonite clay colloids. The potential for colloids to affect radionuclide transport is also being researched in the colloid formation and migration (CFM) experiment at the Grimsel Test Site in Switzerland [30].
- The Nuclear Energy Agency (NEA) Thermochemical Database (TDB) project seeks to make available a comprehensive, internally-consistent, internationally recognised and quality-assured chemical thermodynamic database of selected chemical elements [31]. The project website [32] provides access to thirteen published reports that document reviews of thermodynamic data for key elements, including some important radionuclides and other species such as organics. We are currently working with the French waste management organisation, ANDRA, to develop a broader thermodynamic database [33, 34] that is suited to assessing the behaviour of the wide range of radioactive wastes in the UK and France.
- The NEA Sorption Project has been working to collate sorption data and improve the representation of sorption in safety assessments [35, 36]. The EC RETROCK project also examined sorption in the geosphere [37, 38].
- In order to consider behaviour over the long timescales of interest in radioactive waste disposal various natural system studies have been undertaken. For example, studies of radionuclide migration in natural systems have been made at Poços de Caldas in Brazil [39] and at Cigar Lake in Canada [40]. Further analogue studies are discussed in reference [41].

The following sub-sections introduce key processes that are likely to be important to the migration of radionuclides and non-radiological species derived from the waste in groundwater. The occurrence and extent of the processes will be dependent on the chosen disposal concept and the surrounding rocks. Sections 3 and 0 discuss the possible occurrence and effects of these processes in more detail under specific conditions within the EBS and the geosphere.

2.1 Radioactive decay and ingrowth

Radionuclides exhibit spontaneous radioactive decay. In some instances, the radionuclide decays directly to a stable, non-radioactive isotope. In others case, radioactive 'daughter' nuclides are produced by ingrowth.

Radioactive decay causes the radiological hazard presented by the waste to reduce over time. Over 95% of the radioactivity in higher-activity radioactive waste will decay within the first thousand years.

All radioactive substances decay over time. In some instances, the radionuclide decays directly to a stable, non-radioactive isotope. In other cases, a chain of radioactive 'daughter' nuclides is produced by ingrowth before a stable isotope is eventually formed. It is important to take account of decay and ingrowth when assessing the safety of the GDF as, for example, the ingrowth of radionuclides such as Ra-226 can be important.

The rate of radioactive decay is an intrinsic property of each radionuclide, and can be characterised by the 'half-life' - the time that it takes for half of the radioactive nuclei in the material to decay. Radionuclide half-lives range from fractions of a second to many millions of years. Information on selected radionuclides is given in Box 1.

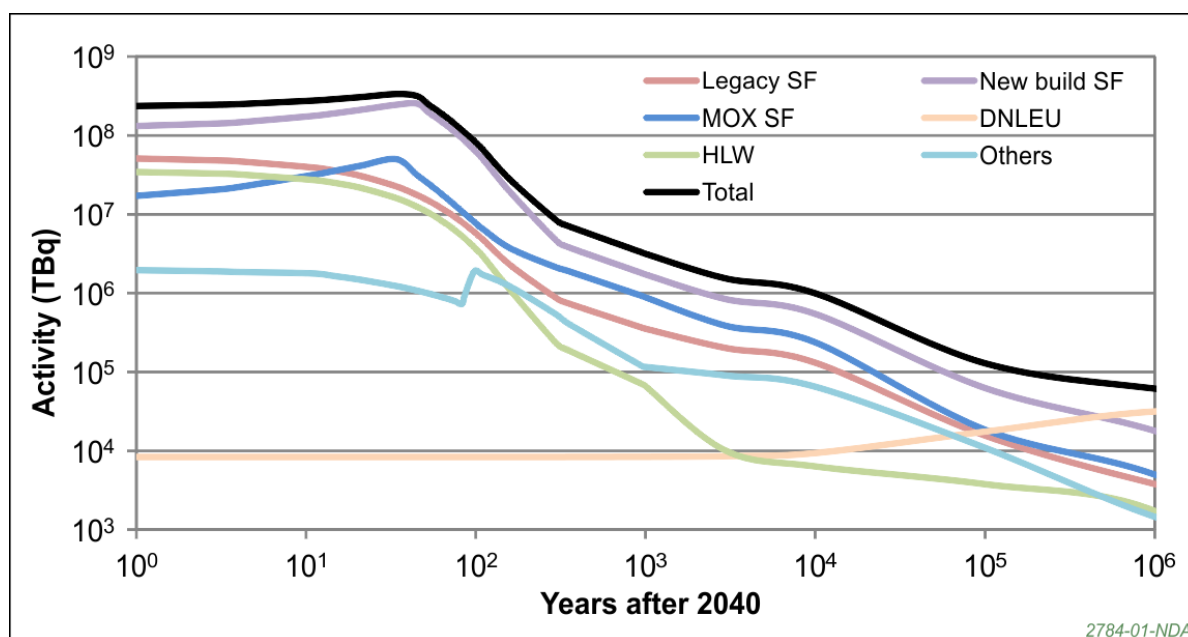
⁵ 'Bentonite Erosion: effects on the Long-term performance of the engineered Barrier and Radionuclide transport' (BELBaR) commenced in 2012. The project is co-funded by the EC under the Euratom research and training programme on nuclear energy within the Seventh Framework Programme.

The effect of radioactive decay on the different types of waste that might be disposed of in the GDF is shown in Figure 3 [13]. The figure shows the activity increasing initially as there is still spent fuel arising. At early times (up to hundreds of years), the radioactivity is dominated by fission and activation products in spent fuel and HLW. At later times, most of the fission and activation products will have decayed and the activity of the wastes will be dominated by actinides⁶ and their daughters. Peak activity occurs in 2075; 1,000 years after the peak, the total activity has decayed by just over 99% of its peak value.

A substantial number of radionuclides occur in the waste inventory. However, not all of these radionuclides are of radiological significance in post-closure performance assessments. Some have half-lives that are so short that they will decay almost completely over the timescales required for release from the GDF and transport in groundwater to the biosphere. Others are present in the inventory only in very small amounts and are not the daughters of other radionuclides present. It is not necessary, therefore, to propagate all of the 112 radionuclides identified in the inventory through the full suite of models required to evaluate post-closure radiological impacts associated with groundwater-mediated release and transport.

Instead, we have conducted radionuclide screening studies to identify which of the many radionuclides in the waste inventory need to be explicitly modelled in post-closure safety assessment studies. The most recent screening study [42] identified 49 radionuclides and several part decay chains that need to be included in safety assessments (Box 1).

Figure 3. The decrease in activity with time from closure of a GDF for the different types of wastes in the 2013 Derived Inventory [13].



⁶ The actinides comprise the 15 metallic chemical elements with atomic numbers from 89 to 103, actinium to lawrencium.

Box 1 Origin and decay of selected radionuclides in higher-activity radioactive wastes

RWM conducts radionuclide screening studies to identify which radionuclides need to be explicitly modelled in safety assessments, for example reference [42]. The most recent screening study identified 49 radionuclides and several decay chains that need to be included in the assessment of the groundwater pathway. This box provides some basic information on the origin and decay of some of the more significant of these radionuclides.

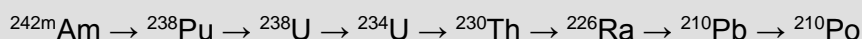
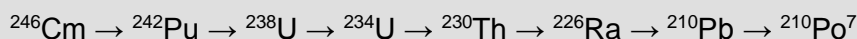
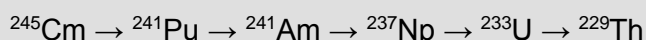
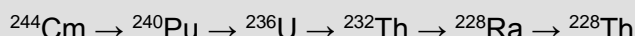
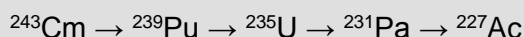
Actinides and their decay series radionuclides

^{238}U (half-life 4.5×10^9 years) and ^{235}U (half-life 7.0×10^8 years) head the natural uranium series decay chains, and are the main components of uranium oxide nuclear fuels. Some of their daughters are also of potential radiological significance; for example, ^{230}Th (half-life 7.5×10^4 years) and ^{226}Ra (half-life 1.6×10^3 years). These radionuclides are initially present in only very small amounts, but will ingrow by decay of their parent radionuclides.

^{239}Pu (half-life 2.4×10^4 years) and ^{240}Pu (half-life 6.6×10^3 years). These radionuclides are produced from ^{238}U by neutron capture in reactor fuel and are also present in greater quantities in mixed oxide (MOX) nuclear fuels.

^{237}Np (half-life 2.1×10^6 years). This radionuclide is produced from ^{235}U by neutron capture in reactor cores, and from the decay of ^{241}Am .

In more detail, the key decay series are [42]:



Fission products

^{79}Se (half-life 1.1×10^6 years), ^{93}Zr (half-life 1.5×10^6 years), ^{99}Tc (half-life 2.1×10^5 years), ^{126}Sn (half-life 2.4×10^5 years), ^{129}I (half-life 1.6×10^7 years) and ^{135}Cs (half-life 2.3×10^6 years). These radionuclides are produced as fission products in nuclear reactors.

Activation products produced from structural components of reactors

^{14}C (half-life 5.7×10^3 years). This radionuclide is produced from ^{14}N and ^{13}C . ^{14}C is generated principally within graphite and steel, but is also present in other waste streams (for example, as barium carbonate, BaCO_3).

^{36}Cl (half-life 3.0×10^5 years). In a nuclear reactor, ^{36}Cl is produced by three main routes; the dominant one being direct activation of the natural chlorine isotope chlorine-35. In the GDF ^{36}Cl would occur principally within graphite wastes.

^{59}Ni (half-life of 7.5×10^4 years) and ^{63}Ni (half-life 9.9×10^1 years). These are produced from the irradiation of stable nickel and are generated principally within steel.

^{94}Nb (half-life 2.0×10^4 years). This radionuclide is produced from ^{93}Nb , the stable isotope of niobium. ^{94}Nb is generated principally within steel.

⁷ Po-210 is of potential significance due to in-growth in the biosphere [42].

2.2 Chemical speciation

The behaviour of radionuclides and non-radiological species in water depends on chemical speciation. Chemical speciation refers to the distribution of an element among the different chemical forms or species that can occur. In water, chemical speciation depends on the composition of the water, the stabilities of the various species that may form, and on the prevailing conditions of, for example, salinity, temperature, pH and redox.

This section is concerned with the chemical speciation of radionuclides and non-radiological species in the porewaters and groundwaters that may be present in a geological disposal system. In this context, chemical speciation refers to the detailed distribution of chemical species dissolved in the water. The chemical speciation within a particular aqueous solution depends on the composition of the water, on the stabilities of the various dissolved species that may form, including inorganic and organic complexes, and on the prevailing conditions of, for example, temperature, pH and redox.

The temperature in the GDF will be influenced by heat emitted from some of the wastes, by the ambient temperature of the rocks at the disposal depth and by other processes such as the hydration of cement (see for example, [43]). The temperatures that may be reached in the GDF are typically less than 100 °C; see the generic Disposal System Technical Specification [44].

Redox conditions in the GDF will be affected by various chemical reactions, such as those involved in the degradation of wastes and the corrosion of steel. Many of these reactions will cause conditions within the GDF to be generally chemically reducing. Chemical speciation may also be influenced by other factors, including colloids and reaction kinetics; these topics are discussed in later sections.

At this stage in the programme to develop the GDF no site has been selected; therefore, many factors including the chemical compositions of groundwaters are not known. Nevertheless, the likely range of conditions that may need to be considered in future site-specific safety assessments can be assessed and bounded. Given this situation, we have focused our research and development work in this area on gathering relevant experimental data and developing and using tools and databases to understand and model the chemical speciation of key radionuclides. For example, chemical speciation codes such as PHREEQC [45] and EQ3NR [47] can be used in conjunction with thermodynamic databases to assess chemical speciation (and related processes such as sorption and solubility – see below). As a result, there is considerable understanding of chemical speciation, but there are still some gaps in data and uncertainties associated with the use of the models under certain conditions. Work is ongoing internationally to further develop the thermodynamic database and to extend the ability to model chemical speciation, for example, in more saline and higher temperature systems.

Our research programme is following a risk-based approach and is therefore focusing any detailed work on radionuclide chemistry on those radionuclides which are potentially important to safety. We are using expert elicitation to develop probability distribution functions (PDFs) of solubility and sorption values for key radionuclides based on available experimental data and taking account of the uncertainties that exist [46].

The chemical properties of elements that are most relevant to this report are those that determine their behaviour in aqueous solutions (groundwaters and EBS porewaters) and their interactions with solid surfaces, for example, through sorption, solubility and precipitation/co-precipitation. Some elements, such as the halogens, are highly soluble and have relatively simple aqueous chemistry. Others, such as the actinides, are only sparingly soluble, and their solubilities are strongly influenced by the chemistry of the water in which they are dissolved and the prevailing conditions. For example, the solubility of plutonium is strongly affected by solution pH and redox [51].

Redox conditions are of particular relevance because several redox sensitive radionuclides are more mobile when they are present in their higher oxidation states. It is important to understand redox reactions because redox disequilibrium is common in natural aqueous systems [47]. This has to be taken into account when assessing the chemistry and mobility of radionuclides and other species in a geological disposal system. Potentially important redox couples in this context include, Fe(II)/Fe(III), S(-II)/S(VI), C(-IV)/C(IV), U(IV)/U(VI), and Tc(IV)/Tc(VII). Examples of redox disequilibrium are common and include:

- the coexistence of dissolved oxygen and organic carbon in nearly all natural waters
- the disequilibrium commonly observed between $\text{CH}_{4(\text{aq})}/\text{HCO}_3^-$ and between $\text{HS}^-/\text{SO}_4^{2-}$ [47].

Redox disequilibrium may be created by radioactive decay, fluid mixing, and transfer of redox components from one phase to another [47]. Biological activity, however, derives energy from redox disequilibrium and in doing so catalyses an overall progression toward redox equilibrium [47]. With sufficient analytical data, the degree of disequilibrium among the various redox couples in a system can be evaluated and assessed using thermodynamic speciation codes.

2.2.1 Radionuclides

There is considerable knowledge of the chemical speciation of radionuclides in dilute, low-temperature groundwater systems, but further data may need to be gathered in some areas and site-specific assessments of groundwater geochemistry and interaction with the wastes will need to be made once a prospective site or sites are identified.

Extensive research has been conducted over the last few decades into the chemical thermodynamics and speciation of radionuclides in dilute, low-temperature groundwater systems, for example within the NEA TDB Project [31, 32]. Further detailed information is provided in [48, 49]. As another recent example, reference [50] provides a short overview of the aqueous complexation of Am(III), lanthanides⁸ (III), U(VI), and Th(IV) by sulphates, silicates, carbonates and phosphates. The research identified in our Science and Technology (S&T) Plan also includes several tasks aimed at developing and maintaining a consistent thermodynamic database [10, tasks 806, 807, 808 and 809].

Detailed systematic thermodynamic modelling studies of radionuclide speciation and solubility under the conditions expected in the geological disposal systems have been documented as part of safety cases developed in overseas disposal programmes, for example [51, 52, 53, 54, 55]. Equivalent studies have not yet been conducted in the UK because a site for the GDF has not been selected and the groundwater compositions of interest are not yet known. Some information from the overseas studies on the chemical speciation of key radionuclides in aqueous solution is given in Box 2. The information given on chemical speciation in Box 2 is at a high level and covers a range of geochemical environments relevant to geological disposal (for example, a range of redox and pH conditions). Box 2 does not, however, consider the impact of organic complexants on radionuclide speciation; this is discussed in Section 2.3.

⁸ The lanthanides series comprise the 15 metallic chemical elements with atomic numbers 57 to 71, from lanthanum to lutetium.

Box 2 Inorganic Aqueous Speciation and Potential Solubility Controls for Selected Radionuclides. After [51, 52, 53].

The following information is based on [51, 52, 53] and references therein, unless otherwise stated. These references are based on, and are generally consistent with, the information in the highly respected NEA TDB reviews [31, 32]. The chemical conditions considered in these references span the pH range 6 to 13, and redox (Eh) conditions from -400 to 0 mV; although the work did consider conditions within cement-conditioned waters, it was primarily focussed on conditions relevant to spent fuel disposal. The comments on solubility control apply to the EBS, which is consistent with the idea that aqueous radionuclide concentrations in the geosphere and biosphere are likely to be too low to result in the precipitation of pure radionuclide solid phases, although there may be cases where precipitation in the geosphere might occur.

The following paragraphs discuss the speciation of the elements according to the groups in the periodic table to which they belong (Figure 4).

Figure 4. Periodic table showing the groups of elements.

Periodic Table																		o																	
IA																		2																	
1	H																	He																	
IIA																		IIIa	IVA	VA	VIIa	VIIIA													
3	Li	4	Be																	5	B	6	C	7	N	8	O	9	F	10	Ne				
11	Na	12	Mg																	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar				
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
55	Cs	56	Ba		72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn	
87	Fr	88	Ra																																
				57	La	58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Re	69	Tm	70	Yb	71	Lu		
				89	Ac	90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr		

Non-metals

Alkali Metals

Alkaline Earth Metals

Transition Metals

Lanthanides

Actinides

Metalloids

Basic Metals

Halogens

Nobel Gasses

3447-01-ND A

3447-01-NDA

Elements of groups IA to VIIIA

Carbon

Carbon speciation is dominated by carbonic acid, $\text{H}_2\text{CO}_{3(\text{aq})}$, below $\sim\text{pH } 6$, bicarbonate, $\text{HCO}_3^-(\text{aq})$, between $\sim\text{pH } 6$ and 10 , and carbonate, $\text{CO}_3^{2-}(\text{aq})$, above $\sim\text{pH } 10$. The reduction of carbonate to form methane, $\text{CH}_{4(\text{g})}$, is thermodynamically plausible, but is kinetically hindered at low temperature and in the absence of microbial activity. In the absence of carbonate reduction, carbon solubility is likely to be controlled by calcite, $\text{CaCO}_{3(\text{s})}$, saturation.

Continued.../

Box 2 Inorganic Aqueous Speciation and Potential Solubility Controls for Selected Radionuclides (continued).

Chlorine

Chlorine speciation is dominated by chloride, $\text{Cl}^-_{(\text{aq})}$. Solubility is considered unlimited.

Iodine

Iodine speciation is dominated by iodide, $\text{I}^-_{(\text{aq})}$, but iodate, $\text{IO}_3^-_{(\text{aq})}$ can form under very oxidising conditions, above $\sim\text{Eh}$ 400 mV [56]. Solubility is considered unlimited.

Caesium

Caesium speciation is dominated by $\text{Cs}^+_{(\text{aq})}$, but $\text{CsCl}_{(\text{aq})}$ also forms depending on water salinity. Solubility is considered unlimited.

Radium

Radium speciation is likely to be dominated by $\text{Ra}^{2+}_{(\text{aq})}$, but $\text{RaSO}_{4(\text{aq})}$ and $\text{RaCO}_{3(\text{aq})}$ species also form, depending on water composition. Solubility may be controlled by solid solution or co-precipitation with $\text{BaSO}_{4(\text{s})}$ [126] or by precipitation of $\text{RaSO}_{4(\text{s})}$ or possibly $\text{RaCO}_{3(\text{s})}$.

Selenium

Selenium speciation depends on redox and pH. Under reducing and relatively less alkaline conditions selenium forms Se(-II) selenide species such as $\text{HSe}^-_{(\text{aq})}$. Under weakly reducing to moderately oxidising conditions Se forms Se(IV) species such as $\text{HSeO}_3^-_{(\text{aq})}$ and $\text{SeO}_3^{2-}_{(\text{aq})}$. Under more strongly oxidising conditions Se forms Se(VI) selenate species, such as $\text{HSeO}_4^-_{(\text{aq})}$ and $\text{SeO}_4^{2-}_{(\text{aq})}$. These anionic species may form complexes with a range of cations depending on water chemistry. Solubility may be controlled by precipitation with iron.

Tin

Tin speciation is dominated by hydrolysis products of Sn(IV) as $\text{Sn}(\text{OH})_{4(\text{aq})}$ below $\sim\text{pH}$ 8, $\text{Sn}(\text{OH})_5^-_{(\text{aq})}$ between $\sim\text{pH}$ 8 and 10, and $\text{Sn}(\text{OH})_6^{2-}_{(\text{aq})}$ above $\sim\text{pH}$ 10. Solubility may be controlled by amorphous $\text{SnO}_{2(\text{s})}$ or $\text{CaSn}(\text{OH})_{6(\text{s})}$, depending on pH and water composition.

Lead

Lead speciation is dominated by Pb(II) species [57]. For a total lead concentration of 1×10^{-6} M, $\text{Pb}^{2+}_{(\text{aq})}$ tends to predominate below $\sim\text{pH}$ 7.5, $\text{Pb}(\text{OH})^+_{(\text{aq})}$ and $\text{Pb}(\text{OH})_{2(\text{aq})}$ between $\sim\text{pH}$ 7.5 and ~ 10 , $\text{Pb}(\text{OH})_3^-_{(\text{aq})}$ between $\sim\text{pH}$ 10 and 11.5, and $\text{Pb}(\text{OH})_4^{2-}_{(\text{aq})}$ above $\sim\text{pH}$ 11.5. However, the positions of these predominance boundaries are dependent on the total lead concentration and at higher concentrations species such as $\text{Pb}_6(\text{OH})_8^{4+}_{(\text{aq})}$ may occur under moderately alkaline conditions [57]. Lead carbonate, phosphate, sulphate and chloride species may also form depending on water chemistry.

In the EBS, if sulphide is present, then lead concentrations will be controlled to low values by the formation of $\text{PbS}_{(\text{s})}$ [57]. Similarly, if the Eh is reduced sufficiently to stabilise metallic lead, then the concentrations of lead will be very low. If such conditions are not present, then it is likely that lead silicate will control the solubility of lead. Depending on water chemistry, prevailing conditions and kinetic factors, a range of solid phases may control lead solubility in other parts of a disposal system [57], including cerussite, $\text{PbCO}_{3(\text{s})}$ and hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_{2(\text{s})}$, lead silicates, lead phosphates, lead chlorides, carbonato-chlorides and hydroxy-chlorides, lead sulphates (such as anglesite, $\text{PbSO}_{4(\text{s})}$) and lead sulphide.

Continued.../

Box 2 Inorganic Aqueous Speciation and Potential Solubility Controls for Selected Radionuclides (continued).

Transition elements

Nickel

Nickel speciation is dominated by Ni(II) species. $\text{Ni}^{2+}_{(\text{aq})}$ tends to predominate below ~pH 9.5, and $\text{Ni}(\text{OH})_{2(\text{aq})}$ and/or $\text{Ni}(\text{OH})_{3^{-}(\text{aq})}$ occur above ~pH 9.5. Ni also forms stable species with chloride and sulphate. The solubility of Ni may be controlled by $\text{NiCO}_{3(\text{s})}$ or $\text{Ni}(\text{OH})_{2(\text{s})}$, with the hydroxide more likely to occur above ~pH 8. The speciation and solubility of nickel may also be affected if there is bacterial reduction of sulphate to sulphide.

Technetium

Technetium speciation depends on redox and pH. Under reducing conditions, technetium forms Tc(IV) species, principally $\text{TcO}(\text{OH})_{2(\text{aq})}$ between ~pH 6 and 11, and $\text{TcO}(\text{OH})_{3^{-}(\text{aq})}$ at higher pH. Tc(IV)-carbonate species may also form at higher pH. Under more oxidising conditions technetium forms the Tc(VII) pertechnetate species, $\text{TcO}_4^{-}(\text{aq})$. Under reducing conditions, the solubility of technetium may be controlled by technetium dioxide (for example, $\text{TcO}_2 \cdot 1.63\text{H}_2\text{O}_{(\text{s})}$). Under more the oxidising conditions in which pertechnetate species occur, the solubility of technetium is considered unlimited.

Actinides

Thorium

Under the conditions of relevance to a GDF, and depending on water chemistry, particularly the concentration of carbonate, thorium is expected to occur as a range of Th(IV) mixed hydroxide-carbonate complexes. Three mixed hydroxide-carbonate thorium species were selected in the NEA thorium review: $\text{Th}(\text{OH})(\text{CO}_3)_{4^{5-}(\text{aq})}$, $\text{Th}(\text{OH})_2(\text{CO}_3)_{2^{2-}(\text{aq})}$ and $\text{Th}(\text{OH})_4(\text{CO}_3)_{2^{2-}(\text{aq})}$. Reference [53] notes that two further mixed complexes, $\text{Th}(\text{OH})_2(\text{CO}_3)_{(\text{aq})}$ and $\text{Th}(\text{OH})_3(\text{CO}_3)^{-}(\text{aq})$, are potentially relevant at low carbonate concentrations in the near neutral pH range. $\text{Th}(\text{CO}_3)_{4^{4-}(\text{aq})}$ may occur at high carbonate concentrations in the near neutral to moderately alkaline pH range. The solubility of thorium is potentially limited by the solubility of amorphous thorium oxide, $\text{ThO}_{2(\text{s})}$.

Uranium

Uranium speciation depends on redox and pH, and is such that a mix of U(IV) and U(VI) may co-exist in the EBS of the GDF. Under reducing conditions, U forms U(IV) species, and $\text{U}(\text{OH})_{4(\text{aq})}$ may dominate. Under less reducing conditions, U(VI) hydroxide and carbonate species may dominate, including $\text{UO}_2\text{CO}_{3(\text{aq})}$ below ~pH 7, $\text{UO}_2(\text{OH})_{3^{-}(\text{aq})}$ between ~pH 7 and 9, and $\text{UO}_2(\text{CO}_3)_{3^{4-}(\text{aq})}$ above ~pH 9. $\text{UO}_2^{2+}(\text{aq})$ may also be important below ~pH 7. Depending on water chemistry, the prevailing chemical conditions and kinetic factors, a range of solid phases may control uranium solubility. Under reducing conditions, $\text{UO}_{(2+x)(\text{s})}$ phases can form. $\text{UO}_{2(\text{s})}$ can accept excess oxygen into its structure up to a non-stoichiometric composition corresponding to $x = 0.33$ (that is, $\text{UO}_{2.33(\text{s})}$ or $\text{U}_3\text{O}_{7(\text{s})}$). Under oxidising conditions, U(VI) uranium solids may form. Depending on water chemistry, potential pure U(VI) solid phases include uranophane, becquerelite, coffinite and soddyite [51]. Uranates have been reported to precipitate under alkaline conditions, giving uranium solubilities on the order of 2.5×10^{-8} to $3 \times 10^{-6} \text{ mol/dm}^{-3}$ [53]. In nature, uranium also occurs in many other minerals, together with elements including phosphates.

Continued.../

Box 2 Inorganic Aqueous Speciation and Potential Solubility Controls for Selected Radionuclides (continued).

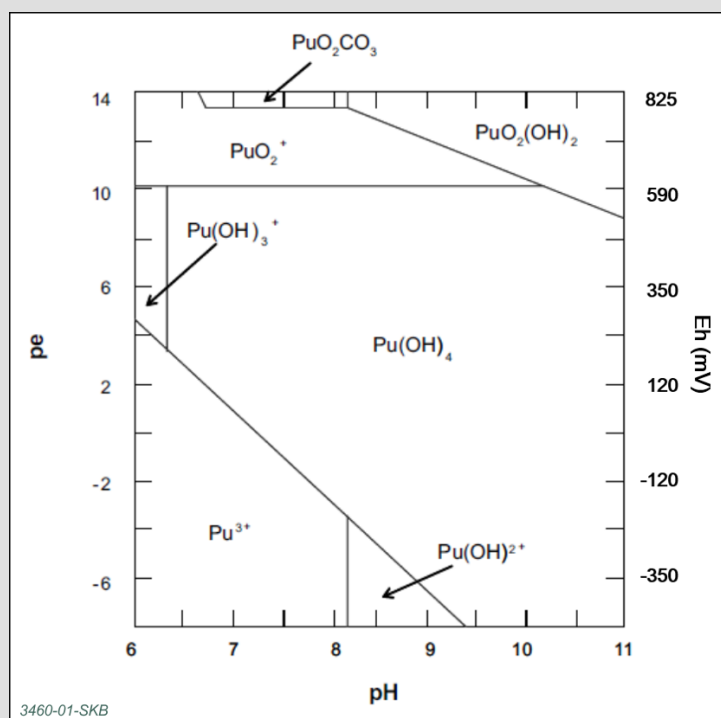
Neptunium

Neptunium may occur in several different oxidation states, III, IV, V and VI, depending on the redox environment. The speciation of neptunium under reducing conditions is likely to be dominated by $\text{Np}(\text{OH})_{4(\text{aq})}$. In more oxidising conditions, Np(V) species may dominate; $\text{NpO}_2^+(\text{aq})$ in the near neutral region and $\text{NpO}_2(\text{OH})_{(\text{aq})}$ in more alkaline conditions. Various Np(V)-carbonate species may form at higher pH. Neptunium dioxide $\text{NpO}_2 \cdot 2\text{H}_2\text{O}_{(\text{s})}$, may exert solubility control in reducing and slightly oxidising environments; in oxic conditions, $\text{Np}_2\text{O}_5_{(\text{s})}$ may control neptunium concentrations in groundwater. Neptunium concentrations governed by the precipitation of neptunium dioxide will depend on environmental conditions and water composition, particularly on dissolved carbonate concentrations.

Plutonium

Plutonium may occur in several different oxidation states, III, IV, V and VI, depending principally on the redox environment, but also on water pH. Figure 5 from [51] shows the predominant plutonium aqueous species as a function of redox conditions and pH for a particular Swedish reference groundwater and a total Pu concentration of 1×10^{-7} M. $\text{Pu}^{3+}_{(\text{aq})}$ occurs under strongly reducing conditions and pH values in the lower part of the range. $\text{Pu}(\text{OH})_{4(\text{aq})}$ is the dominant aqueous species over much of the range of conditions of interest. Pu(V) and Pu(VI) species only become dominant under very oxidising conditions. The speciation of plutonium is also dependent on water composition, particularly in terms of carbonate, sulphate and phosphate concentrations, and species including $\text{PuCO}_3^+(\text{aq})$, $\text{Pu}(\text{CO}_3)_2(\text{aq})$ and $\text{PuSO}_4^+(\text{aq})$ may be important. According to [51] plutonium solubilities may be controlled by Pu(III) (hydr)oxides or hydroxo-carbonate under very reducing conditions and by Pu(IV) (hydr)oxides under slightly reducing or oxidising conditions.

Figure 5. Eh/pH diagram showing the predominant plutonium aqueous species. Calculations performed with total Pu concentration = 1×10^{-7} M for a Swedish reference groundwater. After [51].



Continued.../

Box 2 Inorganic Aqueous Speciation and Potential Solubility Controls for Selected Radionuclides (continued).

Americium

Under the conditions of relevance to a GDF the speciation of americium is expected to be dominated by Am(III) species; $\text{Am}^{3+}_{(\text{aq})}$ dominates in the slightly acid to neutral pH range, with the hydrolysis products, $\text{Am}(\text{OH})^{2+}_{(\text{aq})}$, $\text{Am}(\text{OH})^{+}_{(\text{aq})}$, $\text{Am}(\text{OH})_{3(\text{aq})}$, dominating in the alkaline range. Americium also forms stable carbonate and sulphate species; it may also form carbonate, sulphate and phosphate species depending on water chemistry.

Depending on the chemical conditions and water chemistry, the solubility of americium may be controlled by a range of solid phases, including $\text{Am}(\text{CO}_3)_{3(\text{s})}$, $\text{Am}(\text{OH})_{3(\text{s})}$ or $\text{AmCO}_3\text{OH}_{(\text{s})}$ or, possibly, by phosphate solid phases.

Curium

The chemistry of curium is similar to that of americium.⁹

Lanthanides

Samarium

The chemistry of samarium is similar to that of americium and curium, although the dominance of $\text{Sm}^{3+}_{(\text{aq})}$ extends slightly further than that of $\text{Am}^{3+}_{(\text{aq})}$, up to ~pH 9. A mixture of samarium hydrolysis species is expected in the range ~pH 9 to 11, and $\text{Sm}(\text{OH})^{4-}_{(\text{aq})}$ is expected to dominate above ~pH 11. The most likely precipitating solid phases are samarium hydroxide, samarium carbonate and a mixed samarium hydroxo-carbonate.

Holmium

The chemistry of holmium is similar to that of samarium, although the $\text{Ho}(\text{OH})^{4-}_{(\text{aq})}$ species is dominant throughout the range above ~pH 9. The solubility of holmium may be controlled by solid carbonate phases (eg. $\text{Ho}_2(\text{CO}_3)_{3(\text{s})}$) under near neutral conditions. Under more alkaline conditions, above ~pH 8.5, solubility may be controlled by the solid hydroxide, $\text{Ho}(\text{OH})_{3(\text{s})}$.

2.2.2 Non-radiological species

With the exception of radioactive decay and biodegradation of some organic compounds, the behaviour and transport of non-radiological species in groundwater will be controlled by the same physical and chemical processes that control the behaviour and transport of radionuclides. The impacts of non-radiological species will be compared against different regulatory standards to those for radionuclides.

Some of the wastes and materials used in the construction of a GDF will contain non-radiological species, such as metals and organic compounds. Some of the radionuclides present may also pose a non-radiological hazard. For example, radioactive isotopes of uranium are also toxic.

The Water Framework Directive (2000/60/EC) (WFD) and the Groundwater Daughter Directive (2006/118/EC) (GDD) require EU Member States to protect groundwater against pollution¹⁰ and deterioration by preventing or limiting the entry of pollutants (substances liable to cause pollution) to groundwater.

⁹ It is generally accepted within standard chemistry texts that certain actinides in the same oxidation state have similar chemical behaviour. Where these similarities exist, such as between americium(III) and curium(III), an 'oxidation state analogy' can be used to provide some understanding of the likely behaviour of those actinides for which there is not extensive experimental data.

¹⁰ **Pollution** - the direct or indirect introduction, as a result of human activity, of substances or heat into the air, water or land which may: (i) be harmful to human health or the quality of aquatic ecosystems or terrestrial

Certain provisions of these Directives have been given effect in England and Wales through the Environmental Permitting (England and Wales) Regulations 2010 (EPR10) that apply to the development of the GDF. The adoption of the WFD and GDD into EPR10 emphasises the need to protect the environment and groundwaters in particular, not just from radioactive species but from hazardous substances¹¹ and also non-hazardous pollutants¹².

A hazardous substance is any pollutant identified as such by the UK environment agencies' Joint Agencies Groundwater Directive Advisory Group (JAGDAG). The current JAGDAG list contains approximately 250 substances, including hydrocarbons, organo-halogen compounds, organo-phosphorus compounds, mercury and cadmium. UK Government considers that radioactive substances are hazardous substances within the meaning of the WFD and GWDD [58].

The Environment Agency's Guidance on Requirements for Authorisation (GRA) [59] indicates that *"...solid radioactive waste shall be disposed of in such a way that the level of protection provided to people and the environment against any non-radiological hazards of the waste is consistent with that provided by the national standard for wastes that present a non-radiological hazard"*. This principle does not ask for the specified national standards for non-radiological hazards to be applied, but asks for an equivalent level of protection to that taken into account when radioactive waste is disposed of. Any suitable means can be used to protect against the non-radiological hazards, providing the protection against these hazards is as great as it would be if the wastes were not radioactive [59].

GRA Requirement R10 states:

"Protection against non-radiological hazards: the developer/operator of a disposal facility for solid radioactive waste should demonstrate that the disposal system provides adequate protection against non-radiological hazards."

Environment Agency supplementary guidance [60] states:

"...for a radioactive waste disposal facility, the applicant should take into account the magnitude of the non-radiological hazard and the effectiveness of the barrier to groundwater pollution provided by the geology".

To recognise the requirements, RWM's 2016 Generic Disposal System Specification [61, 62] will include an additional requirement on Environmental Protection:

"In accordance with the groundwater protection provisions of the Environmental Permitting (England and Wales) Regulations 2010, it shall be demonstrated that all necessary technical precautions will be observed to:

- *prevent the input of hazardous substances to groundwater; and*
- *limit the input of non-hazardous pollutants to groundwater so as to ensure that such inputs do not cause pollution of groundwater."*

With the exception of radioactive decay and the biodegradation of some organic compounds, the behaviour of inorganic non-radiological species will be determined by the same physico-chemical processes that control the behaviour in groundwater of radionuclides. For example, metal ions will sorb and precipitate and may form complexes with organic complexants. Organic non-radiological species may degrade radiolytically,

ecosystems directly depending on aquatic ecosystems;(ii) result in damage to material property; or (iii) impair or interfere with amenities or other legitimate uses of the environment [EPR10].

¹¹ **Hazardous substances** - substances or groups of substances that are toxic, persistent and liable to bio-accumulate, and other substances or groups of substances which give rise to an equivalent level of concern [Water Framework Directive].

¹² **Non-hazardous pollutant** - any substance liable to cause pollution [EPR10].

thermally or chemically and could give rise to organic complexing species or other smaller organic molecules. Microbial activity may however degrade small organic molecules [149] and, thus, limit the quantities reaching relevant assessment points.

Assessment of the impact of non-radioactive species is not a new issue. Scoping assessments for non-radiological species have been conducted in the past [63, 64, 65, 66, 67, 68, 69, 70]. Work has also been conducted on behalf of the Low Level Radioactive Waste Repository (LLWR), see for example references [71, 72]. Examples of non-radiological species considered in these earlier studies are given in Box 3.

Box 3 Examples of non-radiological species. After [67].

Hazardous species

Aluminium. Aluminium is the most widely used non-ferrous metal and will therefore be present in numerous waste streams anticipated for disposal in the GDF.

Cadmium. Relatively small amounts of cadmium may be present in the inventory. Ingestion of cadmium may result in kidney failure and bone diseases, while chronic inhalation of cadmium may impair lung and kidney functions. Cadmium and cadmium compounds are also carcinogenic to humans; inhalation increases the risk of lung cancer.

Organics. In addition to inorganic non-radiological species, there is a need to consider the potential impacts of certain hazardous organic non-radiological species such as benzo-pyrene, benzene, dodecyl benzene, toluene, mineral oil, petroleum oil, styrene, mercury compounds, C10 to C13 alkanes, chloroethylene, hexachlorobenzene, 1,1,2,2 tetrachloroethane, 1,2,4-trichlorobenzene, dichloroethane, 2-chloro-1,3-butadiene, trichloroethylene, tributyl-phosphate, triphenyl-phosphate and tributyltin oxide.

Non-hazardous pollutants¹³

Beryllium. Naturally occurring beryllium is often used as a neutron reflector and neutron moderator due to its large scattering cross-section for high-energy neutrons. Beryllium is a highly toxic substance, especially if inhaled as dust.

Chromium. Chromium is a component of stainless steel and will be present in the wastes and waste containers. The toxicity of chromium depends on its oxidation state, with the hexavalent form being more toxic than the trivalent form. In the GDF chromium released from stainless steel waste containers is expected to be in the trivalent form, but this may be oxidised in near-surface conditions [73, 74].

Lead. Lead is commonly used for radiological shielding and so will be present within the wastes and potentially also as shielding material in waste containers [57]. Lead will also be produced in the disposal system by radioactive decay and ingrowth. Lead is a known cumulative neurotoxin and chronic exposures to lead can result in headache, irritability, lethargy, convulsions, muscle weakness, ataxia, tremors and paralysis. Inorganic lead compounds are classified as probably carcinogenic to humans.

Manganese. Manganese is commonly used in metal alloys, particularly stainless steel. It will therefore be present in the waste containers as well as in the wastes themselves. Manganese can cause neurological effects following inhalation and following extended exposure to very high levels in drinking-water.

Uranium. Various isotopes of uranium will be present within the GDF, principally due to its use in nuclear fuel. In addition to the radiological properties of uranium, it is also a well-known nephrotoxin¹⁴.

¹³ Non-radioactive isotopes of the following elements are non-hazardous pollutants. Radioactive isotopes are hazardous species.

¹⁴ A nephrotoxin is a toxic agent or substance that inhibits, damages or destroys the cells and/or tissues of the kidneys.

In these previous studies, the focus was on humans as the receptor (or endpoint), rather than on groundwater and the environment. However, under EPR10 the requirements in the legislation “*to prevent the input*” (in the case of hazardous substances) and to limit the input (for non-hazardous pollutants) into the groundwater, are relatively new and present potential challenges, particularly at the current stage of the programme for geological disposal in which generic assumptions have to be made regarding the geological and hydrogeological characteristics of environment in which the future GDF will be sited.

In support of the ‘prevent the input’ criterion, the Environment Agency has published Minimum Reporting Values (MRVs) for a number of hazardous substances [75]. We propose to use these values (or where they are not available a multiple of the Limit of Detection, LoD) to calculate a threshold inventory (essentially a mass of material) for each substance identified in the inventory for disposal. These will be determined by modelling the performance of the EBS using relevant sorption and solubility data to determine the concentration of the substance at the appropriate compliance point and comparing these with appropriate limits.

Recently, RWM has undertaken both general screening and assessment studies on non-radiological substances, and studies of specific substances, including lead and mercury. Reference [76] looked at the potential post-closure behaviour of a wide range of hazardous substances in the GDF. In this study, the JAGDAG list of hazardous substances was analysed and 49 of the listed species were identified as being present or likely to be present in higher-activity wastes. Within this set of 49 species, priority was given to those for which MRV or LoD values were known and a list of 20 species with a range of different characteristics was identified for modelling and assessment. The 20 species were cadmium, benzo-pyrene, benzene, dodecyl benzene, toluene, mineral oil, petroleum oil, styrene, mercury compounds, C10 to C13 alkanes, chloroethylene, hexachlorobenzene, 1,1,2,2 tetrachloroethane, 1,2,4-trichlorobenzene, 1,2-dichloroethane, 2-chloro-1,3-butadiene, trichloroethylene, tributyl-phosphate, triphenyl-phosphate and tributyltin oxide. However, it should be noted that at this stage it is not clear which of the substances listed by JAGDAG are actually present in the inventory of wastes for disposal. The project [76] was effectively a scoping study, based on conservative assumptions as a first step in furthering understanding of the potential significance of hazardous substances within higher-activity wastes and considering means of calculating disposal capacities.

It is recognised that additional studies, possibly including modelling of further hazardous and non-hazardous substances, covering both aqueous and gaseous species will be required - the research identified in our S&T Plan includes work to:

- identify in more detail the quantities of hazardous substances and non-hazardous pollutants that may be present in the waste inventory [10, task 306]
- collate data to help understand the migration of non-radiological species from a GDF via the groundwater pathway [10, task 051]
- evaluate the current state of knowledge on non-radiological species in the context of the prevailing regulatory setting and propose additional work to satisfy knowledge gaps [10, task 052]
- develop an appropriate methodology for undertaking a full site-specific assessment of non-radiological species [10, task 053]
- develop understanding of possible synergistic effects resulting from exposures to mixtures of chemical contaminants or a combination of radiotoxic and chemotoxic substances and propose additional work to satisfy knowledge gaps [10, task 054].

The manner by which we will ultimately address the requirements of environmental protection from non-radiological species at a specific site will need to take account of the

characteristics of the site and, in particular, the delineation and characteristics of groundwaters at depth and in overlying groundwater bodies.

We are also engaging in dialogue with the regulators to discuss potentially suitable assessment approaches and how assessment results may be considered and applied in the context of the relevant regulations and regulatory guidance.

2.3 Organic complexation

Organic compounds may be present as dissolved and colloidal species and may be transported by advection and diffusion. They may also bind to radionuclides and inorganic non-radioactive species, increasing their solubility and mobility.

Organic compounds, including potentially toxic organic non-radiological species, can form dissolved and colloidal species in aqueous systems and may be transported in groundwater by advection and diffusion. They may also bind to radionuclides and inorganic non-radioactive species (such as metal ions) and by doing so increase their concentration in solution and their potential for transport.

For the waste inventory and disposal concepts under consideration, organic complexants are most relevant to the disposal of ILW/LLW. Relevant organic complexants may be derived from the degradation of cellulosic ILW/LLW, from as-disposed complexants, and from superplasticisers and polymeric waste encapsulants.

Many studies have been conducted to investigate the range of potential organic complexants and their effects on radionuclide behaviour. For example, based on an extensive review of the literature, reference [77] selected thermodynamic data for organic complexes of citrate, oxalate, ethylenediaminetetraacetic acid (EDTA) and isosaccharinic acid (ISA) with uranium, neptunium, plutonium, americium, technetium, nickel, selenium, zirconium and some other competing cations. Further work on organic complexation has been conducted within the Thermochemie database development project, extending the range of organic ligands considered to include acetate, adipate, gluconate, nitrilotriacetate, phthalate and fulvate-like compounds [33, 34]. Reference [78] assesses the potential effects of complexants on contaminant transport at the LLWR.

These studies suggest that, if present at high enough concentrations in the GDF, cellulose degradation products (CDP) and possibly EDTA may be the most important of the organic complexants; radioelement solubility may be increased and sorption decreased, with the magnitude of these effects varies with the concentration of complexants [79, 80, 81]. The available data also suggest that cellulose degradation products may have a stronger effect than as-disposed complexants [82]. In RWM's safety assessments, the effects of organic complexation on solubility and sorption in the EBS are considered using factors that quantify the enhancement of solubility and the reduction in sorption that they can cause (for more detail see [9]).

As water from the EBS moves into and through the geosphere it will be progressively diluted through mixing with groundwater and dispersion. The concentrations of organic complexants may be further reduced by chemical or microbial processes. These processes would reduce the concentration of waste-derived organic species and complexants, and so their effects on radionuclide solubility and sorption would gradually decrease. The distance over which this dilution occurs will depend on the details of groundwater movement at the particular site.

Groundwaters in the geosphere may contain natural organic matter (NOM), for example, in the form of humic and fulvic substances; these may influence the behaviour and transport of dissolved species. Humic and fulvic acids are present in many groundwaters, especially in the near-surface environment. Humic and fulvic acids can be stable over long time periods and are known to form complexes with many radionuclides and metal ions.

More detailed information on organic complexation in the EBS and in the geosphere is provided in Sections 3 and 0.

2.4 Radiolysis

The term radiolysis is used to describe the decomposition of chemical compounds by radiation. Radiolysis is of principal concern inside the waste packages because this is where the radiation field is high enough to have an effect.

Radiolysis of water may lead to the formation of a wide range of product species, including hydrogen gas, hydrogen peroxide and free radicals. Most of these species are short-lived and they are not expected to migrate over any appreciable distance.

Radiolysis is not expected to have a significant effect on spent fuel dissolution because the anaerobic corrosion of steels in the GDF will generate hydrogen pressures that are sufficiently high to overwhelm the effects of oxidising radiolysis products and suppress fuel dissolution rates. HLW glass dissolution rates are typically independent of radiation levels. Radiolysis of water in cements can induce gas generation. Radiolysis of some organic waste materials such as PVC can lead to the production of acids. Radiolysis of polymers may also lead to the production of water soluble organic species that can act as complexants and form NAPLs. The effects of radiation on solid materials outside the waste packages will be insignificant.

The term radiolysis is used to describe the decomposition of chemical compounds by radiation [83]. The effects of radiolysis will depend on the type and energy of the radiation and the spatial distribution and nature of the materials being irradiated. Radiolysis is of principal concern inside the waste packages because this is where the radiation is most intense.

Radiolysis of water

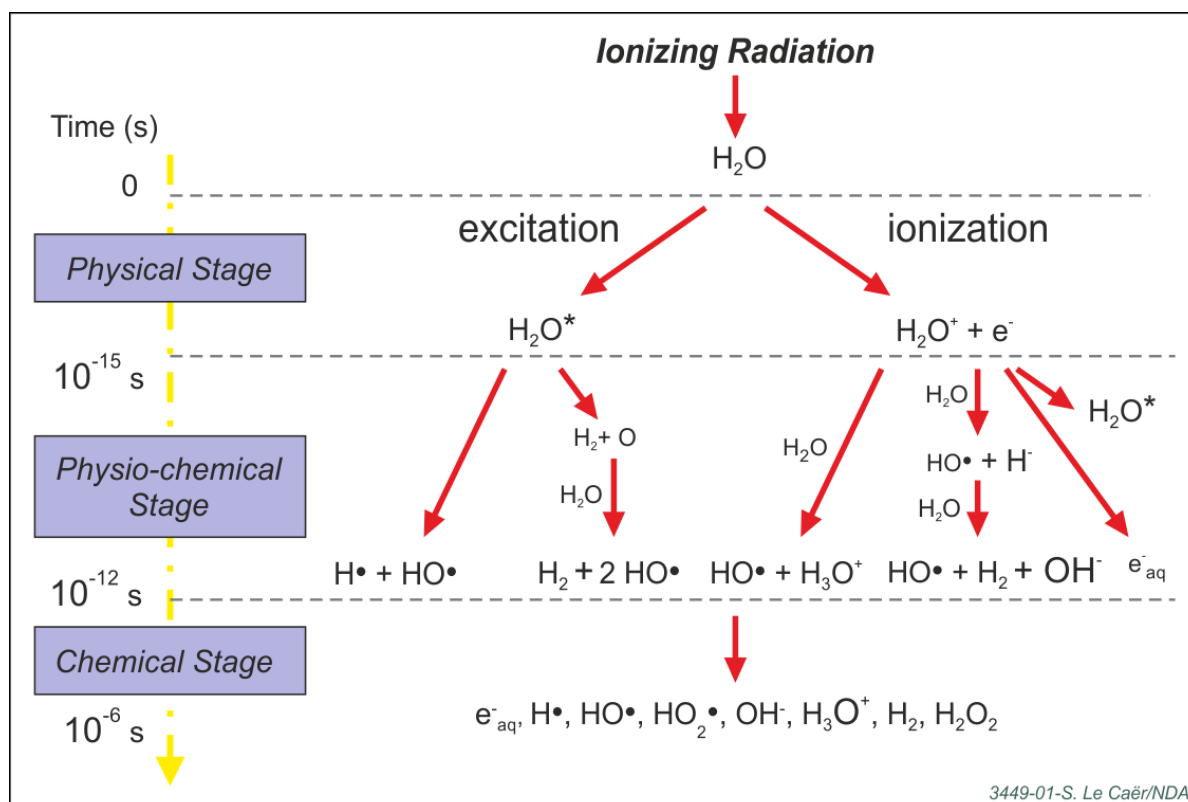
Radiolysis of water may lead to the formation of a wide range of product species, including hydrogen gas, hydrogen peroxide and free radicals - the process is illustrated in Figure 6. These species have varying stabilities and tendencies to react with their surroundings, but many are chemically reactive and very short-lived. Such species are not expected to migrate over any appreciable distances before reacting.

Radiolysis of wastes

Spent fuel and HLW

Redox conditions in the GDF are expected to become generally reducing over a period of tens to hundreds of years, principally due to the corrosion of steel. Redox conditions are expected to remain generally reducing for the subsequent future of the GDF [2]. Anaerobic corrosion of steel produces hydrogen some of which will dissolve in the water inside the GDF and some of which may be present as gas.

Waste containers for spent fuel and HLW are currently designed to ensure that dose rates outside them are below 1 Gy/h [84, 85]. At this level, effects of radiolysis 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 dose rates from HLW and spent fuel will diminish 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 . After a few hundred years, a period over which the waste container is expected to remain intact, the dominant contribution to radiolysis product formation will be alpha radiation from the decay of actinides. Alpha activities of the order of 10^{13} to 10^{14} Bq/teU are expected after thousands of years [86], the minimum lifetime generally expected from spent fuel and HLW containers (see Section 10 of [2]).

Figure 6. Reaction pathways for the radiolysis of water¹⁵. After [87].

The effect of gamma or beta radiolysis on the creation of oxidized species in contact with waste package is expected to be negligible due to the large amounts of hydrogen dissolved in the water [88, 89, 90]. Hydrogen pressures of the order of 1 to 10 MPa are expected in the disposal areas for spent fuel and HLW [90, 91].

Although low redox potentials are expected in the 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 waste [90]. The effect of radiolytic oxidants (in particular $H_2O_2(aq)$) and reductants (predominantly $H_2(g)$) on the dissolution of un-irradiated UO_2 and spent fuel have been studied extensively [90, 92]. In oxygenated water, radiolysis products such as $H_2O_2(aq)$ accelerate the oxidative dissolution of UO_2 [93]. In the absence of oxygen, the dissolution rate is significantly lower; nonetheless, there is still evidence for some impact of radiolytic oxidants on dissolution. Many studies of spent fuel dissolution performed recently have shown that the presence of significant amounts of hydrogen and the absence of oxygen result in a complete suppression of oxidative fuel dissolution [94, 95, 96, 97].

HLW glass dissolution rates are typically independent of radiation levels. The few experimental data that are available from tests performed in radioactive conditions show that the glass corrosion rate does not appear to be significantly affected by either external radiation fields or self-irradiation [98]. Leach tests showed a factor of 2-3 increase in the initial dissolution rate in the presence of radiation. However, the HLW 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.

¹⁵ Key: H^\bullet = an uncharged hydrogen atom or free radical. HO^\bullet = an uncharged free radical. H_2O^* = an excited water molecule. H_2O^+ = an ionised water molecule. e^- = a sub-excitation electron, $e^-_{(aq)}$ = a solvated electron [73].

LLW/ILW

Radiolysis of water in cements can induce gas generation. Gas generation introduces the potential for mechanical damage of cementitious wasteforms (such as cracking) and, although no detrimental effect on wasteform strength is expected [2], gas generation may result in the pressurisation of unvented waste containers and enhance the release of any gaseous radionuclides [5].

Radiolysis of some organic waste materials can lead to the production of acids. Radiolysis of cellulosic wastes is unlikely to yield acidic materials in sufficient quantities to be of concern, but radiolysis of chloride-containing polymers, such as PVC, may lead to production of hydrochloric acid [99]. Radiolysis of polymers may also lead to the production of water soluble organic species that can act as complexants and form NAPLs [100] (see Section 2.9).

Radiolysis of other materials in the disposal system

The effects of radiation on solid materials outside the waste packages (for example cements, metals and rocks) will be insignificant because the intensity of the radiation field will be too low [101].

2.5 Sorption

The term sorption is used here to describe a range of processes that involve the uptake of dissolved species by material surfaces. Sorption has the effect of lowering the dissolved concentration of the species and so retards its transport in groundwater. The rates, strength and reversibility of sorption reactions are dependent on the species, the nature of the sorbing surface and the environmental conditions.

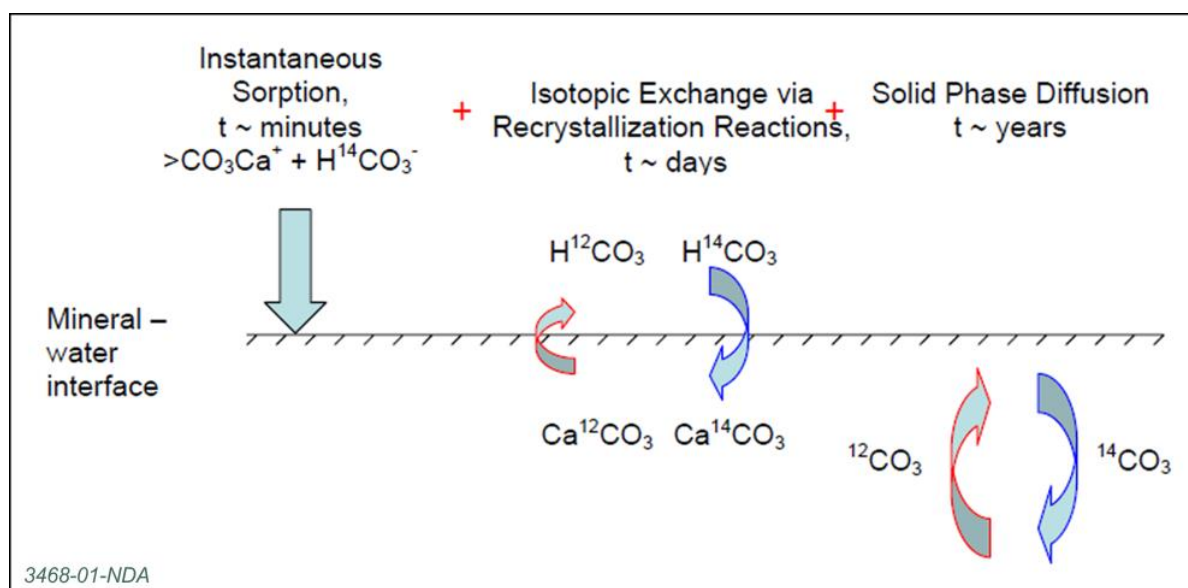
The term sorption is used here to describe a range of processes by which entities such as dissolved ions, gas or other molecules are partitioned between a solution (groundwater or porewater) and a solid surface (for example, the surface of a mineral).

Sorption processes occur at surfaces and, as defined here, do not involve the formation of three-dimensional solid phases. However, in some instances there may be a gradation from sorption processes to processes that do involve the formation of three-dimensional solid phases, such as co-precipitation and solid solution formation – see Section 2.6.2. For example, Figure 7 shows a conceptual model for the uptake and incorporation of $^{14}\text{CO}_3^{2-}(\text{aq})$ by calcite, which involves an initial process of sorption followed by recrystallization and diffusion [130].

The occurrence of processes such as sorption, co-precipitation and precipitation on immobile surfaces during chemical transport leads to a retardation of the solute in question relative to the migration of species that are not involved in such reactions (conservative tracers) and which generally migrate by advection at the average speed of the water or by diffusion.

As defined here, sorption may occur on any material surface exposed to water, including the wasteform and waste container (and any associated corrosion products and secondary minerals formed from their interactions with water), other materials in the rest of the EBS (which, dependent on the disposal concept, may include clay, salt or cement-based engineered barriers) and mineral and other surfaces in the host rocks and the rest of the geosphere and biosphere.

Figure 7. Conceptual model for the uptake and incorporation of $^{14}\text{CO}_3^{2-}(\text{aq})$ by calcite. After [130].



In multiphase solids, such as cements and clays in engineered barriers and most rocks, trace mineral phases may dominate sorption behaviour and can have a significant impact on transport. In fractured rocks, sorption onto minerals on fracture surfaces and fracture filling minerals may occur.

Laboratory observations of sorption are often interpreted in terms of ion exchange or surface complexation reactions. These reactions are generally rapid and can be investigated on laboratory timescales.

- **Ion exchange.** This involves the exchange of ions present at the surface of a mineral with other ions in solution.
- **Surface complexation.** In surface complexation theory, sorption is described in terms of a set of complex formation reactions between dissolved solutes and surface functional groups [102]. The free energies of the reactions can be divided into chemical and electrostatic contributions for modelling purposes. Surface functional groups influence both terms. The nature of the surface functional groups controls the stoichiometry of the sorption reactions, and hence the variation in sorption with solution chemistry. Surface functional groups also influence the electrical properties of the interface, and their density controls the sorption capacity [103].

A variety of materials may sorb radionuclide and other species in a geological disposal system. Hydrous oxide minerals and natural organic particulate matter possess proton-bearing surface functional groups [103]. Consequently, adsorption onto these solid phases is pH dependent. Aluminosilicate minerals can be divided into those that possess a permanent structural charge and those that do not. Aluminosilicate minerals without permanent charge have proton-bearing surface functional groups, and hence may be considered along with hydrous oxides. Minerals with permanent structural charge, such as clay minerals, micas, zeolites and most manganese oxides, have ion-bearing exchange sites in addition to proton-bearing surface functional groups. The surface functional groups of salt-type minerals bear the cation or anion of the salt, for example $\text{Ca}^{2+}(\text{aq})$ or $\text{CO}_3^{2-}(\text{aq})$ on the calcite surface. Sulphide minerals are potentially important sorbing phases in many reducing environments. These minerals possess both proton-bearing and salt-type surface functional groups; however, metal ion sorption by sulphides may be controlled primarily by surface precipitation reactions (see Section 2.6.2).

Sorption can be quantified using two broad approaches. The first approach involves the use of empirical sorption isotherms to describe the relationship between dissolved and sorbed concentrations. The simplest isotherm is termed 'linear sorption'. Other more complex isotherms, such as the Freundlich and Langmuir isotherms, have been developed (see, for example, reference [38]) to represent the concentration dependence of sorption and the sorption capacity of the sorbing surface respectively. The second approach involves developing a more detailed, mechanistic understanding of the sorption processes, often using, or supported by, thermodynamic sorption modelling that may include more or less complex representations of the electrostatic effects that occur at the mineral surface such as the formation of an electrical double layer comprising one layer of surface charges and a diffuse layer of counter charges in solution [111].

Empirical sorption parameters, including the distribution coefficients, K_d , derived purely from experiment are strictly only applicable to the conditions under which they were measured and there can be difficulties in their application to dynamic groundwater systems [104]. Representations of sorption based on thermodynamic sorption models have greater potential to allow extrapolation to other conditions (that is, they have the potential to provide some degree of predictive capability), but this assumes that the system can be well enough defined or characterised, and many such models also assume that chemical equilibrium is achieved, which may not be the case.

The application of thermodynamic sorption models was considered as part of the NEA's Sorption Project Phases II [35] and III [36]. It was concluded that using thermodynamic sorption models to derive sorption data for safety assessment would have significant advantages over the K_d approach, in that they would allow '*a direct coupling of sorption with variable solution chemistry and mineralogy in a thermodynamic framework*'. However, in practice the use of thermodynamic sorption models, particularly for complex materials such as rocks, is often limited by the availability of information on the nature of the sorbing surface. Therefore, to date, thermodynamic sorption models have been used to aid interpretation of experimental data and to allow limited extrapolation to conditions where direct experimental data are unavailable, rather than to obtain sorption parameter values directly for use in safety assessments (see, for example, reference [105]).

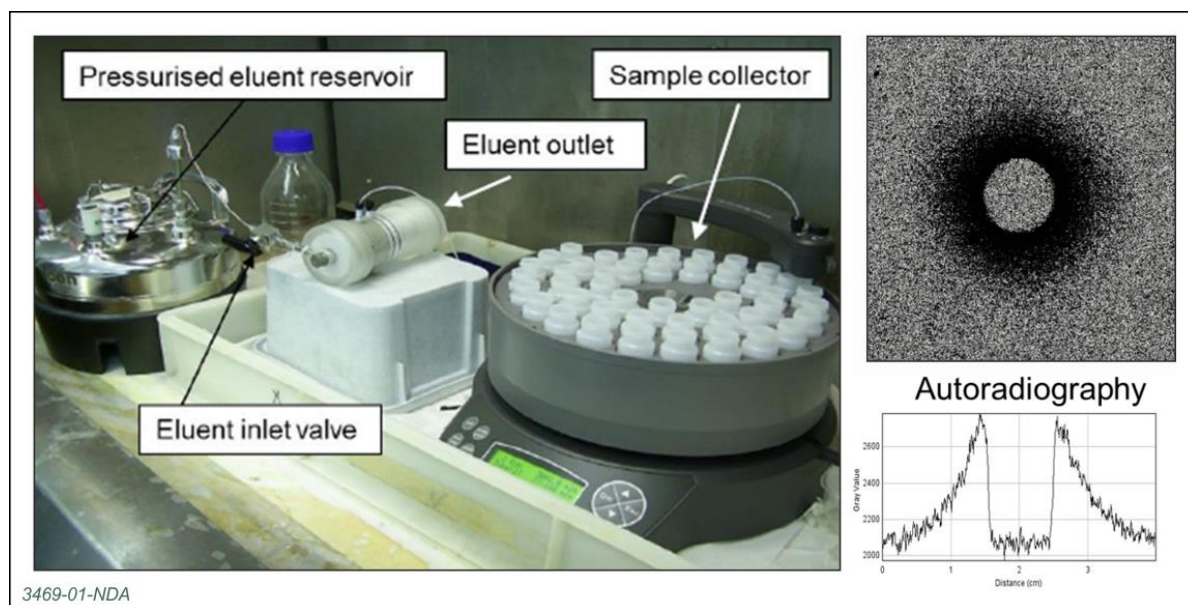
R&D programmes to support geological disposal have conducted many laboratory experiments to measure radionuclide sorption on a wide range of barrier materials, principally buffer/backfill materials and rocks along the expected groundwater pathway from a GDF to the biosphere. An example of one of our sorption studies is shown in Figure 8. These laboratory studies can be complemented by field-scale experiments (typically conducted in, or from, underground rock laboratories, URLs), observations of radionuclide behaviour in natural systems and geochemical modelling. In laboratory experiments, sorption is measured in well-characterised systems on timescales up to a few years and over length-scales typically much less than a few centimetres. The slow migration rates of sorbing radionuclides in many materials limit the distances over which migration can be studied in the laboratory (see, for example, reference [106]).

The most widely used experimental technique for measuring sorption is the 'batch sorption' method. In this method the solid material is crushed to create a high surface area and then contacted with water containing the radionuclide of interest. Sorption causes some of the radionuclide to be removed from the water and to become attached to the surfaces of the solid. At the end of the experiment, the concentration of radionuclide remaining in the water is measured and the amount of sorption calculated (see for example [107, 108]).

Crushing the solid into small particles significantly reduces the time to reach equilibrium and enables experiments to be completed on timescales of weeks or months. Consequently, large numbers of experiments can be undertaken to characterise the radionuclide sorption properties of a range of materials from the engineered barriers and surrounding rocks under a range of chemical conditions. The batch sorption technique is

good for examining how sorption (represented by K_d) is influenced by variables such as radionuclide concentration, temperature, and groundwater chemistry.

Figure 8. Experimental set-up and autoradiography results for radial advection of calcium-45 through an intact specimen of NRVB. The sample is a sealed cylinder of solid NRVB with a cylindrical well drilled along its axis into which a solution with a known concentration of radionuclide is injected and held at an overpressure. During the experiment radial flow occurs outwards from the central well into the sample. The dark area in the autoradiograph (right) shows the extent of radionuclide migration at the end of the experiment. Virtually all of the radionuclide is retained next to the well. After [109].



Crushing the sample can however introduce experimental artefacts, such as producing new surfaces in the sample, which may cause over-estimation of sorption. This artefact is not, however, important in high porosity materials that naturally have high surface areas, such as cements and clays. For example, a Swiss study on Opalinus Clay found excellent agreement between caesium sorption on crushed and intact rock samples [110]. The artefact is more important for low porosity, low surface area materials such as the matrix of fractured rocks. Following on from an approach used previously by Nirex, in performance assessment studies RWM has to date used 'beta factors' to correct sorption data obtained from experiments on crushed samples to allow their application to intact rocks and EBS materials. However, there are uncertainties with this approach and so, particularly for geosphere studies, a smaller number of longer timescale, more complex, laboratory experiments should be undertaken using intact rock samples, where the internal surfaces have not been disturbed. This type of experiment enables understanding of whether sorption in the batch experiment is over-estimated and, if so, to what extent. The most common type of intact rock or material experiment is the diffusion-sorption experiment, in which one face of an intact porous rock sample is exposed to a solution containing the radionuclide. In these experiments, the radionuclide is transported into the pores of the sample by diffusion, and is retarded by sorption onto the pore surfaces. The rate of migration depends on the strength of sorption.

As noted above, the process used by RWM to derive sorption parameters from a range of experimental measurements for use in safety assessment models involves expert elicitation. The approach takes account of many uncertainties, including those associated with the experimental measurements. A linear, reversible sorption model is generally used in the assessment models; uncertainty is captured by specifying appropriate probability

distribution functions of sorption values and making many calculations in a probabilistic framework. The effects of organic complexation on sorption in the EBS are considered using factors that quantify the reduction in sorption (for more detail, see reference [9]).

In the EBS sorption may occur on various materials, including:

- iron oxides and other phases formed as a result of the corrosion of the waste containers
- certain clay minerals such as montmorillonite in bentonite-based barriers
- other solid phases, such as calcium silicate hydrate (CSH), in cement-based barriers.

Little sorption is expected to occur on salt based minerals or salt engineered barriers. More detail on sorption processes in the EBS is given in Section 3.2 and Section 3.3.

In the geosphere the mechanisms of sorption and the extent to which radionuclides and non-radiological species will be removed from groundwater also depend on the chemistry of the solution and the surfaces with which they come into contact. For example, for redox sensitive radionuclides, such as neptunium, plutonium, selenium, technetium and uranium, sorption and, therefore, retardation relative to groundwater flow may be decreased if the groundwater conditions are sufficiently oxidising.

The measurement of radionuclide sorption onto various barrier materials, minerals and rocks has been a key area of research in support of geological disposal of radioactive waste for more than 30 years, and many papers and compilations containing relevant data are available, for example see references [36, 106, 111, 112, 113, 114, 115, 116, 117, 118].

Clay minerals occur commonly in many sedimentary rocks and, under the right conditions, can be strongly sorbing towards many radionuclides. Even in rocks that are not comprised primarily of clays (such as igneous and metamorphic rocks, quartz-rich sandstones and pure limestones), clay minerals and iron oxyhydroxide minerals, which are also strongly sorbing, often occur as surface coatings on the discontinuities in the rock along which groundwater flow and radionuclide migration may occur. Therefore, even though these phases may be only trace minerals in the bulk rock, they can still have a significant impact on radionuclide sorption and transport.

Sorption data obtained from experiments performed on rocks need to be interpreted with care. Trace minerals such as iron oxyhydroxides or phyllosilicate minerals can often dominate sorption, and so rocks of similar bulk composition can exhibit markedly different sorption behaviours. Sorption can also be affected by relatively small changes in aqueous chemistry. It is important, therefore, to emphasise the need for studies of sorption on site-specific rock samples to be conducted under chemical conditions that are as close as possible to those expected at the site of the GDF.

The research identified in our S&T Plan includes:

- re-examination of existing PDFs that describe the sorption of uranium to see if it is possible to disaggregate some of the previously combined uncertainties and make recommendations regarding the need for additional elicitation exercises [10, task 798]
- a new elicitation of uranium sorption coefficients under the EBS conditions expected in the GDF [10, task 796]
- new elicitations of sorption coefficients for both high priority and lower priority radionuclides [10, tasks 800 and 801]
- a review of the appropriateness and use of beta factors to correct sorption data obtained from experiments on crushed samples for application to intact rocks and EBS materials [10, task 802].

A substantial research programme to measure radionuclide sorption onto rock samples from the candidate site will be an important part of the work undertaken during the period of characterising a potential site for the GDF. RWM will carry out an experimental programme of this type once candidate sites have been identified and samples are available. We also expect to build confidence in the understanding of geosphere sorption by studying the behaviour of naturally occurring radionuclides in natural geological systems.

2.6 Solubility and mineral precipitation/co-precipitation

At its simplest, solubility can be thought of as the extent to which one substance will dissolve in another. Solubility and precipitation/co-precipitation may control the dissolved concentrations of radionuclides and other species and, therefore, affect their transport away from the wastes in the GDF.

2.6.1 Solubility

The solubility of a radionuclide-bearing solid phase may, at equilibrium, determine and effectively limit the concentration of a dissolved radionuclide in water within the waste packages.

Solubility refers to the propensity of a solid, liquid, or gaseous chemical substance (the solute) to dissolve in a solvent (often water) to form a solution. The solubility of a substance depends on the physical and chemical properties of the solute and solvent, as well as on the prevailing conditions of, for example, temperature and pressure.

The solubility of gases can be approximated using Henry's Law [119]; this is discussed in the Gas Status Report [5].

The solubility of a radionuclide- or metal-bearing solid phase may, at equilibrium, determine and effectively limit the concentration of a dissolved radionuclide or metal in water within the waste packages ([57, 120])¹⁶. For example, under alkaline EBS conditions, if sulphide is present, then lead (Pb) concentrations may be controlled to low values by the formation of PbS_(s) [57].

In other circumstances, for example where the rate of waste dissolution or metal corrosion is relatively slow compared to the rate at which the solute is being removed from the system (for example, by advection – see section 2.10), the concentration of the dissolved radionuclide or metal may be lower than the theoretical equilibrium solubility. For example, under alkaline EBS conditions, lead corrosion might be reduced or prevented by passivation by silicate species [57].

The most common approach for measuring solubility is to measure the concentration of the element in a solution in contact with a solid phase of the element. For example, the concentration of thorium in water placed in contact with thorium oxide solid phase. The contact time needs to be sufficiently long that thermodynamic equilibrium is reached. Two approaches are commonly used in the laboratory:

- The oversaturation technique, in which the element is added to the solution such that the resulting concentration exceeds the solubility limit and a precipitate forms
- The undersaturation technique in which a known solid phase containing the element is dissolved in the solution.

¹⁶ Under certain typically very clean laboratory conditions, the equilibrium solubility can be exceeded to give a metastable, supersaturated solution. However, such conditions are not expected to occur in the GDF and supersaturated solutions generally equilibrate rapidly by the occurrence of precipitation in response to the presence of features that promote crystal nucleation.

Where data are available, the dissolved concentration of a radionuclide can be calculated using a combination of the 'solubility product' of the solid phase that is in equilibrium with the solution and the 'stability constants' of the relevant aqueous species. Various thermodynamic chemical speciation/solubility codes are available (see, for example, [45, 47]) and these can be used together with an appropriate thermodynamic database [32, 33, 34] to calculate radionuclide solubilities in waters of different composition under a range of conditions.

Further information on radionuclide solubilities can be obtained from observations in the natural environment. The most common approach is to measure the concentrations of radionuclides in groundwater and compare the values with those estimated using chemical thermodynamic models. An early example of the use of natural analogues to build understanding of radionuclide solubility was the Poços de Caldas Analogue Study [39]. Further analogue studies are discussed in Section 7.4 of [4] and references such as [41]. Initial calculations of the solubility of the uranium ore based solely on information about major element solution chemistry suggested dissolved uranium concentrations that were eight orders of magnitude below those observed in the field. A refined model, using a solid that was more representative of the chemistry of the ore body, resulted in modelled concentrations that were in line with those observed [39]. This, and other similar studies (such as reference [121]) illustrate the sensitivity of the chemistry of some important radionuclides to the prevailing chemical conditions and the need to understand and account appropriately for variability and uncertainty in the safety case.

As noted above, the dissolved concentration of an element is partly dependent on the nature of the solid phase. The solid phase may be a so-called 'pure' radionuclide phase, such as uranium oxide, UO_2 , or it may be a solid solution or a co-precipitate in which the radionuclide occurs as a trace component in the structure of the solid. Box 2 identifies some solid phases that may potentially control the solubility of selected radionuclides in the EBS of a GDF for spent fuel.

In most cases, the solid phase that forms in equilibrium with the water will be the one that is most thermodynamically stable, subject to the kinetics of the mineral formation process under the prevailing conditions. Kinetics may mean that meta-stable solids form and some of these may persist for long periods - this needs to be taken into account when estimating radionuclide solubilities for safety assessment calculations.

The degree of crystallinity of the solid phase can also exert a strong influence on its solubility; in general in low-temperature aqueous systems, mineral solubility decreases as the degree of crystallinity of the solid phase increases. Poorly-crystalline solid phases are expected to be present in some circumstances, and this also needs to be taken into account when estimating radionuclide solubilities for safety assessment calculations.

RWM uses expert elicitation to take account of such uncertainties and define probability distribution functions of radionuclide solubilities for use in safety assessment. Quantitative data on the potential solubilities of radionuclides and non-radiological species are documented in the Data Report [9]. The research identified in our S&T Plan includes:

- re-examination of existing PDFs that describe the solubility of uranium to see if it is possible to disaggregate some of the previously combined uncertainties and make recommendations regarding the need for additional elicitation exercises [10, task 798]
- a new elicitation of uranium solubility under the EBS conditions expected in the GDF [10, task 796].

2.6.2 Precipitation and co-precipitation

Chemical precipitation involves the formation from solution of a discrete, separable solid phase (such as a radionuclide containing mineral phase). Precipitation may involve the formation of a 'pure' solid phase. Examples of pure radionuclide solid phases are U_3O_8 and PuO_2 . Alternatively, elements may co-precipitate with other species to form a solid solution.

Chemical precipitation involves the formation from solution of a discrete, separable solid phase (such as a radionuclide containing mineral phase). Precipitation may occur if the concentrations¹⁷ of the constituents of a solid phase in the solution are such that the solubility product of the solid phase is exceeded. This may occur as a result of a change in the prevailing conditions; typically a change in temperature or in the chemistry of the water, as exemplified by the formation of mineral seams in nature.

Precipitation may involve the formation of a 'pure' solid phase. A pure solid phase can be described using one substance only; it has a definite and constant (elemental) stoichiometry that is unequivocally related to its structure. Examples of pure radionuclide solid phases are U_3O_8 and PuO_2 .

Alternatively, many elements may co-precipitate with other species to form a solid solution. A solid solution is a homogeneous crystalline structure in which one or more types of atoms or molecules may be partly substituted for the original atoms and molecules in a solid phase without changing its structure, although the lattice parameters may vary [123]. An example of a radionuclide-bearing solid solution is $(\text{RaBa})\text{SO}_4$ [126]. Co-precipitation could be particularly important for radionuclides that tend to be present at low concentrations in the disposal system, but which have relatively high specific activities, for example ^{63}Ni , ^{226}Ra .

The solubility of a radionuclide controlled by a pure radionuclide phase is generally much higher than in the case where the radionuclide is only present as a trace component in a co-precipitate or solid solution. Consequently, precipitation of pure radionuclide phases is most likely to be relevant in the waste package and its immediate vicinity where radionuclide concentrations could be relatively high, although conceptually it could also occur at redox fronts in the geosphere. Co-precipitation is a potential immobilisation process in the EBS and in the geosphere. For example, in the presence of iron from waste packages, trace quantities of radionuclides may co-precipitate with magnetite [128, 129]. The FUNMIG project and the NEA review of solid solutions recognised that there may be a continuum of processes, starting with surface sorption processes, through co-precipitation processes close to the surface of newly formed solid phases, and ending at the formation of solid solutions [25, 122, 123].

The traditional approach in safety assessments has been to represent the influence of precipitation by considering only pure radionuclide phases. In the international community, significant effort has gone into generating thermodynamic data for a range of potentially relevant pure phases. A recent review [124] describes the nature of the data produced. Compilations of such data appear in publications of projects such as the NEA Thermochemical Database project [32], which has so far published thirteen reports in its Chemical Thermodynamics Series. These reports comprise reviews dealing with data selection for particular elements or groups of elements of relevance to radioactive waste disposal. The data can be used in computer programmes such as PHREEQC [45] and EQ3NR [47] to help identify relevant solid phases and calculate the dissolved concentrations of radionuclides in equilibrium with these phases under specified conditions (for example, of water chemistry and temperature). However, the identification of solubility limiting phases is far from straightforward for reasons relating to the need for sufficient

¹⁷ Strictly, the chemical activities.

characterisation of the chemical system of interest, and to the kinetics of mineral formation, amongst others. This can be a significant source of uncertainty in predicting environmental concentrations of radionuclides and other chemotoxic species and has been another focus of expert judgement and expert elicitation studies [125]. The resultant PDF often covers several orders of magnitude, primarily due to this uncertainty over the composition of the relevant solubility limiting phase.

However, despite the difficulties, thermodynamic modelling of solid solution processes is increasingly being used to support more complex representations in safety assessment models. A 'state-of-the art' study on the chemical thermodynamics of solid solutions of interest in nuclear waste management [123] concluded that the thermodynamics of solid solutions is an established discipline and that the conceptual framework is robust. Some recent safety cases have used such approaches to model radium co-precipitation with barium sulphate following the leaching of spent fuel [126].

In the EBS beyond the waste package, precipitation and co-precipitation of radionuclides and other species may occur in various settings, dependent on the prevailing conditions and the concentrations of radionuclides and other species that will be present. More detail on precipitation and co-precipitation processes in the EBS is given in Section 3.3.

Unless there is a high natural background concentration of the radionuclide in question, or marked redox fronts or changes in groundwater chemistry are present, the precipitation of pure radionuclide phases in the geosphere is unlikely to be important because dilution, dispersion and sorption will cause the dissolved concentrations of radionuclides to be at levels below the solubility limits for such pure solid phases. The Criticality Safety status report considers an unlikely case (a 'what if' scenario) entailing accumulation of fissile material in a localised region of the GDF or the surrounding host rock following its mobilisation from one or more degraded waste packages and transport in groundwater [6]. It is more likely, however, that radionuclides could be immobilised in the geosphere through co-precipitation. This is evidenced by the observation that naturally occurring radionuclides are often found at trace concentrations in minerals such as iron oxides and carbonates (see, for example, reference [127]).

A review of the co-precipitation of trace elements into iron-bearing minerals such as ferrihydrite and goethite [128] concluded that isomorphous substitution of up to 15% of the iron sites in goethite is possible. Magnetite may also sorb certain species [eg. 129]. Carbonate and sulphate minerals also incorporate trace elements into their crystal structure. Of particular relevance to radionuclide behaviour are the incorporation of dissolved inorganic ^{14}C in calcium carbonate minerals such as calcite and dolomite [130] and the incorporation of ^{226}Ra in barium sulphate [126]. Calcium-bearing minerals in the geosphere such as calcite would also be expected to incorporate ^{90}Sr into their mineral structures [131], although it is likely that much of the ^{90}Sr (half-life 29.1 years) would decay in the GDF before reaching the geosphere.

In general terms, co-precipitation and precipitation are most likely to occur in locations that have high hydrochemical gradients, such as:

- at the interfaces between different materials in the EBS and between the EBS and the geosphere (for example, see the discussion of the chemically disturbed zone in Section 4.2).
- at the interface between hydrogeological units, where mixing between different groundwaters can occur. An example could be the interface between lower permeability basement rocks and overlying higher permeability sedimentary strata, where low fluxes of reducing groundwater in basement rocks discharge into higher volumes of more oxygenated groundwater in the overlying sediments. Potentially, precipitation of iron oxyhydroxides could occur at this interface and encourage the co-precipitation of various metals and radionuclide species.

- in the vicinity of saline interfaces. Movement of the saline interface can occur; for example in response to changing sea level (see Section 5.4 of the Geosphere Status Report [4]). The precipitation of carbonate minerals can be affected by movement of the saline interface.

Although co-precipitation of radionuclides can occur in regions of the geosphere where minerals such as carbonates and oxides are actively precipitating, it is often difficult to identify with confidence where co-precipitation might take place. This is a limitation when considering whether or not to represent co-precipitation mechanisms in safety assessment models of the geosphere, but one which might be resolved at least to some extent by site characterisation work. Nevertheless, excluding precipitation and co-precipitation processes from safety assessment models of the geosphere pathway results in a generally conservative treatment of radionuclide transport.

2.6.3 Mineral surface ageing

The mineral surfaces on which sorption takes place, or in which radionuclides may be incorporated, may evolve, or age, with time. Mineralogical changes due to ageing may accelerate or retard radionuclide migration in groundwater.

The minerals on which sorption will take place, or in which radionuclides may be incorporated, are in contact with water and may evolve, or 'age', with time. Ageing processes generally involve the transformation of amorphous phases towards more crystalline and ordered forms. Often the process is accompanied by an increase in crystal size, which in turn is associated with a decrease in surface area. In many cases, the ageing process also involves the loss of water as poorly-crystalline hydrous gels crystallise to less hydrous, but more crystalline phases. These processes may become significant over the long timescales relevant to geological disposal.

A detailed review of the effects of ageing, using understanding gained from laboratory studies and observations in natural systems, can be found in reference [132]. This review also considered the fate of sorbed trace elements and concluded that minerals can incorporate sorbed trace elements into their structure during ageing. This is beneficial as it reduces the possibility of trace elements being re-released to solution. However, there is also evidence, both from laboratory experiments and from studies of natural systems, that a proportion of the trace element within the structure of the host mineral may be re-released to solution as the crystallinity of the host mineral increases for example by Ostwald ripening¹⁸ [133, 134]. Often it is observed that the released trace element is then incorporated in a different mineral. In addition, such ageing processes may result in a significant reduction in surface area (and for clay minerals ion-exchange capacity), reducing the potential for sorption on these materials.

Mineral ageing is a very slow process in most geological environments that are potentially suitable for a GDF because of a combination of geosphere stability, slow groundwater flow rates and long groundwater residence times [132]. However, more rapid mineral transformations can be expected in cement-based materials and in the rocks close to the GDF where the groundwater chemistry may be more significantly disturbed (see Section 4.2). The research identified in our S&T Plan includes undertaking a focussed study to understand the uptake of key radionuclides on aged cement phases [10, task 740].

In the undisturbed geosphere ageing processes are considered unlikely to significantly affect radionuclide sorption. Provided that sorption values for safety assessments are

¹⁸ Ostwald ripening is an observed phenomenon in solid or liquid solutions that describes the change of an inhomogeneous structure over time. For example, small crystals may tend to dissolve and the dissolved material redeposit onto larger crystals. This process is thermodynamically favoured because it results in an overall reduction of the surface energy of the system.

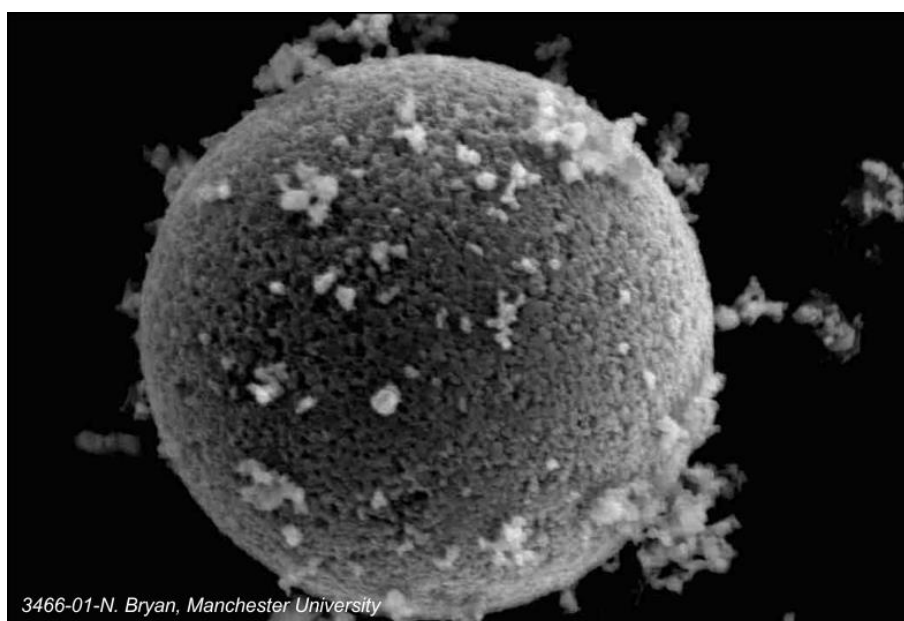
based on naturally aged mineral surfaces, the values are considered appropriate for the timescales of relevance to post-closure safety assessments.

2.7 Colloids

Colloids are small particles, formally in the size range 1 nm to 1 μm , that can remain stably suspended in water. Colloids may be generated as a result of wasteform degradation, or from other engineered barrier materials such as clays, cement-based material and crushed rock. Colloids may also be present in the geosphere. Under some circumstances colloids may enhance the transport of radionuclides and non-radiological species in groundwater.

Colloids are small particles, formally in the size range 1 nm to 1 μm , which can remain stably suspended in water (Figure 9). Over the last 30 years a very considerable amount of research has been conducted into the potential for colloids to affect radionuclide behaviour and transport in the groundwater pathway. The European Commission, for example, has sponsored many international collaborative research programmes on colloids (the CoCo Club, Trancom, HUMICS, HUPA, BENIPA and BELbaR projects); see, for example, references [135, 276]. In addition, several national radioactive waste management programmes have undertaken significant programmes of research and development work focussed specifically on colloids and their potential effects (for example, reference [136]), including both laboratory-based and URL-based experimental work, together with model development and testing. Over these three decades several state of the art reviews have also been published [137, 138, 139, 140, 141].

Figure 9. Scanning electron microscope image of a brucite, $\text{Mg}(\text{OH})_{2(s)}$, colloid of the type that is found in the Magnox nuclear fuel storage ponds at Sellafield (the field of view is approximately 10 μm) [142].



Colloids may be formed during wasteform and waste package degradation (for example, from the dissolution of HLW glass or the corrosion of waste packages). Colloids may also be formed from other parts of the EBS, or as a result of interactions between EBS materials and the geosphere [139, 140, 143]. Some colloids, such as many of those found in groundwater, are naturally occurring. Some microbes (see Section 2.8) are also of a size that falls in the colloidal range. The numbers of colloids, their stability in aqueous suspension, their chemistry and affinity for radionuclides and other species all depend on the prevailing conditions.

Colloids may be generated in any of the barriers of a geological disposal system and can be formed in a variety of ways: including chemical alteration or physical erosion of existing surfaces, or chemical precipitation from solution. For example, plutonium can form polymeric or nanocrystalline PuO_2 colloids by precipitation from solution [138, 141, 144].

Colloids may be mobile in groundwater systems and are, thus, potentially significant because they can enhance the transport of radionuclides in two ways

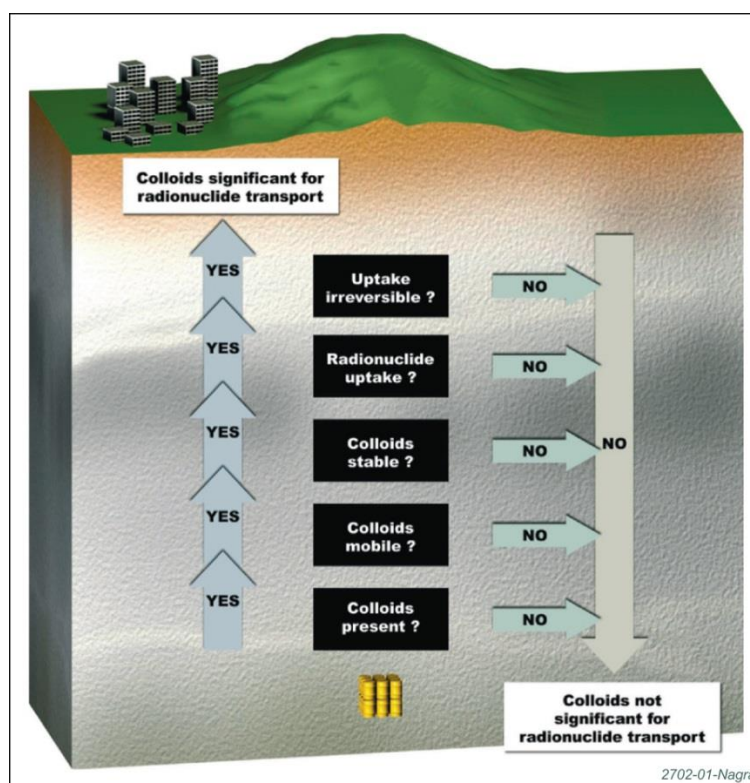
- colloids can incorporate or sorb radionuclides, increasing their effective concentration in groundwater over and above the amount that could be transported in fully dissolved form.
- colloids may also be transported in fractures at velocities that are slightly faster than the average velocity of the groundwater. This is a relatively small effect which results from the distribution of flow velocities across the fracture aperture and the tendency for colloids, because of their size and surface charge, to occupy the centre of the flow channel where the velocities can be slightly higher.

Although colloids have the potential to enhance transport, colloidal dispersions may be destabilised by chemical effects (such as increases in salinity). Colloids may also be sorbed onto surfaces or filtered in pores or fractures with small apertures, which tends to reduce the mobility and potential significance of colloids.

The sensitivity of colloidal suspensions to the prevailing conditions, for example in terms of the stability of the suspensions and flocculation processes, also means that great care has to be taken when obtaining groundwater samples for colloid studies [145].

Colloid-facilitated radionuclide transport may be of significance if several criteria are met. Figure 10 shows a simple conceptual scheme, or decision tree, which can be used as a basis for assessing the potential importance of colloids.

Figure 10. Colloid ‘ladder’ with the requirements for significant colloid-facilitated radionuclide transport in a deep geological repository. After [146].



The decision tree consists of a series of questions concerning possible colloid behaviour. For significant colloid-facilitated radionuclide transport to occur there needs to be a source of colloids (if there are no colloids present, then they cannot affect transport). The colloids need to be stable (to be able to form a stable aqueous suspension) under the prevailing environmental conditions. The colloids need to be mobile within the environment, for example, they would need to be able to pass through the pores in barrier materials. The colloids would also need to sorb or otherwise incorporate radionuclides over timescales that are long enough for them to have a significant effect on radionuclide transport away from the GDF (rapid desorption of radionuclides from the colloids would mean that colloidal transport was not very significant).

The decision tree provides a framework both for assessing the significance of colloids to the safety of the GDF and for designing a focused R&D programme to address the safety significance of colloids.

The research identified in our S&T Plan includes:

- laboratory studies of the potential effects of bentonite colloids on radionuclide behaviour which are being undertaken as part of the EC Belbar project [10, task 754]
- a PhD study to look at the potential effects of non-clay colloids on radionuclide mobility [10, task 753]
- participation in the CFM project at the Grimsel Test Site [10, task 755]
- development and updating of a summary report that consolidates the understanding gained from several related projects on colloids [10, tasks 762 and 769]
- a small experimental programme to investigate whether colloids, organic complexants and microbes may have cumulative effects on radionuclide behaviour [10, task 766]
- development and maintenance of thermodynamic models of sorption and solubility that take account of colloidal effects [10, tasks 816 and 817].

More detailed information on colloids in the EBS and in the geosphere is provided in Sections 3.3 and 0.

2.8 Microbial activity

Microbes may interact directly with radionuclides and non-radiological species, or indirectly, by affecting the local chemical conditions. If microbes are mobile they may act to transport species in a similar manner to colloids.

Microbes will be introduced to the GDF in the wastes and in the materials used to construct the engineered barriers, and during operations. For example, natural bentonite clays contain microbes; microbes are also present naturally from the surface to relevant depths in all geological environments, although microbial activity may be negligible in some geological environments (for example, halite).

Microbes may influence radionuclide behaviour in several ways [147]:

- by causing changes in the chemical and physical environment of the GDF - by changing the pH or redox conditions in localised regions or niches. In this way, microbes may change the chemical speciation of a radionuclide.
- by forming biofilms¹⁹ on surfaces, to which radionuclides may be sorbed.
- by ingesting and precipitating radionuclides internally [148] (Figure 11).
- mobile microbes may act to transport radionuclides in a similar manner to colloids.

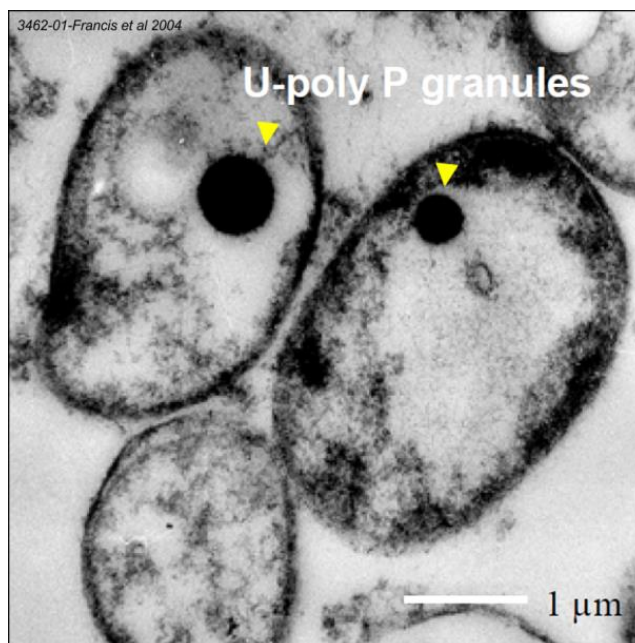
¹⁹ A biofilm is any group of microorganisms in which cells stick to each other on a surface. These adherent cells are frequently embedded within a self-produced matrix of extracellular polymeric substance.

- like colloids, mobile microbes carrying radionuclides may also become trapped by filtration within the EBS or geosphere, thereby retarding further radionuclide transport.

Reference [149] summarised the potential impacts of microbial interactions with the different components of a GDF (waste package, EBS and geosphere) and highlighted how those interactions might influence radionuclide behaviour. The following potential impacts were identified:

- microbes can affect radionuclide speciation by affecting redox reactions, either directly by interaction with the radionuclide itself, or indirectly by interaction with components of the waste (such as organic materials) or with naturally occurring redox-active solutes containing carbon, sulphur, iron, nitrogen or manganese. These interactions may potentially enhance or retard the migration of radionuclides in groundwater (see Section 3.3 of [149]).
- microbial degradation of organic wastes will be significant in some disposal concepts (specifically concepts for the disposal of ILW/LLW) and may result in the production of soluble degradation products that increase radionuclide solubility and decrease radionuclide sorption (see Section 2.3). However, in cement-based wasteforms chemical degradation is expected to be the dominant mechanism by which organic wastes degrade (see [5] for further discussion).
- microbial activity may lead to gas generation - these effects are also discussed in the Gas Status Report [5].

Figure 11. Intra-cellular and extra-cellular accumulation of uranium by *Halomonas* sp. After [148]. Courtesy Brookhaven National Laboratory



Microbial activity may degrade soluble organic compounds, such as cellulose degradation products [150]. The extent of degradation will be determined by the prevailing biogeochemistry. Experimental work has also demonstrated microbial degradation of isosaccharinic acid (ISA) under conditions representative of those around a GDF [151, 152].

The ability of microbes to exist and remain active in bentonite-based engineered barriers has been the subject of various research studies; above a certain swelling pressure in a bentonite-based buffer, microbial activity may be decreased [153, 271].

The tolerance of microbial activity to high pH environments has been subject to some debate; recent studies have shown that the rate and extent of bio-reduction decreased at higher pH, with an upper limit for the processes studied of pH 12 [154, 155]. The upper limit to microbial activity is of importance when considering processes occurring within the EBS of cement-based ILW/LLW disposal concepts. It has also been shown that the organisms involved in these processes have the potential to limit the mobility of many redox-active radionuclides that may be present in the wasteforms (including Tc(VII), U(VI) and Np(V)) via direct and indirect redox transformations or by utilising chelating agents, such as ISA, which may have been produced abiotically under repository conditions, as growth substrates [155].

Microbes occur in groundwaters over a broad range of depths in the Earth's subsurface, and there is evidence that microbes can exist and remain viable to depths of at least 3,000 m [145]. Microbial respiration facilitates redox processes among redox-sensitive solutes in groundwaters. In groundwaters, the energy sources for microbial respiration are typically dissolved organic carbon compounds and/or methane. Dissolved hydrogen might also be a significant energy source in the deep geosphere where abundances of the other energy sources are absent or extremely low. The presence of the GDF will provide multiple additional energy sources for microbial activity.

Reference [149] concluded that all geological environments in the UK potentially suitable for a GDF will have an indigenous microbial ecosystem, which would be influenced by environmental conditions such as the availability of nutrients and energy for microbial use, groundwater flow and the geological characteristics of the site. In addition, the development of the GDF and waste disposal operations will inevitably lead to the introduction of further microbes from the surface environment.

Microbial activity in the geosphere, as in any environment, is often preferentially located on chemical or physical interfaces, usually within biofilms. The impacts can be both physical (for example, altering porosity) and/or chemical (such as changing sorption behaviour). Growth of biofilms can cause pore blocking and thereby reduce permeability; for example, see references [156] and [157] - this process may reduce radionuclide mobility. Conversely, Swedish studies examined the impact of biofilms on radionuclide sorption on granite [158] and concluded that sorption of a range of radionuclides (including ^{241}Am , ^{237}Np and ^{234}Th) was reduced when biofilms were present on the rock surface. It was concluded that biofilms can form a barrier between the rock and groundwater, and that differences in sorption were dependent on the chemical properties of the individual radionuclides and the availability of different surface functional groups modified by the presence or absence of biofilms.

In summary, microbes have the potential to either increase or decrease radionuclide transport in groundwater. The research identified in our S&T Plan includes:

- a study to develop a deeper understanding of the potential microbial processes that could degrade ISA under GDF-relevant conditions [10, task 751]
- a small experimental programme to investigate whether colloids, organic complexants and microbes may have cumulative effects on radionuclide behaviour [10, task 766]
- development of a synthesis report on the understanding of microbial processes and their impact on radionuclide behaviour in GDF-relevant conditions [10, task 768]
- a PhD study to look at the maximum pH at which sulphate reduction and methanogenesis can proceed under the EBS conditions expected in a cementitious GDF for ILW/LLW [10, task 771]

- a PhD study to improve understanding of microbial sulphate reduction and its potential effects on the behaviour of uranium and technetium under the EBS conditions expected in a cementitious GDF for ILW/LLW [10, task 772]
- a PhD study to improve understanding of spatial heterogeneity and microbial niches in a cementitious GDF for ILW/LLW [10, task 773]
- development and maintenance of thermodynamic models of sorption and solubility that take account of colloidal and microbial effects [10, tasks 816 and 817].

Research on microbiology in nuclear waste disposal is also being undertaken within the international MIND Project [159]. It will be important to study microbial activity further once candidate sites become available.

2.9 Non-aqueous phase liquids

Non-aqueous phase liquids (NAPLs) may be present in the waste inventory or may be formed from the degradation of waste components. If radionuclides or other species partition into a buoyant NAPL phase, this may provide an additional carrier for their migration. However, we have recently shown that significant quantities of NAPLs would not be able to escape from the waste packages, survive their passage through the vault, and accumulate as a discrete phase capable of migrating away from the vaults.

NAPLs are organic liquids, such as oils and solvents, which have limited miscibility with water. Some radionuclides and other non-radiological species may partition into a NAPL phase. Figure 12 illustrates a method for evaluating the significance of NAPLs on radionuclide migration from a GDF.

The inventory of wastes for disposal includes a limited quantity of 'as-disposed' NAPLs, such as oils. As-disposed NAPLs are extremely unlikely to be able to migrate from the waste package as a free phase because the disposability assessment process limits waste package NAPL contents. These wasteforms are also designed so that any NAPLs present are dispersed throughout the wasteform and are immobilised by the encapsulation process.

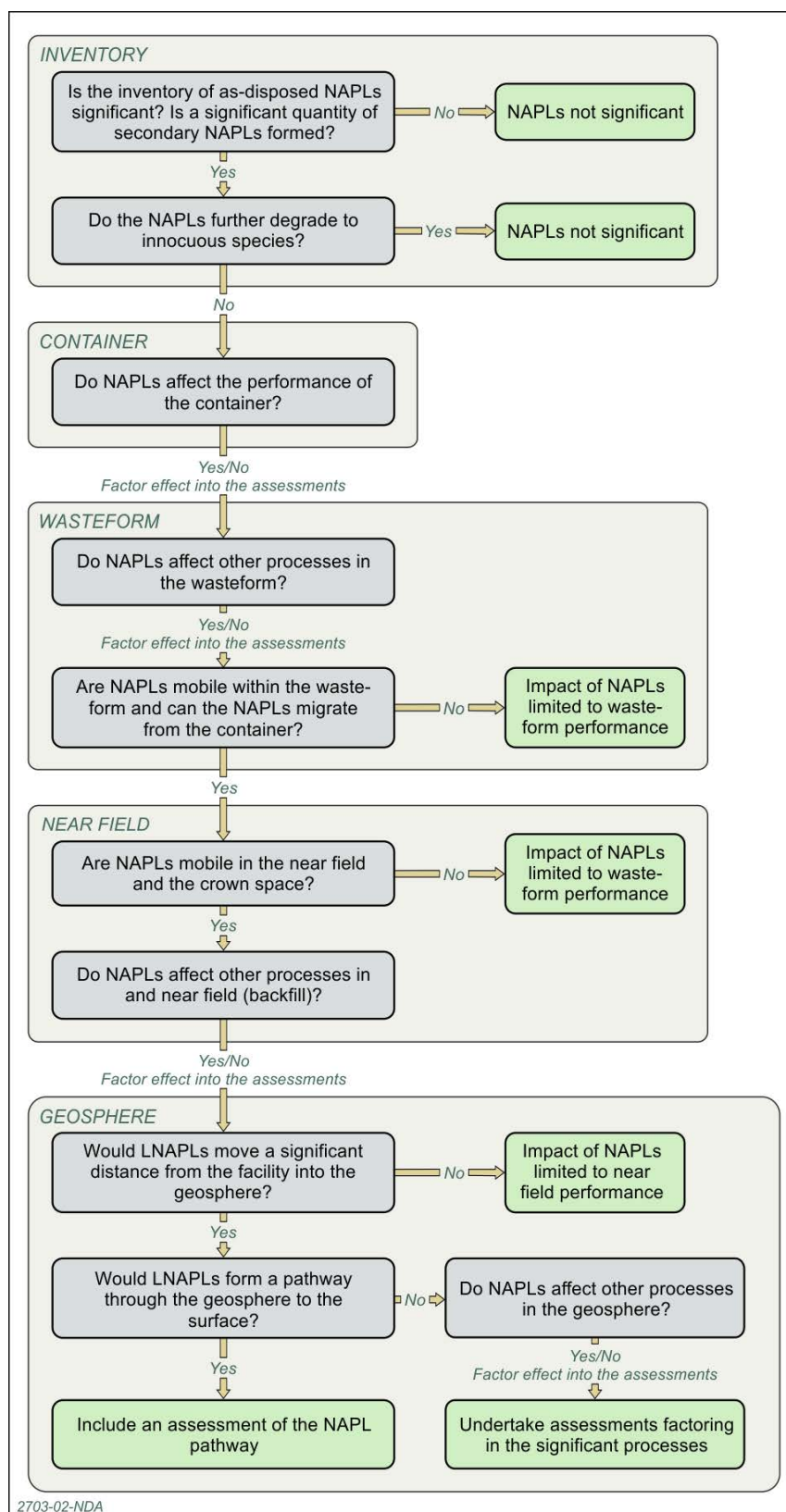
Secondary NAPLs may be created in the GDF, principally as breakdown products from the radiolysis of organic polymers present in the waste. Review of the ILW/LLW inventory and laboratory studies on the degradation of organic materials present, which are mainly plastics, confirmed that 'light' (buoyant) NAPLs formed from the decomposition of disposed organic material, notably the halogenated plastic, PVC, may be the main source of NAPLs in the disposal system [166]. If present in sufficient quantity, light NAPLs could become mobile due to their buoyancy, and thereby act as a carrier for radionuclides and other species that preferentially partition into the organic liquid phase. Because of their buoyancy, light NAPLs are considered more likely than dense NAPLs to have an effect on the performance of a GDF.

However, NAPLs generated from PVC degradation are expected to be high molecular weight phthalate-based compounds with densities similar to water, but with high viscosity; as such they are not expected to be very buoyant or mobile in what is otherwise an aqueous system. Reference [160] reports that a viscous, oily residue developed on samples of PVC film after exposure to $\text{Ca}(\text{OH})_2$ solutions. The component of the residue that could be analysed contained phenolic species similar to those found during analysis of the aqueous solutions. Other than the oily residue, no separate NAPL phase was observed at any time during the ageing experiments, and it was suggested that plasticiser migrated from the PVC and underwent hydrolysis on contact with $\text{Ca}(\text{OH})_2$ solution.

NAPLs also have the potential to affect the surface properties of solids with which they come into contact and therefore have the potential to affect the sorption properties of materials, particularly in the EBS. Our research has however shown that this is not a

significant consideration; the effect of NAPLs on the sorption of caesium and plutonium onto samples of the cement-based Nirex Reference Vault Backfill (NRVB), impregnated with Castrol Nucleol 520 oil (a commercial lubricating oil widely used in nuclear applications), was investigated in reference [161]. No significant decrease in sorption was observed.

Figure 12. Decision tree to aid the evaluation of the impact of NAPLs. After [166].



As well as potentially affecting the transport of radionuclides, many NAPL-forming compounds are themselves toxic, and typical compounds have been considered in toxicity assessments, such as reference [162].

In the presence of NAPLs, radionuclides and non-radiological species will be distributed between the NAPL phase and the aqueous phase. The distribution will depend on the relative stabilities of the relevant species in the two liquid phases under the prevailing conditions. Ionic and polar species will tend to favour the aqueous phase, whereas uncharged less-polar species will tend to favour the NAPL phase. Thus, neutral complexes of radionuclides with organic complexants containing significant hydrophobic groups are more likely to partition into any NAPL phase.

Experimental studies investigating the uptake of radionuclides by NAPLs under the high pH conditions that would be expected in cement-based engineered barriers have confirmed that plutonium and americium may be preferentially partitioned into NAPLs [163]. Another study [164] used simple extraction tests to investigate the uptake from alkaline solutions of nickel, plutonium and americium into n-nonane or Castrol Nucleol 520. The studies were extended to consider the competitive effects of a range of possible complexants, including EDTA, cellulose degradation products and detergents [164, 165]. These studies also indicated that the uptake of radionuclides into some NAPLs can be significant. However, the presence of organic complexants (such as ISA) that stabilise the radionuclide in the aqueous phase tended to lower the observed distribution factors between the NAPL and the aqueous phase.

NAPLs will also be susceptible to degradation by chemical, microbiological and radiolytic mechanisms. Where this leads to the production of water-soluble species, gases or solids, these processes will tend to cause the destruction of the NAPL phase and the cessation its ability to transport radionuclide and non-radiological species. The effects of their water soluble degradation products on the complexation and transport of these species is however uncertain and is the subject of ongoing work [10, task 752]. The timescales on which such degradation occurs are also uncertain, and will depend on the disposal concept and the NAPL's composition because of the different materials and chemical conditions present.

More recent work [166, 167, 168] suggests that the amount of secondary NAPL that may be formed in a GDF from the degradation of polymers in the waste is likely to be very low, and less than the amounts of as-disposed NAPLs originally present in waste. This work has also shown that phthalate esters, which may be formed from the degradation of PVC plasticisers, appear to break down on gamma irradiation to form water-soluble species and a denser insoluble phase. Phthalate esters also hydrolyse in contact with alkaline water. The research identified in our S&T Plan includes further study of the release and degradation behaviour of PVC additives under the EBS conditions expected in a cementitious GDF for ILW/LLW - this work will also examine the impacts of PVC additive breakdown products on the solubility and sorption of uranium, nickel and plutonium [10, task 752].

Modelling results for various cases assuming more or less degraded waste packages, with and without cracks in the waste encapsulation grouts, indicate that the light NAPL viscosity is a key control on their migration within the GDF. For realistic light NAPL compositions, only small amounts of free phase NAPL would migrate from an intact waste package, even if there were cracks in the grout. Thus, any NAPLs originating from waste is unlikely to be sufficiently persistent to allow accumulation in a vault or transport into the geosphere [167, 168]. These references conclude that it is even less likely that NAPL would be sufficiently persistent in the disposal environment, given the aforementioned degradation processes, to accumulate (for example, at the highest point of a vault), overcome the pore-pressure of the host rock and hence move into or through the geosphere. Based on this finding, NAPLs are not regarded as an issue that could challenge the viability of safe geological disposal.

2.10 Advection, diffusion and dispersion

Radionuclides and non-radiological species may be transported away from the GDF in groundwater. Transport may occur by advection and/or diffusion. The relative importance of these processes will depend on concept-specific and site-specific hydrogeochemical conditions.

Radionuclides may be transported in or through groundwater by the processes of advection and/or diffusion. The relative importance of these processes in a particular barrier material or rock depends on the properties of the material and on the thermal, hydraulic, density and chemical gradients in the system. In addition, hydrodynamic dispersion acts to spread radionuclides and other species as they migrate with flowing groundwater.

2.10.1 Advection

Advection refers to the transport of species in flowing water. Advection is of particular relevance in porous rocks and those with open fractures.

In this context, advection refers to the transport of species in flowing water. In contrast to molecular diffusion (see below), advected species can be thought of as being carried along by the groundwater rather than moving through it. Advection is of particular relevance in porous rocks and those with open fractures. Flow and advection are controlled by the permeability of the material through which the water moves and the hydraulic gradient across the material, which provides the driving force for water movement. Thermal gradients such as might be established close to disposed high-heat generating wastes and gradients in water salinity can also cause flow and advection.

Box 3 Quantifying groundwater flow and advection

Groundwater flow in saturated porous media is often approximated using Darcy's Law [169].

$$Q = -(\kappa/\mu) \cdot (\nabla p - \rho g)$$

Where Q is the flux (discharge per unit area) [m/s], κ is the permeability of the rock [m²], μ is the viscosity of the fluid [Pa.s], ∇p is the pressure gradient [Pa/m], ρ is the density of the groundwater [kg/m³], and g is the acceleration due to gravity [m²/s]. Darcy's Law is valid for laminar flow. Flow in partially-saturated media can be approximated using the Richards equation [170].

Advection in groundwater systems is often approximated using the advection-dispersion equation. The three-dimensional advection-diffusion equation in its general form with a distinction between effective and diffusion-accessible porosity can be written as follows [171]:

$$n \partial C / \partial t = \text{div}(n \cdot D_e \cdot \nabla C + n_e \cdot D \cdot \nabla C - n_e \cdot v_e \cdot C)$$

Where n is the diffusion accessible porosity [-], C is the solute concentration [kg/m³], D_e is the effective diffusion coefficient [m²/s] which is related to the molecular diffusion coefficient that occurs in Fick's First Law [172], n_e is the effective porosity [-], D is the dispersion coefficient [m²/s], and v_e is the effective advection velocity [m/s].

The advection-diffusion equation can be used in various forms for application to a particular problem and to take account of retardation and other processes. The specific forms of the equations solved in RWM's post-closure performance modelling are documented in references [11, 173].

2.10.2 Molecular diffusion

Molecular diffusion, often simply called diffusion, results from the thermal motion of particles that occurs at all temperatures above absolute zero. Diffusion explains the net flux of particles from regions of higher concentration to regions of lower concentration.

Molecular diffusion, often simply called diffusion, is the thermal motion of particles that occurs at all temperatures above absolute zero. The rate of this movement is a function of temperature, fluid viscosity and the size (mass) of the particles. Diffusion explains the net flux of particles from regions of higher concentration to regions of lower concentration. If the concentrations become equal, the particles continue to move, but since there is no concentration gradient the process of molecular diffusion has ceased. The diffusive flux and the change in the concentration gradient with time are often approximated using Fick's Laws [172].

Box 4 Quantifying diffusion

Molecular diffusion was described well before its fundamental nature was established. In analogy to earlier work by Fourier on heat conduction, Fick [172] postulated that the negative gradient of the concentration C ($-\nabla C$) was the driving force of the diffusive mass flux J [mol/m².s]. He further proposed a linear relation between flux and driving force:

$$J = -D_m \nabla C$$

which is commonly referred to as Fick's first law. The constant of proportionality, D_m [m²/s], is the coefficient of molecular diffusion. Combining this with the conservation of mass, Fick arrived at the diffusion equation:

$$\partial_t C = D_m \nabla^2 C$$

which is commonly referred to as Fick's second law.

In the context of a GDF, diffusion causes radionuclides and other chemical species to move from the waste package, where concentrations are higher, into the engineered barriers and geosphere, where the concentrations of radionuclides and many other species that are not present in the barrier materials are lower. Diffusion is a slow process, which is only important as a mechanism for transporting radionuclides and other species along the groundwater pathway when advective transport is small. Such conditions may prevail in the saturated pores of clay-based materials, where the small pore sizes impart a very low permeability to the material.

Box 5 The relative importance of diffusion and advection

A Péclet number can be used to determine the relative importance of advection and diffusion in a system. A Péclet number is a dimensionless number that relates the effectiveness of mass transport by advection to the effectiveness of mass transport by either dispersion or diffusion.

A variety of Péclet number definitions can be found in the literature and it is important to use a formulation that is suited to the scale and problem of interest [174]. The following form of the Péclet number has been used in the Belgian and Swiss programmes for the disposal of radioactive wastes in low permeability clay rocks [175, 176]:

$$Pe = (V_D \cdot x) / nRD_{app} = (V_D \cdot x) / nD_e$$

Where V_D is the Darcy velocity [m/s], x is a distance [m], n is the diffusion accessible porosity [-], R is the retardation factor [-], D_{app} is the apparent diffusion coefficient [m²/s] and D_e is the effective diffusion coefficient [m²/s].

For $Pe < 1$, diffusion dominates over advection at the distance x from the source [175, 176].

Reference [174] concludes that since the effective porosity and the diffusion accessible porosity may be very different in low permeability environments such as clays, the use of the effective porosity instead of the diffusion accessible porosity may lead to very different results. For low permeability environments, a Péclet number including the diffusion accessible porosity instead of the effective porosity should therefore be used. The convention in solute transport analysis to use a single lumped value of porosity instead of two different porosity terms is not appropriate for low permeability environments.

2.10.3 Dispersion

Dispersion refers to the spreading of a stream or discrete volume of contaminants (radionuclides or other species) as it flows through the subsurface.

Dispersion refers to the spreading of a stream or discrete volume of contaminants (radionuclides or other species) as it flows through the subsurface.

Dispersion is caused by both microscopic and macroscopic effects. Mechanical dispersion on a microscopic scale (Figure 13) is a result of deviations of velocity on a microscale from the average groundwater flow velocity. These velocity variations arise because water in the centre of a pore space travels faster than water near the wall and because diversion of flow paths around individual grains of porous material causes variations in average velocity among different pore spaces. These two factors create dispersion on a microscopic scale.

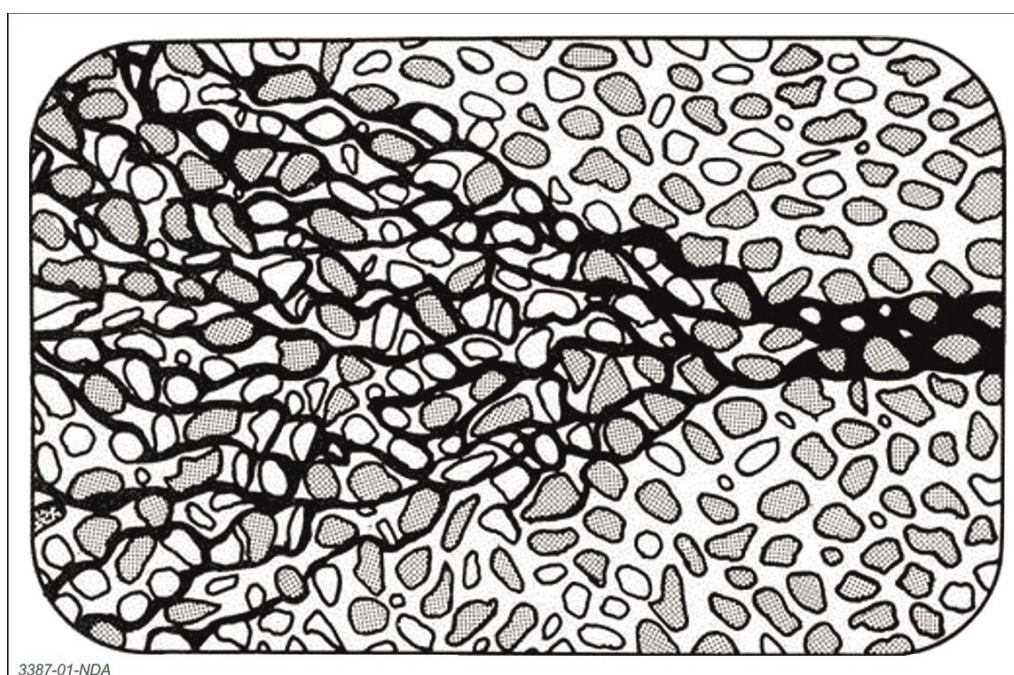
Reference [177] provides the following example. If a spot of dye is injected into porous material through which groundwater is flowing, the spot will enlarge in size as it moves downgradient. More specifically, in a three-dimensional Cartesian coordinate system where the average groundwater velocity is parallel to the x -axis, a sphere of dye moving horizontally along the x -axis will undergo longitudinal spreading, or dispersion, parallel to the x -axis and transverse dispersion parallel to the y - and z -axes. Dispersion causes mixing with uncontaminated groundwater, and hence dispersion is a mechanism that leads to dilution. Moreover, dispersion causes the contaminant to spread over a greater volume of the aquifer than would be predicted solely from an analysis of groundwater velocity vectors.

Dispersion is chiefly of importance in simulating transport away from point sources of contamination, but it also affects the spread of contaminants from non-point sources (for example, the GDF). Contaminants introduced into the subsurface from non-point sources will be spread over a relatively large area. In this case, dispersion merely causes the zone of contaminated water to acquire some 'rough fringes' [177]. Dispersion is also of interest

because it causes contaminants to arrive at a discharge point (such as a stream or a water well) prior to the arrival time calculated from the average groundwater velocity. This is due to the fact that some parts of the contaminant plume move faster than the average groundwater velocity. The possible effects of dispersion during transport away from the GDF are illustrated in the Post-Closure Safety Assessment report [11].

The discussion of dispersion above has focussed on continuous porous media. Dispersion in fractured rocks is more complex. Fractured rocks can be described and modelled as dual porosity media. In such cases, the diffusion of contaminants from fractures to the rock matrix may be a potentially significant retardation mechanism (see below). Dispersion in the fractures can however significantly accelerate the arrival of contaminants at a discharge point when velocities in the fractures are relatively low.

Figure 13. A schematic illustrating the process of dispersion in a porous medium. After [178].



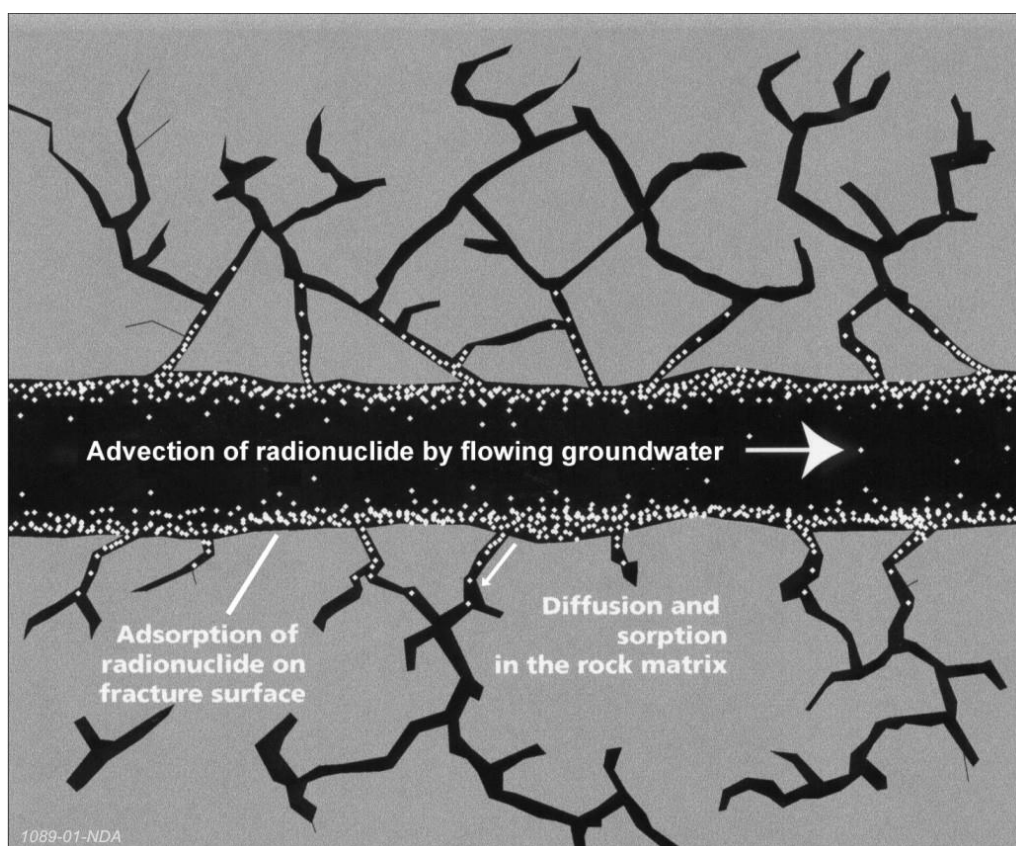
2.11 Rock-matrix diffusion

Rock-matrix diffusion involves the diffusion and dispersion of radionuclides or other species from groundwater in fractures or channels into the pores of the rock matrix. Rock-matrix diffusion, together with any sorption and decay that occurs in the rock matrix, may retard the transport of radionuclides or other species.

The term rock-matrix diffusion is commonly used to refer to the migration of chemical species in groundwater from a fracture or other zone of relatively high permeability rock into a lower permeability rock matrix [179, 180, 181, 182]. Rock-matrix diffusion is illustrated in Figure 14, with the chemical species shown as white dots.

Rock-matrix diffusion can occur in any groundwater system in which there is a significant contrast in advective flow rates among connected zones. For example, it can occur in systems in which groundwater flow occurs primarily in fractures within a porous rock matrix, and in systems comprising intercalated porous rocks of different permeabilities, see for example, references [183, 184] and references therein.

Figure 14. Illustration of advective transport, rock-matrix diffusion and sorption in fractured rock [181].



Based on results from laboratory experiments on a range of fractured granites, simplified analytical modelling studies [179] were undertaken to investigate the potential effects and significance of rock-matrix diffusion. They showed that rock-matrix diffusion has the potential to be significant in retarding radionuclide transport from a GDF, but there was considerable uncertainty in the values of some of the modelling parameters.

Reference [180] presented the theoretical basis for modelling rock-matrix diffusion and reviewed available data from laboratory experiments and natural analogues. The authors noted that:

- The results of laboratory diffusivity measurements can be questioned because of the small size of the samples used (which could mean that they miss the contribution of dead-end pores) and because the sampling procedures used can produce experimental artefacts (such as new fractures) as the rock samples are de-stressed - see also [185].
- Diffusivities and sorption coefficients in most fracture coating materials were found to be of the same magnitude or greater than in unaltered rocks. Fracture coatings did not seem to block the pores of the underlying unaltered rock.
- Natural analogue studies and *in-situ* experiments indicated pore connectivity on the scale of metres but, in most studies, matrix diffusion seemed to be limited to weathered or altered zones, only extending a few centimetres into the rock.
- A lack of knowledge concerning the initial and boundary conditions relevant to many field-based observations, and the possibility of other transport mechanisms being active, makes it difficult to obtain unambiguous data from natural analogues.

Matrix diffusion is commonly conceptualised and described in terms of Fickian diffusion from a fracture or other zone of relatively high permeability into the rock matrix [180].

However, depending on the geological environment, there can be uncertainty as to whether the observed distribution of a chemical species (such as a radionuclide) in the rock matrix close to a fracture actually results from diffusion, or whether advection and dispersion around the zone of higher permeability (for example, in micro-fractures close to the main zone of higher permeability) also plays a role. For example, [186] studied concentrations of tritium in water samples taken from glacial drift and fractured crystalline rock over 4 km in central New Hampshire, U.S. At this site, dispersion and mass transfer to and from fractures has affected the tritium concentration to the extent that the peak tritium concentration of the 1960s is no longer distinguishable. The diffusion coefficient at the kilometre scale was estimated to be at least 3 orders of magnitude greater than laboratory estimates of diffusion in crystalline rock, and this was interpreted as implying that diffusion into the rock matrix was masked at the large scale by advective exchange between fractures with large contrasts in transmissivity. Reference [186] concluded that advective mass transfer from high-permeability fractures to low-permeability fractures resulted in the migration of chemical constituents over short distances in the low-permeability fractures over an extended period of time before re-entering high-permeability fractures. Viewed at the kilometre scale, this process is analogous to the chemical constituent diffusing into and out of an immobile fluid phase.

Similarly to reference [180], [181] reviewed natural analogue data on rock-matrix diffusion and concluded that in low-porosity fractured rocks, such as granites, the available evidence demonstrated diffusion distances up to a few centimetres from fracture surfaces. They argued, however, that there was no justification for the view that diffusive migration of less strongly retarded solutes would be restricted to this narrow region around the fracture.

Reference [335] gave an overview of work undertaken within the Nirex Safety Assessment Research Programme on solute diffusion through groundwater in rocks. The authors noted that experiments on samples of Upper Caithness Flagstone, St Bees Sandstone and Borrowdale Volcanic Group rocks showed no evidence for a reduction in porosity or diffusivity close to any fracture face studied, and that in the case of the Caithness Flagstone, diffusivity and porosity were enhanced close to the fracture face in three samples studied. They also noted, however, that a number of experiments had been unsuccessful due to sample failure when a confining pressure was applied and that irreversible changes to the rock along planes of weakness resulted from borehole drilling and sample de-stressing.

Reference [187] reports experiments conducted at the Äspö Hard Rock Laboratory in Sweden in order to improve understanding of radionuclide transport and retention in fractured crystalline rocks at the 10 to 100 m scale. The experiments involved a series of tracer experiments using sorbing tracers in three different flow paths. Four tests were performed using different mixtures of sorbing radioactive tracers. For each tracer injection, the breakthrough of sorbing tracers was compared to the breakthrough of a conservative tracer. Selected tracer test results were modelled and interpreted using a one-dimensional advection-dispersion model, including sorption and unlimited matrix diffusion. The modelling indicated that there was a slightly higher mass transfer into a highly porous material in a block-scale experiment as compared with in situ experiments performed over shorter distances, and significantly higher than what would have been expected from laboratory data obtained from studies of the interactions in unaltered rock.

References [188 and 189] discuss a literature survey of forty field tracer tests at 15 fractured geological sites. Field-scale effective matrix diffusion coefficient values were obtained, either directly using data reported in the literature or by reanalysing the field tracer tests reviewed. The reanalysis was conducted using analytic or semi-analytic solutions for tracer transport in linear, radial, or inter-well flow fields. The data showed that the ratio of the field-scale effective matrix diffusion coefficient to the laboratory-scale matrix diffusion coefficient for the same tracer is generally greater than one, indicating that the effective matrix diffusion coefficient in the field is larger than the matrix diffusion coefficient

measured at the rock-core scale. This effect was attributed to mass-transfer processes at different scales in naturally heterogeneous, fractured rock systems. At a given scale, the ratio varied by two orders of magnitude, reflecting the influence of differing degrees of fractured rock heterogeneity at different geological sites. The data also showed a moderate, on average, trend toward systematic increase in the scale factor with observation scale.

Further uncertainties exist related to quantifying the transport of radionuclides and other species in water flowing through fractures:

- Heterogeneities are found at all scales in fractured rocks; from the scale of individual fractures, to the scale of fracture networks, and to the largest regional scales.
- Aperture variability within a fracture can cause a channelling of flow. The water flow can be focused in just a few channels and other areas of the fracture may have practically stagnant water. The degree of channelling can be quantified by defining the flow-wetted surface area; this is the area where the flowing water is in contact with the fracture. The flow-wetted surface is an important parameter that influences diffusion into the rock matrix and sorption to the fracture rock surface [182, 190].
- Anion exclusion may reduce the pore space available to anions, and may reduce the diffusivity of the rock matrix towards anions and other charged species such as colloids.

In summary, in some geological environments radionuclides and other species in groundwater may move from fractures or other zones of relatively high permeability into the surrounding rock matrix by diffusion and/or advection and dispersion in microfractures. These processes have the potential to retard and delay the transport of radionuclides from the GDF to the biosphere. The scale over which these processes operate, and the significance of the processes, are uncertain and will depend on a range of site-specific factors [191, 192].

The research identified in our S&T Plan includes a forthcoming review of understanding and approaches to modelling rock matrix diffusion [10, task 372]. Investigations of the potential for these processes at potential GDF sites will need to be made using a range of techniques; due attention will also need to be given to the potential for artefacts in laboratory scale experiments and to the effect of measurement scale. In particular, the work of [185] suggests that any future experimental studies on rock matrix diffusion should be carried out under a confining pressure appropriate to GDF conditions and only after rock cores have been cycled to sufficiently high temperatures and pressures to seal any microcracks caused as an artefact of sampling and exhumation.

2.12 Filtration and ion exclusion

During transport in groundwater, some species may be too large to pass through the pores of the engineered barrier materials or rocks and this may result in a filtration effect. Dissolved species with a charge of the same sign as on the surface are repelled and may be excluded from regions close to the surfaces, a process known as ion exclusion.

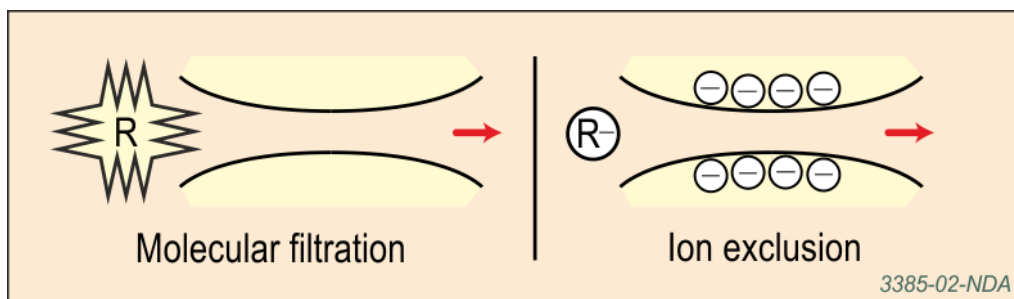
A wide range of materials are under consideration for the engineered and natural barriers of the GDF. Some of these materials contain pores that are on the scale of nanometres. Some entities in the groundwater, such as some colloids, microbes and aqueous complexes may be too large to pass through these pores and can, therefore, be prevented from migrating by a filtration effect. This process, molecular filtration, is illustrated schematically in Figure 15. There is a considerable literature on filtration (see, for example, references [136, 193]).

As discussed in Section 2.5, many mineral surfaces have a permanent or pH-dependent surface charge. The surfaces of many minerals of relevance to geological disposal, such as silicates (such as clays) and oxides, are negatively charged at neutral and high pH. This leads to the development of a region close to the mineral surface from which anions in the water are excluded by electrostatic repulsion. Ion exclusion is illustrated schematically in Figure 15.

In the context of radionuclide transport in groundwater, ion exclusion is only important for materials with pores on the length scale of nanometres, as this is the maximum length scale on which electrostatic interactions between the negatively-charged pore surfaces and anions in the groundwater can occur. A good qualitative understanding of these coupled phenomena comes from the application of the classical theory of electrical double layers: see, for example, standard textbooks such as [194]. There are, however, difficulties in applying these ideas to some materials, including highly compacted bentonite (see Section 3.3.1). A review of the theory of electrical double layers and its application to anion exclusion in rocks, addressing the reduced porosity accessible to anions, the reduced anion diffusivity compared to water and how anion exclusion is suppressed at high ionic strength, is contained in [195].

In un-fractured materials, solute and colloid transport takes place through the pores of the bulk of the material. In such cases, ion exclusion can act to reduce the transport of anionic species if it reduces the connectivity of free pore spaces (that is, those beyond the diffuse layer – see [111] and Section 4.3.3). However, in fractured materials, where groundwater flow takes place through a network of much larger pores (the fractures), ion exclusion may enhance anion transport. This is because this process may reduce the diffusion of colloids, microbes, larger aqueous complexes or anions into the pores of the rocks adjacent to the fractures. Further discussion of such effects is given in Sections 3.3.1 and 4.3.

Figure 15. Schematic representation of molecular filtration and ion exclusion.



3 Behaviour and transport in engineered barrier systems

Section 3 discusses the behaviour and transport of radionuclides and non-radiological species in engineered barrier systems, including the wasteform, buffer and backfill.

Wastes will be disposed of as wasteforms that are resistant to degradation:

- HLW is converted into a borosilicate glass wasteform. The glass will be packaged inside steel containers for disposal [2]. Fission and activation products separated during reprocessing are distributed throughout the glass. The glass is a durable wasteform that is suitable for geological disposal because it will only dissolve slowly in any groundwater in the GDF (see Section 3.1.1).
- Almost all of the radioactivity in the spent fuel inventory is contained in ceramic uranium dioxide (UO₂) pellets, but a small proportion is present in what is known as the Instant Release Fraction (IRF), and in other types of spent fuel. Research has demonstrated that ceramic uranium dioxide pellets can provide significant long-term containment of radionuclides. Section 3.1.2 discusses the release of radionuclides from the spent fuel.
- If they are declared as waste, suitable wasteforms will need to be selected for separated nuclear materials (plutonium and uranium). It is currently assumed that almost all of the plutonium will be converted into MOX fuel. It is further assumed that the small proportion of plutonium that is unsuitable for conversion to MOX fuel, and the HEU in the inventory, will be converted into a titanium-based ceramic wasteform. A range of disposal options for DNLEU is being evaluated [15], including overpacking of the current mild steel storage containers containing powdered DNLEU in more robust and durable waste packages. The use of cement grouts to intimately immobilise the DNLEU waste followed by packaging in stainless steel containers is also being evaluated. Another alternative being considered is the entombment of the existing waste storage containers containing the uranium oxide powders in cement. The release of radionuclides from these materials is discussed in Section 3.1.3.
- ILW/LLW incorporates a diverse range of wastes including metallic wastes, flocs²⁰, sludges, plastics and cellulosic materials. The LLW that will be disposed of in the GDF is that which is unsuitable for near-surface disposal. Much of this LLW comprises graphite which is unsuitable for near-surface disposal because of its ¹⁴C content. Most ILW/LLW will be conditioned using cement-based grouts. However, some ILW/LLW items may be disposed of in an unconditioned form, for example in robust shielded containers. Some ILW may be disposed of in vitrified form and other waste encapsulants such as polymers may also be used. In some cases, the radionuclides in ILW/LLW are present within solids and these may be expected to be released into groundwater slowly as the matrix dissolves. In other cases, the radionuclides may be more readily available for release to groundwater; for example they may be on the surfaces of waste items or sorbed onto floc which has then been grouted. The release of radionuclides from these materials is discussed in Section 3.1.4.

More details of the waste containers and waste packages in use or under consideration, and of their evolution in the GDF, are presented in the Package Evolution Status Report [2]. The corrosion of ferrous metal waste containers generates corrosion products on which radionuclides may sorb - radionuclide sorption onto such corrosion products is

²⁰ Floc - the product of flocculation. It consists of flakes of precipitate that come out of solution during the process of flocculation.

discussed in Section 3.2. Radionuclide sorption onto other engineered barriers is considered in Section 3.3.

3.1 Release from the wastes

Water may enter the waste containers and, as a result, some radionuclides and other species will dissolve and become mobile. The timescales for this will be dependent on numerous factors, including the flowrate and chemistry of the water, the container material, the wasteform and the radionuclides.

This section provides a brief summary of how radionuclides will be released to groundwater from the main types of higher-activity wastes in the GDF – this section is based on the more detailed account provided in the Waste Package Evolution status report [2]. The Waste Package Evolution status report [2] provides the basis for the parameter values on wasteform dissolution used in the 2016 generic Post-Closure Safety Assessment [11].

The dissolution behaviour of the wasteforms and the associated release of radionuclides is influenced by the nature of the wasteform and by the chemistry of the water that it contacts. This water will have been chemically conditioned by the materials of the EBS, such as cement, bentonite or metal. Where radionuclides are distributed and chemically bound throughout the matrix of the wasteform, the rate at which the radionuclides are released is largely controlled by the wasteform dissolution rate. If radionuclides are present at the surface of wastes, such as on contaminated items, they may be released more quickly.

The concentrations of dissolved radionuclides in water within the waste packages may be limited by solubility constraints. The extent to which solubility limitation is important in the waste packages depends on the interplay of a number of processes:

- the rate of water ingress into the waste package and the effects of any chemical reactions that consume water (for example, corrosion)
- the chemistry of the water in the container and its evolution
- any instantaneous release of radionuclides and the rate of wasteform dissolution
- the solubility of radionuclide bearing solid phases and the speciation of released radionuclides
- the rate at which radionuclides are transported out of the container
- the extent to which radionuclides released from the wasteform are incorporated in secondary minerals that precipitate in the waste package or are sorbed on the surfaces of corrosion products or other materials in the container
- microbial activity.

Slow wasteform dissolution, radionuclide sorption on surfaces in the waste packages, and transport of radionuclides out of the packages may keep concentrations below solubility constraints. Radionuclides may be sorbed onto various materials, such as corrosion products formed during the degradation of many waste containers, for example [196, 197].

The water that will eventually enter the waste containers will be derived from the surrounding rocks. The chemistry of this water will be influenced by the type of rocks and engineered barrier materials with which it has come into contact, the rate of any water flow through these barriers, and the extent of the water/rock interactions. In the UK, groundwater chemistry ranges from low to medium salinity waters, to more saline waters and brines [4].

Once released from the wasteform, radionuclides may be transported by diffusion and/or advection into the backfill or buffer. The possible impacts of water chemistry on radionuclide behaviour in the EBS are discussed in Section 2.2 and in references such as

Appendix F of [19]. For example, a range of water chemistries is possible in compacted bentonite, largely controlled by the presence or absence of trace minerals such as carbonates, which may buffer pH, and ferrous iron-bearing minerals such as pyrite (FeS_2) and siderite (FeCO_3), which may buffer Eh [198].

In addition, all of the disposal concepts under consideration by RWM include metals in the EBS [2, 3]. The metals are present principally as waste containers, but also occur as components of some of the wastes and their encapsulants (for example, blast furnace slag, which is a common constituent of the cementitious grouts used for waste conditioning, contains significant quantities of iron). Further metals may be present in the form of structural supports, rock bolts, etc. The corrosion of ferrous metals will consume any oxygen present in the GDF and the immediately surrounding rocks. After the oxygen initially present has been consumed, some of the remaining metals may corrode anaerobically and produce hydrogen gas. Corrosion is expected to maintain generally reducing conditions near the wasteform for long periods of time, although processes such as radiolysis and the release of nitrates from some wastes may cause conditions to be relatively less reduced / more oxidised locally.

The extent and timescale of redox buffering will be influenced by several processes (such as corrosion, radiolysis and waste dissolution), as well as by the chemistry and rate of any groundwater flow into the facility, the volumes and types of metal and other materials in the GDF and their spatial distributions. Research into the timescales and consequences of GDF redox evolution is continuing [10, tasks 445, 551, 701] - see the Engineered Barrier System Status Report for further discussion [3].

The following subsections provide summary information on the release of radionuclides and other species from the main wasteforms. More detailed information on wasteform dissolution processes (particularly for HLW, spent fuel and some vitrified ILW and potential plutonium wasteforms) is provided in the Waste Package Evolution Status Report [2].

3.1.1 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.

Radionuclide release from calcium-rich HLW is expected to occur over hundreds of thousands of years. Radionuclide release from magnesium-rich HLW is expected to occur over tens of thousands of years.

Earlier release of up to about 1% of the radionuclide inventory in HLW is possible due to the dissolution of highly soluble phases (in particular yellow phase) and due to faster initial rates of glass dissolution, before longer-term dissolution rates are established.

The radionuclides in HLW are vitrified into a form of borosilicate glass which is highly resistant to leaching. In such glass, silicon atoms, together with other elements known as 'glass formers' (for example, aluminium, zirconium or boron) that readily form bridging bonds with oxygen atoms, provide a highly cross-linked glass network. Alkali metal cations, known as 'glass modifiers' (for example, the ions Li^+ , Na^+ or K^+), alter the network structure; they are usually present as ions, and are charge compensated by nearby non-bridging oxygen atoms. The structure of a waste glass is illustrated in Figure 16 [199].

Numerous studies have been conducted on the dissolution of silicate glasses in water, and many have considered actual or simulated HLW borosilicate glasses (for example, see [200, 201, 202, 203, 204] and references therein).

The mechanisms of glass dissolution are relatively well understood [200, 204] and their rates are shown schematically below in Figure 17 [202]. 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 16. Schematic diagram showing a typical structure of waste glass. After [199].

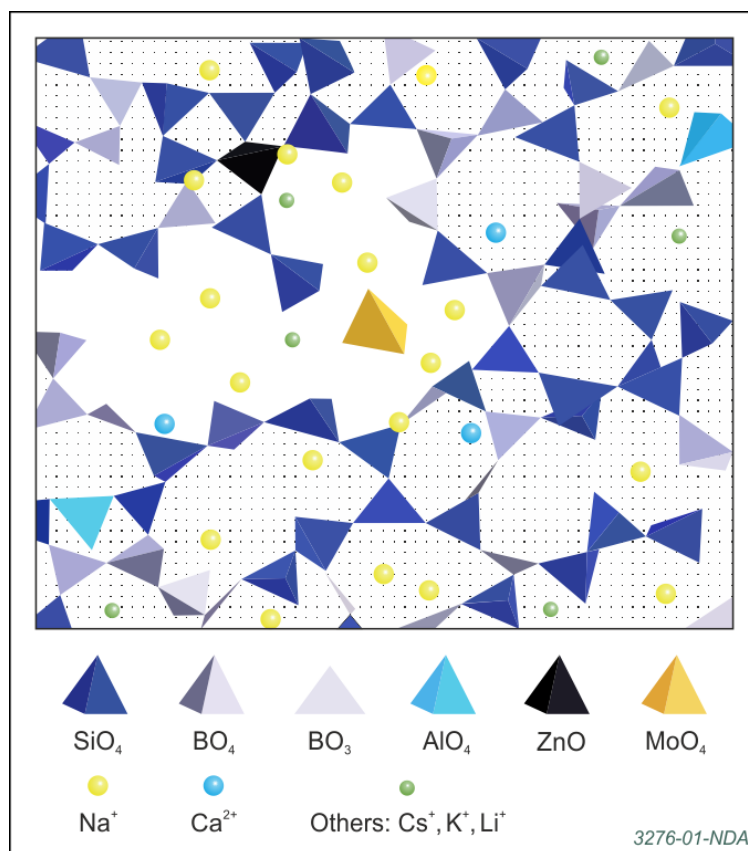
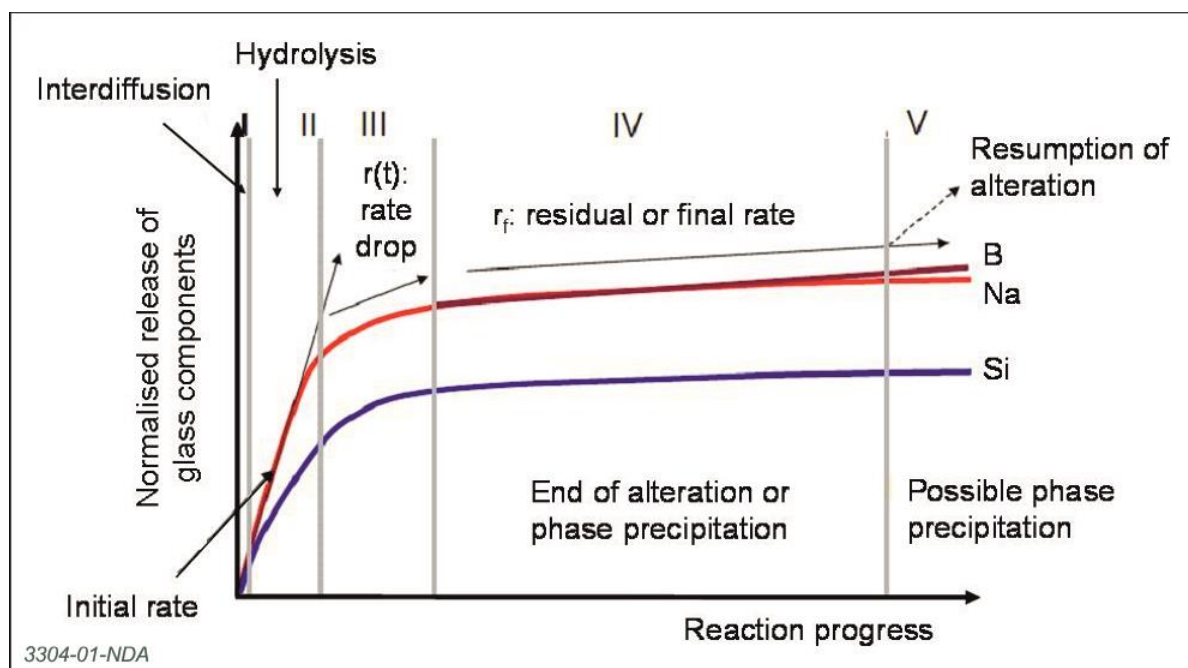


Figure 17. Different rate regimes for glass dissolution in near-neutral pH conditions [202].



In conditions of near-neutral pH, when glasses come into contact with water, the initial stages of dissolution are characterised first by inter-diffusion (diffusion of water molecules into the glass surface layer) and ion-exchange of network modifier elements (Stage I in Figure 17) and then by the hydrolysis of the borosilicate glass network (Stage II in Figure 17), resulting in the release of boron and silicon [205]. 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 in Figure 17).

Available evidence from relatively long-term experiments indicates that, in many circumstances, once the residual rate regime (Stage IV in Figure 17) has become established, the glass will continue to dissolve at the residual rate.

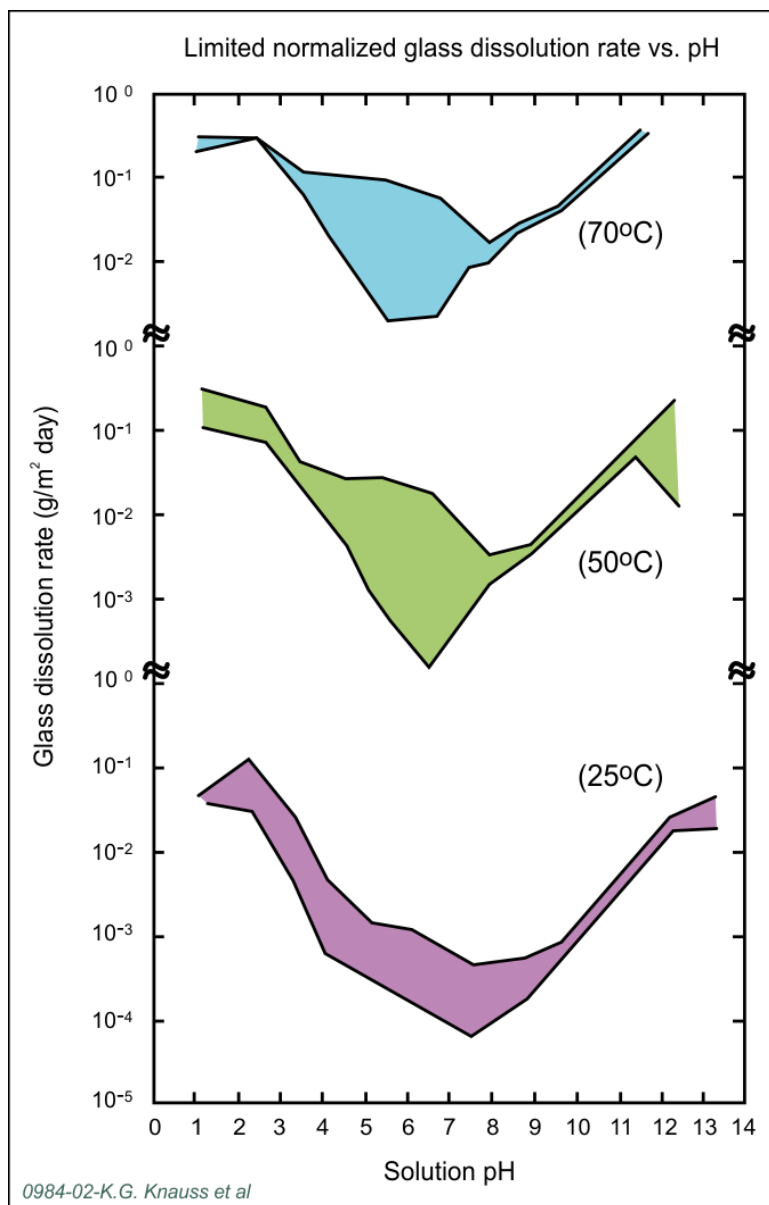
Recent work carried out in the UK programme indicates that potentially more soluble elements like caesium can be retained in the gel layer that forms on the surface of the glass under certain conditions [206]. It is important to note that, for radionuclides that are adsorbed or retained in the gel layer or in secondary solids, measured glass dissolution rates based on the release of weakly or non-sorbing elements can be used to define an upper limit for the rate of radionuclide release [207].

The rate of borosilicate glass dissolution (particularly Stage II in Figure 17) 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.

Figure 18 shows the dissolution rates of a simple borosilicate glass (as evidenced by the release of aluminium, boron, calcium, silicon and sodium) as a function of temperature and pH [208]. The shaded regions bound the range of dissolution rates for the five elements considered. HLW glass dissolution rate data are more fully discussed in the Waste Package Evolution status report [2] and are documented in the Data Report [9].

Reviews of international research on the long-term behaviour of vitrified HLW [209, 210] concluded that both glass dissolution and radionuclide behaviour are influenced by glass composition. Most published research has been on the French R7T7 glass, which is produced from reprocessing wastes derived from Pressurised Water Reactor (PWR) fuel. Less research has been undertaken on the glass compositions produced in the UK, which have higher magnesium contents. This is due to the fact that the UK HLW glass is a blend of the product from reprocessing of Advanced Gas-cooled Reactor (AGR) spent fuel and the product from reprocessing of Magnox spent fuel, and so inherits a greater concentration of magnesium from the Magnox fuels which are not used so extensively elsewhere [2].

The behaviour of UK specific glasses in the GDF is an area of research. 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 [207]. 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. Some of the UK glasses may also include micro-segregated phases (known as 'yellow phase') and this may also lead to initially higher releases of certain radionuclides [2].

Figure 18. Dissolution rates of a borosilicate glass. After [208].

Results from further tests [206, 211] to characterise the dissolution behaviour of UK-specific HLW compositions are discussed in [2], and our S&T Plan includes several further studies on the durability and dissolution of HLW glasses, including simulant Magnox and Magnox-blend glasses [10, tasks 536, 537, 538, 540 and 541].

Glass dissolution rates are typically independent of radiation levels and redox conditions because most of the major glass-forming elements in HLW are not redox sensitive. The few experimental data available from tests performed under radioactive conditions show that the glass corrosion rate does not appear to be significantly affected by either external radiation fields or self-irradiation [212]. Although leach tests showed a factor of 2-3 increase in the initial dissolution rate in the presence of radiation, the 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. However, the rates of release of some redox-sensitive species within the glass (such as ⁹⁹Tc, see [213]) 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.

The precipitation of secondary phases during the dissolution of HLW glass wasteforms is a beneficial process as it will remove radionuclides from solution and cause them to be re-immobilised inside the waste container. However, there is evidence that some of these secondary precipitates, which are mainly phyllosilicate minerals, such as smectite, binessite, saponite and nontronite, could form colloids [140]. The mechanisms by which colloids may be generated from glass surfaces are similar to the weathering processes by which mineral colloids may be generated from rock surfaces in contact with water; the principal secondary minerals are broadly similar. The major difference is the likelihood for the direct incorporation of radioelements in the colloids and the formation of intrinsic radioelement colloids [140].

Colloids could enhance the release rates of some radioelements from glass wasteforms if they are mobile in the pore waters and incorporate or adsorb radionuclides that otherwise would be contained in the vicinity of the wasteform. The stability and mobility of colloids and their significance will depend on site-specific factors that will need to be considered in future as the disposal programme is progressed. The research identified in our S&T Plan includes several further studies on the durability and dissolution of HLW glasses [10, tasks 539 and 541].

3.1.2 Spent fuel

In the presence of water, radionuclides may be released from UO_2 spent fuels in stages. First, easily accessible radionuclides are released in what is known as the Instant Release Fraction (IRF). IRFs of up to ~10% are expected for LWR and AGR spent fuels. The fuel matrix may dissolve at much lower rates, with the simultaneous release of fission and activation products and their daughters. In the conditions expected in a GDF, the release of radionuclide from the fuel matrix is expected to occur over millions of years.

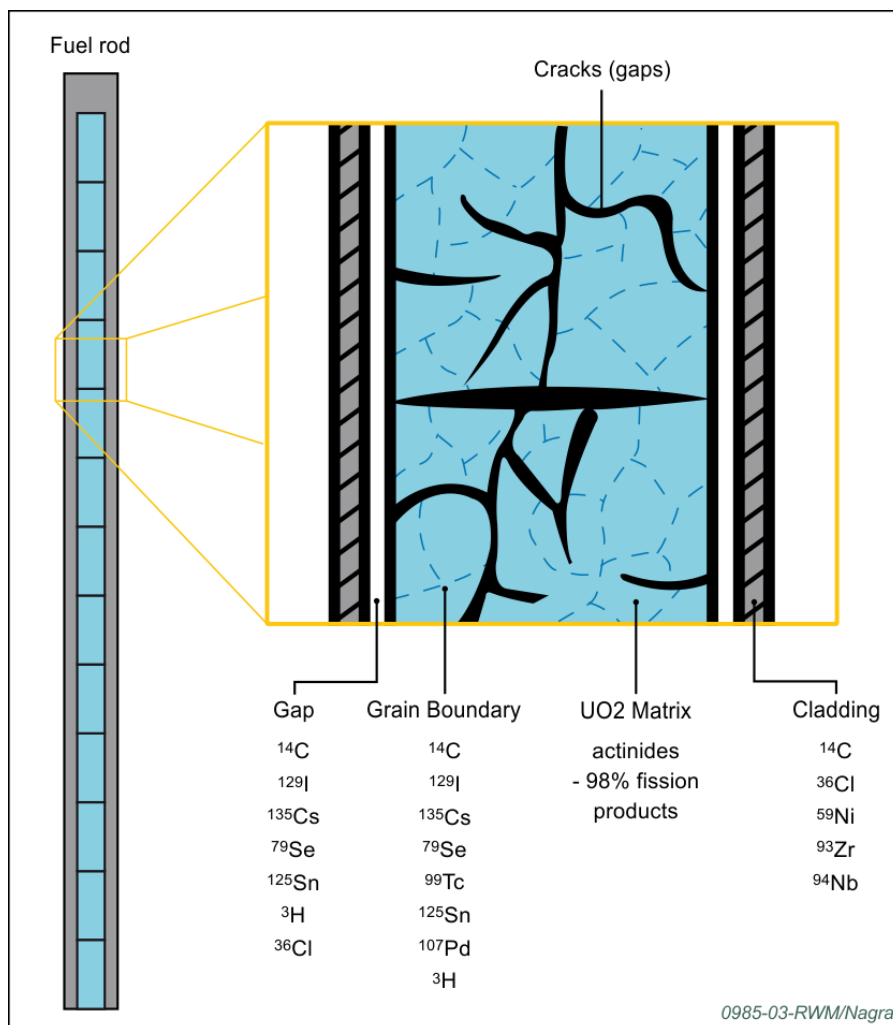
Metallic spent fuel is expected to degrade rapidly in a GDF, leading to a release of its radioactive inventory over relatively short periods of time. Exotic and plutonium-bearing spent fuels (for example, MOX) are expected to behave similarly to metallic or oxide fuels, depending on their chemical form. Very high burn-up fuels will require specific consideration.

Most of the spent fuel in the waste inventory (AGR and PWR fuels) consists of ceramic uranium dioxide (UO_2) pellets, contained in stainless steel, zirconium or nickel alloy cladding. The inventory also includes a much smaller amount of metallic uranium spent fuel contained in Magnox cladding. There are also some 'exotic' spent fuels from experimental reactors – see [2] for more details.

Many national and international studies have examined the dissolution of spent fuel [for example, 23, 214, 215, 216, 221].

UO_2 spent fuels

In UO_2 spent fuels, radionuclides occur along grain boundaries on fracture surfaces and in any cracks and gaps in the fuel and between the fuel and the cladding, in the cladding and in the fuel matrix (see Figure 19). In the presence of water, radionuclides are released from the spent fuel in stages.

Figure 19. Location of radionuclides in UO₂ PWR spent fuel. After [217].

- Instant release fraction

Once contacted by water, radionuclides on exposed surfaces of the fuel will be released over a period of days [23]. Further easily accessible radionuclides (from the pellet-cladding gaps, fracture surfaces, grain boundaries and any other accessible segregated phases) will be released as part of what is described as the IRF. Over longer periods (years to hundreds of years), the grain boundary inventory and possibly, in the case of high burn-up spent fuel, the rim region²¹ will also be released.

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 [2]. These studies show that the IRFs of 'volatile' radionuclides (for example, ¹³⁵Cs and ¹²⁹I) tend to increase with fuel burn-up and power rating. For these radionuclides conservative estimates of the IRF can be made on the basis of fission gas release data obtained at the highest levels of burn-up and power rating. The IRF of other radionuclides (particularly ¹⁴C and ³⁶Cl) is currently more uncertain [2].

An initial study [218] was completed in 2011 to estimate specific values of the IRF for a variety of radionuclides in UK-specific spent fuels types, including AGR, Magnox and some exotic fuels.

²¹ The rim region is the part of the spent fuel that has undergone restructuring as a result of burn-up. It is more porous than un-restructured spent fuel, and radionuclides can therefore be leached from it more easily.

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 [20, 219, 220]. Values of 1% or less have been estimated for other radionuclides [2]. In the conditions expected in a GDF, the release of the remaining inventory is expected to occur over periods of millions of years [2].

Figure 20 shows some example IRF data from the recent EC FIRST-Nuclides Project [216]. Note that the IRF data from the FIRST Nuclides Project may tend to over-estimate the instant release fraction because the study looked at relatively high burn-up fuels and many of the experiments considered were performed under oxidising conditions.

- Release from cladding materials

General corrosion of the Zircaloy, stainless steel and nickel alloy cladding materials upon exposure to groundwater is likely to be slow. Localised corrosion and other degradation processes are however likely to result in cladding perforation. The corrosion rate of Magnox cladding is expected to be fast and the cladding may be in a partly corroded state at the time of disposal. Corrosion of the cladding and other fuel assembly components is important as it will influence the release of activation products (for example, ^{14}C , ^{36}Cl , ^{59}Ni , ^{93}Zr and ^{94}Nb), some of which can be significant to post-closure safety [11]. ^{14}C may be present in the oxide films on Zircaloy and stainless steel cladding, and Magnox cladding fuel also contains significant quantities of ^{14}C . More detail on the processes that may affect radionuclide release from the various cladding materials is given in [2].

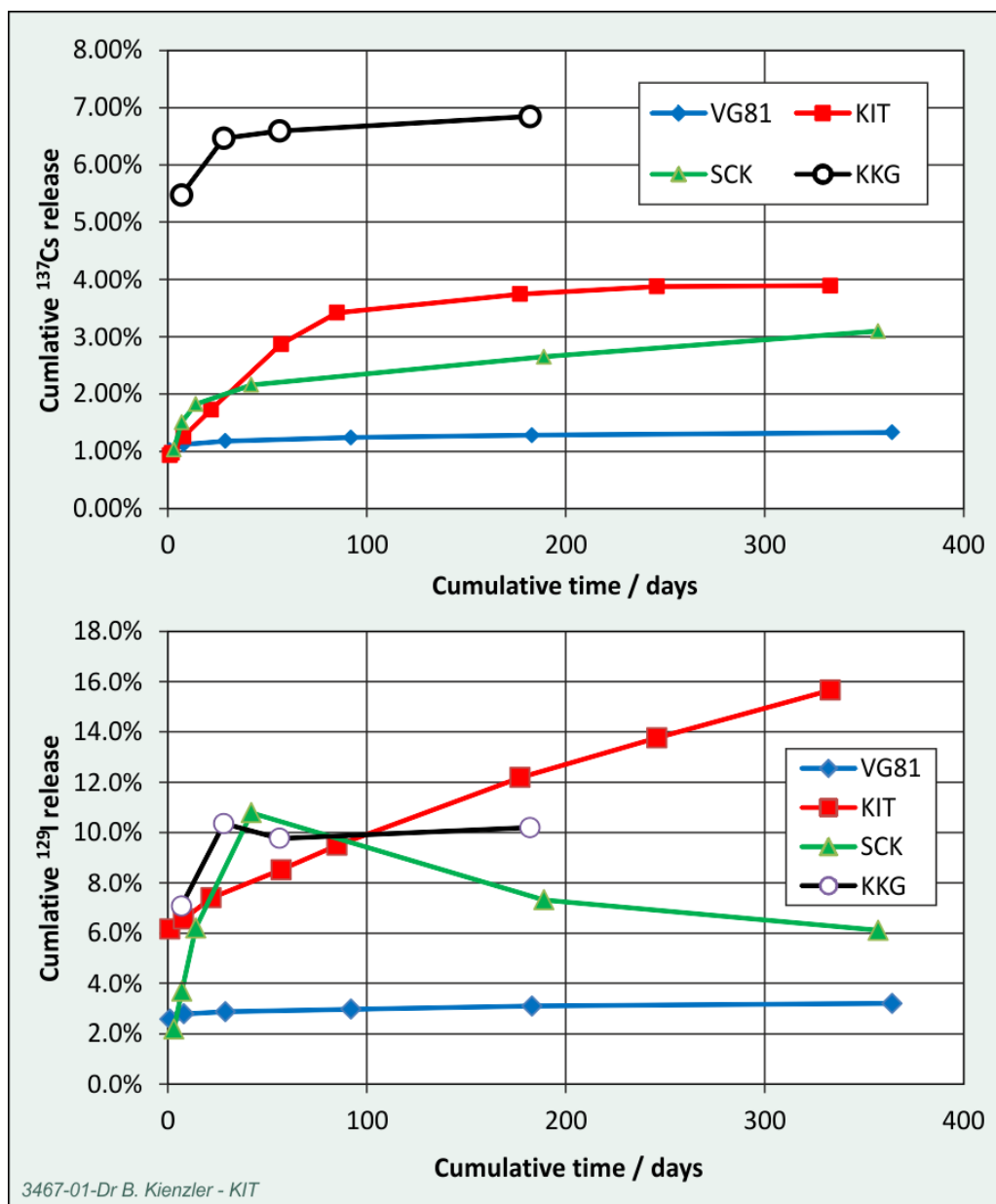
- Fuel matrix dissolution

In the presence of water, the matrix of uranium dioxide fuels will gradually dissolve, with the congruent release of fission and activation products and their daughters. The rate of spent fuel matrix dissolution will depend on a range of factors.

The key influence on the fuel matrix dissolution rate is the redox chemistry of the aqueous/solid phase system, as affected by the process of radiolysis and any supply of oxidants from outside the waste container [2, 20, 221 and references therein]. Significant dissolution of the spent fuel matrix would only occur under conditions in which the relatively stable uranium dioxide was oxidised to more soluble forms. The chemistry of the water that could possibly come into contact with the wasteforms after failure of the waste container will be dependent on the disposal concept and the nature of the site and its future evolution. The current expectation is that, despite these uncertainties and the localised effects of radiolysis, overall reducing chemical conditions will be established in the waste package, in part due to the presence of iron or steel, and that these conditions will persist in the vicinity of the spent fuel for a long period.

In disposal concepts that include ferrous metal waste container components (such as a steel waste container and/or a cast iron insert) hydrogen gas would be produced during corrosion of ferrous metals. Corrosion of ferrous metals may affect dissolved iron concentrations, contribute to the maintenance of reducing conditions and influence the rate of spent fuel matrix dissolution [221].

Figure 20. Example data on the cumulative IRF of caesium-137, an analogue for caesium-135, (top) and of iodine-129 (bottom), from various PWR spent fuel pellets and segments measured as a function of time²² [216].



As an example, reference [221] concludes that for (CANDU) fuel with an age of 1,000 years or greater, at concentrations of dissolved Fe^{2+} greater than $4.2 \mu\text{mol/l}$, even the radiolytically produced H_2 alone can suppress fuel corrosion without assistance from external H_2 . Depending on fuel burn-up, H_2 concentrations of the order of $0.1 \mu\text{mol/l}$ may almost completely suppress fuel corrosion [221]. In the presence of hydrogen from

²² Key:

VG81 = 2.8% enriched fuel with 8% Gd from the Vandellòs PWR with a burn up of $54.4 \text{ GWd/t}_{\text{HM}}$.

KIT = 3.8% enriched fuel from the Gösgen PWR with a burn up of $50.4 \text{ GWd/t}_{\text{HM}}$.

SCK = 4.3% enriched fuel from the Tihange 1 PWR with a burn up of $63 \text{ GWd/t}_{\text{HM}}$.

KKG = 4.3% enriched fuel from the Gösgen PWR with a burn up of $56.6 \text{ GWd/t}_{\text{HM}}$.

anaerobic corrosion, the rate of spent fuel matrix dissolution may be extremely low [for example, see Section 3.3.10 of 20].

Fuel matrix dissolution rates have been reviewed in several national programmes. Shoesmith [94] proposes a best estimate dissolution rate of UO_2 for hydrogen-dominated conditions of $\sim 2 \times 10^{-6} \text{ mol m}^{-2} \text{ year}^{-1}$. Consistent with this, recent reviews by SKB [20, 222] and Nagra [219] have proposed a best estimate fractional dissolution rate of spent fuel of $10^{-7} \text{ year}^{-1}$ 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. 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.

Other spent fuels

Metallic uranium fuel is expected to degrade rapidly in a GDF, leading to a release of its radioactive inventory over relatively short periods of time. 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 [2].

Exotic and plutonium-bearing spent fuels (for example, MOX) are expected to behave similarly to metallic or oxide fuels, depending on their chemical form. However, the behaviour of oxide fuel irradiated at very high burn-up ($>70 \text{ GWd tU}^{-1}$) would require specific consideration. Some work on the behaviour of MOX fuel has already been carried out in international programmes [216, 223] and further studies are expected to be completed in the future.

Although fuel matrix dissolution rates may be very low, dissolved radionuclide concentrations in water that contacts the fuel may rise, depending on the prevailing conditions, the rate at which the radionuclides are released from the fuel and the rate at which they are transported out of the container by advection or diffusion. Depending on the concentrations reached and the prevailing chemical conditions, some radionuclides may precipitate or co-precipitate as secondary solid phases.

As the discussion above has shown, both the mechanisms of radionuclide release from the main spent fuels and the factors which influence them are generally well understood. In addition, a significant body of data on spent fuel performance and dissolution rates has been obtained and collated by overseas waste management organisations. Spent fuel dissolution rate data are discussed in more detail in the Waste Package Evolution status report [2] and the values used in the 2016 post-closure safety assessment calculations are documented in the Data Report [9]. Our S&T Plan includes several further studies on the durability and dissolution of spent fuel [10, tasks 541, 546, 547 and 549 to 559].

3.1.3 Plutonium and uranium

A range of wasteforms and disposal concepts is feasible for plutonium and uranium, including synroc-type mineral phases, ceramic materials, and borosilicate or phosphate glasses. There is sufficient understanding of the chemistry of plutonium and uranium, and of the relevant matrices, to derive indicative release rates, but further research and development will be required.

Plutonium and uranium materials are included in the waste inventory, but have not yet been formally declared as wastes. Therefore, wasteforms for these materials have yet to be decided. A range of wasteforms and disposal concepts are feasible, including ceramic UO_2 -based materials and borosilicate or phosphate glasses.

It is currently assumed that almost all of the plutonium will be converted into MOX fuel. It is further assumed that the small proportion of plutonium that is unsuitable for conversion to MOX fuel, and the HEU in the inventory, will be converted into a titanium-based ceramic

wasteform. The majority of DNLEU is either in the form of ceramic oxides (UO_2 , UO_3 or U_3O_8) or gaseous (UF_6) which will have to be converted to a more stable form before disposal (current plans are to convert UF_6 into U_3O_8). A range of disposal options for DNLEU is being evaluated [15], including overpacking of the current mild steel storage containers containing powdered DNLEU in more robust and durable waste packages. The use of cement grouts to intimately immobilise the DNLEU waste followed by packaging in stainless steel containers is also being evaluated. Another alternative being considered is the entombment of the existing waste storage containers containing the uranium oxide powders in cement.

The release of radionuclides from these potential wasteforms has not been studied extensively, but there is sufficient information (from studies of UO_2 spent fuel dissolution) to estimate indicative release rates for use in generic safety assessments.

Plutonium

There is large body of published research on trials for the immobilisation of plutonium and other actinides in ceramic and glass-ceramic wasteforms [203, 224, 225, 226]. The Waste Package Evolution status report [2] summarises key aspects details of the experimental work undertaken in these studies. Based on the available information, reference [203] used expert elicitation to derive indicative dissolution rates for potential plutonium wasteforms (Table 1). Table 1 provides a 'non-conservative lower bound', a 'conservative upper bound' and a 'current best estimate' for the dissolution rate of, and the plutonium release from, relevant wasteforms under consideration for plutonium disposal. The environmental conditions considered in the elicitation were a pH range from 7 to 13. The higher part of this pH range was included to take account of the possible effects of interactions between the wasteforms and a plume of high-pH waters from cementitious materials in the GDF²³.

Although experimental data on the durability of potential wasteforms for plutonium under GDF-relevant conditions are limited, or in many cases absent, a large amount of information on relevant processes affecting their long-term durability in different disposal environments exists from laboratory and *in-situ* studies. In contrast, the database regarding the long-term leaching behaviour of phosphate-based glasses is comparatively small. Data on the durability of ceramic wasteforms is also rather scarce. Detailed understanding of the durability of the different ceramic matrices (regarding their dissolution behaviour as a function of crystallographic structure, chemical composition, lattice substitutions, radiation damage, etc.) is still lacking. Furthermore, even for nominally similar matrices, the dissolution rate data can show a considerable spread and the data are often difficult to compare due to different processing and fabrication routes employed, different experimental conditions and sample treatment, as well as the usage of plutonium-surrogates in some experiments. In addition, it is often the case that rather different chemical formulations have been investigated within a particular ceramic system (for example, pyrochlore or zirconolite).

Experimental investigations on the dissolution and performance of 'storage MOX'²⁴ and/or high-fired, calcined PuO_2 are also rather limited to date. Thus, the assessments and the elicitation of the dissolution rates for this potential wasteform are based on experiments and modelling studies related to the matrix dissolution of spent nuclear fuels (UO_2 and

²³ The current preferred approach to geological disposal is for a single 'co-located' facility consisting of two distinct disposal systems for ILW/LLW (and potentially DNLEU) and HHGW. It is anticipated that ILW/LLW and HHGW will be disposed of in separate disposal modules that implement different EBS designs appropriate to the different wastes and that share common access and surface facilities. These modules will be separated by an appropriate distance to ensure detrimental interactions cannot affect the performance of the disposal system (see Section 6.7 of [4]).

²⁴ The 'Storage MOX' wasteform concept comprises the use of unirradiated MOX pellets as a wasteform for plutonium. Storage MOX is also sometimes referred to as 'low specification MOX' or 'low spec MOX'.

MOX), and the knowledge that has been derived throughout the last three decades on relevant processes affecting their long-term behaviour in a GDF.

The data on which the elicited values in Table 1 are based are discussed in more detail in reference [200]. With these dissolution rates, the release of radioactivity is expected to occur over periods of tens or hundreds of thousands of years [2].

Table 1. Indicative dissolution rates for potential plutonium wasteforms [203].

Potential Pu wasteform	Lower bound g/m ² /d	Best estimate g/m ² /d	Upper bound g/m ² /d
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 x 10 ⁻¹
Storage MOX	<10 ⁻⁷	5 x 10 ⁻⁶	10 ⁻²

Uranium

Disposal of depleted, natural and low-enriched uranium has been the focus of a recent project [15]. This work has investigated a range of wasteforms and disposal concepts in order to determine the preferred option for any DNLEU that is declared as a waste. This work concluded that the preferred disposal strategy is for DNLEU to be disposed of as UO₃ and U₃O₈ powders in mild or stainless steel containers in order to minimise the need for pre-treatment ('conversion') and repackaging of the waste materials, whilst still meeting requirements of the wasteform and waste container as specified in the generic waste package specification.

The data used in the generic DSSC are documented fully in the Data Report [9]. The understanding of plutonium and uranium wasteforms and data for their dissolution will be the subject of review and refinement as more information becomes available. Our S&T Plan includes several studies on the dissolution of potential wasteforms for plutonium [10, tasks 616 to 620] and a study on the dissolution of uranium wasteforms which will also define needs for further research in that area [10, task 631].

3.1.4 ILW/LLW

The majority of ILW/LLW is packaged as a cementitious wasteform, but some unconditioned wastes may be disposed of within robust shielded containers and some ILW may be disposed of in vitrified form; other waste encapsulants such as polymers may also be used. Consequently, radionuclides will be released from ILW/LLW over a wide range of timescales.

The ILW and LLW disposed of to the GDF will be quite variable in nature. The wastes will therefore corrode or degrade by a range of processes, over a range of timescales, as discussed in the Waste Package Evolution Status Report [2]. Radionuclides may be incorporated in the structure of these wastes, or they may be present on their surfaces. Additionally, the waste containers (although vented, and therefore not sealed from groundwater flow) will provide a substantial barrier for some time. Consequently, radionuclides will be released over a wide range of timescales, as determined by the rates of groundwater flow, dissolution, corrosion and leaching, and by sorption and solubility in the EBS (as affected by any organic complexation, colloids and microbial activity).

The release of radionuclides from ILW/LLW into water within the waste package has not been subject to significant research in the UK programme; largely because, to date, safety

assessment calculations for the groundwater pathway have conservatively assumed that the release of radionuclides into the backfill will be instantaneous. Where leaching of radionuclides from ILW/LLW has been studied, for example [227], leach tests have been performed using simulated or actual wastes and wasteforms. Further leach tests could be performed in the future if it becomes necessary to understand the performance (specifically, dissolution rates) of ILW/LLW wasteforms in more detail.

A slightly different approach has been taken for some key radionuclides whose release is assumed to be controlled by the corrosion rate of the waste in which they occur. For example, RWM has recently conducted an extensive study of carbon-14 [228]. This work has shown that a proportion of the carbon-14 released from the wasteforms may enter backfill porewater in the form of carbonate, which is likely to precipitate, or as small organic molecules [229]. We are also leading research within the EC CAST project (CARbon-14 Source Term) to better understand potential mechanisms that may lead to the release of carbon-14 from the wastes under conditions relevant to waste packaging and geological disposal.

In most ILW/LLW disposal concepts, both the waste grouts and the backfill around the waste packages are cement-based. Reaction of water with cement results in alkaline conditions being established in the water (more details are provided in Section 3.3.2). The presence of the cement materials also provides a high surface-area substrate that sorbs many radionuclides quite strongly. Further, a large amount of iron and steel will be present; both as the material from which many waste packages are made and as a component of the waste. Although hyperalkaline conditions may limit the corrosion of some steels, it is expected that sufficient corrosion will occur to promote the establishment and maintenance of generally reducing conditions throughout the majority of the wastes and the EBS. Such chemical conditioning is important for the containment of radionuclides in the EBS of a cementitious GDF (more details are provided in [3]); however, some wastes may contain substances such as nitrates or other oxidants that could affect redox conditions in localised areas.

Although many ILW/LLW concepts involve packaging in a cementitious wasteform, there are also plans for the disposal of unconditioned wastes, possibly with lead shielding, in robust shielded containers and for the disposal of some ILW in vitrified form or with polymeric encapsulants. In some cases, for example for reactive metal wastes, corrosion rates are sufficiently fast that partial reaction will have occurred during curing of the cement grout in the waste package. For organic wastes, degradation of the waste material by radiolysis, hydrolysis and microbial effects may also begin during storage. In other wastes, such as graphite, ILW in vitrified form, effluent process wastes (such as barium carbonate, $\text{BaCO}_{3(s)}$) and steels, corrosion/degradation rates are much slower, and the wastes are not expected to react significantly during the storage phase. More detailed discussion is provided in Section 7 of [2]. Despite the potential for some wastes to corrode or degrade rapidly in the waste package, the potential for the subsequent transport of radionuclides through the EBS is limited by the chemical conditioning effects (solubility/sorption) in the surrounding cementitious encapsulants and/or backfill materials.

Radiolysis

The levels of radioactivity in ILW/LLW are significantly less than those in HLW/spent fuel. Therefore, radiolysis of water might be expected to be less significant in ILW/LLW disposal concepts than in HLW/spent fuel disposal concepts. The potential for radiolysis to promote oxidising conditions in the EBS was considered in the 2014 Compliance Recertification Application for the U.S. Waste Isolation Pilot Plant (WIPP) [230]. For that system it was concluded that the reductants present in WIPP waste (reduced metals and organics) would overwhelm potential radiolytic effects. However, ILW/LLW is comprised of a range of materials and the consequences of radiolysis on some of these materials can be significant. The more significant radiolysis effects in ILW/LLW are likely to be associated with the radiolysis of organic materials and the formation of degradation products such as

hydrogen and potential complexants (as introduced in Section 2.3 and discussed further below).

Organic complexation

Organic complexants relevant to the disposal of ILW/LLW may affect the solubility and sorption of radionuclides released from the wastes. Relevant organic complexants may be derived from the degradation of cellulosic wastes, from as-disposed complexants, from superplasticisers, and from polymeric encapsulants.

- Cellulose degradation products

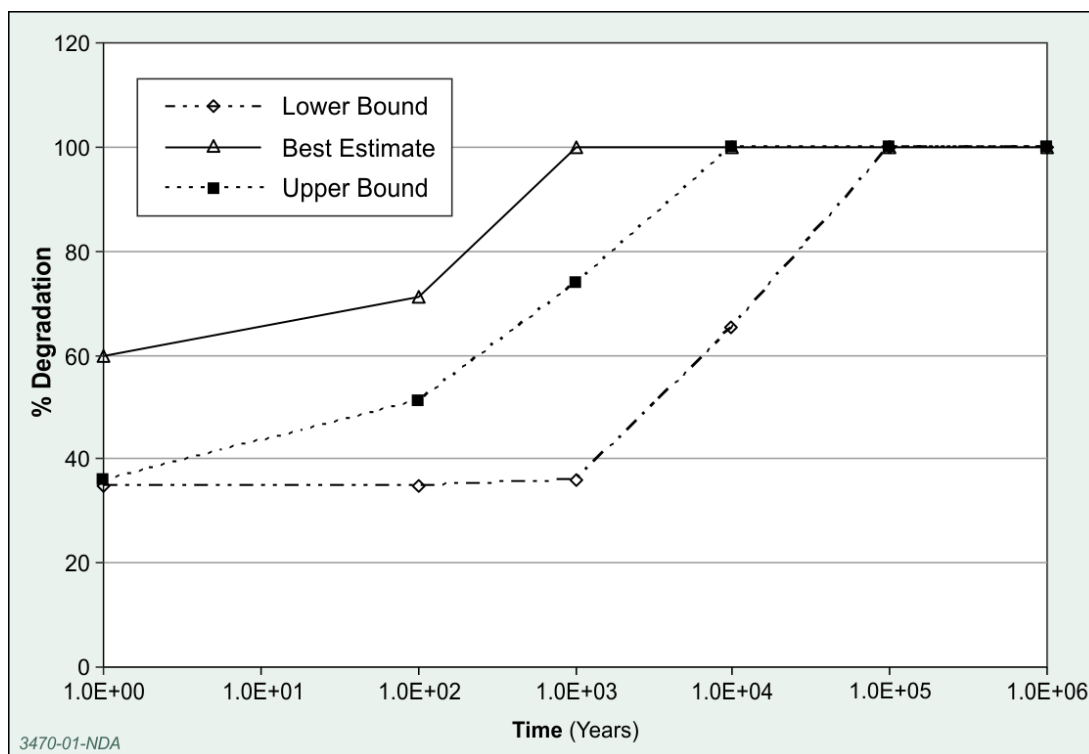
Early studies commissioned by UK Nirex Limited [231, 232] investigated the effect of various organic degradation products on the solubility of plutonium. This work found that increases in plutonium solubility occurred in the presence of degradation products from cellulosic wastes such as wood and paper. These early studies used products that were produced experimentally by degrading cellulose under simulated EBS conditions. Subsequently, Nirex investigated different fractions of this material to identify which had the greatest effect on plutonium solubility (see). These studies concluded that ISA was probably responsible for much of the increase in plutonium solubility observed ([233] and references therein); however it should be noted that the ISA concentrations used in those early experiments were higher than are actually expected to occur in the GDF.

Sorption of organic complexants may reduce their effect in enhancing the concentrations of mobile radionuclides; reference [234] reports experiments that show that ferric floc can reduce the concentrations of complexed plutonium in solution, possibly by sorbing the complexants, so that they are no longer available to complex plutonium.

The concentrations of organic complexants with the ability to enhance dissolved radionuclide concentrations may gradually reduce due to chemical, radiolytic and/or microbial degradation, as well as by processes such as advection, dispersion and dilution or sorption. More recent work [235, 236, 237, 238] has therefore involved building our understanding of the actual concentrations of ISA that are likely to be present in the EBS, of ISA's ability to persist under EBS conditions and of whether the period of ISA stability would coincide with the period when radionuclides would be released from the waste packages in order to understand the timescale over which any increased solubility would persist. This work has also considered whether there is an ISA concentration threshold below which no significant radionuclide solubility enhancement occurs. A range of CDPs were studied, including ISA, lactic acid, acetic acid, glycolic acid and other low molecular weight organic acids and alcohols. This research concluded that:

- the oxidative decomposition of ISA would not be significant in a GDF due to the limited period of oxidising conditions expected [235].
- the extent of alkaline hydrolysis of cellulose remains somewhat uncertain due to the relatively limited amount of experimental data available, but [235] presents estimates which suggest that in a cementitious GDF for the disposal of ILW/LLW (at ~pH 13.3 and temperatures of 60°C to 90°C), between ~35 and 100% of the cellulose initially present might be degraded after 1,000 years (Figure 21).

Figure 21. Estimates of the extent of cellulose degradation as a function of time (based on data at ~pH 13.3 and temperatures of 60°C to 90°C) - see Section 6.1.1 of [235].



- microbial degradation of CDPs may occur in localised volumes of the GDF (for example, where biofilms develop), but is more generally likely to be inhibited by the high pH conditions (see Section 2.8).
- exposure of CDPs to ionizing radiation is expected to induce their decomposition to even lower molecular weight species and gases. Data describing the degradation rates of CDPs by radiolysis are scarce; however, the factors that affect the radiolysis of CDPs are likely to be the same as those that affect the radiolysis of the original cellulose material [235].

Reference [238] concluded that the effective solubility of europium and thorium (which were used as chemical analogues for Am(III) and Pu(IV) respectively) in the presence of cellulose degradation products could be represented by assuming that ISA is responsible for the entire enhancement in solubility. The work also concluded that ISA only has a significant impact on radionuclide sorption and solubility when it is present in approximately millimolar concentrations; below this level no change in solubility or sorption was observed. This latter point is important because it implies that organic complexation by CDP is unlikely to be important in the geosphere, where the concentrations of CDP will be lowered by dilution and dispersion. In addition to the work outlined above, related research has been conducted as part of overseas waste disposal programmes [239, 240, 241, 242]. The research identified in our S&T Plan includes work to develop and update a process model to simulate cellulose degradation and model the subsequent interactions between CDP and radionuclides [10, tasks 758 and 764].

- As-disposed complexants

As noted above, work has been conducted to investigate the effects of other known strong complexants such as EDTA, picolinate, oxalate and diethylenetriaminepentaacetic acid (DTPA). These materials may be present in the waste, either as a result of their use as decontamination agents in decommissioning or due to their use in chemical processing/research activities. A number of studies has been conducted into the effects of

as-disposed complexants on radionuclide solubility [243, 244, 245]. The increases in radionuclide solubility seen in these studies were much lower than those observed for CDPs and so it is currently assumed that their impact will be less significant. However further work may be needed to confirm this and, for example, to determine if the same millimolar concentration cut-off level identified for ISA also applies to these complexants.

As noted above, EDTA is known to form strong complexes with a range of metal ions, including some non-radiological species such as lead (see, for example, references [78 and 246]) and so further work on the organic complexation of non-radiological species may, therefore, be needed to inform assessments of their potential impacts.

The research identified in our S&T Plan includes a review of Letter of Compliance submissions to consider the effects of organic components of wasteforms that may be present as decontamination agents, cement additives and/or grinding agents etc. [10, tasks 763 and 767].

- Superplasticisers

Additives, including superplasticisers, retarders and setting agents are often included in cementitious materials to improve their workability and potentially to allow a reduction in the quantity of water required in the mixture [247]. Superplasticisers are generally linear polymers containing acid groups that are attached to the polymer backbone at regular intervals; most commercial formulations belong to one of four families:

- sulphonated melamine-formaldehyde condensates
- sulphonated naphthalene-formaldehyde condensates
- modified lignosulphonates
- polycarboxylate derivatives.

The sulphonic acid groups are responsible for neutralizing the surface charges on the cement particles, causing dispersion and thus releasing water tied up in the cement particle agglomerations. This has the result of reducing the viscosity of the paste and concrete [248].

Experimental studies have been undertaken to measure the effect of varying superplasticiser concentrations on the solubility of radionuclides under the chemical conditions anticipated within a cementitious GDF for ILW/LLW [249, 250, 251, 252]. Early studies showed that even at low concentrations, ADVA Cast 551 (a polycarboxylate ether-based superplasticiser, which was being assessed for potential use as a grout additive in waste packaging applications) acted as a strong complexant and can significantly increase the solubility of some radionuclides in high-pH solutions if it is added directly to the solution [249]. It is noted, however, that these 'free solution' experiments are overly conservative since, in practice, the superplasticiser would be bound into the cement matrix and not readily releasable into solution. Furthermore, it has been shown that irradiation decreases the complexing ability of ADVA Cast 551, leading to the conclusion that irradiation breaks down the superplasticiser to smaller, less complexing species [249]. Along with chemical and radiolytic degradation, superplasticisers may also degrade microbially. A summary of these degradation processes is given in Section 1.6 of reference [253].

Recent research [254], investigating radionuclide solubility and mobility in the presence of polycarboxylate ethers (PCE), suggests that although the solubility of the radionuclides investigated is observed to increase in the presence of PCE in aqueous solution this does not correspond to an increase in the mobility of radionuclides released from PCE-amended grouts. Further, the research undertaken to date suggests that the PCE used in cementitious materials in the GDF (for example, in wasteforms, concrete waste containers, backfill or vault reinforcement) may be sorbed or otherwise incorporated onto cement surfaces and may only be released in low concentrations over very long timescales as the

CSH structure is leached or otherwise evolves. It is concluded, therefore, that the overall impact of PCE in a GDF environment will be limited to the potential for small concentrations of superplasticiser to cause an increase in the mobility of some available radionuclides once the superplasticisers have migrated from cementitious structures and become available in GDF porewater. This conclusion may not, however, apply to wastes in which radionuclides may be in solution during the liquid phase of the grout encapsulation process. The potential for chelation²⁵ by superplasticisers during this phase may result in mobile species being created in the cement structure. Further research may be required to develop a mechanistic understanding of the release of PCE from cementitious matrices and the potential for superplasticisers to degrade under chemical, thermal and radiolytic conditions [254] - the research identified in our S&T Plan includes several tasks aimed at the selection of suitable superplasticisers [10, tasks 757, 761, 765 and 770]. Our S&T Plan also includes a desk study of the composition and particularly the superplasticiser content of decommissioned building materials [10, task 759].

- Polymeric encapsulants

Epoxy resins and other polymeric encapsulant materials (such as Vinyl Ester Styrene (VES)) have been used for immobilisation of certain wastes that may be emplaced within the GDF as an alternative to cement-based encapsulants. Over the timescales of geological disposal the polymeric encapsulants will degrade, which will allow the release of radionuclides and organic species into solution. Experimental work has been undertaken to determine radionuclide solubilities in irradiated, high-pH leachates from a number of candidate polymeric encapsulant materials [255]. Measured radionuclide solubility enhancement factors in the prepared leachates were generally less than one order of magnitude. However, there were a few exceptions. For example, the solubility of Am(III) in leachate from irradiated low-temperature cured Advanced Polymer System (APS) was enhanced by more than three orders of magnitude. A one order of magnitude enhancement in the solubility of Am(III) was seen using leachate from irradiated VES and APS. Similarly, a one order of magnitude enhancement of Th(IV) solubility was observed in leachate from irradiated low-temperature cured Alchemix 4760 [255].

3.2 Retardation on waste package corrosion products

Iron and steel wastes and waste containers will corrode and degrade over time. The corrosion products formed may have a strong effect on the local chemical environment of the GDF, with the consequence that the chemical environment within the EBS is expected to become generally reducing. Corrosion products may provide substrates to which radionuclides may sorb.

Iron and steel wastes and waste containers will corrode and degrade over time. Iron and steel corrosion is discussed in detail in the Package Evolution Status Report [2] and the Engineered Barrier System Status Report [3]. This section considers the impact of iron-bearing corrosion products on radionuclide mobility.

Steel corrosion in the GDF will promote generally reducing conditions in the EBS. The metals and oxide corrosion products formed will provide abundant surfaces and may promote the reduction of redox-sensitive radionuclides. As a consequence, redox-sensitive radionuclides are expected to be present in their lower oxidation states.

Radionuclides may sorb or otherwise associate with iron-bearing corrosion products. The possible chemical evolutions of the EBS of various GDF disposal concepts are described in

²⁵ A chelate is a chemical compound composed of a metal ion and a chelating agent. A chelating agent is a substance whose molecules can form more than one bond to a single metal ion. Chelating agents are often organic species.

detail in the Engineered Barrier System Status Report [3]. $\text{Fe}(\text{OH})_{2(s)}$ and magnetite ($\text{Fe}_3\text{O}_{4(s)}$) are expected to be the principal corrosion products produced by anaerobic steel corrosion, with the former potentially transforming to the latter over time [256]. However, the conversion to magnetite may be inhibited in some environments because of the high concentration of magnesium present in some waters (for example, as a result of Magnox dissolution [256]), and goethite may persist as an important corrosion product. Other possible iron-bearing corrosion products include the family of minerals known as green rusts²⁶ [257] and these may also sorb or incorporate radionuclides [258, 259].

Under the conditions expected in the high pH EBS of a cementitious GDF for ILW/LLW, measured distribution ratios for americium and plutonium in batch experiments on magnetite were at least $100 \text{ m}^3/\text{kg}$ [260]. Under these conditions it appears that the association of americium and plutonium with magnetite is at least as strong as on cementitious materials.

Similar studies have investigated the mechanisms by which radionuclides and iron corrosion products interact under conditions relevant to a GDF for spent fuel. Under anoxic conditions, uranium(VI) is sorbed on magnetite surfaces, whereas under reducing conditions, reduction to uranium(IV) is inferred to occur [261].

Other experimental studies have demonstrated weak sorption of anions on minerals such as magnetite. For example, a study of the sorption of selenium(IV) and selenium(VI) onto magnetite found weak sorption, typically less than $0.01 \text{ m}^3/\text{kg}$, in both cases [129]. Technetium is mobile in its oxidised pertechnetate form ($\text{Tc}(\text{VII})\text{O}_4^-$), but when it is reduced to Tc(IV) it immobilises readily via precipitation or sorption [196, 197, 262].

The research identified in our S&T Plan includes undertaking a focussed study to understand the uptake of key radionuclides on waste container corrosion products [10, task 741].

3.3 Behaviour in buffers and backfills

Bentonite-based materials are being considered mainly for use in the buffer and the mass backfill in HLW/spent fuel disposal concepts. Cement-based materials are proposed for backfilling caverns, tunnels and shafts in many ILW/LLW disposal concepts. Cement-based materials may also be used in some HLW/spent fuel disposal concepts. Salt-based materials are being considered for buffer/backfills in evaporite rocks.

The excavated voids in the GDF will be filled with a material known as the buffer or backfill, while the access tunnels and shafts will be closed using mass backfill and seals. A range of materials is currently being considered for the buffer, backfill and seals, as discussed in the Engineered Barrier System Status Report [3]. This section describes how buffers and backfill placed around waste packages will affect the behaviour of radionuclides and other species.

The characteristics required of the buffer/backfill are dependent on the role that the barriers play in the specific disposal concept. Physical factors that might be considered include the strength of the material and its permeability to gas and groundwater. Chemical factors might include the surface area of the material (which influences sorption), and/or the ability of the material to chemically condition the EBS environment so that it remains within a particular pH and/or Eh range over long time periods.

²⁶ Green rusts belong to a family of minerals known as layered double hydroxides. They comprise alternating layers of positively-charged hydroxide and hydrated anions and contain a mixture of ferrous and ferric iron.

3.3.1 Bentonite-based barriers

A buffer composed of dense compacted bentonite will protect spent fuel and HLW disposal containers from mechanical deformation, forming a low permeability barrier to water flow, preventing or significantly limiting the activity of microbes, and precluding mobility of colloids. Bentonite barriers may sorb some radionuclides and thus act to retard their transport. If dilute groundwaters interact with bentonite, erosion may cause some loss of buffer function and lead to the generation of colloids.

Bentonite-based materials are being considered mainly for use in HLW/spent fuel disposal concepts. Two types of barrier are generally considered: a bentonite buffer that would be placed immediately around the waste containers, and a mass backfill for filling caverns and tunnels. Bentonite is a suitable material for these engineered barriers because, as long as it is emplaced in the GDF at suitable density, it will, when confined, provide a sufficiently high swelling pressure and low permeability barrier following resaturation. Bentonite also has a high sorption capacity for some radionuclides. In addition, the small pore sizes in bentonite are expected to preclude the movement of colloids through the barrier and limit the growth and mobility of microbes [263]. Because of the low permeability developed, diffusion is the dominant transport mechanism by which radionuclides and other species would be transported through the bentonite.

Transport and retardation in bentonite-based barriers

Transport and retardation in compacted bentonite barriers is likely to occur by diffusion and sorption, and can be quantified to a first approximation using approaches based on the apparent diffusion coefficient.

Bentonites owe their low permeability, high swelling capacity, high plasticity and high sorption to their high content (typically ~50% to 90%) of expandable 2:1 smectite clays, such as montmorillonite. Montmorillonite is the most abundant mineral in natural bentonite deposits such as Wyoming Bentonite, which is the source of the commercial bentonite product MX-80. The remaining minerals in bentonites are largely carbonates and silica; other clay minerals and metal oxides are typically only present at trace levels or not at all. Some bentonites also contain small amounts of pyrite. More information on the composition and properties of bentonite barriers can be found in [3].

Box 6 Quantifying diffusion and retardation in bentonite-based barriers

In a diffusion-dominated system the migration of radionuclides is mainly determined by the element-specific apparent diffusion coefficient, D_a . D_a can either be measured directly or it can be derived using K_d values from batch sorption experiments in dilute systems using the equation [338]:

$$D_a = D_e / (\varepsilon + K_d \rho_d) = D_e / \varepsilon R$$

Where D_e is the effective diffusion coefficient [m^2/s], ρ_d is the dry density [kg/m^3], ε is the accessible porosity [-], K_d is the distribution coefficient [m^3/kg], and R is the retardation factor [-].

As discussed in [338], one of the benefits of this approach is that batch sorption measurements can be used to derive the required parameters. However, reference [36] notes that for reasons of pragmatism and data limitations, typically only D_e values for a few reference species (for example HTO, $\text{Cs}^+_{(\text{aq})}$ and $\text{Cl}^-_{(\text{aq})}$) are used to represent the diffusion behaviour of cations, neutral species and anions. Data on radionuclide diffusivities in bentonite are specified in the Data Report [9].

Given their mineralogical composition, radionuclide sorption in bentonite is dominated by smectite clays and the interlayer is the dominant type of pore space (see Section 4.3.6). The planar siloxane surfaces of these clays are crystallographically well defined and chemically relatively inert. Sorption on these surfaces can be modelled as ion exchange involving the exchange of counter-ions. The edges of the clay platelets feature exposed aluminium, silicon and oxygen atoms with broken bonds, forming amphoteric hydroxyl surface functional groups similar to a typical metal oxide surface - sorption here can be modelled as surface complexation [36, 267].

Radionuclide sorption on bentonite has been studied by various waste management organisations overseas, largely using batch sorption and through diffusion experiments. Reviews of available data can be found in references [36, 264, 265, 266] - these references are the source of the discussion in the following paragraphs.

There are significant experimental difficulties in obtaining pore water and actual sorption data from compacted bentonite, especially as a function of pH and other conditions²⁷. This normally prevents the parameterisation of sorption models on the basis of data directly corresponding to compacted conditions. Sorption model parameters have, thus, to be obtained from experiments on dispersed systems. The principal challenge of modelling sorption in compacted clay systems is therefore the quantification of radionuclide surface complexation and ion exchange based on information obtained from dispersed systems/batch experiments, while maintaining consistency with concepts of narrow pore spaces and electrostatic effects.

Because experimental evidence allowing the description of pore space in compacted bentonite is scarce, and not free of contradictions, various different model concepts have been developed [36]. These can be categorised into two groups [36, 267]. One group comprises models that, as a first approximation, treat the clay as a homogeneous charged porous medium and represent just a single porosity type, for example [268]. The second group comprises models in which more than one type of porosity is recognised, for example [338].

²⁷ The boundary between 'dilute' and 'compact' bentonite systems lies at $\sim 1,300 \text{ kg}/\text{m}^3$, which marks the point where the number of water layers in the interlayer of the bentonite starts to decrease and the swelling pressure starts to increase dramatically with further compaction [36].

Although the models in the second group differ in several details, importantly the effects of cation and anion diffusion are described on the basis of different processes in corresponding different types of pores (interlayer pores and inter-particle pores, respectively). Cations are assumed to diffuse (at least partly) through the interlayer pores, whereas anions cannot access the interlayer pores. Some of these models also evaluate the mobility of cationic species close to the surface of the clay minerals by enhanced diffusion in the diffuse layer – this latter effect has been termed ‘surface diffusion’ [338].

Although there are no indications that sorption sites become inaccessible upon compaction, there are open questions on how sorption sites should be apportioned to different pore types in cases where several types of porosities are considered [36]. In particular, there are questions regarding the mobility of ions (especially alkaline and alkaline earth elements) in the electrical double layer near the planar surface of clays (and possibly also near the edges of the clay minerals) [36].

In summary, transport and retardation in compacted bentonite barriers is likely to occur by diffusion and sorption, and can be quantified to a first approximation using approaches based on the apparent diffusion coefficient. However, there are open questions relating to the fundamental understanding of porosity and the precise mechanisms of transport and retardation in compacted clays.

Bentonite erosion

If dilute groundwaters interact with bentonite, erosion may cause some loss of buffer function and lead to the generation of colloids. RWM is undertaking research on the potential significance of bentonite erosion.

One further issue that could have an effect on radionuclide transport through bentonite and in the surrounding geosphere is the potential for some of the bentonite to be eroded by dilute flowing groundwaters. This could lead to the formation of bentonite colloids and some degradation of the properties of the bentonite barriers, including a reduction in density and degree of compaction [136, 270, 271].

Various research projects on bentonite colloids have been undertaken, both by individual radioactive waste management programmes and within international co-operations (sponsored by the European Commission - see Section 2.7). Most recently, we have been participating in the BELBaR project, which has several work packages, each one investigating one of the questions highlighted in Figure 10.

The potential for bentonite erosion depends on the chemical composition of the bentonite materials, the chemistry and salinity of the groundwater and the velocity of groundwater flow in the vicinity of the buffer. The stability of bentonite is strongly linked to its composition (primarily the sodium and calcium content) and to the composition of the water present. In particular, if the concentration of divalent cations, particularly calcium, in solution is low and falls below the critical coagulation concentration (CCC), bentonite colloids may be released and carried away by the groundwater. Such chemical erosion processes may provide a mechanism for radionuclide transport if radionuclides are sorbed onto bentonite colloids. Bentonite erosion is more likely to occur in the presence of dilute waters. At present, there are limited data that allow quantification of bentonite erosion rates, and in any case, colloid release rates from bentonite will be site-specific. Relevant research has been conducted as part of the waste disposal programmes in Finland and Sweden, and further research is continuing as part of the EC BELBaR project and elsewhere, for example, see reference [269]. The potential for colloids to be released from bentonite barriers is also being studied in the colloid formation and migration experiment (CFM) at the Grimsel Test Site in Switzerland [30].

The main aim of the BELBaR project is to increase knowledge of the processes that control the generation, stability and ability to transport radionuclides by association with clay colloids. The project is investigating three main topics: bentonite erosion, colloid stability and colloid-radionuclide and colloid-host rock interactions. The process of bentonite erosion may proceed by several different mechanisms:

- the transport of fast-flowing water across a bentonite surface can shear off particles by physical forces
- in low salinity waters (and in unconfined conditions) repulsive forces between smectite clay particles can expand the colloids in a repulsive gel²⁸ such that they are eventually so far away from each other that they form a stable sol²⁹ with low viscosity
- dilute gels and sols can flow as a liquid if the viscosity of the gel is low and the hydraulic gradient is high.

These mechanisms are discussed in various references (see, for example, [136, 270, 271, 272, 273 and 274]).

The stability of clay colloids under site-specific host rock conditions will be important for assessments of long-term performance of radioactive waste repositories [275, 276, 277, 278]. The stability of clay colloids in groundwaters is primarily a function of water chemistry, as defined, for example, by pH, salinity and dissolved cation concentrations, and the distribution and magnitude of electrostatic charges on the clay-mineral surfaces and edges which are, themselves, also a function of pH. Further factors may need to be taken into account when assessing colloid mobility, such as water-flow rates and filtration effects [136, 269].

The CFM project is being conducted in a URL at the Grimsel Test Site in Switzerland and aims to understand the formation and transport of colloids and colloid-associated radionuclides in a granitic rock. The experiment emplaced a potential source of radionuclides and colloids within an advective flow system (a fracture) in the host rock, allowing the formation and transport of colloids and colloid-associated radionuclides to be monitored (Figure 22).

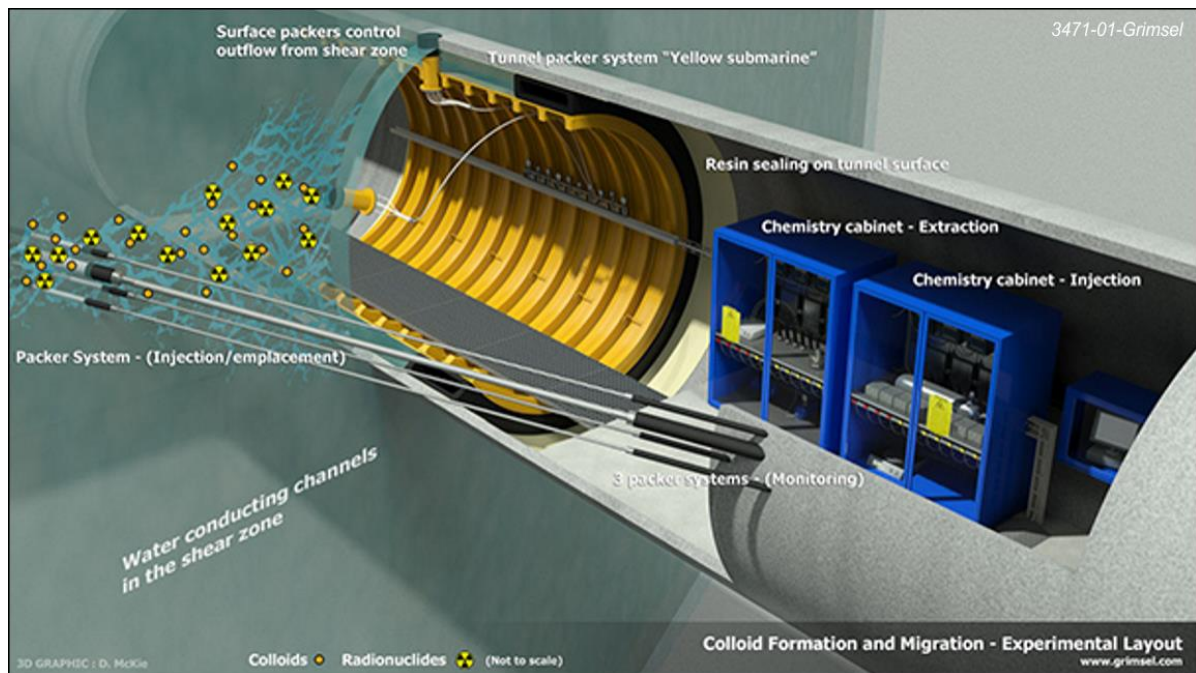
The research identified in our S&T Plan includes:

- review and testing of sorption processes in potential clay buffer/backfill materials [10, task 739]
- a focussed study to understand the uptake of key radionuclides on clays [10, task 741]
- participation in the CFM project at the Grimsel Test Site [10, task 755]
- studies on diffusion processes in saturated bentonite [10, tasks 462 and 470]
- a study of bentonite erosion [10, task 463]
- a study of microbial activity in bentonite [10, task 467]
- a future review of research needs on bentonite-based materials [10, task 468].

²⁸ A gel is a colloidal system with a finite, usually rather small, yield stress.

²⁹ A sol is a colloidal suspension of very small solid particles in a continuous liquid medium.

Figure 22. Illustration of the Colloid Formation and Migration (CFM) experiment at the Grimsel Test Site in Switzerland [30].



3.3.2 Cement-based barriers

Cement-based barriers are proposed for backfilling caverns, vaults, tunnels and shafts in many ILW/LLW disposal concepts and are proposed for use as a buffer in some HLW/spent fuel disposal concepts.

Cement-based barriers are proposed for backfilling caverns, vaults, tunnels and shafts in many ILW/LLW disposal concepts and are proposed for use as a buffer in some HLW/spent fuel disposal concepts (for example, in the Belgian supercontainer concept). Cement-based materials are also used as the wasteform in many ILW/LLW disposal concepts. In some disposal concepts, cement-based materials have further roles as engineered seals, supports, etc. [323].

Transport and retardation in cement-based barriers

Transport in cement-based backfills may occur by advection and diffusion in the pores of the materials and in any open cracks and fractures (within the backfill or between the backfill and the waste packages or host rock). The initial permeability to water of the Nirex Reference Vault Backfill is of the order 6×10^{-17} to $3 \times 10^{-16} \text{ m}^2$ and this may tend to decrease with time as a result of groundwater interaction and calcite precipitation.

In the presence of a hydraulic gradient, radionuclide transport in cement-based engineered barriers will occur by advection as a result of water flow, mainly through the pores of the materials - but it may also occur through any open cracks and fractures (within the backfill or along the interfaces between the backfill and the waste packages or host rock) [279]. Diffusion will also occur in cement-based barriers; in cases where there is no significant hydraulic gradient and/or where the permeability to water of the materials is very low, diffusion may be the dominant transport process. The initial permeability to water of NRVB has been measured to be in the range $6 \times 10^{-17} \text{ m}^2$ to $3 \times 10^{-16} \text{ m}^2$ [280] and this may tend to decrease with time as a result of groundwater interaction and calcite precipitation [281].

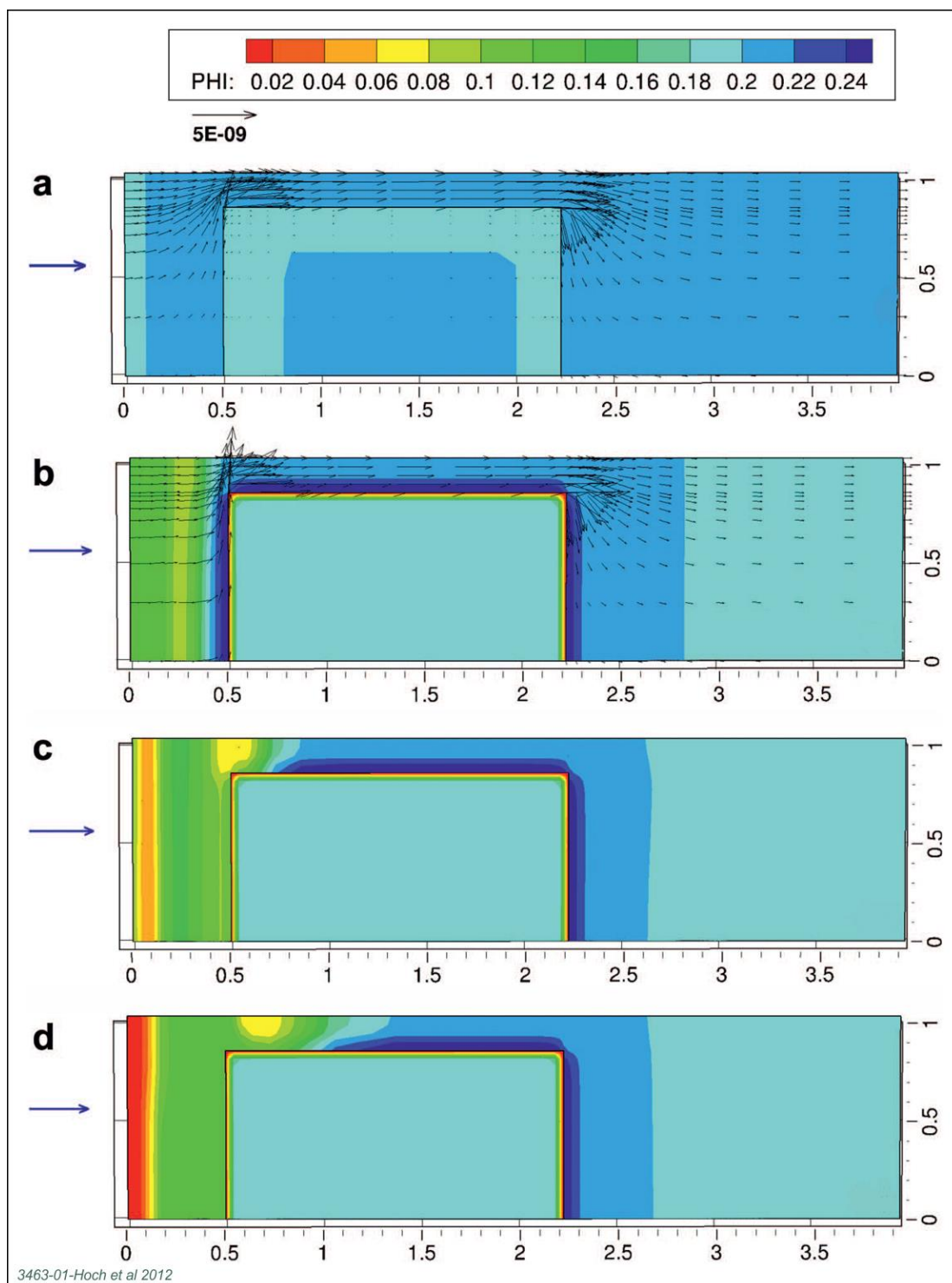
Reference [281] describes modelling that has been carried out to develop an understanding of the possible spatial and temporal evolution of a GDF vault filled with waste and cement-based backfill. In the modelling work (Figure 23) a single waste package was assumed to be filled with an encapsulation grout, placed in an underground vault and surrounded by a cementitious backfill. Groundwater was assumed to flow from the host rock into the vault and through the backfill. A simplified model was used to examine the interactions between groundwater, cementitious backfill and grout. In most cases the model predicted a reduction in the backfill porosity due to precipitation reactions, particularly at the upstream edge of the vault. The degree to which this occurs in the model depends on the assumed groundwater composition. The model also predicted that precipitation and dissolution reactions would occur in the grouts close to their interface with the backfill, reducing the local porosity significantly; this may isolate the grouts from the backfill, so that the pH within the grouts may remain largely unchanged over an extended period.

Investigations have been made into the potential significance of colloids in cementitious environments [139]. Cement-derived colloids comprise small particles composed primarily of the same minerals as those found within the cement-based barriers (for example CSH, calcium carbonate, ettringite-like and hydrotalcite-like particles) [139]. There are a few published studies of radionuclide sorption specifically onto cementitious colloids and the sorption properties of the colloids can also be inferred from the general understanding that exists of the sorption properties of the cement minerals.

Telchadder et al. [282] conducted batch experiments to assess the sorption properties of the Nirex reference vault backfill, using Eu^{3+} as a model trivalent radionuclide and EDTA as a competing ligand. The NRVB is an effective scavenger of europium from solution, with most sorbed within minutes onto the crushed material and less than 1.5% remaining in solution after one day. Ultrafiltration showed that nearly all of this remaining europium (>94%) was associated with NRVB-derived colloids or particulates that were mainly retained by a 100 kDa ultrafilter.

Bots et al. [283] applied conventional geochemical and microscopy techniques, combined with synchrotron based X-ray techniques, to characterise colloidal U(VI) colloids in a synthetic cement leachate ($\text{pH} > 13$) containing 4.2 to 252 μM U(VI). They showed that in cement leachates with 42 μM U(VI), colloids formed within hours and remained stable for several years. The colloids consisted of 1.5 to 1.8 nm nanoparticles with a proportion forming 20 to 60 nm aggregates. X-ray absorption spectroscopy (XAS) and electron microscopy indicated that the colloids had a Clarkeite (sodium-uranate) type crystallographic structure.

Figure 23. Predicted evolution of porosity (PHI) and flow in and around a ILW/LLW Vault at (a) 10 years, (b) 2,500 years, (c) 10,000 years and (d) 50,000 years, for groundwater with a 'saline' composition flowing through NRVB surrounding a 3:1 BFS/OPC grout. The blue arrow represents the direction of groundwater flow. The length of the flow vectors corresponds to the magnitude and direction of flow, with the legend showing a flow arrow corresponding to 5×10^{-9} m/s. The flow vectors at 10,000 years and at 50,000 years cannot be seen because the flow is very low [281].

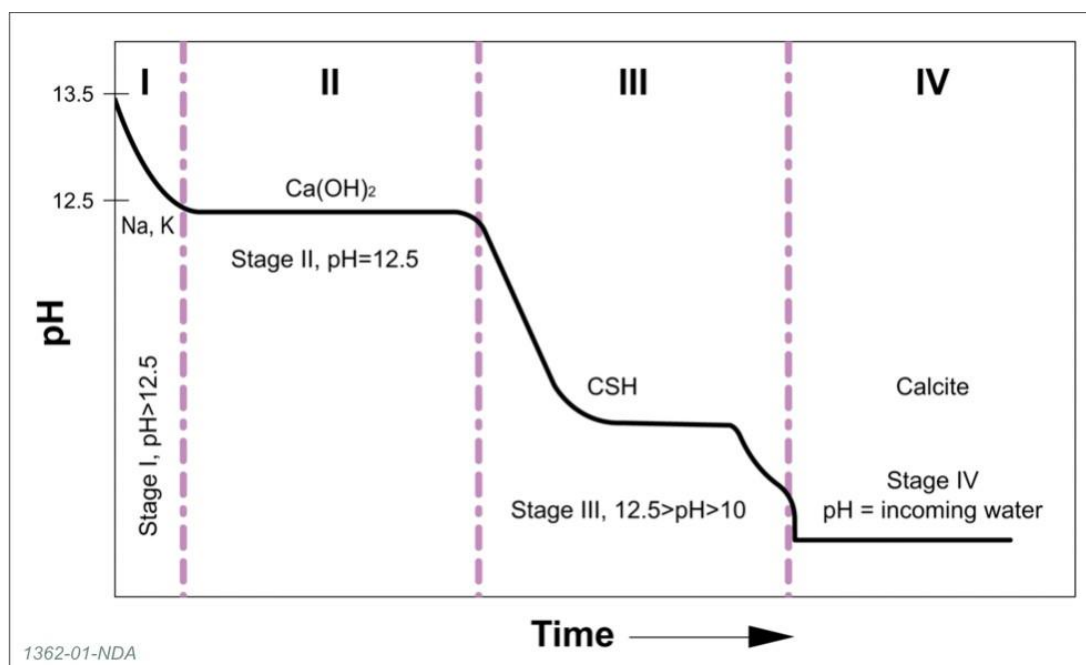


Cementitious colloids may, therefore, have some effect on the concentrations of radionuclides in EBS porewaters. However, relatively little work has been conducted to investigate the migration behaviour of colloids in cementitious barriers. Cementitious colloids are not expected to be chemically stable in the undisturbed geosphere beyond the chemically disturbed zone (see Section 4); instead, they are expected to dissolve and release any radionuclides that they had been transporting to the aqueous phase. In summary, colloid formation and colloid-enhanced radionuclide transport in cement-based materials is unlikely to be significant, but site-specific consideration of the stability of cement-derived colloids in groundwaters may be needed once candidate sites become available.

Experimental studies have demonstrated that the very small size of some pores in cementitious backfills can result in ion exclusion [284]. Around a fifth of the total pore volume of the cementitious backfill studied by Nirex may be accessible to anions such as iodide, whereas neutral and cationic aqueous species access nearly all of the total pore volume. These effects may lead to some enhancement of the transport of anionic species where there is water flow.

The chemical conditions within a cementitious backfill will evolve over time as the cement continues to hydrate and the mineralogy of the backfill evolves. Assuming there is groundwater flow through the GDF, the sodium and potassium initially present in the cements would be fairly rapidly leached away. The porewater would then be maintained at a pH of approximately pH 12.5 for as long as calcium hydroxide, Ca(OH)_2 , is present [308] (see Figure 24). If the calcium hydroxide is fully dissolved (Nirex estimated a groundwater volume several hundred times the volume of the cement backfill would be required to achieve this [285]), the pH of the porewater will be buffered to pH values greater than ~10 by reaction with CSH. If the CSH were to be dissolved then calcite may buffer the pH, depending on the chemistry of the groundwater.

Figure 24. The evolution of pH at 25°C in cement pore fluid as a result of cement degradation. After [308].



Note: The scales of pH and time are indicative and depend on many factors, such as rate of pore fluid replacement, aggressiveness of the environment and temperature. State I is controlled by soluble sodium (Na) and potassium (K) salts, State II by portlandite (Ca(OH)_2), State III by calcium silica hydrates (CSH), and State IV by calcite (CaCO_3).

The longevity of chemical conditioning by Ca(OH)_2 and CSH will depend on:

- the amounts of these phases present; which depends on the composition of cementitious materials, and details such as mineral surface areas and the kinetics of mineral dissolution [286]
- the amount and composition of water flow through the backfill
- the influence of any acidic waters generated by the degradation of organic wastes.

Over a number of years, we undertook an extensive experimental programme to measure the solubility of radionuclides under conditions that simulated the EBS of a cementitious GDF for ILW/LLW [292]. Most of these experiments were performed in the laboratory at room temperature, but a small number of studies were also carried out at higher temperatures (up to 85° C) to provide data for the early period after closure, when heat is produced by cement hydration [287]. Current estimates are that the temperature in an ILW/LLW backfill might rise to ~45°C for a period of up to a decade or so [288].

More recent work has included investigating the solubility of technetium [289] and the degree of chemical containment that cements can provide [290, 291].

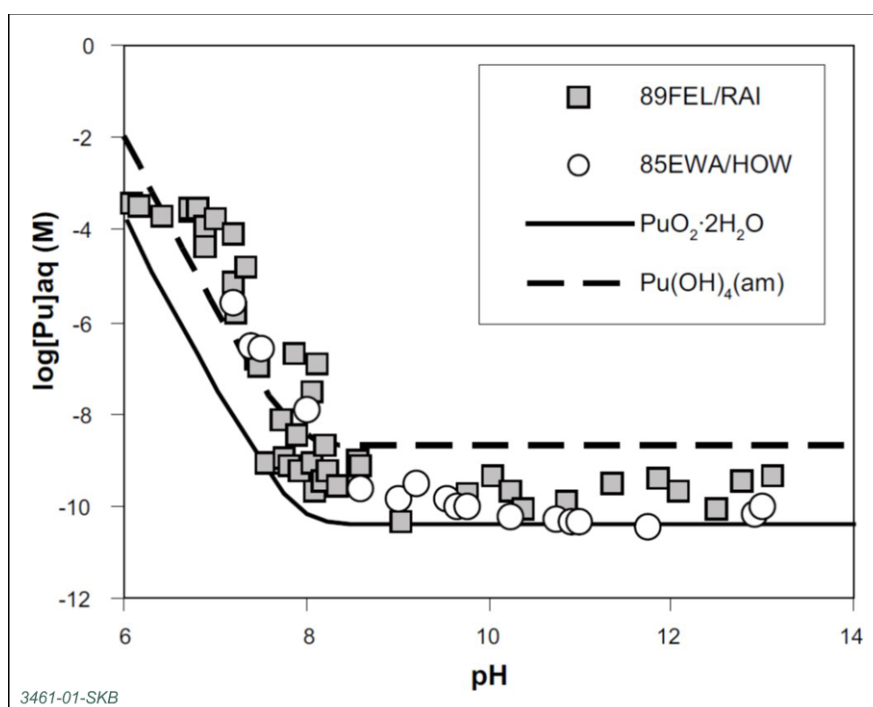
In addition to the UK studies, many overseas waste management organisations have undertaken similar experimental programmes to determine the solubility of key radionuclides under environmental conditions relevant to their geological disposal concepts. A large experimental dataset is therefore available. The data confirm that in cement systems the aqueous concentrations of some radionuclides are much lower than in near-neutral pH groundwater conditions. This is because of the high pH in cements and because carbonate is removed from the porewater by reaction with minerals in the cement. This ensures that the chemistry of the EBS is dominated by the hydroxyl ion (OH⁻), which favours the formation of metal hydroxides; many of which have low solubility at high pH [49, 292, 301]. In addition to solubility control, many radionuclides are retarded in cement-based barriers by sorption [293] and some may be effectively immobilised by co-precipitation and incorporation into the structure of minerals such as CSH [117, 307].

In order to build confidence in the understanding of radionuclide solubility and speciation, experimental results are often used to develop and test thermodynamic models of the behaviour of radioelements under EBS conditions. Thermodynamic modelling is used to help interpret experimental results and to estimate solubilities under conditions for which experimental data are not available. A combined experimental and modelling approach is used by many waste management organisations and, as a consequence, there is now a good understanding of the solubility of key radionuclides under a wide range of potentially relevant EBS conditions. For example, Nirex developed, tested and gradually refined the HATCHES thermodynamic database, which has been used to calculate radionuclide solubility [294, 295]. A similar approach has been used in Switzerland to develop the CEMDATA database, which includes thermodynamic data for many hydrated solids in cementitious materials [296], in France to develop the ThermoChimie database [33, 33] and in Germany to develop the Thereda database, which is appropriate to saline systems and evaporite host rocks [297]. After a review of potential commonalities of purpose and in view of our aspirations for future database development, we are collaborating with the French waste management organisation, ANDRA, on the further development of the ThermoChimie database. This work is targeting potentially important uncertainties, such as those which are known to exist relating to speciation at high pH [109, 298].

As an illustration of the combined experimental and modelling approach described above, the solubility of plutonium as a function of pH is shown in Figure 25 (from [51]). The experimental data shown in Figure 25 are from references [299] and [300]. The modelled solubility of plutonium is also shown in this figure, based on the thermodynamic data used as the basis for Box 2. Very similar results were obtained in reference [292]. At pH greater than 9 the modelled solubility is <10⁻⁹ M and Pu(IV) hydroxide dominates. The experimental data fall between the solubility calculated by equilibrating the water with PuO_{2(am, hyd)} and

the one obtained for $\text{Pu}(\text{OH})_{4(\text{am})}$. At pH less than 9 the modelled plutonium solubility increases significantly (by ~5 orders of magnitude at pH 7) and Pu(III) carbonate species dominate. For comparison, the pH of deep groundwaters is typically in the range pH 7 to 8. The modelled plutonium solubilities are in good agreement with the experimental data, and the figure shows how plutonium solubility decreases significantly in the cement system at pH greater than ~9. Similar successful comparisons of experimental solubility data and modelling results for americium showing a significant decrease in solubility with increase in pH are presented in [301].

Figure 25. Solubility of plutonium as a function of pH³⁰. After [51].



With regards to sorption on cementitious materials, RWM's studies have included examining evidence on the mechanisms of radionuclide uptake on cementitious materials [302] and measurements of sorption of uranium(VI), neptunium(IV), zirconium and tin on unaltered, leached and hydrothermally altered NRVB [303, 304]. Typical sorption values for uranium(VI), neptunium(IV), zirconium and tin on NRVB were all greater than 10 m³/kg.

Other work in Switzerland focussed on the mechanisms of radionuclide-cement interactions and has included advanced spectroscopic investigations of uptake processes (see for example, references [305, 306, 307]).

In 2009 a panel of experts was drawn from European radioactive waste management organisations (including RWM) and their contractors to review the available sorption data for sixteen radioelements [308]. The elements considered were chlorine, iodine, niobium, nickel, radium, strontium, caesium, thorium, uranium, plutonium, neptunium, protactinium, americium, carbon, hydrogen (tritium) and technetium. The review panel assessed many of the batch sorption data that Nirex had published in the 1990s - see, for example, reference [309], as well as data from other sources. The 2009 expert panel advised on the relative quality of different studies and, where experimental data were available, produced best-estimate, upper limit and lower limit sorption values. They also identified sorption mechanisms, and discussed areas where further work may be needed to resolve outstanding issues. The study included consideration of four stages of cement leaching

³⁰ Key: 89FEL/RAI = [253], 85EWA/HOW = [254]

(see Figure 24, [308]) and the potential effects of cellulosic degradation products on radionuclide sorption. The work has recently been published in reference [310].

The data from the 2009 compilation and some more recently reported experimental work was also considered and reviewed in reference [117]. Reference [117] provides a detailed commentary on the uptake of radionuclides on cementitious materials. The study concluded that in the GDF, cementitious materials will be influenced by geochemical processes, such as:

- carbonation due to the trapping of CO₂ arising from the degradation of organic waste materials
- the presence of dissolved metal ions, arising from metallic wastes, containers and vault construction materials
- externally induced geochemical processes, such as degradation due to interaction of inflowing saline and non-saline groundwater from the host rock.

These processes can change the mineral composition of cementitious materials and/or the composition of the pore solution, which could have an effect on radionuclide uptake.

The research identified in our S&T Plan includes:

- laboratory studies to investigate radionuclide retardation and isolation in NRVB and demonstrate chemical containment [10, task 736]
- studies to demonstrate a mechanistic understanding of the processes by which radionuclides are taken up by cement phases [10, task 737]
- studies to demonstrate a mechanistic understanding of radionuclide speciation and interaction with EBS phases [10, task 738].

Over a number of years RWM has used expert elicitation to derive PDFs of radionuclide solubilities and sorption coefficients relevant to cementitious conditions. These PDFs are intended to capture the broad range of chemical conditions that may occur in the GDF during the entire evolution of the EBS. While they do capture a wide range of chemical conditions, they do not permit explicit representation of the different stages of EBS chemical evolution illustrated in Figure 24 that may occur as a result of groundwater interactions and gradual dissolution of particular cement phases. In addition, although the basis for the PDFs was published in 2006 and 2010 [46, 235], most of the data on which the PDFs are based originates from the 1990s and early 2000s. Therefore, work to update the data input to the expert elicitation process and possibly allow explicit representation of the chemical evolution of the EBS may form the subject of future work [10, tasks 798, 800 and 801].

3.3.3 Barriers in evaporites

Engineered barriers in a GDF developed in evaporite host rocks could be formed using salt-based materials or magnesium oxide.

Transport and retardation in evaporite-based barriers

Once compacted as a result of rock creep, salt based barriers are assumed to attain very low permeabilities, such that there would be no groundwater flow - solute transport is, therefore, not expected.

Radionuclide retardation in barrier materials in evaporite host rocks would only be relevant for unlikely alternative scenarios. It is generally assumed in safety assessment studies that no radionuclide retardation occurs to salt materials.

The minerals in evaporite rocks are very soluble; therefore the persistence of these rocks over geological timescales demonstrates that there has been negligible groundwater flow in the system. Although they often contain many small fluid inclusions, evaporite rocks typically have essentially no connected porosity and, because of this, very low permeability. Thermal gradients may cause fluid inclusions to migrate towards the heat source in a GDF for heat generating wastes. The volumes of fluid involved would likely be low, but would need to be assessed for a specific site and disposal concept. Depending on the waste container material, these fluids could have some impact on waste container corrosion and gas generation. Again, such issues and whether they might affect the transport of radionuclides or other species away from the GDF would need to be assessed on a site and disposal concept specific basis.

A key characteristic of many evaporite rocks is their ability to creep; that is, to flow plastically at relatively fast rates. For example, reference [311] presents measurements of the closure of a long, 2.9 m diameter tunnel at the WIPP, which show that the tunnel diameter decreased by ~0.8 m after ~3 years. The process of creep gradually eliminates the voids created in the rocks by excavation and also tends to eliminate any pores through which water and gas might otherwise flow.

Experience has shown that it is relatively straightforward to backfill the excavated volumes around the waste packages in a GDF with crushed rock salt. Various studies (for example, in Germany) have shown that the effect of creep on crushed salt backfills or other granular mixtures of crushed rock salt and Portland cement, or crushed rock salt and magnesium oxide (MgO) would be to gradually compact the material and lead to the formation of a very low permeability barrier around the waste [312, 313, 314]. Once compacted as a result of rock creep, salt based barriers are assumed to attain very low permeabilities, such that there would be no groundwater flow - solute transport is, therefore, not expected. The compacted backfill would also support the host rock in a mechanical sense and prevent the excavations having too great an effect on the host rock. Compacted crushed salt is chemically compatible with the host rocks and would, therefore, be stable in the long-term.

Given the characteristics of evaporite host rocks, the use of crushed salt as a buffer/backfill material for High Heat Generating Waste (HHGW) in an evaporite host rock is assumed to [44]:

- contribute to protecting the container by initially isolating the container from the rock
- stabilise the structure and geometry of the engineered barriers by creeping under the influence of overburden pressure and temperature to eventually become solid with almost identical properties to the surrounding undisturbed rock
- prevent access of water from surrounding formations so long as the salt remains stable.

It may, however, also be desirable that the backfill materials have some beneficial effect on the chemistry (or the predictability of the chemistry) of the EBS. The WIPP provides an interesting example that follows such an approach.

The WIPP facility comprises a series of disposal rooms and tunnels excavated at depth in a thick sequence of evaporite (mainly halite) rocks called the Salado formation. The long-term safety of the WIPP disposal facility, relies largely on the self-sealing (creep) behaviour of the salt host rock, together with the exclusion of groundwater from the facility by a series of shaft and borehole seals. However, in addition to an 'undisturbed scenario', the 2014 WIPP Compliance Recertification Application (CRA) included a series of alternative scenarios in which a brine reaches the disposal facility.

Figure 26. Contact-handled transuranic waste within a disposal vault at the WIPP.



The engineered barrier system at WIPP includes the use of solid MgO in the EBS [315]. The MgO is placed as dry granules in bags on top of the waste containers. MgO granules, rather than powder, are used to ensure that the permeability of the material is high enough to allow any gas or brine to move through the material and to promote the establishment of homogeneous chemical conditions around the waste packages. Creep closure of the host rock is expected to rupture the bags of MgO and disperse it among the waste containers. This will, in turn, expose the MgO to the atmosphere of the disposal facility, including any CO₂ gas, water vapour and brine present.

The MgO used at WIPP has two key functions [315] that directly affect the calculation of actinide concentrations in brine:

- MgO consumes carbon dioxide gas - produced by microbial degradation of organic waste materials (and bicarbonate / carbonate in any brine that enters the system). It therefore, maintains a low carbon dioxide fugacity in the repository. The reaction also maintains a low aqueous carbonate concentration in the WIPP brine, which avoids the formation of highly soluble actinide-carbonate aqueous complexes.
- The chemical reaction of MgO with the brine buffers the EBS environment to a pH of about 9 by the precipitation of minerals such as brucite, hydromagnesite and magnesite. This chemical buffering reduces uncertainty in the actinide solubility calculations that would otherwise be present if the pH was more variable.

Colloids have been considered in developing the radionuclide source term for the WIPP. In this case the contribution of colloids to the calculated releases was shown to be less than for dissolved actinides due to a variety of factors, such as colloid destabilisation and flocculation in brines and due to the large size of many of the anticipated colloidal particles, which leads to filtration during fluid movement [230].

At the WIPP, a number of potential pathways for actinide release from the EBS have been considered and these are discussed in detail in Appendices PA-2014 and SOTERM-2014 of the 2014 WIPP CRA [315, 316]. Under conditions relevant to the EBS of the WIPP, actinides are expected to be in their lower oxidation states, which are less soluble than more oxidised forms. Neptunium and plutonium are believed to be present predominantly as Np(IV) and Pu(IV). Curium and americium would be present in the (III) oxidation state.

In the reference (undisturbed) scenario, actinide releases up the shafts or laterally through the rocks around the WIPP facility are insignificant and have no impact on regulatory compliance or safety. Human intrusion involving drilling could result in a scenario whereby water flows into the facility from overlying or underlying more permeable formations via a borehole. As the minerals in evaporite are highly soluble, any groundwater contacting the evaporite would become highly saline and form a brine. For example, measurements at WIPP show brines have salinities ranging from that of seawater to eight times that of seawater [315]; the brines at Gorleben in Germany where HLW disposal has been considered have salinities of up to nine times seawater [312] (the salinity of open seawater is ~600 mM).

In the WIPP human intrusion scenario, the brines flowing into the facility were postulated to contact the waste and dissolve some of the radionuclide inventory. The brines could then migrate via the borehole to the overlying or underlying rock formations, where radionuclides would be retarded relative to groundwater flow by processes such as sorption. In order to assess this scenario, radionuclide solubilities in brines and sorption from brines onto rocks overlying or underlying the salt have been investigated [315].

Such scenarios might also be relevant to GDFs developed in bedded halite host rocks in the UK, although this would have to be assessed on a site-specific basis. In such scenarios, it is possible that radionuclides released from the waste would be retarded in the buffer materials by processes such as sorption. However, radionuclide sorption is likely to be relatively weak because of competition for sorption sites by the high concentrations of inactive ions in the brines. Moreover, the intrinsic sorption capacity of minerals in salt barriers is low, much lower than in clay or cement barriers, for example.

Given the WIPP example and experience, the use of MgO as a buffer/backfill for Low Heat Generating Waste (LHGW) in an evaporite host rock in the UK would be assumed to [44]:

- protect the waste containers by absorbing water, which helps delay the onset of water contacting the waste packages thus reducing corrosion
- stabilise the structure and geometry of the EBS by filling voids
- limit the release of radionuclides by:
 - providing a measure of physical containment as the MgO hydrates and swells, reducing porosity and permeability of the EBS
 - buffering the pH to alkaline conditions which reduces solubility of key radionuclides
 - providing a cation exchange capability for the sorption of radionuclides
- limit over-pressurisation by absorbing CO₂(g).

4 Behaviour and transport in the geosphere

The principal functions of the geological barrier (the 'geosphere') are to isolate the waste from direct human contact and to contain the radionuclides until they have decayed to levels at which any possible future radiological impacts are acceptably low.

This section begins with a description of how a GDF may impact upon the geosphere immediately around the excavations and affect transport and retardation in this region (Sections 4.1 and 4.2). The geosphere immediately around the GDF will be disturbed by a variety of thermal, hydrogeological, mechanical, chemical and biological processes. For example, the geosphere immediately around the GDF will be disturbed as a consequence of the excavation of tunnels, caverns and boreholes and by chemical interactions between the engineered barriers (including any mechanical support / hydrogeological control measures used, such as spraycrete and rock bolts) and the surrounding rock. This status report deals mainly with chemical aspects of the disturbed zone and, in particular, with those aspects that affect the behaviour of radionuclides and other waste derived species. Other aspects of interactions between the GDF and the geosphere are mainly discussed in the Geosphere Status Report [4]. The potential changes to the groundwater flow-field resulting from such damage are also addressed in references such as [24].

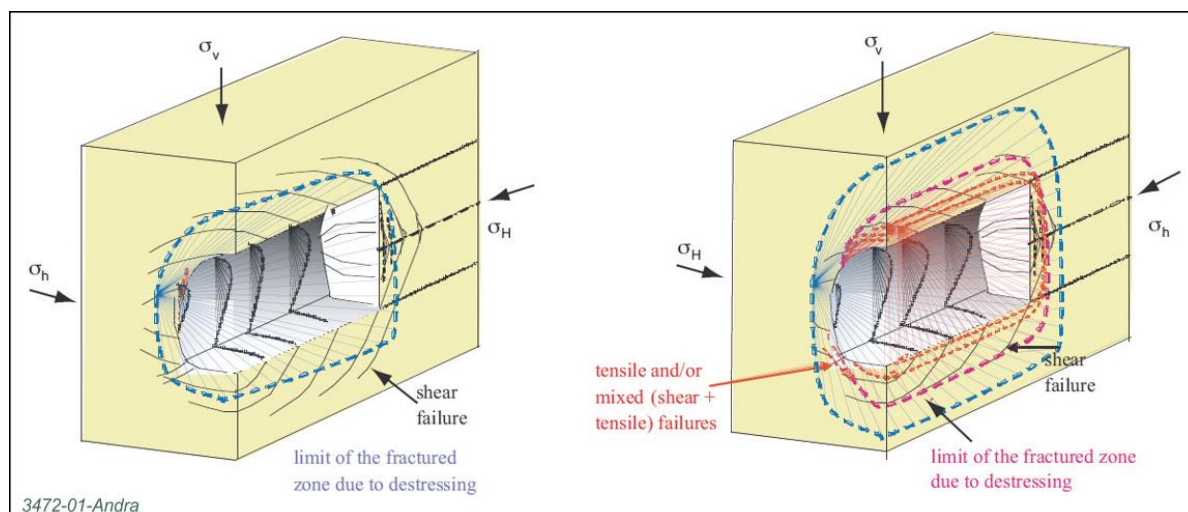
Section 4.3 discusses transport and retardation in the undisturbed geosphere. Beyond the disturbed zone close to the GDF, the potential for transport in groundwater and retardation of radionuclides and other species in the geosphere will depend on the geological environment. In some geological environments there may be no significant groundwater flow. This might be the case for a GDF constructed beneath the sea where there is no appreciable hydraulic gradient. It might also be true for a GDF developed in evaporite rocks where there is little or no connected porosity and, therefore, little or no flow. Groundwater flow may also be very limited or absent in some other rocks with low permeability (for example, some clay rocks). In such settings, the dominant transport mechanism is likely to be diffusion. In other geological environments, where there is a sufficient hydraulic gradient and the rocks have connected porosity and relatively greater permeability, advection may be the dominant transport mechanism. Where there is appreciable groundwater flow, two different cases can be distinguished. A case in which groundwater flow occurs through the pores in the matrix of the rock (simple porous flow) and a case in which the rock has discontinuities such as fractures or other zones of higher permeability (forming channels). In the latter (dual porosity) case, some or possibly all of the groundwater flow may occur in the fractures or channels and there may be relatively little or no flow through the pores in the rock matrix between the fractures or channels. It is also possible that all of these behaviours could occur in different rocks at a particular site.

4.1 The excavation disturbed zone

Excavation of the GDF may affect the conditions and properties of the host rock close to the GDF, leading to the formation of an Excavation Disturbed Zone (EDZ). Localised areas of altered permeability may develop that could affect transport. The spatial extent and properties of the EDZ will be very dependent on the host rock.

Excavation of underground disposal vaults, shafts, tunnels and boreholes for the GDF will alter the stresses and physically disturb the surrounding rocks and this, in turn, may induce mechanical and other changes in the host rocks. This zone of perturbation is called the Excavation Disturbed Zone (EDZ). Figure 27 shows an illustration of fracture patterns around drifts at the 490 m depth level of the underground rock laboratory at Bure, France [317].

Figure 27. Schematic of fracture patterns around drifts at the 490 m depth level of the underground rock laboratory at Bure, France. The figure illustrates the effect of tunnel orientation relative to the stress field [317]



EDZ formation and evolution can be complex. In the short-term the rock will respond to excavation (for example, by stress relief, fracturing and oxidation). In the longer term, after GDF closure and sealing, conditions will tend to return to the natural underground conditions, but localised areas of altered permeability may remain that may act as potential pathways for transport [318]. The significance of the fractures or other zones with modified porosity forming the EDZ will depend on their spatial extent and on the extent to which they provide connected pathways for flow and transport.

Extensive research programmes, including large-scale experiments in URLs, have shown that in some circumstances both the chemical and physical properties of the rock in the EDZ can change appreciably, but that in other cases the effects can be minor [319, 320, 321].

Experience from studies of the excavation damaged and disturbed zones in sedimentary rocks has been reviewed in reference [322], which notes the importance to post-closure performance of the conductivity and connectivity of the EDZ over tens or hundreds of metres. Reference [322] suggests that the fracture network within the EDZ may be unconnected over greater length scales, although this conclusion would need to be confirmed at any particular site. Reference [322] also notes that in the long-term, in argillaceous rocks, self-sealing processes may result in a significant reduction in EDZ permeability as compared with that measured soon after excavation, and that such processes will be particularly important in rocks with clay content greater than 40%. Again, however, this conclusion would need to be confirmed for the particular rocks and circumstances at a specific site.

4.2 The chemically disturbed zone

Chemical alterations are likely to occur at the interface between the engineered barrier systems and the surrounding rocks. In particular, the rock directly in contact with a cementitious backfill will undergo chemical changes. Processes occurring in the chemically disturbed zone may enhance or retard radionuclide transport, but it is most likely that the net effect will be beneficial to disposal system performance because of new mineral formation and fracture sealing.

4.2.1 Oxidation

During the operation of a GDF, the rocks adjacent to the excavations will be exposed to the air and some oxidation may occur. For example, iron oxyhydroxide minerals may form in place of ferrous iron minerals. Microbiological activity may play a role in sulphide mineral oxidation. Radionuclides may sorb or associate strongly with iron oxyhydroxide minerals.

During the operation of a GDF, the rocks adjacent to the excavations will be exposed to the air in the GDF. The precise consequences will depend on the extent of rock fracturing, the duration of exposure of the rock to the air, and the mineralogy of the rock surfaces, as well as on the volume and chemistry of any groundwater flowing into the excavations. Based on observations in many underground excavations, dissolution of ferrous iron minerals and precipitation of iron oxyhydroxide and carbonate minerals, such as calcite, is expected to occur. Many radionuclides sorb or associate strongly with iron oxyhydroxide minerals, and so their formation may be beneficial from the standpoint of radionuclide retardation (as discussed in Section 3.2 and [322]). Microbiological activity may also play a role in sulphide mineral oxidation, which may have implications for retardation and for the corrosion of some types of waste containers.

4.2.2 Resaturation and precipitation

After a GDF in porous or fractured rocks has been sealed, it will gradually resaturate. The chemistry of any groundwater flowing into the GDF is expected to be conditioned by interaction with the engineered barriers. If this conditioned groundwater subsequently flows out of the GDF, or if solutes diffuse out of the GDF into the surrounding rocks, further chemical reaction will likely take place because the water will not be in equilibrium with the rock. Mineralogical changes may occur in the rock including the precipitation of secondary mineral phases. The precipitation of secondary minerals, such as calcite and CSH, may effectively seal fractures around the repository and sorb radionuclides and other species.

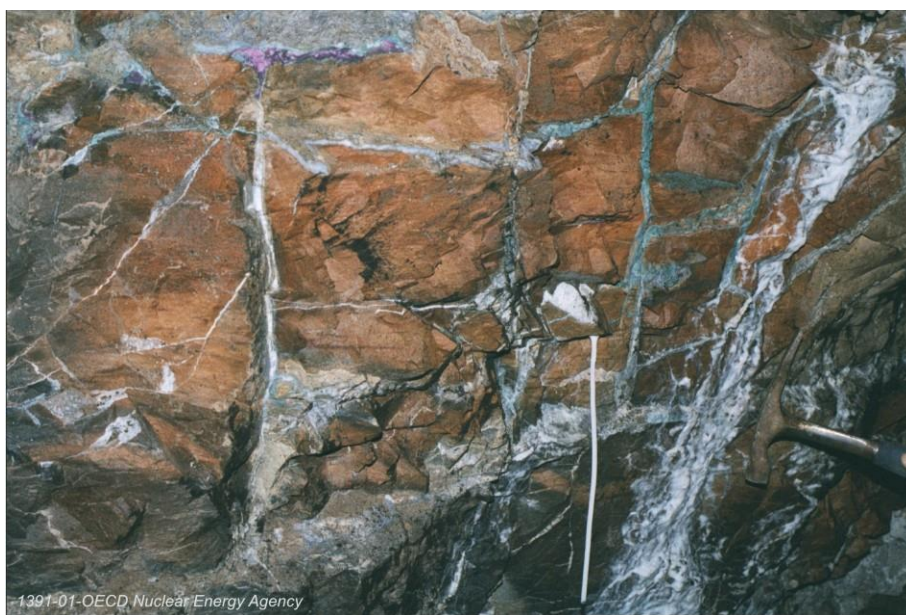
After a GDF in porous or fractured rocks has been sealed, it will gradually resaturate. During resaturation, the GDF will become part of a modified regional groundwater system and, for host rocks with appreciable connected porosity and permeability, groundwater may begin to flow towards and into the GDF. Depending on the hydraulic gradient, groundwater may flow through the GDF. The movement of groundwater toward the GDF will tend to re-establish the ambient natural, generally-reducing chemical conditions close to the GDF excavations. The chemistry of any groundwater flowing into the GDF is expected to become modified and conditioned by interaction with materials in the engineered barriers. If this conditioned groundwater subsequently flows out of the GDF, or if solutes diffuse out of the GDF into the surrounding rocks, further chemical reaction will be likely to take place because the water will no longer be in equilibrium with the rock.

The magnitude of the chemical reactions between the EBS and the geosphere is expected to be greatest for those disposal concepts where the chemical environment in the EBS is most different from that of the surrounding geosphere. Hence, the greatest chemical disturbance is expected to occur around a GDF containing large amounts of cement-based materials. Less chemical disturbance is expected around a GDF containing bentonite-based buffer/backfill materials because these materials contain clay minerals similar to those found in many rocks. Little or no chemical disturbance would occur around a GDF constructed in evaporite rocks if crushed rock salt is used as the backfill.

Chemical disturbance may perturb the geosphere in a number of ways; the most important involve mineralogical changes in the rock and the precipitation of secondary mineral phases - especially during interactions between the rocks and hyperalkaline waters derived from early leachate from cementitious materials.

The precipitation of secondary minerals, such as calcite, may effectively seal fractures around the repository [323]. The volume of rock affected will depend on the nature of the chemical disturbance and its spatial extent. The reactivation of fractures as a result of later rock movements could however cause some of them to re-open and then exist in a state with surfaces coated, or armoured, with fracture-filling minerals such as calcite. Some rock fractures show signs of having experienced multiple cycles of fluid flow, fracture sealing, and reactivation.

Figure 28. Photograph of fractures sealed by calcite due to the passage of high pH fluids through a fractured zone at Maqarin in Jordan. After [323].



The largest chemical gradients are expected to occur in the rocks surrounding the backfilled tunnels and vaults of the ILW/LLW. In this region, high pH groundwater flowing or diffusing from the EBS will react with the surrounding rocks. In the absence of flow, diffusion will tend to reduce the chemical gradients and will have a similar, although possibly less extensive, effect. For example, two-dimensional reactive-transport modelling [324] for a hypothetical body of cement surrounded by a groundwater-saturated clay rock showed that precipitation reactions (due to the diffusion of solutes) blocked porosity at the interface between the cement and the host rock, even where there was no chemical transport by advection.

The effects of flow and/or diffusion are expected to result in some initial dissolution of the rocks, followed by the precipitation of new minerals such as CSH phases, carbonates and oxides. Chemical changes resulting in precipitation may have a beneficial effect on retardation, but colloid formation could also occur and this might have the opposite effect. The pH of the waters flowing from the cement-based materials into the geosphere will be gradually lowered as a result of these reactions, and the chemical composition of the water will change correspondingly.

Although there may be a long period (tens or hundreds of thousands of years) during which alkaline porewaters will be produced in the EBS of a GDF containing cement-based materials, the formation of a chemically disturbed zone (CDZ) in the surrounding geosphere with decreased permeability due to mineral precipitation may lead to a gradual reduction in any flow of water through the disposal vaults and into the geosphere [281].

In order to understand how the CDZ might develop, Nirex carried out laboratory studies to react a range of rock-forming minerals with high-pH groundwaters [325]. The nature of the newly formed minerals and the rate at which the original minerals dissolved in the high-pH

water had been previously characterised. The work showed precipitation of secondary CSH on albite after four months exposure to high pH solutions at 70°C. The experiments were supported by geochemical modelling to aid interpretation and to investigate the possible long-term mineralogical evolution and extent of the CDZ.

As illustrated in Figure 28, additional understanding of the CDZ has been obtained through an international collaborative natural analogue study of a site in north-west Jordan. The Maqarin site [326] is underlain by organic-rich marls that have spontaneously combusted in the past to produce marbles containing calcite, lime (a key ingredient in the production of cement) and a range of other calcium-bearing minerals. Subsequently, groundwater has flowed through the marbles and has hydrated the minerals in them to produce a rock that can be considered as an analogue of the cementitious materials in a GDF. As a result of this process the present day groundwater at the site has been buffered to a high pH and, when it flows out into the surrounding undisturbed rocks, it has reacted with them to form a chemically disturbed zone; a natural analogue of the CDZ that would form around a cementitious GDF. A mechanism whereby minor earth movements cause periodic reactivation of fractures and breakthrough of the armoured reaction zone (allowing groundwater fresh access to the cementitious materials) has been used to explain the observed periodic reactivation of fractures that otherwise appear completely closed by reaction products of the hyperalkaline groundwater system at Maqarin [327].

Reference [57] describes a recent study of the behaviour of lead in and around a GDF. A set of generic solubility calculations has shown that several solid phases involving three different common anions (silicate, sulphide and carbonate) that could control lead concentrations across the pH gradient in the CDZ between the EBS and the undisturbed geosphere. If sulphide is present, lead concentrations much less than 10 ppb are expected, whilst carbonate and silicate could control lead concentrations to 100 ppb and chloride to 240 ppb. Reference [57] concludes that it is unlikely that high concentrations of lead would be able to cross the CDZ.

4.2.3 Retardation

The transport of radionuclides and other species in the CDZ may be retarded by several processes, including sorption and co-precipitation in newly forming minerals.

The transport of radionuclides and other species in the CDZ may be retarded by several processes, including sorption and co-precipitation in newly forming minerals.

Our understanding of radionuclide behaviour in the CDZ is largely derived from sorption experiments. For example, Nirex undertook two types of batch sorption experiment [328]. In the first type of experiments, the radionuclide and high pH groundwater were added simultaneously to unreacted rock samples. This was designed to simulate the unlikely situation where migration of radionuclides from the EBS occurs at the same time as development of the CDZ. In the second type of experiments, sorption was measured on crushed rock samples that had previously been reacted with high-pH groundwater to produce secondary minerals. This simulated the situation where radionuclides migrate into the rock around a GDF after the CDZ has developed; this is the most likely way in which the GDF will evolve - due to the initial containment of the wastes within packages.

As described above, some of the principal mineral phases that may form in a CDZ close to a cementitious GDF for ILW/LLW are typical cement phases, such as CSH and calcite. Section 3.3.2 identified a number of sources of data on the sorption of radionuclides to cementitious materials at different stages of evolution/degradation (for example, reference [310]); some of those data for the later stages of cement degradation may be applicable to the CDZ.

In addition to the examples described in the preceding paragraphs, RWM has been involved in an advisory capacity on Research Council funded projects such as BIGRAD

(Biogeochemical Gradients and Radionuclide Transport) [329]. BIGRAD had two overarching objectives:

- to gain a mechanistic understanding of biogeochemical processes and their controls on radionuclide behaviour in the chemically disturbed zone around the GDF
- to develop a predictive modelling capability, firmly rooted in scientific advances and experimental results, to quantify radionuclide mobility in the chemically disturbed zone.

The research identified in our S&T Plan includes a desk study to review and synthesise the knowledge obtained by the NERC-funded BIGRAD project [10, task 760].

In summary, processes occurring in the chemically disturbed zone may enhance or retard radionuclide transport, but it is most likely that the net effect will be beneficial to disposal system performance because of new mineral formation and fracture sealing. These processes may reduce groundwater fluxes and provide radionuclide retardation in the CDZ. However, the formation of a CDZ and its effects at a particular GDF site will depend on the details of the EBS materials used, the properties of the rocks and the site's hydrogeochemistry [325].

4.3 The undisturbed geosphere

The pattern of groundwater flow at a site is determined by the forces driving the flow (such as hydraulic head gradients), the properties of the rocks (primarily permeabilities and porosities), and the properties of the groundwater (density and viscosity). Sorption, co-precipitation, precipitation and rock-matrix diffusion may retard transport in groundwater. Other processes, such as colloidal transport and complexation by organic matter, may enhance transport under certain circumstances.

The pattern of groundwater flow at a site is determined by the forces driving the flow (such as hydraulic head gradients), the properties of the rocks which determine the resistance to groundwater flow and which may vary from rock to rock and within an individual rock type (primarily permeabilities and porosities), and the properties of the groundwater (density and viscosity, which in turn depend on temperature and salinity). When considering the transport of radionuclides and other species it is important to consider the characteristics of the groundwater flow paths at a micro-scale, smaller than that necessary for representing the overall pattern of flow at the site.

Some rocks, such as halite formations, have very little connected porosity and very low permeabilities, such that there would be no groundwater flow. In many rocks, such as some sandstone formations, groundwater flow in response to the presence of a hydraulic gradient is predominantly through narrow pores in the rock-matrix (the matrix porosity), which may be connected over large volumes of the rock. This is termed porous flow. In other rocks, such as many granites, where there is a significant hydraulic gradient, groundwater moves mainly through networks of fractures or other discrete geological features, for example, at the zone of contact between different rock units. This is often termed fracture flow. In reality there are many intermediates between these three cases. In some 'dual porosity', fractured rocks, flow may occur both in the fractures and the rock matrix. An example is that some flow may occur in discrete fracture zones and/or channels in sedimentary rocks such as clays, limestones and sandstones that otherwise exhibit porous flow.

The Geosphere Status Report [4] identifies and discusses the broad hydrological properties of the various rock types present in England, Wales and Northern Ireland. The rock types considered are evaporites, clays (clays and mudstones), 'metamudstones' (shales and slates), sandstones, low-grade metasandstones, limestones (including chalk), extrusive igneous rocks, intrusive igneous rocks, and medium- to high-grade metamorphic rocks. Of

these, [4] identifies evaporites and mudrocks as being diffusive settings, sandstones and low-grade metasandstones as being porous settings, and the rest as being dual porosity rocks with fracture flow.

4.3.1 Transport in dual porosity rocks with fracture flow

Groundwater flow in dual porosity rocks may lead to the transport of dissolved and colloidal radionuclides and non-radiological species by advection and diffusion. Transport may occur primarily by advection in fractures. Some transport may also occur by advection and diffusion in the rock matrix. Rock matrix diffusion may retard transport of some species.

Dual porosity, fractured rocks are being investigated and developed as potential host rocks for GDFs in several countries, including Finland and Sweden.

At depths of more than a few hundred metres, many rock fractures are closed and do not allow active groundwater flow. Nevertheless, where there is a significant hydraulic gradient radionuclides and other dissolved or colloidal species may be transported through dual porosity rocks, principally by advection through the proportion of fractures or other discontinuities (eg. channels) in the rock that have active flow. Transport in the rock matrix between the fractures or other discontinuities may also occur by advection and diffusion, but is likely to be less significant, particularly if the matrix has relatively low permeability. This situation has been demonstrated for some granitic rocks through *in-situ* experiments, such as those undertaken at the Aspö underground rock laboratory in Sweden [330].

The hydrogeological properties of fracture networks are likely to be scale-dependent and, as a consequence, this introduces uncertainty into models of groundwater flow. The difficulty of characterising groundwater flow in fractured rocks is well-recognised. In particular, upscaling of groundwater flow properties can be problematic and relies on a good understanding of the length-dependence and connectivity of the different types of fractures and other discontinuities in the rock. Significant effort has been spent in characterising and modelling fracture networks in such rocks at different length scales. For example, see references [331, 332].

Although fractured media may include fast flow and transport pathways, resulting in short residence times for some species, they also promote mixing and dilution due to strong heterogeneity. Enhanced mixing and dilution can have two effects. Firstly, peak radionuclide (or non-radiological contaminant) concentrations may be attenuated and, secondly, mixing-induced precipitation reactions may lead to radionuclide immobilisation [333].

Radionuclides and other species in groundwater may move from fractures or other zones of relatively high permeability into the surrounding rock matrix by diffusion and/or advection in microfractures. These processes have the potential to retard and delay the transport of radionuclides and other species from the GDF. The scale over which these processes operate and the significance of the processes are uncertain and will depend on a range of site-specific factors.

Investigations of the potential for all of these processes at a specific site will need to be made using a range of techniques; due attention will need to be given to the potential for artefacts in laboratory-scale experiments and to the effects of spatial heterogeneity and measurement scale.

4.3.2 Transport in rocks with porous flow

Groundwater flow in un-fractured porous rocks may lead to the transport of dissolved and colloidal radionuclides and non-radiological species by advection and diffusion. The pores in some of these rocks may be too small to allow colloidal transport.

Although at some scales most rocks have fractures, faults or other discontinuities, there are some in which flow and advection occurs, or can be represented reasonably as occurring, principally through the pores of the rock over appreciable distances. For example, many types of sandstone are porous and permeable and act as aquifers.

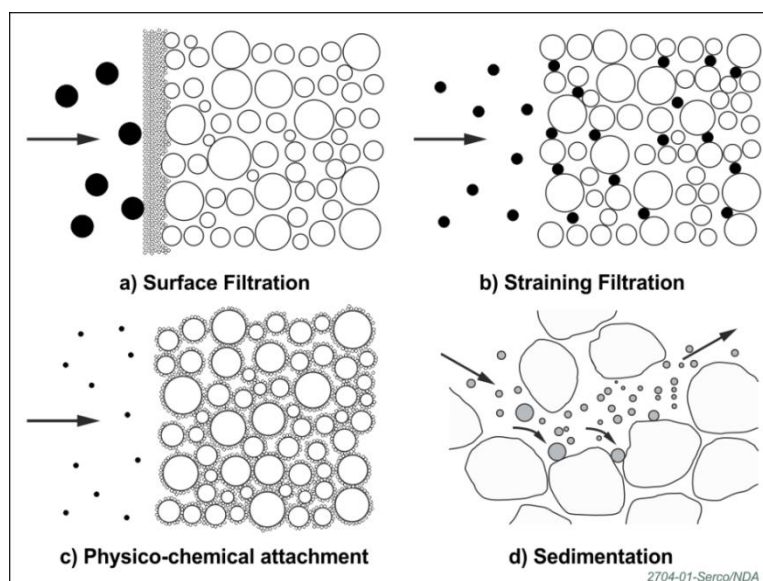
Although the more permeable examples of such rocks may not be suitable for use as a host rock for the GDF [4], they may occur in the rock sequence at or near the GDF site, for example in a sequence of sedimentary rocks overlying crystalline basement or other suitable host rock. There is considerable knowledge, understanding and experience of characterising and modelling flow and transport in such porous rocks, including much experience from outside the radioactive waste disposal industry [171, 334].

Colloids and complexation by naturally occurring organic matter have the potential to enhance transport in some circumstances, but the pores in some rocks may be too small to allow colloidal transport (Figure 29, see also Section 4.3.5).

Transport may be retarded by radioactive decay and, depending on various factors including mineralogy and groundwater chemistry, by sorption. Minor mineral phases in the rocks (such as iron oxide or carbonate cements in sandstones) may dominate sorption behaviour. Again, depending on various factors, including mineralogy and groundwater chemistry, some species may be retarded by processes such as isotopic exchange and mineral (co)precipitation (see Section 4.3.6).

Characterisation of the rocks at a specific site for the GDF will need to be undertaken to understand the potential for flow and transport and their significance to the safety of waste disposal.

Figure 29. Mechanisms of colloid capture by the rock in a porous medium (note the particle size dependence and the differences in deposit morphologies). After [140].



4.3.3 Transport in diffusive settings

In the absence of a significant hydraulic gradient and/or in rocks with very low permeabilities or connected porosities, transport may occur primarily by diffusion. The pores in these rocks may not be connected and/or may be too small to allow colloidal transport. Diffusion rates in clay rocks may be affected by electrostatic effects.

In some potential GDF host rocks (such as halite), radionuclides and other species would only be transported in groundwater following the occurrence of an event that has caused unexpected groundwater movement in these systems (such as human intrusion). The potential for a groundwater pathway to develop following an unlikely event such as human intrusion would be assessed at the site-specific stage should an evaporite host rock be selected.

In the absence of a significant hydraulic gradient and/or in rocks with very low permeabilities or connected porosities, transport may occur primarily by diffusion [29, 335]. Where diffusion dominates, the rates of solute and colloid migration will be much lower than in rocks with significant groundwater flow.

Many clay rocks contain very small pores, have very low permeabilities and could provide a diffusive setting for the GDF. Some evaporite rocks have very low connected porosity and may also provide a diffusive setting for the GDF.

Clays

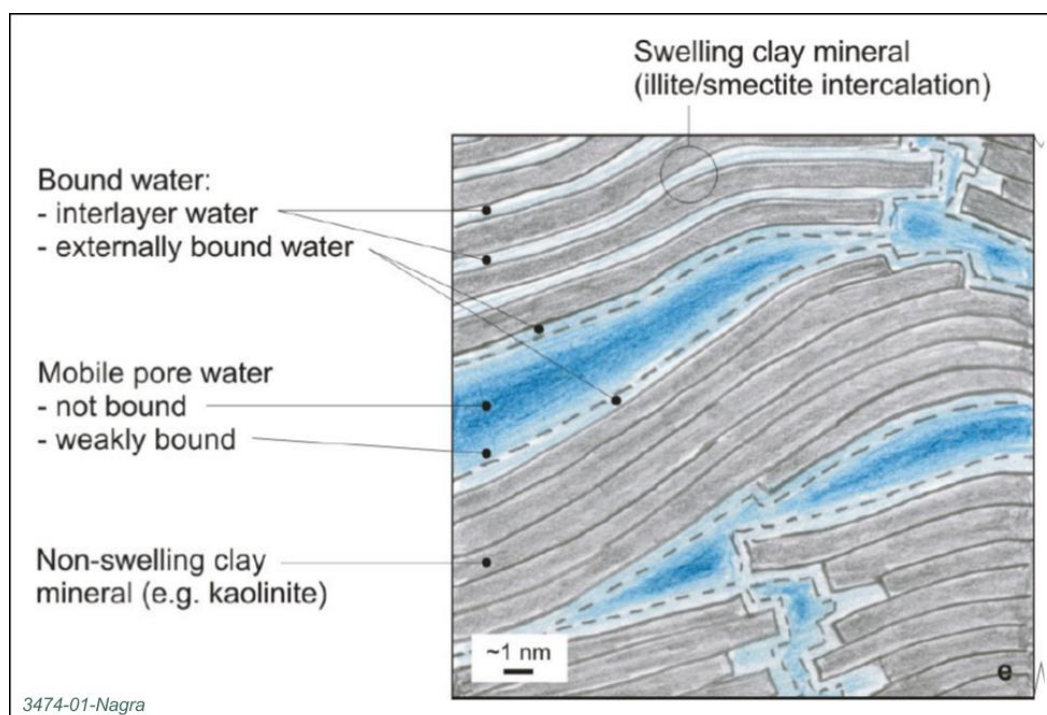
Clay rocks are being investigated as potential host rocks for GDFs in several countries, including Belgium, France and Switzerland. In Belgium, a poorly-indurated, plastic clay, the Boom Clay, is being researched as a potential host rock for a GDF [336]. In France and Switzerland, indurated, mechanically-stronger mudstones (the French Callovo-Oxfordian Clay [16]) and siltstones/claystones (the Swiss Opalinus Clay [337]) are being considered.

There is an extensive literature on diffusion in clays (see, for example, references [29, 335, 338]). In clay rocks transport may occur in the water-filled pore spaces; typically, different types of pores can be distinguished. In general, the pore space in clay rocks can be subdivided into the interlayer pore space and the inter-particle pore space. Depending on the density of the clay and the solution conditions, the latter can be further sub-divided into the pore space influenced by the diffuse layer extending from the charged pore wall (diffuse-layer pore space) and the free-pore space. Figure 30 illustrates the different types of pores (or types of water) present in the Opalinus Clay.

Because clay minerals have permanent electrostatic charge, the water in the pore spaces and any solutes may be affected by electrostatic effects. The diffusion accessible porosity for neutral species and cations equals the total porosity of the medium. Cations, such as $\text{Cs}^+_{(\text{aq})}$, may diffuse at relatively higher rates than neutral species because of surface diffusion in the diffuse layer. In the case of anionic species, however, only part of the pore space is available due to anion exclusion: the negatively charged anions are repulsed by the permanent negative charges present on the surface of clay particles. For some highly compacted clays, anions may be virtually excluded [338].

Transport in a diffusion-dominated system can be quantified using the relevant diffusion coefficient, as described in Section 3.3.1. Reference [338] describes a procedure for estimating the effective diffusion coefficients for clay rocks, based on an extended version of Archie's Law [339]. Diffusion is faster at higher temperatures and may also be strongly affected by anisotropy.

Figure 30. Conceptual model of the different types of pores and waters present in Opalinus Clay. The figure distinguishes between bound water in the interlayer pore space or close to the external surface of the clay minerals, and mobile pore water in the inter-particle pores, that may either be in the free pore space or in the diffuse layer. After [337].



Characterisation of the rocks at a specific site for the GDF will need to be undertaken to understand the potential for flow and transport and their significance to the safety of waste disposal. For example, if a site with a clay host rock was to be considered, it would need to be shown that the potential for groundwater flow through any faults or other discontinuities was not a concern and that, therefore, transport could be represented using a suitable diffusion model.

Evaporites

Evaporite rocks have been investigated as potential host rocks for GDFs in several countries, including Germany, the Netherlands and the U.S.A.

Potentially suitable evaporites include those comprised principally of rock-salt (halite, $\text{NaCl}_{(s)}$) because excavations in these rocks can provide a disposal environment, with little possibility of fluid flow. Other evaporite rocks comprising potash (sylvite, $\text{KCl}_{(s)}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}_{(s)}$) or anhydrite ($\text{CaSO}_4_{(s)}$) are not considered to be suitable host rocks for a GDF [4] because they can maintain open fractures through which fluid movement is possible over extended periods of time, bringing with it the threat of rock dissolution.

As evaporites are comprised mainly of soluble minerals, the existence of such rocks over geological time implies that the rocks have come into contact with relatively small quantities of groundwater in which its minerals could dissolve. For example, the Gorleben salt dome in Germany formed around 250 million years ago. The host rock at the WIPP in the U.S.A. (the thickly bedded halites of the Salado formation) also formed in the late Permian period ~250 million years ago.

In contrast to most other rocks, potentially suitable evaporites do not contain mobile groundwater - solute transport is, therefore, not expected³¹. For this reason, less research has been undertaken to study radionuclide transport through evaporites than for other rock types. Nevertheless, any evaporite formations considered as potential host rocks for the GDF would need careful investigation in order to develop a good understanding of the existence of porewaters (in the host rock and neighbouring horizons) and isolated pockets of water or brine, so that the possibility for any flow and transport can be understood and assessed. The potential for a groundwater pathway to develop following an unlikely event such as human intrusion would be assessed at the site-specific stage should an evaporite host rock be selected.

4.3.4 Organic complexation in the geosphere

In the geosphere, the transport of radionuclides and non-radiological species may be influenced by complexation with natural organic matter (NOM). The importance of NOM will be strongly dependent of the characteristics of the site and may enhance or reduce the mobility of radionuclides and inorganic non-radiological species. For these reasons, the characterisation of the NOM at a potential GDF site and the assessment of its potential effects will form an important part of a site-specific research programme.

As discussed in Section 2.3, organic complexation has the potential to enhance the transport of radionuclides and non-radiological species under some circumstances. Radionuclide behaviour only appears to be affected significantly by CDP at concentrations in excess of 10^{-4} M [340, 341]. These concentrations are greater than those expected in the geosphere owing to the effects of dilution, dispersion and degradation along the groundwater pathway. However, other types of organic complexants in the geosphere need to be considered.

Natural organic matter (NOM), such as humic and fulvic substances resulting from the decomposition of plant matter, and other natural chelating agents and siderophores³² have the potential to influence the behaviour of metals and radionuclides [342, 343, 344; 345].

Humic and fulvic acids comprise a range of organic molecules with sizes that extend up to masses on the order of a few hundred thousand Da. For example, fulvic acid type organics have been identified in crystalline environments and plastic Clay formations (Boom Clay) with molecular sizes up to ~300,000 Da [351].

The larger molecules may form colloidal species in groundwater, but the smaller molecules are soluble to some extent, depending on the water composition and prevailing conditions. Fulvic acids are, on average, smaller molecules than humic acids. They tend to be relatively more oxidised and are soluble over a wide range of water chemistries and conditions. Humic and fulvic acids contain a range of functional groups (for example, carboxylic and phenolic) that may interact with and bind radionuclides and metals. The smaller of these molecules can be susceptible to microbial degradation.

Concentrations of natural organic colloids (predominantly humic materials) are significant in some deep groundwater systems, particularly if there is a deep source of fossil organic material, such as the brown coal sands found at Gorleben in Germany [140].

At the Gorleben site, over 70% of uranium and 99% of total thorium in the groundwater is associated with colloidal NOM. The isotopic 'signatures' of uranium and thorium in the

³¹ Fluid inclusions may move towards the GDF as a result of thermal gradients near heat-generating wastes, but these fluids would be small in volume. Although these fluids might have some effect in causing waste container corrosion, they would not provide a mechanism for the subsequent transport of radionuclides or other species away from the GDF.

³² Siderophores are small, high-affinity iron chelating compounds secreted by microorganisms such as bacteria, fungi and grasses.

colloid fraction and in ultrafiltered groundwater are different, which suggests that the association of radionuclides with the NOM could be controlled by relatively slow kinetics relative to the rate of transport occurring at the site. Reference [135] concluded that studies in natural aquifer systems (including the Gorleben system) on the origin, stability and mobility of humic colloids show no indication for humic colloid retention or decomposition and suggested that this leads to a situation where humic colloids need to be treated as stable, non-retarded species. They did however note two exceptions to this conclusion relating, (i) to the retention of humic and fulvic acids in brines, and (ii) to the ultrafiltration of colloids in low permeability natural compacted clays where the transport of colloids is strongly hindered. Reference [346] provides more information on the importance of kinetics in colloid enhanced radionuclide transport.

NOM may be mobile in surface waters and in some groundwater systems (for example, in some advective systems in fractured rocks and in permeable horizons in sedimentary rocks) and they may be transported over significant distances. In other rock types, such as low permeability clays (such as the Boom clay), research suggests that the NOM present may be relatively less mobile and that the effect of NOM in enhancing radionuclide transport depends on the kinetic release (de-complexation) of radionuclides from the NOM [347, 348, 349].

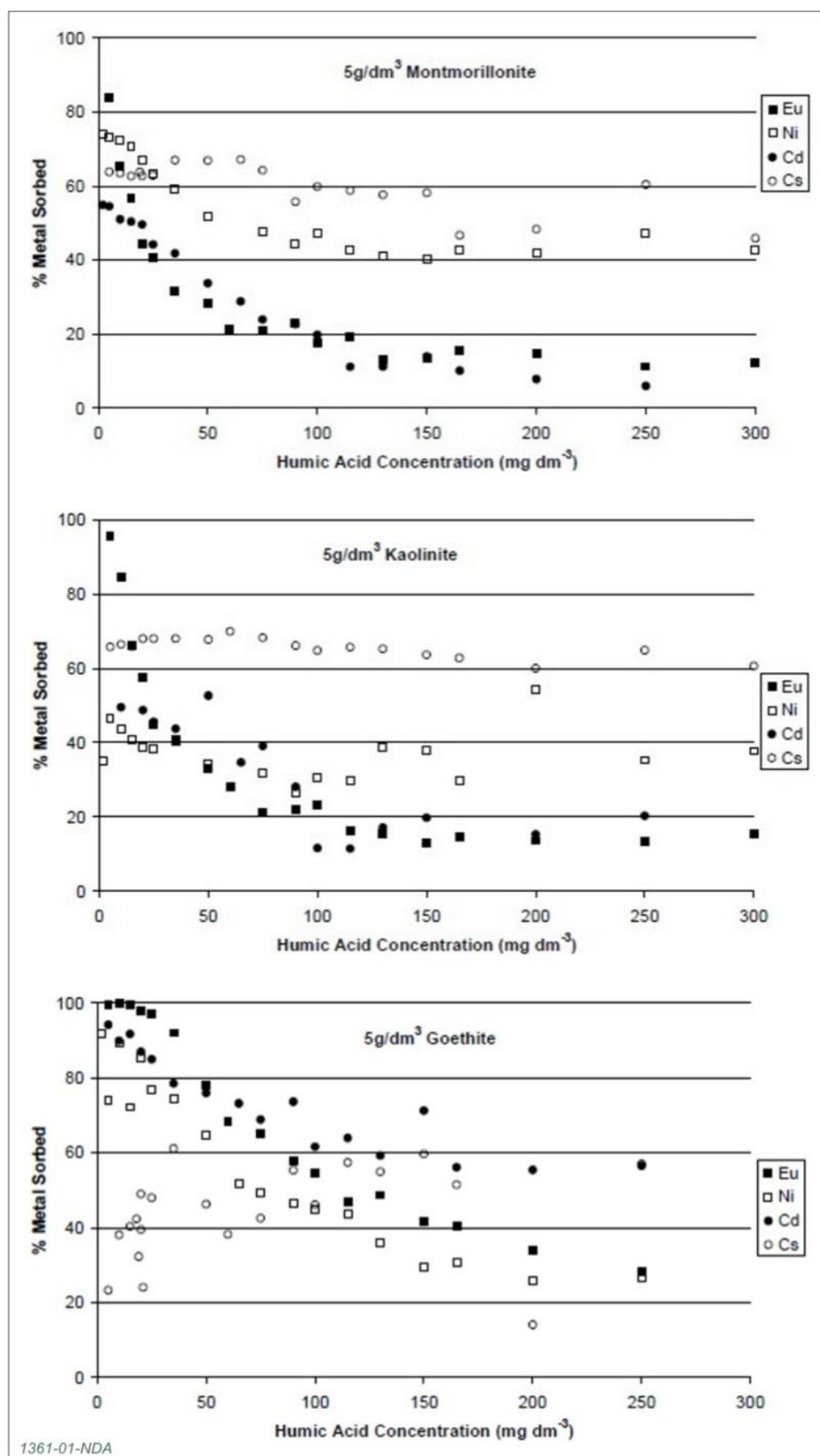
The EC-funded FUNMIG project [29, 351] included significant research on this topic. Experimental projects within FUNMIG confirmed that radionuclide sorption on mineral surfaces decreases in the presence of humic acids. For example, Figure 31 shows how the sorption of europium, nickel, cadmium and caesium on a range of commonly-occurring minerals decreases with increasing humic acid concentrations [25]. Similar results (reported in [26]) were obtained from a study of europium(III) sorption on illite in the presence of NOM representative of that in Boom Clay. In these latter experiments, the sorption of europium decreased by an order of magnitude in the presence of the dissolved organic matter. A range of modelling approaches has been developed to account for the interactions between NOM, mineral surfaces and radionuclides. Work has also studied the binding of U(VI) to humic acid at pH values of ~10 to 13 to determine the expected behaviour within the chemically disturbed zone around a cementitious ILW/LLW disposal area [350]. This work showed that humic acid can bind UO_2^{2+} ions over this pH range, including in the presence of competing ions (Ca^{2+} or Cu^{2+}).

As with organic degradation products in the EBS, there are a number of open questions concerning the overall significance of NOM. The reactive groups on NOM, which can complex with metal and radionuclide ions in solution, are also electrostatically attracted to mineral surfaces and so the NOM or the NOM-complexed radionuclides or metals may sorb onto mineral surfaces. Further, because the size of NOM extends into the colloidal size range they can also be subject to filtration effects. Therefore, depending on the relative strengths and kinetics of the interactions with the NOM and the solid phase, NOM may enhance or reduce the mobility of radionuclides and inorganic non-radiological species. For these reasons, the research identified in our S&T Plan includes:

- work to develop numerical coupled process models of tracer and colloid transport to investigate whether NOM may lead to increases actinide mobility in fractured rocks [10, task 756]
- a small experimental programme to investigate whether colloids, organic complexants and microbes may have cumulative effects on radionuclide behaviour [10, task 766].

The characterization of the NOM at a potential GDF site and the assessment of its potential effects will form an important part of a site-specific disposal programme.

Figure 31. Sorption of europium(III), nickel, cadmium and caesium in the presence of varying concentrations of humic acid. After [25].



4.3.5 Colloids in the geosphere

The presence of colloids that comprise, contain or sorb radionuclides or other species of interest can increase the amounts that may be transported in groundwater. The potential importance of colloid-mediated transport will be strongly influenced by the rocks and flow paths that exist at a site. Colloids are often unstable in high ionic-strength waters, and measured populations in such systems are consequently low. Observations of the association of natural radionuclides and other species with colloids in a range of groundwater systems suggests that organic colloids may be more significant than inorganic colloids in facilitating transport in deep groundwaters, but this will depend on site-specific factors and is an area of continuing research.

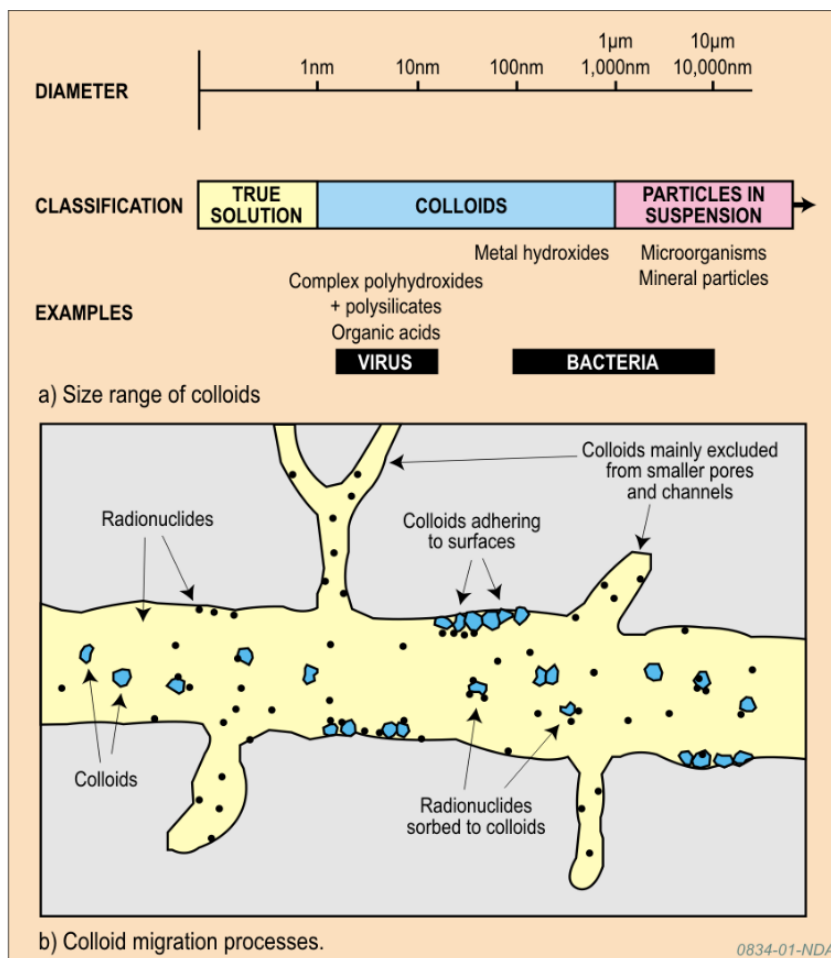
As noted above, the presence of colloids that comprise, contain or sorb radionuclides or other species of interest can increase the amounts that may be transported in groundwater. The potential importance of colloid-mediated transport will be strongly influenced by the rocks and flow paths that exist at the site. Colloids may be advected with groundwater flow through flowing porosity. In some systems (for instance, where water flow occurs in fractures) colloids have the potential to be advected at slightly faster rates than the average velocity of the water.

Inorganic colloids typically comprise mineral fragments derived from local rock surfaces. A wide range of colloid concentrations has been measured [140]. According to reference [351] the inorganic colloid concentration in deep groundwaters of advection dominated systems rarely exceeds 1 mg/l and is expected to be in the ng/l range in diffusion controlled systems. Organic colloid concentrations of up to tens of milligrams have been found in diffusion-controlled indurated clays. The range of observed groundwater colloid concentrations in part reflects the range of groundwater salinities present in the systems studied, which varies from low ionic strength to brines. Colloids are often unstable in high ionic strength waters, and measured populations in such systems are consequently low.

Colloid-mediated radionuclide transport has been demonstrated in a number of shallow groundwater systems (see, for example, the summary in reference [140]). In deep systems, however, groundwater salinities and residence times are often higher than in shallow systems, and these factors tend to reduce the potential importance of colloid-mediated transport of radionuclides.

Figure 32 illustrates various processes that may influence the stability and mobility of inorganic and organic colloids and associated radionuclides in fractured rocks. The potential significance of colloidal transport is increased if the colloids are stable and the radionuclides or other species of interest are bound to the colloids (or otherwise associated with the colloids) in a partly or fully irreversible way.

To date there is only questionable evidence for the transport of radionuclides with inorganic colloids over distances of more than a few tens of metres in deep groundwater systems. Examples from US and Russian nuclear test sites have been reported in which low solubility radioelements have been found associated with colloidal fractions in groundwaters. For example, plutonium migration over a distance of kilometres has been reported from nuclear test areas at the Nevada Test Site [352], and colloid-facilitated transport has been proposed as the explanation. However, this is a disrupted site where there is significant uncertainty about the nature of the transport processes and alternative explanations have been proposed involving explosive injection during the nuclear tests. Although these examples show the possible importance of colloids, they may not be the sole explanation for radionuclide migration at these sites.

Figure 32. Colloid behaviour and radionuclide transport in fractured rocks.

Similarly, natural analogue studies of uranium and thorium transport from deep ore bodies have to date not found evidence of significant long-range transport of radioelements in inorganic colloidal form. For example, studies of the uranium ore body at Cigar Lake, Canada, indicated that although significant colloidal uranium was present in some groundwaters close to the ore zone, groundwaters in the surrounding rocks were found to contain mainly dissolved uranium, suggesting that the clay alteration zone that surrounds the ore body was an effective barrier to colloid migration [139, 140]. Despite these observations in natural systems, it is recognised that radionuclide transport with inorganic colloids may occur in deep groundwaters, particularly in rocks where advective transport is dominant. Colloid-mediated transport may be potentially important for highly sorbing, low solubility radioelements such as thorium, americium and plutonium.

In summary, there are a number of lines of evidence that suggest that inorganic colloid-mediated radionuclide transport may not be significant [139, 140]. However, this is an area of ongoing research; in particular, the reversibility of radionuclide sorption onto mobile colloids is being addressed (see, for example, reference [353]). The likelihood of increased radionuclide transport to the biosphere is increased if radionuclide-colloid association (by sorption, co-precipitation or another mechanism) is partly or fully irreversible. In such cases, the potential impact of colloids depends on:

- the amounts of radionuclides associated with colloids
- the stability and mobility of those colloids in the groundwater system
- the strengths and kinetics of the association and dissociation reactions between the radionuclides, the colloids and the rocks

- the duration of transport
- the persistence and stability of the colloids.

Given the observations of the association of natural radionuclides and other species with colloids in a range of groundwater systems, organic colloids may be more significant than inorganic colloids in facilitating transport in deep groundwaters, but again this will depend on site-specific factors and is also an area of continuing research [354, 355].

In evaporite rocks, groundwater salinity would be expected to be high and groundwater movement would under normal circumstances be expected to be negligible, such that colloids could only possibly become important when considering alternative scenarios, such as those involving human intrusion.

Given the above, the research identified in our S&T Plan includes:

- work to develop numerical coupled process models of tracer and colloid transport to investigate whether colloids may lead to increases actinide mobility in fractured rocks [10, task 756]
- development and updating of a summary report that consolidates the understanding gained from several related projects on colloids [10, tasks 762 and 769]
- a small experimental programme to investigate whether colloids, organic complexants and microbes may have cumulative effects on radionuclide behaviour [10, task 766].

The characterisation of colloids at a potential GDF site, and the assessment of their potential effects will form an important part of a site-specific research programme.

4.3.6 Retardation in the geosphere

Processes such as decay, sorption, co-precipitation, precipitation, rock matrix diffusion and isotopic exchange may lead to retardation in the geosphere. Many individual studies of radionuclide retardation processes have been undertaken and several sorption databases have been developed, but there will need to be significant programme of work to characterise the geology, mineralogy, hydrogeology and geochemistry of the system at a potential site for the GDF and to develop an approach for representing sorption and other retardation processes in the particular rocks of interest.

Retardation in dual porosity rocks

Because the dual porosity fractured rocks of interest for geological disposal consist of a wide range of primary minerals, fractures may contain various secondary minerals. The nature of fracture fillings will depend to a large extent on the nature of the rock, but minerals commonly found are:

- iron oxy-hydroxides (typically magnetite, hematite, goethite, hydrous ferric oxides)
- other oxides (alumina, titanite, silica, etc.)
- calcite and other carbonates
- clay minerals (montmorillonite, kaolinite, etc.)
- secondary mica minerals
- zeolites
- residual (unaltered) quartz.

Fractures may thus possess diverse physico-chemical properties, with varying porosity and a different mineralogy - with higher surface area and cation exchange capacity - than the rock matrix.

Because of the mineralogical heterogeneity of both the rock matrix and the fracture fillings, retardation processes may comprise a variety of ion-exchange reactions (with constant-charge minerals like micas and clay minerals) and surface complexation reactions (with minerals exhibiting pH-dependent surface charge: micas, oxides, clays, etc.). This may lead to further (co)precipitation with, for example, carbonates, iron oxides, etc.

Sorption onto the fracture surface or the fracture filling materials may be the main retardation process for solutes in preferential fracture flow paths. However, the volume of the fractures typically represents only a small fraction of the total volume of a given rock. The pore system of the rock matrix includes the majority of the aqueous phase. This pore network may provide a large solid/liquid interface area, far larger than the surface area of fracture walls, so that diffusion into the rock matrix and sorption onto matrix pore surfaces may reduce radionuclide concentrations in flowing groundwater.

The overall effect of interactions between radionuclides and other species, with fracture fills and surfaces and the rock matrix will depend on various physical parameters, including the amount of surface area in contact with the flowing water (the flow-wetted surface area), the water flow rate in the fractures, the porosity of the matrix, and the extent of matrix diffusion and anion exclusion processes [190].

It can be understood, therefore, that although many individual studies of radionuclide retardation have been undertaken, and several sorption databases have been developed, (see, for example, references [114, 115, 338]) there will need to be significant programme of work to characterise the geology, mineralogy, hydrogeology and geochemistry of the system at a potential site for the GDF and to develop an approach for representing sorption and other retardation processes in the particular rocks of interest.

Retardation in clays

Argillaceous rocks are typically comprised mainly of minerals such as illite, smectite, illite/smectite mixed-layer clays and kaolinite. These minerals are abundant, have high reactive-surface areas and dominate sorption in such rocks. They also exert a significant chemical buffering effect on the pore solutions present.

Typical accessory minerals include quartz, carbonates and smaller amounts of pyrite, gypsum, and feldspars. These minerals are less important than the clays in terms of sorption. Similarly, the content of iron and aluminium oxides present is also typically insignificant compared to the reactive surfaces provided by the clay minerals.

Clay rocks often contain organic matter. Where this material is humic-like it may have an important effect on the sorption and transport of radionuclides and other dissolved species, see, for example, reference [356]. In clay rocks such as the Opalinus Clay and the Callovo-Oxfordian Clay, the organic matter is not humic-like and the effect on sorption and transport is likely to be small or even absent [36].

Many individual studies of radionuclide sorption to clays have been undertaken [108, 356, 357, 358] and several sorption databases have been developed [112, 115, 116, 118].

Two broad approaches have been tested for representing sorption on clay rocks: 'bottom-up' and 'top-down'. In bottom-up or 'mineral additivity' models, the sorption of the rock is derived from the quantities, distributions and sorption site densities of the individual component minerals. In contrast, in top-down or 'general composite' models, sorption onto the mineral assemblage is represented by a number of generalised surface sorption sites. The NEA has led a number of comparison exercises to evaluate different models of sorption and has developed guidelines for the development of sorption models for clay mineral assemblages [36, 35]. In terms of quantifying sorption, the relatively complex

mineralogy of argillaceous rocks can often be modelled adequately by considering the contributions of the main clay components (such as smectite and illite) in an additive manner [36].

Retardation in evaporites

Little experimental work has been undertaken to measure radionuclide sorption or retardation in evaporite minerals or rocks.

Reference [359] describes some basic studies on the interaction between selected radionuclide species ($^{134}\text{Cs}^+$, $^{85}\text{Sr}^{2+}$, $^{60}\text{Co}^{2+}$, $^{151}\text{Eu}^{3+}$, $^{241}\text{Am}^{3+}$ and $^{99}\text{TcO}_4^-$) in saturated sodium chloride solutions and: (a) pure halite, (b) pure halite, artificially contaminated with impurities typical for salt formations - hematite (Fe_2O_3) and anhydrite (CaSO_4), and (c) anhydrite. On the basis of their experiments they concluded that europium and americium in the form of MCl_2^+ species interacted with the halite surface, apparently forming solid europium / americium chloride (MCl_3) moieties, which were desorbed only with difficulty. Batch-type experiments revealed distribution ratios on the order of 0.02 and 0.075 m^3/kg for europium and americium, respectively. Impurities in the halite, such as hematite or anhydrite strongly increased the sorption efficiency. In these cases cobalt, and to a minor extent caesium and strontium, were also found to be sorbed.

Although a few data exist, most safety assessments for disposal in salt have assumed that no sorption occurs on evaporite minerals. Instead, experimental programmes (at Gorleben and WIPP) have focused on measuring radionuclide sorption on more permeable rocks in the evaporite sequences and the surrounding geosphere.

For example, work at the WIPP included measuring actinide sorption onto the Culebra Dolomite, a fractured dolomite overlying the repository horizon [316]. At the Gorleben site in Germany, the reference safety assessment model showed that no water from outside the EBS reached the disposal areas and all radionuclides were contained within the GDF [312, 360]. Alternative assessment scenarios considered a slower compaction rate and a higher final porosity of the compacted crushed salt backfill. This variant scenario showed that water would be able to reach the waste containers and that the radionuclides would be mobilised [361]. However, the transport of radionuclides towards the drift seals was assumed to be dominated by diffusion and, therefore, to be very slow. The safety assessment calculations did not consider sorption of radionuclides [360].

Given the site-specific controls on the processes that will control transport and retardation in the geosphere, there will need to be a significant programme of work at any potential evaporite site for the GDF to characterise the hydrogeochemical system, understand which processes may be of significance and hence assess the overall safety of waste disposal.

In the meantime, the research identified in our S&T Plan includes participation in a five-year collaborative study to characterise and model radionuclide speciation and transport, and ecological transfers and transformations at four near-surface sites in the UK. This work will look principally at ^{14}C , uranium and radium, but will also collect information on ^{137}Cs , ^{241}Am , plutonium, ^{90}Sr and ^{129}I [10, tasks 786, 787 and 788]. Two related follow-on tasks will assess the outputs from the collaborative project, verify their relevance to a GDF and incorporate relevant aspects into models as appropriate [10, tasks 789 and 790].

The research identified in our S&T Plan also includes development of a conceptual model of the transport of uranium and its daughters that takes account of interactions with naturally-occurring uranium and daughters in the geosphere [10, task 797].

5 Concluding remarks

The science and technology underpinning disposal of the materials currently considered in the inventory of higher activity wastes for geological disposal is well established. The knowledge base includes information from laboratory studies, demonstration experiments, models and studies of 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 there is a good understanding of the processes that are likely to control the behaviour and transport of radionuclides and non-radiological species in groundwater, and considerable research has been conducted into their behaviour and transport in the more common engineered barrier materials. There are, however, several areas where understanding is incomplete and further research may be necessary (for example, relating to the content of non-radiological species in the wastes, to the dissolution of UK-specific spent fuels and HLW glasses, to wasteforms for plutonium and to transport in and erosion of bentonite). We use an expert elicitation process to develop PDFs of solubility and sorption values for use in safety assessments, based on available experimental data and taking account of uncertainties - there is a need to update the information input to this process to take account of the most recent research results. Our Science and Technology Plan sets out the range of generic research that is being conducted and planned, as well as an approach for moving to site-specific research. Given the site-specific nature of groundwater species behaviour and transport in the geosphere, there will need to be a significant programme of work at any potential site for the GDF to characterise the hydrogeochemical system, understand which processes may be of significance and assess the overall safety of waste disposal.

Information contained in the suite of Research Status Reports has been used to underpin the development of the 2016 generic DSSC. In particular, information from this status report has been used to provide technical underpinning for the illustrative post-closure safety assessment calculations and the Science and Technology Plan.

Appendix A

Various processes may influence the behaviour and transport of radionuclides and non-radiological species in groundwater. These processes include radioactive decay and ingrowth, chemical speciation, organic complexation, radiolysis, sorption, solubility, precipitation and co-precipitation, mineral-surface ageing, colloids, microbial activity, non-aqueous phase liquids, advection, diffusion, dispersion, rock-matrix diffusion, filtration and ion exclusion.

Based on the descriptions and discussions given in this report of results from many years of research that has been carried out into the geological disposal of radioactive waste, Table A1 summarises the locations in a geological disposal system where certain key processes may be relevant in controlling the behaviour and transport in groundwater of radionuclides and other species.

Table A1: The possible occurrence of key processes in the disposal system

Process	Location in disposal system						
	Near Field				Far Field		
	EBS		Geosphere				
	Waste package	Buffer/backfill	Excavation disturbed zone	Chemically disturbed zone	Undisturbed geosphere		
Dual porosity rocks with flow					Rocks with porous flow	Diffusive settings	
Decay and ingrowth	Decay and ingrowth would occur throughout the disposal system						
Chemical speciation, pH, redox, organic complexation	Chemical speciation would have an influence throughout the disposal system						
	Organic complexation potentially important for ILW/LLW (for example, CDP)	CDP of lesser importance further away from the wasteform			NOM possibly important at some sites		NOM may be less significant
Radiolysis	Could be important for HLW, spent fuel, U/Pu wastes and ILW/LLW encapsulated in polymeric and other organic materials, less so for cement grouted ILW/LLW	Importance reduces further away from the waste					
Sorption	May limit or delay the build-up of dissolved concentrations of many radionuclides and other species	Important for long-lived sorbing radionuclides and other sorbing species	Relevant for species that sorb to newly formed surfaces and mineral phases (eg. calcite and CSH)		Important in fractures and rock matrix	Important in rock matrix	Important in rock matrix
Solubility, precipitation and co-precipitation	Solubility may limit the dissolved concentrations of some elements	Solubility of lesser importance further away from the waste, but could be relevant at reaction fronts or where there are changes in groundwater chemistry					
	Precipitation and co-precipitation of radionuclides possible		May see precipitation of calcite, CSH and other phases around cementitious ILW/LLW vaults		Less likely further away from the GDF, but could occur where groundwater chemistry changes and at reaction fronts		
Mineral surface ageing	Ageing of mineral surfaces may release sorbed radionuclides or lead to radionuclides becoming more strongly retarded						

Process	Location in disposal system						
	Near Field				Far Field		
	EBS		Geosphere				
	Waste package	Buffer/backfill	Excavation disturbed zone	Chemically disturbed zone	Undisturbed geosphere		
Dual porosity rocks with flow					Rocks with porous flow	Diffusive settings	
Colloids	Colloids may form during waste degradation (for example, from HLW glass, container corrosion and cementitious materials)	Filtration of colloids by a bentonite buffer possibly important. Cementitious materials may de-stabilise colloids or have very low colloid populations	May see colloid formation or destabilisation of GDF-derived colloids with the changes in conditions in the zone between the EBS and the far-field		Natural inorganic and/or organic groundwater colloids may be present, but their significance would depend on site specific factors		Probably not significant
Microbial activity	Could be present in niches or biofilms and more generally throughout the disposal system. May influence groundwater chemistry, waste package degradation and radionuclide transport. Microbial activity may be suppressed in high-density bentonite buffers, and at high pH. Microbes may degrade organic waste species and organic complexants						
NAPLs	Possibly present as a separate liquid phase	Unlikely to be significant	Waste-derived NAPLs unlikely to be present or significant				
Advection, dispersion and diffusion	Diffusion should be the dominant transport mechanism in a GDF for spent fuel, HLW and U/Pu with a bentonite-based buffer; advection likely to occur in a GDF for ILW/LLW with a cement-based backfill		Advection in fractures likely to be dominant	Advection and diffusion may occur	Advection in fractures likely to be dominant	Diffusion or advection dominant depending on hydraulic gradient and rock properties	Diffusion dominant
Rock matrix diffusion	Not relevant				Possibly important	Not relevant	
Filtration	Not significant	Filtration of colloids by a bentonite buffer possibly important	Not significant	Not significant	Some rocks may filter colloids		
Ion exclusion	Not significant	Ion exclusion may influence transport of some key nuclides (for example, ¹²⁹ I, ³⁶ Cl)					

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Certificate No LRQ 4008580

Radioactive Waste Management Limited
Building 587
Curie Avenue
Harwell Oxford
Didcot
Oxfordshire OX11 0RH

t +44 (0)1925 802820

f +44 (0)1925 802932

w www.gov.uk/rwm

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