Geological Disposal
Carbon-14 Project Phase 2: Overview Report

March 2016
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ISBN 978-1-84029-536-8

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Abstract

Carbon-14 is a key radionuclide in the assessment of the safety of a geological disposal facility for radioactive waste because of the potential radiological impact of gaseous carbon-14 bearing species.

RWM has established a project team, in which the partners work together to develop an holistic approach to carbon-14 management in a geological disposal system. The overall aim of the project is:

“To support geological disposal of UK wastes containing carbon-14, by integrating our evolving understanding from current and pre-existing projects, in order to develop an holistic approach to carbon-14 management in the disposal system”.

This report provides an overview of the work that has been completed in Phase 2 (the final phase) of the project, which has delivered the work mapped out at the end of Phase 1. The report updates our understanding of the key generation and migration processes and in particular focuses on the knowledge gaps that have now been filled. The improved understanding and data have been used to develop updated and new models, which have been used to provide a revised assessment of the implications of carbon-14 bearing gases that may be released from intermediate-level waste. Alternative treatment, packaging or design options are also discussed.

As a result of this focused programme of work, we now have the knowledge base required to support packaging decisions for specific wastes and understand the envelope of conditions within which disposal of the UK’s wastes containing carbon-14 can be managed.
Preface

This report is part of an ongoing programme of research conducted by the Radioactive Waste Management and its contractors. It is a component of the research into the implementation of geological disposal for radioactive wastes in the UK.

Geological disposal is the UK Government’s policy for the higher-activity radioactive wastes. The principle of geological disposal is to isolate the waste deep inside a suitable rock formation to ensure that no harmful quantities of radioactivity reach the surface environment. To achieve this, the waste will be placed in an engineered underground containment facility – the geological disposal facility. The facility will be designed so that natural and man-made barriers work together to minimise the escape of radioactivity.

Radioactive Waste Management Limited has developed a multi-barrier concept for geological disposal of higher-activity radioactive wastes. These wastes include high-level waste (HLW), spent nuclear fuel, intermediate-level (ILW) and certain low-level (LLW) radioactive wastes.

A geological disposal facility for wastes including ILW and LLW will be carefully designed and engineered to provide deep, excavated vaults together with the necessary access ways. Typically, the ILW and LLW wastes will be packaged in steel or concrete containers, usually with a cement grout, and subsequently placed in the vaults. Sometime later, the vaults will be backfilled with a cement-based material, completely surrounding the waste packages. Engineered barriers will be provided by the cement grout, the containers and the backfill. Natural barriers will be provided by geological formations that surround the repository and that lie between the repository and the accessible human environment. The concept for dealing with HLW and spent nuclear fuel is slightly different in that these materials could be placed in high integrity containers and these placed directly into deposition tunnels, again using engineered and natural barriers.

RWM has established a project to develop an integrated approach to support the geological disposal of wastes containing carbon-14. In particular this project addresses carbon-14 bearing gases that are expected to be generated from wastes emplaced in the GDF. The technical approach is informed by the key generation and migration processes that affect the fate of carbon-14 in the derived inventory. This report provides an overview of the work undertaken in Phase 2 of the project.
Executive Summary

Background
Carbon-14 is a key radionuclide in the assessment of the safety of a geological disposal facility (GDF) for radioactive waste. It has a half-life of 5,730 years. If it can be retained within the engineered barrier system (EBS) for a number of half-lives it will decay to insignificant levels. However, the radiological impact of gaseous carbon-14 bearing species is potentially an issue.

RWM has established a project to develop an integrated approach to support the geological disposal of wastes containing carbon-14. The technical approach is informed by the key generation and migration processes that affect the fate of carbon-14. The approach has become known as the ‘AND’ approach and is described in the box below.

For the radiological impact of gaseous carbon-14 to be an issue:

- There must be a significant inventory of carbon-14;
- That waste has to generate carbon-14 bearing gas;
- A bulk gas has to entrain the carbon-14 bearing gas;
- These gases must migrate through the engineered barriers in significant quantities;
- These gases must migrate through the overlying geological environment (either as a distinct gas phase or as dissolved gas);
- These gases must interact with materials in the biosphere (i.e. plants) in a manner that leads to significant doses and risks to exposed groups or potentially exposed groups.

These processes have been investigated in the current project. The conclusions are summarised below. The inventory and gas generation are considered first. Then the approaches to assessing the implications of releases during the operational period and following closure are described; this discussion groups the other processes shown in the ‘AND’ approach above. This is followed by a consideration of the important groups of wastes. The implications for the groundwater pathway have also been considered.

Inventory
There are 17,700 TBq of carbon-14 in the 2013 Derived Inventory. The main groups of wastes containing carbon-14 are: irradiated graphite, irradiated steels, irradiated reactive metals and spent fuel. The inventory of these streams has been examined and improvements made to the understanding of the inventory, the quantities of carbon-14, and the nature of the materials with which the carbon-14 is associated. The improvements for particular categories of waste are discussed below.

The work on the inventory has been undertaken in parallel with the work on the 2013 Derived Inventory, and the understanding developed has been incorporated into the 2013 Derived Inventory.
Gas generation

A number of mechanisms will lead to gas being generated in a GDF for intermediate-level radioactive waste during the operational and post-closure phases, including bulk hydrogen, carbon dioxide and methane and carbon-14 bearing methane, carbon dioxide and carbon monoxide.

There have been improvements in the understanding of:

- steel corrosion – the anaerobic stainless steel corrosion rate used in the modelling has been reduced;
- radiolytic gas generation – the parameterisation of the model has been revised; and
- microbial degradation – there is an improved understanding of the conditions required to sustain a microbial population.

These have been taken into account in the revised assessments.

The availability of water is important for a number of gas generation processes. There are a number of sources of water in a GDF, and a number of processes that consume water. Corrosion of certain wastes consumes water. Encapsulated wastes contain a significant quantity of water in the grout. Resaturation may provide additional water depending on the geological environment. Gas generation may be less in environments with longer resaturation times once the initial water in the encapsulation grout is consumed.

Assessing operational discharges

The initial approach to operational discharges was to use the assessment methodology adopted in the generic Disposal System Safety Case. In the light of the results, an updated methodology has been developed. This methodology addresses some of the simplifications in the initial methodology that are not well tailored to assessing the particular nature of the release of carbon-14 being considered, and leads to lower calculated doses. The calculated effective dose rates are below the source-related dose constraint for members of the public for a new facility of 0.15 mSv yr⁻¹.

Assessing post-closure releases

Gas that is formed in a GDF may dissolve in water, undergo chemical reactions or form a free gas phase. The amount of free gas and its migration through the EBS and the geosphere depend strongly on site-specific conditions, and may also depend on the design of the GDF. Two important aspects of the geological environment are the amount of water available to dissolve the gas and the permeability and porosity of the host rock.

A small amount of gas could dissolve in groundwater in the EBS. This dissolved gas will undergo advection along with the groundwater and diffusion due to concentration gradients in the groundwater. The majority of the gas is expected to form a free gas phase (although this may not be retained at longer times in certain environments). To avoid pressurisation, the EBS will be designed to allow migration of gases out of the vented waste packages and through any backfill. Limited amounts of carbon dioxide are expected to be generated from carbon-14 bearing waste streams. This carbon dioxide is expected to react with cement-based materials that are likely to be used in the part of the GDF for ILW and LLW, and thus will be retained in the EBS.

Three generic host rock environments have been considered, along with the important features that may be found in the overlying rocks.

In a higher-strength host rock, the gas will migrate through fractures in the host rock. Other site specific features (e.g. cap rocks, faults, gas traps and aquifers) could be present in the overlying geological environment and these features could delay or prevent gas reaching the biosphere and affect the area over which any gas would be released. Depending on
the hydrogeological properties of the rock, resaturation times may be relatively short in higher-strength rock or they may be longer (possibly around a thousand years).

Because a lower-strength host rock would have low permeability and very small pores, it will be more difficult for the gas to migrate across the host rock than in a higher-strength rock. Gas would also migrate across the host rock more slowly. Resaturation will be slower in this environment and water ingress may be reduced or prevented by pressurisation of the GDF. In a lower strength sedimentary rock, it may be appropriate to manage gas pressure in the GDF through the use of gas permeable seals and backfill materials, but these requirements would be site specific.

In the case of an evaporite, the gas phase would be expected to be confined to the host rock immediately surrounding the GDF and would not be expected to reach the biosphere. This would depend on the details of the actual geological environment and the efficacy of the sealing of access routes.

Any carbon-14 bearing gases that reach the biosphere following closure would be released to the deep soil. Recently a combined experimental and modelling programme has been completed, which focused on whether methane would be oxidised to carbon dioxide in the soil. This has been complemented by a wider review of the understanding of methane oxidation in soils from other fields. This work shows that the bulk of the methane will be oxidised. In the light of the results of this programme, a revised assessment model has been developed. This model is consistent with those used by the Low Level Waste Repository (LLWR).

The calculated post-closure consequences are dependent on the migration time relative to the half-life of carbon-14 and the area over which the carbon-14 is released to the deep soil. Six illustrative cases have been developed to enable the implications of the release of carbon-14 to be assessed; they include a case where there is no release of carbon-14. These cases span the geological environments that may be considered in the future to host a GDF. Given that there is no specific site currently being investigated, none of these cases is given more weight than any other.

**Irradiated graphite wastes**

There are about 7,000 TBq of carbon-14 associated with graphite. Improved understanding has shown that not all of the carbon-14 is releasable on relevant timescales, and not all of it that is released is released as gas. A revised model has been developed. Leaching experiments on Oldbury graphite have been extended to longer times to determine whether the release slows further or stops. The implications of these results will be considered once they are available.

In the operational period, if the graphite is packaged in a cement-based encapsulation grout, then any carbon dioxide generated would react with the cement and be immobilised. Small amounts of methane and carbon monoxide would also be generated, but the resulting effective dose rates would be below the source-related dose constraint for members of the public for a new facility. If graphite is not packaged in a cementitious grout, then it should remain dry during the operational period, and as a consequence no carbon-14 would be released in gaseous or aqueous form.

In the post-closure period, the radiological impact of any release of gaseous carbon-14 from graphite would be site specific. In the first thousand years following closure, risks would be below the risk guidance level provided it is released to an area which is comparable to the repository footprint. Therefore it will be important to understand the gas migration characteristics of any site proposed for the disposal of these wastes. After the first thousand years risks are assessed to be negligible.

It has been proposed that graphite could be disposed of in separate vaults. This could have the advantage that it might be possible to package the waste in such a way as to limit
the amount of metal and thus avoid the production of a bulk gas phase. A number of alternative packaging options have been investigated as part of this project and it has been concluded that, although disposal in separate vaults is feasible, it is not necessary for the management of carbon-14.

**Irradiated steel wastes**

There are about 7,000 TBq of carbon-14 associated with irradiated steel wastes. The overall inventory has increased in the 2013 Derived Inventory, because wastes associated with new build reactors are now included, but the inventory of certain key waste streams has decreased as a result of the improved understanding of the nitrogen impurity concentrations in the wastes. The inventory of carbon-14 in legacy steel wastes has been reduced by over 50%.

Post-closure release of carbon-14 depends particularly on the anaerobic corrosion rate of the stainless steel. As part of the international CAST project, a detailed review of corrosion rates has been undertaken, and as a consequence the anaerobic corrosion rate of stainless steel under alkaline conditions has been reduced by over an order of magnitude. The overall gas generation rate is also dependent on the geometry of the steel wastes, particularly on the thickness of the steel plates and the ‘diameter’ of more bulky items. The understanding and data for these have been improved for some of the important waste streams.

Not all of the carbon-14 may be released to the gas phase; some of it may remain in the aqueous or in solid phases. Experimental measurements are planned to measure this.

In the operational period, effective dose rates from gases released from the stainless steels are assessed to be below the source-related dose constraint for members of the public for a new facility.

In the post-closure period, the radiological impact of any release of carbon-14 from steels would be site specific. Steel wastes are the major contributor to the risks at times greater than a thousand years post-closure. However, it is not expected that risks arising from steel wastes will be above the risk guidance level, providing the planned experimental measurements confirm that a significant proportion of the carbon-14 is retained in aqueous or solid phases and is not released as a gas.

**Irradiated reactive metal wastes**

There are about 100 TBq of carbon-14 associated with reactive metal wastes. This inventory is small compared with the inventories of carbon-14 in graphite and steels. However, it is potentially significant as the carbon-14 could be released over a shorter period of time. Although the inventory has changed little, there is a better understanding of the nature of the material with which the carbon-14 is associated. In particular about a quarter of the Magnox and a third of the uranium is declared in the 2013 Derived Inventory as already corroded, and is therefore not available for future gaseous release of carbon-14.

The releases are sensitive to the corrosion rates of Magnox and uranium. The Magnox rate is sensitive to the presence of chloride (the corrosion rate is higher in the presence of chloride), and the uranium rate is sensitive to whether the conditions are aerobic or anaerobic (the corrosion rate is higher under anaerobic conditions). Both Magnox and uranium corrosion rates depend on temperature. Reviews have been undertaken and support the corrosion rates used. However, as a result of these reviews, it is expected that the uranium will be corroding under anaerobic conditions by the time the waste is emplaced in the GDF. Most of the uranium is expected to have corroded before the vaults are backfilled.

On the basis of vault-scale and package-scale modelling of the migration of chloride, it is assessed that the times at which chloride reaches the Magnox waste will be spread over at
least a thousand years. Thus Magnox will corrode at an enhanced rate resulting from the
presence of chloride at different times in different parts of the GDF. As a consequence the
‘effective’ or ‘average’ corrosion rate is only slightly higher than the rate without chloride.
This reduces the rate at which Magnox corrodes in the post-closure period compared to the
rate if chloride reached all the waste at the same time, and thus reduces the gas
generation rates.

The releases from reactive metals are higher than those from any of the other wastes
during the emplacement and backfilling phases and first thousand years following closure:

- Effective dose rates during the operational period will be below the source-related
dose constraint for members of the public for a new facility.
- The post-closure risks from Magnox are substantially lower than in earlier work,
  arising from the spreading of the times that chloride affects the corrosion of the
  wastes; however, these risks persist for much longer.
- The post-closure risks from Magnox will be site specific. Taking the best estimate
  of the fraction of carbon-14 released as a gas, the calculated risk is below the risk
  guidance level in four of the six illustrative cases. It is less than a factor of two
  above the risk guidance level in one of the illustrative cases. In the remaining
  illustrative case, corresponding to a focused release to an area which is
  considerably smaller than the repository footprint, risks are expected to be
  substantially above the risk guidance level. Therefore it will be important to
  understand the gas migration characteristics of any site proposed for the disposal of
  these wastes.
- Post-closure risks arising from any uranium metal remaining at closure are not
  expected to be significant, as the uranium is expected to have fully corroded by the
  time the GDF is closed.
- In the longer term, after a thousand years, the reactive metals have corroded unless
  there is very limited water availability, and there are no calculated risks.

In some circumstances, an alternative approach to the management of these wastes, such
as pre-treatment, may be appropriate. However, it is recognised that for a substantial
proportion of these wastes either they are already packaged or packaging plans are in
place. As a consequence, pre-treatment could be considered as part of option studies for
wastes that are neither currently packaged nor being packaged.

Spent fuel

There are about 3,300 TBq of carbon-14 in spent fuel. Spent fuel is likely to be packaged
in long-lived containers that are not vented. The carbon-14 would therefore decay
significantly before any water was able to breach the container. Even for an early release
from oxide fuels, where the carbon-14 is associated with stainless steel and Zircaloy
cladding, the calculated release rate would be low (i.e. even if released directly to the
biosphere the calculated risk would be below the risk guidance level).

Overview

The project has successfully updated the understanding of the key gas generation and
migration processes that determine the potential impact of UK wastes containing
carbon-14. The integrated approach has covered a wide range of technical areas,
gathering evidence to improve the knowledge base that supports our approach to
management of these wastes.

A large number of knowledge gaps have been filled and the improved knowledge base has
been captured in updated and new models. The calculated consequences have been
reduced. The calculated impact is site specific and is dominated over the first thousand
years following closure by the release of carbon-14 from the corrosion of irradiated Magnox.

In the first thousand years following closure, the calculated impact from gaseous carbon-14 would be below the risk guidance level, provided that:

- the proportion of carbon-14 released from Magnox as methane or carbon monoxide is limited (less than around 30%); and
- any gas that is released to the biosphere is released over an area roughly equivalent to the repository footprint or larger.

If there were a focused release of gas to a small area, risks may be above the risk guidance level. Therefore it will be important to understand the gas migration characteristics of any site proposed for the disposal of these wastes.

In some circumstances, alternative treatment or disposal options may be appropriate. At this time it is considered beneficial to retain:

- options to dispose of graphite wastes in separate vaults, with minimal packaging to minimise generation of bulk gas; and
- the option for alternative treatment of wastes containing irradiated reactive metals (recognising that this would not be undertaken lightly since many of these wastes are already packaged).

The results presented here will be updated once experimental measurements on the speciation of carbon-14 released from irradiated Magnox and irradiated stainless steels become available. Consideration should be given to developing a better understanding of the rate and extent of corrosion of reactive metal wastes prior to closure of a GDF. Sellafield is working towards measuring gas release from active waste packages, but these data will take several years to obtain. Such data would be valuable for comparison with the assessed releases.

Our improved understanding also has implications for the assessment of the groundwater pathway in terms of the inventory available for release and the speciation of carbon-14 in the aqueous phase. Account could be taken of the significant proportion of carbon-14 in graphite that would not be released on relevant timescales and the long timescales over which carbon-14 would be released from steels.

Carbon-14 remains a key radionuclide in the assessment of the safety of a GDF for radioactive waste, because of the potential radiological impact of gaseous carbon-14 bearing species. As a result of this focused programme of work, we now have the knowledge base required to support packaging decisions for specific wastes and understand the envelope of conditions within which disposal of the UK’s wastes containing carbon-14 can be managed.
List of Contents

1 Introduction 1
   1.1 Why carbon-14 is a key issue for geological disposal 1
   1.2 The illustrative disposal concepts 2
   1.3 Key generation and migration processes 6
   1.4 The integrated approach 6
   1.5 Structure of this report 9

2 Inventory 10
   2.1 The 2013 Derived Inventory 10
   2.2 Progress on understanding the carbon-14 inventory 11
   2.3 Summary of the current inventory 12

3 Gas Generation 15
   3.1 Recent progress 16
   3.2 Calculated bulk gas generation rates 17
   3.3 Impact of geological environment on gas generation 21

4 Gas in the Engineered Barrier System 27
   4.1 Formation of a free gas phase 28
   4.2 Gas migration in the EBS 31
   4.3 Carbonation 33
   4.4 Microbes in the EBS 35

5 Gas in the Geosphere 37
   5.1 Gas migration 37
   5.2 Illustrative geological environments 41
   5.3 Modelling gas migration 43
   5.4 Microbes in the geosphere 45
   5.5 Dissolution of gas in the geosphere 46
   5.6 Release of gas to the biosphere 47

6 Biosphere 50
   6.1 Pre-closure releases of gas 50
   6.2 Post-closure releases of gas 53
   6.3 Dissolution in an aquifer 58
7 Migration and Release Scenarios 60
  7.1 Stages in the evolution of the GDF 60
  7.2 Waste emplacement 61
  7.3 Backfilling and closure 61
  7.4 Post-closure 61
  7.5 Species and pathways 63
  7.6 Summary of calculations undertaken 65

8 Irradiated Graphite Wastes 66
  8.1 Inventory 66
  8.2 Experimental evidence on the release of carbon-14 from irradiated graphite 68
  8.3 Modelling the release of carbon-14 from irradiated graphite 72
  8.4 Application of the revised model 75
  8.5 Implications for release of carbon-14 from irradiated graphite 78
  8.6 Alternative approaches for the management of graphite wastes 79
  8.7 Additional graphite samples 83
  8.8 Summary and next steps 83

9 Irradiated Steel Wastes 86
  9.1 Inventory 86
  9.2 Steel corrosion rates 89
  9.3 The release of carbon-14 from irradiated steels 92
  9.4 Modelling 93
  9.5 Implications for release of carbon-14 from irradiated steels 97
  9.6 Alternative approaches 99
  9.7 Summary and next steps 100

10 Irradiated Reactive Metal Wastes 102
  10.1 Inventory 102
  10.2 Magnox 105
  10.3 Uranium 119
  10.4 Aluminium 129
  10.5 Alternative approaches 129
  10.6 Summary and next steps 130

11 Spent fuel 134
11.1 Inventory 134
11.2 Potential for release of carbon-14 135

12 Other Wastes 137
12.1 Inventory of other wastes 137
12.2 ILW organics from GE Healthcare 138
12.3 Encapsulated LWR cladding (Zircaloy) 138
12.4 Encapsulated barium carbonate slurry/multi-element bottle crud 140
12.5 Other ILW containing carbon-14 140
12.6 Aluminium nitride cartridges 141
12.7 Summary position for the other waste groups 141

13 Summary and Conclusions 143
13.1 Overview of the modelling results 143
13.2 Summary of the current position 149
13.3 Integrated conclusions – the ‘AND’ approach 150

14 References 153
## List of Acronyms and Abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGR</td>
<td>Advanced Gas-cooled Reactor</td>
</tr>
<tr>
<td>Andra</td>
<td>The French radioactive waste management organisation</td>
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<tr>
<td>BEP</td>
<td>Box Encapsulation Plant (at Sellafield)</td>
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<tr>
<td>BEP0</td>
<td>British Experimental Pile 0 – air-cooled graphite-moderated pile (at Harwell)</td>
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<td>BGS</td>
<td>British Geological Survey</td>
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<tr>
<td>BWR</td>
<td>Boiling Water Reactor</td>
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<tr>
<td>CAST</td>
<td>Carbon-14 Source Term (International collaborative project supported by European Commission)</td>
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<td>CVCS</td>
<td>Chemical and Volume Control System</td>
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<td>DBE</td>
<td>The German radioactive waste management organisation</td>
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<tr>
<td>DI</td>
<td>Derived inventory</td>
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<td>DNLEU</td>
<td>Depleted, natural and low-enriched uranium</td>
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<td>DSSC</td>
<td>Disposal System Safety Case</td>
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<tr>
<td>EA</td>
<td>Environment Agency</td>
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<tr>
<td>EARP</td>
<td>Enhanced Actinide Removal Plant</td>
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<td>EBS</td>
<td>Engineered barrier system</td>
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<td>EDZ</td>
<td>Excavation disturbed zone</td>
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<td>FED</td>
<td>Fuel Element Debris</td>
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<td>FGMSP</td>
<td>First Generation Magnox Storage Pond</td>
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<tr>
<td>FT</td>
<td>Fischer-Tropsch – a synthesis methodology</td>
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<tr>
<td>GDF</td>
<td>Geological disposal facility</td>
</tr>
<tr>
<td>GPA (03)</td>
<td>Generic Performance Assessment 2003</td>
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<tr>
<td>HEU</td>
<td>Highly enriched uranium</td>
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<td>HLW</td>
<td>High-level waste</td>
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<tr>
<td>HSR</td>
<td>Higher strength rock</td>
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<td>ILW</td>
<td>Intermediate-level waste</td>
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<tr>
<td>IPT</td>
<td>Integrated Project Team</td>
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<tr>
<td>LLW</td>
<td>Low-level waste</td>
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<td>LLWR</td>
<td>Low Level Waste Repository</td>
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<tr>
<td>LP&amp;S</td>
<td>Legacy Ponds and Silos</td>
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<tr>
<td>LSSR</td>
<td>Lower strength sedimentary rocks</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>MEP</td>
<td>Magnox Encapsulation Plant</td>
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<td>MSSS</td>
<td>Magnox Swarf Storage Silos</td>
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<td>MTR</td>
<td>Materials test reactor</td>
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<td>Nagra</td>
<td>The Swiss radioactive waste management organisation</td>
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<td>NNB</td>
<td>Nuclear New Build</td>
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<td>NRVB</td>
<td>Nirex Reference Vault Backfill</td>
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<tr>
<td>OESA</td>
<td>Operational environmental safety assessment</td>
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<td>PCSA</td>
<td>Post-closure safety assessment</td>
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<td>PETF</td>
<td>Product Evaluation Task Force</td>
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<tr>
<td>PGA</td>
<td>Pile Grade A – a type of graphite</td>
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<td>PGB</td>
<td>Pile Grade B – a type of graphite</td>
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<tr>
<td>PhD</td>
<td>Doctor of Philosophy</td>
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<td>PWR</td>
<td>Pressurised Water Reactor</td>
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<td>RWM</td>
<td>Radioactive Waste Management Limited</td>
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<td>RWMD</td>
<td>Radioactive Waste Management Directorate</td>
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<td>SFL</td>
<td>Springfield Fuel Ltd</td>
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<td>SILW</td>
<td>Shielded intermediate-level waste</td>
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<td>SKB</td>
<td>The Swedish radioactive waste management organisation</td>
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<tr>
<td>SMOGG</td>
<td>Simplified Model of Gas Generation</td>
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<td>TBq</td>
<td>Terabecquerel, $10^{12}$ Becquerels – the Becquerel is the standard international unit of measurement of radioactivity</td>
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<tr>
<td>UILW</td>
<td>Unshielded intermediate-level waste</td>
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<td>UK</td>
<td>United Kingdom</td>
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<td>UK RWI</td>
<td>UK Radioactive Waste Inventory</td>
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<td>US DOE</td>
<td>US Department of Energy</td>
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<tr>
<td>WAGR</td>
<td>Windscale Advanced Gas-cooled Reactor</td>
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1 Introduction

Carbon-14 is a key radionuclide in the assessment of the safety of a geological disposal facility for radioactive waste. In particular, the radiological impact of gaseous carbon-14 bearing species is a potential issue and has been recognised as such in a number of recent reports.

The main sources of carbon-14 are: irradiated graphite, irradiated steels, irradiated reactive metals and spent fuel. There are 17,700 TBq of carbon-14 in the 2013 Derived Inventory1.

RWM has established an integrated project to develop an holistic approach to carbon-14 management in a geological disposal facility. The technical approach is informed by the key generation and migration processes that affect the fate of carbon-14 in the derived inventory.

The Nuclear Decommissioning Authority (NDA) has established a wholly owned subsidiary, Radioactive Waste Management (RWM), to manage the delivery of geological disposal for higher activity radioactive wastes as required under UK Government policy, and published in the Implementing Geological Disposal White Paper [1].

Carbon-14 (half-life 5,730 years) is a key radionuclide in the assessment of the safety of a geological disposal facility (GDF) for radioactive waste [2]. In particular, the radiological impact of gaseous carbon-14 bearing species is a potential issue and has been recognised as such in Nirex report N/122 [3], in the 2010 generic Disposal System Safety Case (DSSC) [4], and in the issues register [5]. Carbon-14 is expected to be released from a GDF over a timescale of several thousand years. A number of radioactive gases will be generated from waste materials within a GDF, with carbon-14 bearing methane (14CH4) likely to be the dominant carbon-14 species transported in the gas phase, potentially reaching the biosphere at low activity concentrations.

RWM has been carrying out a range of research and assessment tasks on carbon-14 to improve the understanding of the expected evolution of the disposal system and the consequences for the calculated annual risk. Much of this work is summarised in the 2010 gas status report [6], the 2010 radionuclide behaviour status report [7], the 2010 biosphere status report [8] and in the 2014 Science & Technology Plan [9]. However, following publication of the 2010 DSSC, it was decided to adopt a collaborative approach to tackling issues related to carbon-14 by establishing a project team, in which the partners work together to develop an holistic approach to carbon-14 management in a geological disposal facility.

1.1 Why carbon-14 is a key issue for geological disposal

Carbon-14 is a key radionuclide in the assessment of the safety of a geological disposal facility for radioactive waste. In particular, the radiological consequences of gaseous carbon-14 bearing species have been recognised as a potential issue [4].

Carbon-14 is produced by thermal neutron activation of nitrogen-14, carbon-13 and oxygen-17 ‘precursor’ species when nuclear fuel components and reactor cores are irradiated. The half-life of carbon-14 is 5,730 years, so if it can be retained within the multi-barrier system for sufficient time, then it will decay (to stable nitrogen-14). However, it is possible for carbon-14 to be released as a gas, such as methane (14CH4). If carbon-14 is released in this form and the gas is able to migrate relatively quickly to the biosphere

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1 1,000 TBq (terabequerel) can be written as 1 PBq (petabequerel). However, all the inventories in this report are written as TBq to enable ready comparison. 1 TBq is 10^12 Bq.
following closure, the calculated risk could exceed the risk guidance level provided by the environment agencies in the Guidance on Requirements for Authorisation [10].

The 2013 Derived Inventory (DI) contains approximately 17,700 TBq of carbon-14. The main components of the carbon-14 inventory are irradiated graphite, irradiated steels, irradiated reactive metals (Magnox and uranium) and spent fuel.

The inventory of carbon-14 in the 2013 UK Radioactive Waste Inventory (UK RWI) is different from that in the 2010 UK RWI in that it reflects the improved understanding gained by the project; it also includes additional wastes and spent fuel from a proposed new nuclear build programme and excludes Scottish wastes since Scottish policy is that these will not be disposed in a GDF. The work on the inventory is discussed further in Section 2. A detailed description of the inventory of carbon-14 in UK wastes and the changes made as a result of improved understanding can be found in reference [11].

The potential radiological consequence of gaseous carbon-14 was recognised as a key challenge to a GDF in reference [3], where calculations were presented for two scenarios. In the first of these, it was assumed that carbon-14 is all dissolved in groundwater and is released to the biosphere in solution; in this case the calculated risk was well below the regulatory risk guidance level. A second scenario was presented in which it was assumed that methane containing carbon-14 could be generated from irradiated metals, graphite and organic molecules and that any methane generated is released to the biosphere. In this scenario, the calculated risk was above the regulatory risk guidance level. However it was recognised that, in a multi-barrier system, the geosphere would be expected to play a role and that further work was required to better understand the extent to which different geological environments have the potential to retard gas migration and to reduce uncertainties in the rates and quantities of carbon-14 generated.

Since that time, RWM has been carrying out a range of research and assessment tasks on carbon-14 to improve the understanding of the expected evolution of the disposal system and the consequences for the calculated annual risk. Carbon-14 is also recognised as a key issue for geological disposal in other countries and the European Commission is supporting a project called CArbon-14 Source Term (CAST), in which around 30 partner organisations are participating in a project to better understand the carbon-14 source term.

Carbon-14 is an issue in RWM’s issues register, where it has been raised by a number of stakeholders [5] and it was a key issue in the 2010 generic DSSC [4]. Following publication of the 2010 DSSC, and recognising that the potential release of gaseous carbon-14 was one of the key challenges in the safety case, RWM established an Integrated Project Team (IPT), in which the partners would work together to integrate evolving understanding from current and pre-existing projects to develop an holistic approach to carbon-14 management in the disposal system. The project team includes members from a number of contracting organisations and from the different technical functions within RWM. The contract is managed collaboratively by a representative of RWM and the Lead Technical Manager (who is from Amec Foster Wheeler).

1.2 The illustrative disposal concepts

RWM are using a number of illustrative disposal concepts, which are based on examples of disposal concepts developed by waste management organisations across the world. Illustrative disposal concepts have been developed for each of three geological environments, for both low-heat-generating waste (LHGW), which includes intermediate-level waste (ILW), low-level waste (LLW) and depleted, natural and low-enriched uranium (DNLEU), and high-heat-generating waste (HHGW), which includes high-level waste (HLW), spent fuel, plutonium and highly enriched uranium (HEU).
The examples are given in Table 1.

**Table 1** Examples of disposal concepts developed by waste management organisations around the world

<table>
<thead>
<tr>
<th>Host Rock</th>
<th>Example of Illustrative Disposal Concept (Developer, Country)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher strength rock¹</td>
<td>Low-heat-generating wastes (ILW, LLW, DNLEU)</td>
</tr>
<tr>
<td></td>
<td>UK ILW/LLW concept (NDA, UK)</td>
</tr>
<tr>
<td></td>
<td>High-heat-generating wastes (HLW, spent fuel, plutonium and HEU)</td>
</tr>
<tr>
<td></td>
<td>KBS-3V concept (SKB, Sweden)</td>
</tr>
<tr>
<td>Lower strength sedimentary rock²</td>
<td>Opalinus clay concept (Nagra, Switzerland)</td>
</tr>
<tr>
<td>Evaporites³</td>
<td>WIPP Bedded Salt Concept (US DOE, United States)</td>
</tr>
<tr>
<td></td>
<td>Gorleben Salt Dome Concept (DBE, Germany)</td>
</tr>
</tbody>
</table>

**Notes:**

1. Higher strength rock – the UK ILW/LLW concept and SKB’s KBS-3V disposal concept were selected because of the availability of information on these concepts for the UK context.

2. Lower-strength sedimentary rock – Nagra’s concepts for Opalinus Clay were selected because an NEA review regarded the Nagra work as state of the art. However, it should be noted that there is similarly extensive information available for the French (Andra) concepts (for Callovo-Oxfordian Clay), which have also been accorded strong endorsement from international peer review. Although the Swiss concepts are used as the basis of the illustrative disposal concepts, information from the French programme and from the Belgian HLW/spent fuel supercontainer concept would be drawn upon, should a potential site be identified in an area of the UK providing access to suitable lower strength sedimentary rock at GDF depth.

3. Evaporites – the concept developed by the US DOE for transuranic wastes at the WIPP was selected because of the wealth of information available from a licensed facility that operated for more than 10 years. The concept developed by the German Company for the Construction and Operation of Waste Repositories (DBE) for HLW/spent fuel was also selected because of the level of information it provides.

Further details of the concepts are provided in Table 2 and Table 3. These illustrative concepts form the basis of the work on the carbon-14 project.

Many of the waste streams containing carbon-14 are ILW, and these are the focus of much of the report. There is also carbon-14 in spent fuel, but this is likely to be packaged in long-lived containers, which are not vented. The carbon-14 associated with these wastes would therefore decay significantly before any water was able to breach the container. These wastes are discussed later in the report (Section 11), but the treatment is not as detailed.
Table 2  Illustrative disposal concepts for low heat generating waste

<table>
<thead>
<tr>
<th>Rock</th>
<th>Description of illustrative disposal concept (LHGW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher Strength Rock</td>
<td>Cement grouted waste in standardised containers, disposed of in large horseshoe-shaped vaults (e.g. 16 m x 16 m x 300 m), which are unlined. Support to prevent rockfall and water ingress provided by rock bolting, mesh and shotcrete as required. Vaults are backfilled with high pH, high porosity and permeability cementitious backfill (NRVB) during closure.</td>
</tr>
<tr>
<td>Lower Strength Sedimentary Rock</td>
<td>Cement grouted waste in standardised containers in oval-shaped vaults (e.g. 9.5 m wide by 11.5 m high and 100 m in length), which are unlined. Support to prevent rockfall and water ingress provided by rock bolting, mesh and shotcrete as required. A concrete floor is installed. Stack dimensions are approx. 6 m x 6 m. High pH, high porosity and permeability cementitious backfill surrounding waste packages which has some structural strength to resist creep of the host rock and is emplaced as soon as each vault has been filled.</td>
</tr>
<tr>
<td>Evaporites</td>
<td>Cement grouted waste in standardised containers in rectangular-shaped vaults (e.g. 10 m wide by 5.5 m high by 100 m long), which are unlined. Stack dimensions are approx. 8.5 m wide by 4 m high. Sacks of MgO are placed on top of each waste stack to absorb CO₂ and water and buffer pH and the remaining void space left open. The vault is closed as soon as it has been filled. Underground access is by shaft instead of the more normal drift access.</td>
</tr>
</tbody>
</table>
### Table 3  Illustrative disposal concepts for high heat generating waste

<table>
<thead>
<tr>
<th>Rock</th>
<th>Description of illustrative disposal concept (HHGW)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Higher Strength Rock</strong></td>
<td>Copper waste containers with cast iron inserts disposed of in vertical boreholes (1.5m wide by 8-10m deep) drilled from the floor of deposition tunnels. Each borehole accommodates one waste package surrounded by compacted bentonite blocks. The disposal tunnels are backfilled with a mixture of bentonite and crushed rock and the access tunnels are backfilled with crushed rock.</td>
</tr>
<tr>
<td><strong>Lower strength sedimentary rock</strong></td>
<td>Thick-walled carbon steel containers disposed of in 2.5 m diameter unlined tunnels with a concrete floor, nominally 800 metres in length. Pellet bentonite buffer, although compacted bentonite pedestal used to support waste package. Backfilled with crushed host rock.</td>
</tr>
<tr>
<td><strong>Evaporites</strong></td>
<td>Thick-walled carbon steel container placed on the floor of the rectangular unlined tunnels, e.g. 4.5 m wide by 3.5m high and nominally 800 metres in length. Crushed host rock buffer and crushed host rock mass backfill.</td>
</tr>
</tbody>
</table>
1.3 Key generation and migration processes

An overview of the key processes affecting the fate of carbon-14 in the geological disposal system is shown in Figure 1 below.

**Figure 1** Key generation and migration processes affecting the fate of carbon-14 in the disposal system

The main sources of carbon-14 include activated metals, graphite and spent fuel. As these materials are corroded, leached or otherwise degraded, carbon-14 could be released in aqueous or gaseous form.

At the same time corrosion of metals, radiolysis and degradation of organic materials will generate hydrogen, referred to as ‘bulk gas’ in the figure above. ILW containers are generally vented and any gas generated will be released into the surrounding near field. Depending on the amount of bulk gas generated, some species containing carbon-14 will dissolve in the near field and some will remain in the gas phase. Carbon dioxide is likely to be retained within the engineered barrier system through carbonation (see Section 4). However, methane and carbon monoxide are likely to be either dissolved or entrained within a bulk gas phase.

The geosphere may contain features that delay or prevent the migration of gas, but if gas is able to reach the biosphere, it could be released directly as methane or carbon monoxide or it could be converted to carbon dioxide by microbes in the soil zone. This carbon dioxide could then be taken up by plants and enter the food chain; leading to a consequent dose to any exposed groups or potentially exposed groups.

Spent fuel is not shown in the diagram above. The source term for these wastes is somewhat different, because spent fuel is likely to be packaged in long-lived containers, which are not vented. The carbon-14 would therefore decay significantly before any water was able to breach the container. This is discussed further in Section 11.

1.4 The integrated approach

The project team has developed an integrated technical approach to the work, based on an understanding of the key processes affecting the fate of carbon-14. The approach is known as the ‘AND’ approach and is described in Figure 2 below. The project team has used this approach as a way of considering the problem comprehensively and to underpin the prioritisation of the work. The ‘AND’ approach has been used for each of the key waste streams in order to break the problem down in a manageable way and to form the basis for the structure of this report.
For the radiological impact of gaseous carbon-14 to be an issue:

- There must be a significant inventory of carbon-14;
  **AND**
- That waste has to generate carbon-14 bearing gas;
  **AND**
- A bulk gas has to entrain the carbon-14 bearing gas;
  **AND**
- These gases must migrate through the engineered barriers in significant quantities;
  **AND**
- These gases must migrate through the overlying geological environment (either as a distinct gas phase or as dissolved gas);
  **AND**
- These gases must interact with materials in the biosphere (i.e. plants) in a manner that leads to significant doses and risks to exposed groups or potentially exposed groups.

The overall aim of the project is:

“To support geological disposal of UK wastes containing carbon-14, by integrating our evolving understanding from current and pre-existing projects, in order to develop an holistic approach to carbon-14 management in the disposal system. This includes the following sub-objectives:

- To inform strategic decisions on disposal options for specific waste types and inform packaging decisions for specific waste streams;
- To provide data and understanding and, if necessary, develop conceptual and component-level models to support the transport, operational and environmental safety cases;
- To develop options for an integrated waste management approach to disposal of these wastes;
- To establish whether mitigation measures or design solutions are required;
- To develop data and understanding required to inform the siting process;
- To inform the requirements for site characterisation;
- To deliver value for money.

A successful outcome from this project would be that we understand the envelope of conditions within which disposal of the UK’s wastes containing carbon-14 can be managed.”

The project consisted of two phases. In Phase 1, the project team carried out a six month programme of work to summarise the current understanding and set out a roadmap for Phase 2 [2]. The work concluded that the calculated release of carbon-14 from a GDF
would be dominated by: corrosion of reactive metals (in the operational and early post-closure time frame); corrosion of irradiated stainless steel and leaching of irradiated graphite. It also concluded that there was considerable scope for reducing the calculated radiological consequences for these wastes in Phase 2. It was also concluded that there was scope for considering approaches to alternative management strategies that would mitigate the consequences, and for considering how site-specific issues might affect the consequences once sites are identified.

Phase 2 of the project has now been completed, and this report provides an overview of the work undertaken and the conclusions reached. It is one of a suite of reports issued by the project; the main reports are listed in Table 4, along with some of the key supporting references written as part of associated projects.

Table 4  Main reports issued as part of Phase 2 of the Carbon-14 project (and associated projects)

<table>
<thead>
<tr>
<th>Title</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Main reports written on the project</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon-14 Project Phase 2: Inventory</td>
<td>AMEC/200047/003 [11]</td>
</tr>
<tr>
<td>Carbon-14 Project Phase 2: Irradiated Graphite Wastes</td>
<td>AMEC/200047/004 [12]</td>
</tr>
<tr>
<td>Carbon-14 Project Phase 2: Irradiated Steel Wastes</td>
<td>AMEC/200047/005 [13]</td>
</tr>
<tr>
<td>Carbon-14 Project Phase 2: Irradiated Reactive Metals Wastes</td>
<td>AMEC/200047/006 [14]</td>
</tr>
<tr>
<td>Carbon-14 Project Phase 2: Gas Formation and Migration</td>
<td>AMEC/200047/007 [15]</td>
</tr>
<tr>
<td>The Oxidation of Methane in Soil as a factor in Determining the Radiological Impact of a Geological Disposal Facility</td>
<td>AMEC/200047/001 [16]</td>
</tr>
<tr>
<td>Operational Impacts from Aerial Discharges of C-14 Labelled Gases</td>
<td>AMEC/200047/002 [17]</td>
</tr>
<tr>
<td>Carbon-14 Project Phase 2: Modelling</td>
<td>AMEC/200047/008 [18]</td>
</tr>
<tr>
<td>Carbon-14 Project Phase 2: Overview Report</td>
<td>This report</td>
</tr>
<tr>
<td><strong>Key supporting references written as part of associated projects</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon-14 Release from Oldbury Graphite</td>
<td>AMEC/5352/002 [19]</td>
</tr>
<tr>
<td>Rates of steel corrosion and carbon-14 release from irradiated steels – state of the art review</td>
<td>AMEC/201265/001 [20]</td>
</tr>
<tr>
<td>Field &amp; laboratory experiments to determine the fate &amp; behaviour of $^{14}$CH$_4$ injected into agricultural subsoil – Progress Report for Year 3</td>
<td>AMEC/Nott/004041/005 [22]</td>
</tr>
<tr>
<td>Uptake of Gaseous Carbon-14 in the Biosphere: Modelling of Field and Laboratory Experiments</td>
<td>AMEC/Nott/004041/006 [23]</td>
</tr>
<tr>
<td>Uptake of Gaseous Carbon-14 in the Biosphere: Development of an Assessment Model</td>
<td>AMEC/004041/007 [24]</td>
</tr>
</tbody>
</table>

Further supporting reports are expected on a longer timescale.
1.5 Structure of this report

The following sections of the report describe the work carried out within the project, as follows:

Section 2 describes the work on developing a better understanding of the carbon-14 inventory;
Section 3 summarises the main gas generation processes;
Section 4 describes how gases interact in the engineered barrier system;
Section 5 describes how gases migrate through the geosphere;
Section 6 describes how carbon-14 interacts with the biosphere and calculates dose to risk conversion factors for the relevant species in the time frames of interest;
Section 7 provides a summary of the release and migration cases on the basis of the work on the engineered barrier system, the geosphere and the biosphere described in the previous sections;
Section 8 describes the extent to which irradiated graphite wastes generate carbon-14 bearing gas, and the implications of any gas released to the biosphere;
Section 9 describes the extent to which irradiated steel wastes generate carbon-14 bearing gas, and the implications of any gas released to the biosphere;
Section 10 describes the extent to which irradiated reactive metal wastes generate carbon-14 bearing gas, and the implications of any gas released to the biosphere;
Section 11 considers the implications of carbon-14 in any spent fuel disposed in the GDF;
Section 12 considers the implications of carbon-14 in other wastes; and
Section 13 presents the overall modelling calculations, which summarise the behaviour of carbon-14 in the geological disposal system; and presents the overall conclusions of the work.
2 Inventory

As part of the project, we have sought to develop a better understanding of the inventory of carbon-14 in the key waste streams, and to seek to address the key uncertainties. The work on inventory has been undertaken in parallel with the work on the 2013 Derived Inventory, and the understanding developed has been incorporated into the 2013 Derived Inventory.

The Department of Energy and Climate Change (DECC) and NDA periodically publish an inventory of all radioactive waste in the UK. The most recently published UK Radioactive Waste Inventory, the 2013 UK RWI [26], contains information on radioactive wastes in the UK that existed on the 1 April 2013 and those that were projected to arise after that date. The UK RWI only considers stocks and arisings from existing sources, often referred to as legacy wastes.

In addition to existing wastes, there are some radioactive materials that are not currently classified as waste but would, if it were decided at some point that they had no further use, need to be managed as wastes through geological disposal. These include spent fuel, uranium and plutonium. As part of the UK RWI process, summary information on the quantities of these radioactive materials is published [27].

During Phase 1 of the project’s work, the 2010 Derived Inventory [28] was the best estimate of the wastes destined for geological disposal. However, the gas generation calculations reported as part of Phase 1 used the Derived Inventory based on the 2007 UK Radioactive Waste Inventory (referred to as ‘the 2007 Derived Inventory’) [29, 30, 31], as this dataset was more complete and was consistent with the information used in the 2010 DSSC [4].

2.1 The 2013 Derived Inventory

Phase 2 of the project uses the 2013 Derived Inventory. This is based on the 2013 Radioactive Waste Inventory, but it excludes wastes not destined for geological disposal and includes other wastes reflecting industry best estimates and UK Government policy.

The UK RWI contains an extensive amount of data on radioactive wastes, and these require modification before they can be used in RWM’s generic design and assessment work to support the implementation of geological disposal. For this purpose, a more detailed inventory for disposal, referred to as the ‘Derived Inventory’, is prepared. This differs from the UK RWI in a number of respects and the most important of these, from the perspective of the carbon-14 project, are:

- Wastes not destined for geological disposal are removed; and
- Other wastes are added to reflect industry best estimates and Government policy.

In particular, the 2013 Derived Inventory differs in three significant ways from the 2010 Derived Inventory [28]:

- It includes the waste and spent fuel from a 16 GW(e) nuclear new build programme (NNB)³.

³ The 2013 UK RWI does not include estimates of radioactive waste and spent fuel from a new nuclear build programme. This is because they will depend on the type and number of reactors, and how long they operate. Although a number of operators have plans to construct new nuclear generation in the UK, it is only EDF Energy (EDFE) that has been awarded the licences and construction consents for two European Pressurised Reactors (EPRs) at Hinkley Point in Somerset.
• It is assumed that 95% of the plutonium inventory will be disposed of as mixed oxide (MOX) spent fuel [32] in line with Government’s preferred policy for long-term plutonium management. This spent fuel is included in the 2013 Derived Inventory; and

• It excludes wastes that are managed under the Scottish Government’s policy for higher activity radioactive wastes [33].

At the same time as the carbon-14 project’s Phase 2 work, RWM has been undertaking a programme of work to develop the 2013 Derived Inventory. The results of the Phase 2 work have been integrated into the 2013 Derived Inventory4.

The radionuclide content in the 2013 Derived Inventory is decayed to the expected GDF closure year of 22005. Material content, such as the quantity of uncorroded uranium and Magnox are taken from returns from the waste producers, and correspond to an earlier date, such as the date of packaging or the date when the information was determined.

### 2.2 Progress on understanding the carbon-14 inventory

<table>
<thead>
<tr>
<th>Key areas of progress on the inventory have included:</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Significant reduction in the inventory of carbon-14 associated with AGR stainless steel fuel cladding and fuel assembly components;</td>
</tr>
<tr>
<td>• Improved geometry data for steels, and in particular the AGR stainless steel fuel cladding and fuel assembly components;</td>
</tr>
<tr>
<td>• Recognition that about a quarter of the Magnox and a third of the uranium has already corroded at the time of encapsulation.</td>
</tr>
</tbody>
</table>

The aims of the Phase 2 work on inventory have been to improve the understanding of, and clarify uncertainties in, the carbon-14 inventory data, to improve knowledge of composition data for those materials important for the carbon-14 inventory, and to improve the data on the geometry of certain key waste streams. These aims have been achieved, particularly for graphite and stainless steel wastes, which are the largest contributors to the carbon-14 inventory. The key areas of progress are summarised below. Additional information is given in the sections relating to irradiated graphite, irradiated steels and irradiated reactive metals. Further detail is provided in a supporting reference [11].

The neutron activation calculation methodology and assumed nitrogen precursor concentrations used for determining the carbon-14 activity for Magnox fuel (uranium metal) and AGR (graphite and steel) reactor components has been established. Information regarding calculation uncertainties associated with nitrogen precursor concentrations and other inputs for activation calculations was obtained.

Some information regarding metal grades, composition and geometry has been obtained for stainless steel and other ferrous metal reactor components.

No further information was determined regarding the basis of carbon-14 activity associated with reactive metals. However, Sellafield Ltd has undertaken a characterisation study for Magnox Swarf Storage Silo wastes, and when available the results should provide greater confidence in their carbon-14 content. However, we have taken into account information on the quantities of Magnox and uranium that are already corroded.

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4 The UK National RWI is updated every 3 years and is expected to undergo continuous improvement as the understanding of wastes improves.

5 The change from year 2150 used in the Phase 1 report is not significant given the long half-life of carbon-14.
Relevant areas are discussed in more detail in the overviews below on the conclusions for irradiated graphite wastes (Section 7), irradiated steel wastes (Section 9) and irradiated reactive metal wastes (Section 10).

2.3 Summary of the current inventory

The 2013 Derived Inventory contains approximately 17,700 TBq of carbon-14. The main components of the carbon-14 inventory are irradiated graphite, irradiated steels, irradiated reactive metals (Magnox and uranium) and spent fuel. There is also carbon-14 in the form of small organic molecules produced by GE Healthcare. These GE Healthcare wastes are included in the inventory, but are in the process of being incinerated and are therefore unlikely to be disposed of in a GDF, and have therefore not been included in the calculations included in this report. A summary of the inventory is given in Table 5.

The inventory of carbon-14 in the 2013 UK RWI is different from that in the 2010 UK RWI in that it reflects the improved understanding gained by the project. The overall result of the project’s investigations has allowed a 239 TBq reduction in the carbon-14 inventory for geological disposal [11]. This has been integrated into RWM’s 2013 Derived Inventory. However, the inventory includes additional wastes and spent fuel from a proposed new nuclear build programme and excludes Scottish wastes since Scottish policy is that these would not be disposed in a GDF. A detailed description of the inventory of carbon-14 in UK wastes and the changes made as a result of improved understanding can be found in [11].

Table 5 presents the inventory by grouping similar waste streams together (for example, the graphite values are for waste streams for which graphite is the major constituent, grouped together). However, certain waste streams contain more than one material. To support the gas generation calculations discussed later, the inventory has been analysed, and has been divided amongst the important material types. This is presented in Table 6.6,7.

The 2013 Derived Inventory includes the waste and spent fuel from a 16 GW(e) nuclear new build programme. There is considerable uncertainty in the programme, and therefore also in the extent of wastes that will arise from it.

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6 The division of the waste inventory by grouping the waste streams is given in Appendix A of reference [11]. The more detailed division by material type is given in Appendix B of reference [11].

7 ILW is divided into shielded ILW (SILW) and unshielded ILW (UILW). SILW packages would generally be expected to be capable of being transported through the public domain without additional protection and would therefore qualify as transport packages in their own right. Because of their high external radiation dose rate, or requirements for the containment of their contents,UILW packages would be expected to be transported through the public domain in reusable shielded transport containers.
### Table 5  Carbon-14 activity in the 2013 Derived Inventory, compared with the 2010 Derived Inventory

<table>
<thead>
<tr>
<th>Waste Category</th>
<th>2010 Derived Inventory $^{14}$C activity (TBq)</th>
<th>2013 Derived Inventory $^{14}$C activity (TBq)</th>
<th>Change (TBq)</th>
<th>Contribution to the 2013 Derived Inventory (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite – ILW core graphite</td>
<td>7,090</td>
<td>6,880</td>
<td>-214</td>
<td>38.8</td>
</tr>
<tr>
<td>Graphite – ILW AGR fuel assembly graphite</td>
<td>45.0</td>
<td>45.1</td>
<td>+0.11</td>
<td>0.25</td>
</tr>
<tr>
<td>Graphite – ILW Magnox fuel element graphite</td>
<td>6.15</td>
<td>1.75</td>
<td>-4.40</td>
<td>0.010</td>
</tr>
<tr>
<td>Graphite – LLW core graphite</td>
<td>5.74</td>
<td>2.13</td>
<td>-3.61</td>
<td>0.012</td>
</tr>
<tr>
<td>Steels – ILW AGR stainless steel fuel cladding</td>
<td>171</td>
<td>29.4</td>
<td>-141</td>
<td>0.17</td>
</tr>
<tr>
<td>Steels – ILW AGR stainless steel fuel assembly components</td>
<td>235</td>
<td>38.3</td>
<td>-196</td>
<td>0.22</td>
</tr>
<tr>
<td>Steels – Fuel stringer debris</td>
<td>122</td>
<td>99.5</td>
<td>-22.0</td>
<td>0.56</td>
</tr>
<tr>
<td>Steels – ILW stainless steels from reactor decommissioning</td>
<td>225</td>
<td>6,770</td>
<td>+6,540</td>
<td>38.2</td>
</tr>
<tr>
<td>Steels – ILW stainless steel reactor wastes</td>
<td>4.45</td>
<td>7.78</td>
<td>+3.34</td>
<td>0.044</td>
</tr>
<tr>
<td>Steels – ILW other ferrous metal decommissioning wastes</td>
<td>198</td>
<td>124</td>
<td>-73.8</td>
<td>0.70</td>
</tr>
<tr>
<td>Steels – ILW other ferrous metal reactor wastes</td>
<td>41.0</td>
<td>29.4</td>
<td>-11.6</td>
<td>0.17</td>
</tr>
<tr>
<td>Reactive metals - ILW reactive metals (Magnox and uranium)</td>
<td>117</td>
<td>115</td>
<td>-1.88</td>
<td>0.65</td>
</tr>
<tr>
<td>Other wastes – ILW organics from GE Healthcare (3)</td>
<td>556</td>
<td>204</td>
<td>-352</td>
<td>1.15</td>
</tr>
<tr>
<td>Other wastes – Other ILW</td>
<td>68.4</td>
<td>77.1</td>
<td>+8.6</td>
<td>0.44</td>
</tr>
<tr>
<td>Other wastes – Spent fuels</td>
<td>920</td>
<td>3,290</td>
<td>+2,370</td>
<td>18.6</td>
</tr>
<tr>
<td>Other wastes – Miscellaneous not assigned (4)</td>
<td>14.4</td>
<td>8.22</td>
<td>-6.17</td>
<td>0.046</td>
</tr>
<tr>
<td><strong>Total Carbon-14</strong></td>
<td><strong>9,820</strong></td>
<td><strong>17,700</strong></td>
<td><strong>+7,890</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

**Notes:**

1. All numbers are reported with up to 3 significant figures. This can mean that the change in activity does not exactly equal the difference between the 2010 Derived Inventory and the 2013 Derived Inventory.
2. Enhancements carried forward from the 2007 Derived Inventory are included (as used in the Phase 1 work [2]).
3. All ILW organics from GE Healthcare may not be disposed of to a GDF.
4. This group comprises those waste streams that contain low concentrations of carbon-14.
<table>
<thead>
<tr>
<th>Material category – Waste package group</th>
<th>Carbon-14 activity (TBq)</th>
<th>Contribution to Carbon-14 activity in 2013 Derived Inventory (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite – Legacy SILW/LLW</td>
<td>6,190</td>
<td>35</td>
</tr>
<tr>
<td>Graphite – Legacy UILW</td>
<td>735</td>
<td>4.15</td>
</tr>
<tr>
<td><strong>Graphite – Total</strong></td>
<td><strong>6,930</strong></td>
<td><strong>39</strong></td>
</tr>
<tr>
<td>Steels – Legacy SILW stainless steels</td>
<td>58.9</td>
<td>0.33</td>
</tr>
<tr>
<td>Steels – Legacy UILW stainless steel (2F03/C)</td>
<td>29.4</td>
<td>0.17</td>
</tr>
<tr>
<td>Steels – Legacy UILW stainless steel (2F08)</td>
<td>38.3</td>
<td>0.22</td>
</tr>
<tr>
<td>Steels – Legacy UILW stainless steels (excluding 2F03/C and 2F08)</td>
<td>83.6</td>
<td>0.47</td>
</tr>
<tr>
<td>Steels – NNB UILW stainless steels (AP301)</td>
<td>1,180</td>
<td>6.67</td>
</tr>
<tr>
<td>Steels – NNB UILW stainless steels (AP01)</td>
<td>0.0662</td>
<td>0.0004</td>
</tr>
<tr>
<td>Steels – NNB SILW stainless steels</td>
<td>3.32</td>
<td>0.02</td>
</tr>
<tr>
<td>Steels – Legacy SILW other ferrous metal</td>
<td>137</td>
<td>0.78</td>
</tr>
<tr>
<td>Steels – Legacy UILW other ferrous metal</td>
<td>42.0</td>
<td>0.24</td>
</tr>
<tr>
<td><strong>Steels – Total</strong></td>
<td><strong>7050</strong></td>
<td><strong>40</strong></td>
</tr>
<tr>
<td>Reactive metals – Legacy SILW/UILW Magnox</td>
<td>66.3</td>
<td>0.37</td>
</tr>
<tr>
<td>Reactive metals – Legacy UILW uranium</td>
<td>17.7</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Uncorroded reactive metals – Total</strong></td>
<td><strong>84</strong></td>
<td><strong>0.5</strong></td>
</tr>
<tr>
<td>All wastes – DCIC</td>
<td>7.43</td>
<td>0.042</td>
</tr>
<tr>
<td>Other wastes – ILW organics from GE Healthcare</td>
<td>204</td>
<td>1.15</td>
</tr>
<tr>
<td>Other wastes – Other ILW</td>
<td>140</td>
<td>0.79</td>
</tr>
<tr>
<td>Other wastes – Spent fuels</td>
<td>3,290</td>
<td>18.6</td>
</tr>
<tr>
<td>Other wastes – Miscellaneous not assigned</td>
<td>5.13</td>
<td>0.029</td>
</tr>
<tr>
<td><strong>Other – Total</strong></td>
<td><strong>3650</strong></td>
<td><strong>20.6</strong></td>
</tr>
<tr>
<td><strong>Total Carbon-14</strong></td>
<td><strong>17,700</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

**Note:** All numbers are reported with up to 3 significant figures.
3 Gas Generation

Gas will be generated in a GDF for intermediate-level radioactive waste by a number of mechanisms. To understand the implications for the release of carbon-14 in the gas phase, a necessary first step is to understand the bulk gas phase. The main gas generation mechanisms are corrosion of metals, radiolysis and microbial degradation of organic materials.

Before summarising the processes that lead to the generation of carbon-14 bearing gases, the main mechanisms for the generation of bulk gas in a GDF are considered. These mechanisms have been reviewed in a joint EC/NEA status report [34], and are reviewed in the Gas Status Report [6]. In a GDF, the processes that could generate either large volumes of bulk gases or significant amounts of radioactive gases are:

- corrosion of metals (including the release of carbon-14 from neutron-irradiated metals as these corrode);
- radiolysis, in particular of water and some organic materials;
- microbial degradation of organic materials, including the prior hydrolysis of cellulose to smaller organic compounds;

but would also include:

- diffusion, notably the release of tritium by solid-state diffusion from metals;
- radioactive decay of radium, which leads to the generation of radon-222; and
- the release of radioactive gases containing tritium or carbon-14 by leaching of irradiated graphite.

The rates at which most of the gases will be generated are sensitive to environmental factors, which might change with time, such as: the presence of oxygen or water; the presence of hydrogen or chloride ions; and temperature.

The bulk of the gas will be hydrogen, which will be generated by the corrosion of metals and the radiolysis of water and organic materials. Methane and carbon dioxide may also be generated, mainly by microbial degradation of organic materials. The relative amounts of gas generated by these processes will depend on the waste materials and the geological disposal concept. The overwhelming fraction of the volume of the generated gas will be non-radioactive, with only a very small fraction of the volume being radioactive. The radioactive component will consist mainly of tritiated hydrogen, (with one atom of hydrogen in a molecule replaced by an atom of its radioactive isotope, $^3$H), radioactive methane, carbon dioxide and carbon monoxide (with the carbon atom in the respective molecules replaced by an atom of its radioactive isotope, carbon-14), and radon. Although the volumes of these gases may be small, their safety significance is considered because of their radioactivity.

Further details are also given in the 2010 status report [6]. International understanding of the processes that could form gas from radioactive wastes has been reviewed, for example, in an EC/NEA-funded status report [34], from a project report from the EC FORGE project [35], and from an assessment perspective in another EC report [36].

Assessment of gas generation during transport, storage and disposal of radioactive wastes is carried out using the Simple Model of Gas Generation (SMOGG) software tool [37, 38]. This tool considers a range of gas generation processes including metal corrosion, the degradation of organic materials and the radiolysis of water and waste materials.
3.1 Recent progress

Improvements in the understanding of steel corrosion, radiolytic gas generation and microbial degradation have been reflected in the bulk gas generation calculations (reported in Section 3.2).

During Phase 2 of the work of this project, there have been three main areas where the understanding of the generation of a bulk gas phase has progressed.

### 3.1.1 Stainless steel corrosion

Further information has become available on the corrosion rate of stainless steel in anaerobic conditions (very low levels of oxygen) from a review undertaken as part of the international CAST project [20].

Previously the value used was essentially a ‘less than’ value, or minimum detectable value. New work has enabled us to use a value that is over an order of magnitude lower [20]. This has significant implications for both the generation rates of bulk gas and for the generation rates of gases containing carbon-14. These aspects are discussed further in Section 9.2.

### 3.1.2 Microbial degradation

Further consideration has been given to the role of microbial gas generation in high pH environments. Recent work suggests that provided that the pH is 12 or higher then microbial activity in the near field will be suppressed [39]. The pH is expected to be higher than 12 in the wastes containing a significant quantity of carbon-14. So although any organic material present may degrade chemically, it will not degrade further due to microbial activity until the pH starts to drop, which will be on a significantly longer timescale than the half-life of carbon-14. There remains the possibility of microbial activity in niches within the waste where the pH is not conditioned to such a high value.

This is discussed in more detail in Section 4.4.

### 3.1.3 Radiolysis

A recent study [40] has been undertaken to review the data required to calculate the quantities of gas generated by radiolysis in relation both to materials present in the UK UK RWI and to the operational and post-closure evolution of a GDF. The relationship between the amount of gas, typically hydrogen gas, and the radiation dose is usually formulated in terms of a G-value (also known as radiation chemical yield or yield). In the recent study:

- the current approach to gas generation by radiolysis was reviewed;
- the UK RWI was analysed to help determine the most sensible waste category groupings for the calculations of the quantities of gas generated by radiolysis;
- the available information on G-values, for water, cementitious materials and organic materials was critically reviewed; and
- the best estimate and upper bound G-values for relevant waste materials were summarised, along with their uncertainties and key data gaps.

These values are used in the work presented in this report.

### 3.1.4 Implications

The implications of these different aspects have been to decrease the importance of bulk gas generated by steel corrosion and microbial activity and to increase the importance of bulk gas generated by radiolysis.
3.2 Calculated bulk gas generation rates

It is helpful to understand the bulk gas generation rates. For the Phase 2 calculations, the rates are at a maximum shortly after closure; the overall generation rate is just above $10^5$ m$^3$ at STP yr$^{-1}$. They drop by about an order of magnitude over the next 30 years, and by 3000 AD they have fallen by a further order of magnitude. These rates could be lower in environments where resaturation takes longer.

It is helpful to develop an understanding of the bulk gas generation rates. Using the modelling basis adopted in the project (which is described in more detail in [18]), the calculated rates of bulk gas generation are shown below for different types of waste.

- Figure 3 is the rate of bulk gas generation from seventeen vaults of UILW / ULLW;
- Figure 4 is the rate of bulk gas generation from five vaults of SILW / SLLW; and
- Figure 5 is the rate of bulk gas generation from two vaults of NNB UILW.

The generation rates are expressed as m$^3$ at STP yr$^{-1}$. Actual volumes once the GDF has re-pressurised will be considerably less. However, the adopted approach for expressing the generation rates enables them to be considered on a common basis. These generation rates are based on a resaturation time of 5 years. These rates could be lower in environments where resaturation takes longer. They could also be lower if there is less microbial activity than is assumed.

The maximum generation rates are summarised in Table 7 (expressed per vault) and Table 8 (expressed as a total for that type of waste). The values in Table 8 are also summed over the whole GDF. It is seen that the overall gas generation rate is a maximum in the early post-closure period (up to 30 years after closure). It falls by almost an order of magnitude after that, and by 3000 AD it has fallen by another order of magnitude.

**Table 7 Maximum bulk gas generation rate per vault for a number of post-closure time periods**

<table>
<thead>
<tr>
<th>Waste group</th>
<th>Maximum bulk gas generation rate per vault (m$^3$ at STP yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Early post-closure (2200 to 2230 AD)</td>
</tr>
<tr>
<td>Legacy UILW / ULLW</td>
<td>5080</td>
</tr>
<tr>
<td>Legacy SILW / SLLW</td>
<td>193</td>
</tr>
<tr>
<td>NNB UILW</td>
<td>14.7</td>
</tr>
</tbody>
</table>

**Table 8 Maximum bulk gas generation rate from GDF for a number of post-closure time periods**

<table>
<thead>
<tr>
<th>Waste group</th>
<th>Maximum bulk gas generation rate from GDF (m$^3$ at STP yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Early post-closure (2200 to 2230 AD)</td>
</tr>
<tr>
<td>Legacy UILW / ULLW</td>
<td>$8.64 \times 10^4$</td>
</tr>
<tr>
<td>Legacy SILW / SLLW</td>
<td>$9.67 \times 10^2$</td>
</tr>
<tr>
<td>NNB UILW</td>
<td>$2.95 \times 10^4$</td>
</tr>
<tr>
<td>Total</td>
<td>$8.74 \times 10^4$</td>
</tr>
</tbody>
</table>
Figure 3  Breakdown by waste group of calculated generation rates for bulk gases from seventeen vaults of Legacy UILW / ULLW in the long term
Figure 4  Breakdown by waste group of calculated generation rates for bulk gases from five vaults of Legacy SILW / SLLW in the long term
Figure 5  Breakdown by waste group of calculated generation rates for bulk gases from two vaults of NNB UILW in the long term
3.3 Impact of geological environment on gas generation

The availability of water is important for a number of gas generation processes. There are a number of sources of water in a GDF, and a number of processes that consume water. Some of the sources depend on the nature of the host rock. Encapsulated wastes contain a significant quantity of water in the grout. Resaturation may provide additional water relatively rapidly in certain environments, more slowly in other environments, or in certain environments there may essentially be no water at all. Gas generation may be less in environments with longer resaturation times.

It is expected that there will be sufficient water in the packages for steel and Zircaloy wastes to corrode for a very long time. For aluminium wastes the water might be consumed during storage. For Magnox wastes, there is expected to be sufficient water for corrosion to continue for several tens of years, and perhaps as much as a hundred and fifty years, after closure. Further corrosion of aluminium and Magnox will be dependent on water becoming available from the backfill or surrounding host rock.

The calculations presented in Section 3.2 assume unlimited availability of water from the host rock following resaturation of the GDF. Some of the geological formations that are being considered as a potential host rock for a GDF either have very limited water availability (e.g. an evaporite) or may substantially limit the flow of water into the GDF after closure (e.g. a lower strength sedimentary rock). In these environments, it is possible that the gas generation processes could consume all of the water that is present at the location of the wastes. Thereafter, the rate of gas generation would be limited by the rate at which water could be supplied to the wastes from the surrounding rock.

The purpose of this section is to consider qualitatively how the generation rate may differ in the various geological environments being considered.

3.3.1 Water availability in packages

Encapsulated wastes contain a significant quantity of water in the grout. Resaturation may provide additional water relatively rapidly in certain environments, more slowly in other environments, or in certain environments there may be essentially no water at all.

Three illustrative host rocks being considered for disposal of radioactive waste are:

- Higher-strength rocks (HSR);
- Lower-strength sedimentary rocks (LSSR); and
- Evaporites.

Each of these host rocks may have various overlying rock strata.

The main sources of water in a GDF and the main processes that consume water are summarised in Table 9. Their significance in the different geological environments is also discussed qualitatively.

The sources of water in a GDF become available at different times (at encapsulation, following backfilling and following resaturation). Cementitious materials are structurally complex with water bound in different ways [15]. Water from the grout will be available for corrosion; however, there is uncertainty over how much will be accessible. Water from the backfill and from resaturation will have to enter packages to become available for corrosion of waste materials. Even in environments where water is readily available, this will take time. To help in the understanding of these processes, vault-scale and package-scale modelling for packages of Magnox waste is described in Section 10.2.3.

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8 These are discussed in more detail in Section 5.2.
There are also a number of processes that consume water. These are also listed in Table 9. The significance of the sources and consuming processes may differ in these three geological environments.

### Table 9  The main sources of water in the illustrative designs for a GDF for ILW/LLW, and the main processes by which the water may be consumed

<table>
<thead>
<tr>
<th>Source / Process</th>
<th>Discussion</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sources of Water</strong></td>
<td></td>
<td>HSR</td>
</tr>
<tr>
<td>Encapsulation grout</td>
<td>Important source – some will be readily available</td>
<td>Yes</td>
</tr>
<tr>
<td>Backfill</td>
<td>Potentially an important source after backfilling – for concepts with a backfill</td>
<td>May take time to enter packages</td>
</tr>
<tr>
<td>Surrounding rock – resaturation</td>
<td>Potentially important</td>
<td>May take time to enter packages</td>
</tr>
</tbody>
</table>

| **Processes that Use Water**     |                                                                           | Until backfilling – limited thereafter | Until backfilling – limited thereafter | Limited once vaults are closed |
| Drying of the encapsulation grout| In surface stores and underground emplacement before backfilling. Drying during underground emplacement before backfilling may be limited in more permeable environments because of the high relative humidity | Until backfilling – limited thereafter | Until backfilling – limited thereafter | Limited once vaults are closed |
| Backfill drying                  | Limited water loss because of the large volumes of backfill emplaced      | Limited                              | Limited                              | No backfill                   |
| Steel corrosion                  | Once the system is anaerobic                                             |                                     |                                     | Yes                           |
| Magnonx corrosion                | All times                                                                |                                     |                                     | Yes                           |
| Uranium corrosion                | Once the system is anaerobic                                             |                                     |                                     | Yes                           |
| Aluminium corrosion              | All times                                                                |                                     |                                     | Yes                           |
| Zircaloy corrosion               | Once the system is anaerobic                                             |                                     |                                     | Yes                           |
| Radiolysis                       | Radiolysis of the water                                                  |                                     | Uses water – but the amount is determined by the activity of a range of radionuclides associated with the waste |
| Microbial degradation            | Possibly a net user of water                                             |                                     | Limited sink of water for wastes that contain organic material (these are not a major source of carbon-14 bearing gases) |
| Leaching of graphite             | When water is available                                                  |                                     | Leaching of graphite requires, but does not consume water |

A number of these processes that consume water are judged to have limited significance. These are:
• Microbial degradation of organic materials, including small organic molecules that would be formed from the previous hydrolysis of cellulose. Such organic materials are not associated with the main waste groups responsible for the generation of carbon-14 bearing gases.

• Backfill drying. Whereas drying of the encapsulation grout during storage is potentially significant, drying of the backfill is considered to be less important. This is because it is anticipated that it will be installed in relatively large volumes.

• Leaching of graphite. Although gas generation from graphite requires water to be in contact with the graphite, the leaching process does not consume a significant quantity of water. Leaching of graphite is discussed further in Section 8.

From Figure 3, it is seen that radiolysis is a significant source of gas, and therefore will be a potentially significant consumer of water. However, the wastes that are responsible for the generation of carbon-14 bearing gases are not necessarily those that generate radiolytic gases (where a wide range of radionuclides can contribute).

The following subsections focus on three of the important aspects that affect gas generation, namely drying of the encapsulation grout, the quantity of water required to corrode the various metals, and the resaturation of the GDF in the three generic environments.

3.3.2 Drying of encapsulation grouts

One of the important processes that is not included in the gas generation modelling using SMOGG is wasteform drying, i.e. drying of the grout while the packaged waste is stored on the surface or in the GDF prior to backfilling.

Wong et al. [41] and Sun [42] have undertaken experimental measurements of the water saturation of 3:1 PFA / OPC9 and 3:1 BFS / OPC9 grouts as a function of external relative humidity (RH), over a time period of five months. A typical set of results, plotting the change in the degree of water saturation with conditioning at different RH, is shown in Figure 6.

Figure 6 Change in degree of water saturation with conditioning period and relative humidity for PFA grouts (A – left) and BFS grouts (B – right) (from Reference [41])

9 BFS is Blast Furnace Slag, OPC is Ordinary Portland Cement and PFA is Pulverised Fuel Ash.

10 In the figure legend, P refers to PFA, S to BFS, with 4 samples sectioned into 7 sub-samples.
The results show that both grouts were able to maintain a water saturation of almost 100% during the five year period of curing in a high RH environment. When exposed to a lower RH (< 90%), both grouts began to dry out, with the PFA grout drying at a faster rate than the BFS grout. BFS grout conditioned at a particular RH had a significantly higher degree of water saturation than the corresponding PFA grout. At the end of the five month conditioning period, and considering only RH values that are relevant to a waste store (i.e. 55% to 86%), the degree of water saturation ranged:

- Between ~40% and ~80% for the PFA grout; and
- Between ~80% and ~97% for the BFS grout.

It seems that PFA grouts could lose a significant fraction (i.e. up to about half) of their water content during a long period of storage, but BFS grouts would lose rather little of their water content.

3.3.3 Water consumption by corrosion

The amount of water from the encapsulation grout that is available for corrosion will depend on the assumed water content of the grout and on the conditioning factor (the ratio of the conditioned volume (waste plus grout) to the volume of waste). The nature of the coupling between the water content of a waste encapsulation grout and, for example, the corrosion of a packaged waste metal is uncertain. Corrosion scientists have not determined the water content below which corrosion would slow down in the grout. Therefore, an assumption about how much of the water in the grout might be available to take part in the gas generation processes has to be made in the modelling.

The gas generation models assume that the grout has a porosity of about 0.2, and when the metal wastes are packaged this porosity is fully saturated with porewater. From a literature review presented in Reference [15], it appears that this corresponds to about half the amount of evaporable water (i.e. about 20% by volume) which will be present in the grout soon after the metal wastes are packaged, although some of this evaporable water may be lost due to drying of the grout during storage.

The conditioning factor varies between different types of waste. Consideration of the conditioning factors of typical wastes enables the amounts of water available in typical packages to be estimated. Thus the fraction of the water required for complete corrosion that is available from the encapsulation grout can be calculated for different types of waste. Further corrosion will require additional water from the backfill or from the surrounding geosphere. The timescale on which this becomes available will depend on the geological environment and the timing of backfilling.

The ratios of the amounts of water available from the encapsulation grout to the amounts of water required for the different metals to corrode away are shown in Table 10. The waste types can be considered separately as the bulk steel wastes are separate from the main streams containing Magnox and uranium, which in turn are separate from the main aluminium streams. However, Magnox and uranium occur together in certain reactive metal waste streams.

---

11 The gas generation models assume that the grout has a porosity of about 0.2, and when the metal wastes are packaged this porosity is fully saturated with porewater. The water content of grout is higher, but not all the water is considered to be available for corrosion [15].
Table 10  Ratio of the amounts of water available to the amounts of water required for the metal to corrode away\(^\text{12}\)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Fraction of Water Requirement (^1) (–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel</td>
<td>0.53</td>
</tr>
<tr>
<td>Mild Steel</td>
<td>0.53</td>
</tr>
<tr>
<td>Zircaloy</td>
<td>0.71</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.11</td>
</tr>
<tr>
<td>Magnox</td>
<td>0.23</td>
</tr>
<tr>
<td>Uranium</td>
<td>0.17</td>
</tr>
</tbody>
</table>

\textbf{Note}  
\(^1\) This fraction assumes anaerobic corrosion of the metals; some of the metals (i.e. the steels and uranium) will corrode aerobically at first, consuming oxygen (and metal), before they switch to consuming water.

Packages of steels or Zircaloy contain enough pore water initially to ensure the anaerobic corrosion of much of their waste metal inventories. Furthermore, these particular metals are assessed to corrode very slowly, taking more than \(10^5\) years to corrode away completely (see Figure 3 to Figure 5), the initial inventory of water in the packages is sufficient to ensure that the anaerobic corrosion of steels or Zircaloy will persist for several tens of thousands of years post closure, which represents many half-lives of carbon-14.

In contrast, packages of reactive metals will have consumed all of their initial pore water when between 11\% and 23\% of their waste metal inventories have corroded. Because the reactive metals corrode relatively quickly (it takes aluminium until only 30 years after closure, and Magnox around a thousand years after closure to corrode away), it is possible that these packages could exhaust the water before their inventory of carbon-14 has decayed away.

\subsection*{3.3.4 Resaturation}

Once water from the encapsulation grout is exhausted, further water may become available from the backfill and host rock as a result of resaturation. The timescales for this will be different in the three illustrative host rocks being considered.

- **Higher-strength rocks.** These potentially have the shortest resaturation time, depending on the hydraulic conductivity of the host rock. Reference [15] estimates a resaturation time of 1 year for a hydraulic conductivity of \(10^{-9}\) m s\(^{-1}\) and 1,000 years for a hydraulic conductivity of \(10^{-12}\) m s\(^{-1}\). The SMOGG calculations reported earlier use a resaturation time of 5 years. In practice the resaturation time may be significantly longer, depending on the properties of the rock. As the hydrogeological properties of the rock may be spatially variable, the resaturation time may also be spatially variable.

- **Lower-strength sedimentary rocks.** The hydraulic conductivities of these rocks are typically lower than higher-strength rocks, e.g. in the range \(10^{-14} - 10^{-13}\) m s\(^{-1}\) and reference [15] estimates a resaturation time of 10,000 years.

- **Evaporites.** There will be little, if any, water available in these environments, apart from the water in the encapsulation grouts.

\subsection*{3.3.5 Implications for gas generation}

The main conclusions are as follows:

\(^{12}\) No account is taken of corrosion of the container,
There is considerable uncertainty about how much of the water in a waste encapsulation grout will be available to take part in the gas generation processes. In the absence of pertinent experimental data, the gas generation models have assumed that 50% of the evaporable water in the grout (equating to approximately 20% of the grout volume) will be available.

On this basis packages of steels and Zircaloy will contain enough water to ensure corrosion of much of their waste metal inventories, which will carry on over many tens of thousands of years.

Packages of aluminium could dry out during storage, when approximately 10% – 20% of their aluminium inventories will have corroded. Thus the early peak from bulk gas from aluminium in Figure 3 may not occur in drier environments, such as LSSR and evaporite.

Packages of Magnox are likely to contain enough water, even after storage in a ventilated store, for corrosion to persist for several tens of years, and perhaps as much as a hundred and fifty years, post-closure. Thus the high generation rates may not persist for as long as shown on Figure 3 in environments such as LSSR and evaporite.

In a relatively permeable host rock (such as a higher-strength rock with a hydraulic conductivity of \( \sim 10^{-9} \) m s\(^{-1}\)), there will be a large enough flow of groundwater through the GDF to ensure that both the aluminium wastes and the Magnox wastes can corrode away. The corrosion of Magnox is discussed further in Section 10.2.

In a lower-strength sedimentary rock, some water may enter the packages containing aluminium, and then there will be additional corrosion of this metal. There may be additional corrosion of the Magnox wastes as well. The rate of gas generation will depend on the slow flow of groundwater into the GDF and the gradual pressurisation of both the packages and the vaults.

In an evaporite, there will be little post-closure corrosion of the aluminium wastes, and there will be little corrosion of the Magnox wastes when the inventory of water that is associated with them has been consumed.

Table 10 indicates that only part of the water required to corrode the uranium is readily available. However, the uranium is found in small quantities in waste streams containing Magnox, and so further water will be available to allow complete corrosion. This is not expected to reduce significantly the quantity of water available for Magnox corrosion.

The fate of the gas that is generated will depend on the geological environment (this is discussed in Section 5).
4 Gas in the Engineered Barrier System

Once gas is released from wastes, it will enter the surrounding wasteform, potentially leave the container and migrate into the buffer/backfill. These components, together, are known as the engineered barrier system (EBS). There are a number of questions around the behaviour of gas in the EBS, including: does it enter solution or form a free gas phase; does it react with materials within the EBS where it would then be immobilised; and does it migrate through the EBS? The answers to these questions depend on the design of the EBS and the materials included within it.

In order to contain the radionuclides associated with radioactive wastes and to isolate the wastes from the biosphere, geological disposal facilities are designed as multiple barrier systems [43]. A schematic representation of a multiple barrier system is provided in Figure 7. The engineered components of the system (the wasteform, the waste container and the buffer and/or backfill) are termed the engineered barrier system. Illustrative designs for a range of generic host rocks are presented in [44].

This section considers the behaviour of a gas phase in the engineered EBS, which here is understood to comprise the wasteform, the waste container and the surrounding buffer or backfill, as well as the engineered seals. In particular, it addresses in turn the following questions:

- Will the gas generated by the wastes dissolve in groundwater flowing through the GDF, or will a free gas phase form (Section 4.1)?
- Will the gas phase migrate through the EBS to the host rock (Section 4.2)?
- Will all of the carbon dioxide generated by the wastes react with mineral phases (i.e. portlandite and calcium silicate hydrates) in the cementitious backfill to form calcium carbonate (Section 4.3)?
- Will the presence of microbes affect the release of gases from the near field (Section 4.4)?
4.1 Formation of a free gas phase

If sufficient gas is generated then it will be unable to dissolve in the groundwater and a free gas phase will form. The overall generation rates decrease with time, as materials associated with higher rates are exhausted. Simple arguments show that the expected gas generation rates at early times are sufficiently high for a free gas phase to form. However, whether the gas phase is maintained at longer times (over a thousand years after closure) may be a site-specific issue, and may also depend on the nature of the wastes in particular vaults.

A simple argument can be used to determine whether a free gas phase will form.

The rate of bulk gas generation per vault (m$^3$ at STP yr$^{-1}$; see Section 4.1.1) can be compared with the capacity of the groundwater to transport gas in solution away from the vault, where the latter quantity can be estimated from the flow of groundwater through the vault (m$^3$yr$^{-1}$; see Subsection 4.1.2) multiplied by the solubility of the bulk gas at the depth of the GDF (m$^3$ at STP m$^{-3}$; see Subsection 4.1.3).

4.1.1 Rates of bulk gas generation

The calculated rates of bulk gas generation have been summarised in Section 3.2. These calculations use the modelling basis adopted in this project [18].

In the case of Legacy UILW / ULLW, the gas generation model calculates that closure of the GDF will be followed by a short-term peak in the rate of bulk gas generation (i.e. up to 5,000 m$^3$ at STP yr$^{-1}$ per vault$^{13}$ for a period of a few tens of years) due mostly to aluminium corrosion. The peak will be followed by bulk gas generation at a rate of up to 760 m$^3$ at STP yr$^{-1}$ per vault for several hundred years, due mostly to Magnox corrosion. After all of the Magnox has been consumed, the rate of bulk gas generation will drop by an order of magnitude, and then will continue to decline slowly to about 20 m$^3$ at STP yr$^{-1}$ per vault by 10,000 A.D.

In the case of Legacy SILW / SLLW, aluminium corrosion will generate bulk gas at a rate of up to 190 m$^3$ at STP yr$^{-1}$ per vault for a few tens of years post-closure, depending on the rate of resaturation. After all of the aluminium has been consumed, the rate of bulk gas generation will drop by more than an order of magnitude to about 10 m$^3$ at STP yr$^{-1}$ per vault, due mostly to Magnox corrosion. Several hundred years later, the rate will drop again when all of the Magnox has been consumed, to about 5 m$^3$ at STP yr$^{-1}$ per vault due mostly to steel corrosion. Thereafter gas generation will continue at this rate for a very long time.

In the case of NNB UILW, closure will be followed by a short-term peak in the rate of bulk gas generation (i.e. up to 13 m$^3$ at STP yr$^{-1}$ per vault) due mostly to radiolysis. The rate of bulk gas generation will fall to about 1 m$^3$ at STP yr$^{-1}$ per vault at a thousand years post-closure, as the radioactive inventory decays, and then will decline more slowly.

As discussed in Section 3.3, the rates of gas generation could be reduced in certain environments with longer resaturation times once the initial water in the encapsulation grout is consumed; this is likely to be the case for evaporites and lower-strength-sedimentary rocks and may be the case for higher-strength rocks. In addition the rates include gas generation from microbial degradation of cellulose, which may not occur at higher pH. The rates given above would therefore be upper bounds.

$^{13}$ Note that here (and subsequently) the gas generation rate shown in Figure 3 has been scaled by the number of vaults to give a gas generation rate per vault, rather than a total rate.
4.1.2 Flow of groundwater through a vault

The flow of groundwater $(Q)$ through a vault will be given by:

$$Q = AKiY$$

where $A$ is the area of the vault normal to the flow of the groundwater $(m^2)$, $K$ is the hydraulic conductivity of the host rock $(m \text{ s}^{-1})$, $i$ is the head gradient, and $Y$ is a flow-enhancement factor, which accounts for the possible focusing of flow into the GDF. Thus the flow of groundwater through a vault will depend on properties of the host rock.

In the absence of a site, a range of rocks are being considered as potential host rocks for a geological disposal facility. These are higher-strength rocks, lower-strength sedimentary rocks and evaporites.

Of these potential host rocks, the more permeable (and therefore those with the highest groundwater flow) are higher-strength rocks. In particular:

- The hydraulic conductivity of a higher-strength host rock is likely to be in the range $10^{-12}$ – $10^{-9} \text{ m s}^{-1}$ (over length scales of tens of metres) [45]. (For comparison, the hydraulic conductivities of clays are typically less than $10^{-12} \text{ m s}^{-1}$.)
- The head gradient might be in the range from zero to a few percent [45], determined, to some degree, by the topography of the surface.

Assuming values of the hydraulic conductivity ($10^{-9} \text{ m s}^{-1}$) and head gradient (0.02) towards the upper ends of the ranges given above, an estimate of the specific discharge in the host rock is given by $2 \times 10^{-11} \text{ m s}^{-1}$ (or $6 \times 10^{-4} \text{ m yr}^{-1}$; the 2010 generic DSSC [46] assumed that this is the central value for the specific discharge in a higher-strength host rock, with an order of magnitude uncertainty).

The vaults, in general, could have a markedly higher hydraulic conductivity than the surrounding rock, because the backfill will be designed to provide chemical conditioning rather than to have a low hydraulic conductivity. The presence of a vault leads to a focusing of the flow into the vault. The degree of flow enhancement will depend on both the geometry of the vault and the hydraulic conductivity contrast. This is illustrated in Figure 8.

Generic GDF designs have been developed for the various potential host rocks [44]. In the case of a higher-strength rock the illustrative design assumes that the vaults for ILW / LLW will be ~300m long, ~16m wide, and between ~15m and ~16m high.

The effect of a vault on the specific discharge can be estimated from analytical results [47] that assume simplified representations of the GDF layout and of the flow around the GDF. It turns out that the various components of the specific discharge inside a vault will be equal to the values that they would have in the absence of the GDF multiplied by ‘flow enhancement factors’. The flow enhancement factors \(^{14}\) will be [15]:

- Almost two orders of magnitude for horizontal flow parallel to the axes of the vaults; and
- Approximately two for flows in the orthogonal directions.

Combining all of the above factors, it is possible to compute that the groundwater flow through a vault could be as much as 16 $\text{m}^3\text{yr}^{-1}$ for flow parallel to the axes of the vaults, and 6 $\text{m}^3\text{yr}^{-1}$ for the orthogonal directions. These flows are for a relatively permeable GDF host rock, with a hydraulic conductivity of $10^{-9} \text{ m s}^{-1}$, and are directly proportional to the hydraulic conductivity of the host rock.

\(^{14}\) This factor accounts for both the enhancement of flow arising from the presence of the GDF and further focusing because the GDF is made up of a number of vaults separated by low permeability rock.
4.1.3 Solubility of the bulk gas

In order to estimate the capacity of the groundwater to transport gas in solution away from the vault, the flow of groundwater through the vault (m$^3$ yr$^{-1}$) has to be multiplied by the solubility of the bulk gas (m$^3$ at STP m$^{-3}$).

In all of the vaults throughout the post-closure period, the dominant bulk gas generating process will be one or more of: corrosion of aluminium, corrosion of Magnox, anaerobic corrosion of steels, and radiolysis of pore water. These processes will generate hydrogen. Other processes that will provide minor contributions to the bulk gas generation may generate other gases. Therefore, much of the bulk gas will be hydrogen. For simplicity, the solubility of this particular gas is only considered.

To a very good approximation, the solubility of a gas in water is proportional to the partial pressure of the gas, $p_g$, that is (Henry’s law):

$$c = H p_g$$

where $c$ is the concentration of dissolved gas (m$^3$ at STP m$^{-3}$), and $H$ is Henry’s constant (m$^3$ at STP m$^{-3}$Pa$^{-1}$).

Actually, Henry’s ‘constant’ varies with both temperature and salinity (the ‘salting out’ effect), decreasing as the temperature and salinity increase. In the calculation reported below, it is assumed that the temperature at the repository is 35 °C and the salinity is zero. For these conditions, the Henry’s constant for hydrogen is $1.7 \times 10^{-7}$ m$^3$ at STP m$^{-3}$Pa$^{-1}$ [48, 49].
A gas phase will start to form when the partial pressure of the gas becomes comparable to the pressure of the groundwater, which to a good approximation can be taken to mean that a gas phase will start to form when:

\[ p_g = \rho_l g z \]

where \( \rho_l \) is the density of the groundwater (kg m\(^{-3}\)), and \( g \) is the acceleration due to gravity with a standard value of 9.81 m s\(^{-2}\), and \( z \) is the depth.

It follows that the solubility of hydrogen in the groundwater will vary linearly with depth, and will be: 0.33 m\(^3\) at STP m\(^{-3}\) at a depth of 200m, increasing to 1.06 m\(^3\) at STP m\(^{-3}\) at a depth of 650m, and 1.63 m\(^3\) at STP m\(^{-3}\) at a depth of 1,000m.

4.1.4 Conclusion

In a case with a large amount of dissolution, i.e.:

- A host rock with a hydraulic conductivity of \( 10^{-9} \) m s\(^{-1}\);
- A GDF at a depth of 1,000m; and
- Groundwater flow parallel to the axes of the vaults;

about 26 m\(^3\) at STP of hydrogen could dissolve in the groundwater that will be flowing through a vault.

Referring back to Section 4.1.1, the conclusion is that a gas phase certainly will form at early times in the vaults containing Legacy ILW / LLW, and is likely to persist for many thousands of years in all but the most permeable of the potential host rocks (i.e. host rocks with a hydraulic conductivity of the order of \( 10^{-9} \) m s\(^{-1}\), or larger).

In the long term, once the reactive metals (i.e. aluminium and Magnox) have been consumed and the short-lived radionuclides have decayed away, corrosion of steel will become the dominant source of bulk gas in the vaults containing Legacy SILW / SLLW or NNB UILW. This process will generate hydrogen at a rate that is in the range from about 1 m\(^3\) at STP yr\(^{-1}\) per vault (NNB UILW) to about 5 m\(^3\) at STP yr\(^{-1}\) per vault (Legacy SILW / SLLW). All of this gas could dissolve in the groundwater that will be flowing through a vault, even in a slightly less permeable host rock than has been assumed here, or at a shallower depth. This conclusion is site specific, and depends, in particular, on the hydraulic conductivity of the potential host rock and the depth of the GDF.

4.2 Gas migration in the EBS

Gas will be generated in a GDF for intermediate-level radioactive waste by a number of mechanisms. If, as expected, a bulk gas phase forms, then it is better to allow it to escape from the packages, so that there is no build-up of pressure. For this reason, most ILW packages are vented. Although the characteristics of any backfill have not been finalised, it is expected that it will be designed to allow gas to move through it.

Wherever a free gas phase has formed, the pressure associated with it will continue to increase due to ongoing gas generation. (Gas generation will occur mostly within the waste packages, but anaerobic corrosion of the outer surfaces of steel containers will contribute as well.)

Eventually, the pressure of the free gas phase will reach a threshold value, when it will be able to migrate away from its source and through the surrounding backfill. Gas migration can be described by the multiphase extension of Darcy’s law [50], and will be facilitated by:
• The inclusion of vents in some waste packages (it is expected that ILW which could generate gas will be placed in vented containers to mitigate the possibility of over-pressurisation of the container; also see Section 10.2.3); and

• In the case of higher-strength or lower-strength sedimentary host rocks, the use of a cement backfill with a relatively high hydraulic conductivity.

Management of the gas pressure will be an important design consideration for a GDF.

The illustrative design for a higher-strength rock [44] assumes that the vaults will be backfilled using NRVB, which will have a relatively high hydraulic conductivity of about $10^{-9}$ m s$^{-1}$ [51]. For this particular design, two-phase flow calculations (e.g. package-scale simulations for this project [14]) have shown that gas from a waste package will be able to migrate through the backfill at an excess gas pressure (i.e. gas pressure minus the in situ hydrostatic pressure) of up to a few atmospheres provided the rate of gas generation per package is less than 10 m$^3$ at STP yr$^{-1}$.

Once the gas phase has reached the vault boundary, it will migrate easily into the fractures, first in the Excavation Disturbed Zone (EDZ), assuming that the fractures have not been grouted, and then in the host rock. That is because the fractures typically will have apertures of the order of 1 μm to 100 μm, and therefore from the Young-Laplace equation [52], only a small capillary pressure (i.e. the pressure difference between the gas phase and the liquid phase) will be needed before the gas phase can migrate away from the vault into the surrounding host rock.

Low permeability seals, comprising compacted bentonite retained by a concrete structure [44], will isolate each vault from the access tunnels, and the remainder of the GDF infrastructure.

The illustrative design for ILW / LLW in a lower-strength sedimentary rock [44] assumes that the backfill will be a cement-based material. If the backfill has a similar hydraulic conductivity to the NRVB, then, as was the case for a higher-strength rock, the gas phase will be able to migrate relatively easily within a vault.

The difference from a higher-strength rock is the size of the pores in the host rock. In a lower-strength sedimentary rock, the pores will be very small, and so a large capillary pressure will be needed before the gas phase can start to migrate into the surrounding host rock.

The mechanisms by which the gas will migrate into the host rock, arranged in increasing order according to the pressure at which they become significant, are considered to be [53, 54]:

• Diffusion of gas in solution;

• Two-phase flow;

• Porosity dilation and localised micro-fissuring; and eventually

• If the pressure were to continue increasing and exceed the strength of the rock, fracturing.

For disposal concepts in a lower-strength sedimentary rock, one aim of the design will be to ensure that the peak gas pressure in the GDF does not exceed the strength of the host rock, and thus avoid fracturing the rock. It may be necessary to develop an engineering solution to this problem. For example, Nagra are considering the use of an Engineered Gas Transport System in their disposal concept [55].

Seals, possibly constructed from compacted bentonite and concrete [44], will isolate each vault from the remainder of the GDF infrastructure.
Because the host rock will provide a significant obstacle to gas migration, the EDZ, which is likely to comprise stress relief fractures in the rock, could be an important pathway for gas. The access tunnels and shafts, as well as the EDZ around those features, could provide a preferential pathway for groundwater flow and gas migration; that is because they will be more permeable, and have a lower gas entry pressure, than the undisturbed rock. However, the host rock around the GDF will creep slowly and the fractures in the EDZ may be healed as the rock converges under the lithostatic pressure.

Lastly, the illustrative design for an evaporite [44] assumes that the waste packages will be emplaced in open vaults. Understanding from the German radioactive waste management programme [56] suggests that:

- Wastes will continue to generate gas post-closure from water in the grout, and therefore the gas pressure within a vault will increase.
- Simultaneously with gas production, rock convergence will occur.
- If the gas pressure within a vault were to continue to increase, and approach, or eventually exceed, the minimum principal stress in the host rock, then the following two processes might become important:
  - The salt will become permeable leading to gas infiltration;
  - Because there is no limit on creep in salt, the void space within the GDF will increase until there is equilibrium between the rate of gas production and the (negative) rate of rock convergence.

The first process (‘gas infiltration’) is considered the more likely to occur, and will result in a limited flow of gas into the salt [56]. A zone of gas pressurised rock will develop (i.e. gas will be stored in the salt matrix, which is similar to many observations that have been made in the field [56]).

### 4.3 Carbonation

A number of the disposal concepts for ILW propose the use of cementitious materials. Grout is used in many waste packages, and a cementitious material has been identified as a candidate vault backfill in some geological environments. Cementitious materials react with carbon dioxide. There is a substantial body of evidence supporting this view that carbonation will occur. The wastes that will contain significant amounts of carbon-14 (i.e. graphite, steels and reactive metals) are expected to generate only small amounts of carbon dioxide compared with the carbonation capacities of the cement materials that will be present in the GDF. Therefore, it is reasonable to assume that the carbonation reactions will occur, and any carbon-14 bearing carbon dioxide that is generated will be immobilised as solid carbonate minerals.

In GDF concepts that use large quantities of cementitious materials, either for construction or as a backfill, there is potential for species such as $^{14}$CO$_2$, H$^{14}$CO$_3^-$ and $^{14}$CO$_3^{2-}$ to react with dissolved calcium and precipitate carbonate minerals (such as calcite). These carbonation reactions could immobilise any $^{14}$CO$_2$ that is generated as solid carbonate minerals.

The kinetics of the carbonation reactions are controlled by a number of distinct timescales, of which the longest is thought to be of the order of $10^3$s [57]. Thus, the rate-limiting step is generally the transport of CO$_2$ through the cement matrix, rather than the chemical reaction between CO$_2$ and calcium. This is supported by experimental observations which show sharp fronts separating carbonated from un-carbonated cement.

The evidence for cement carbonation has been reviewed in relation to both cement-based radioactive waste repositories, and also borehole cements used in CO$_2$-rich environments.
environments [15]. Of most relevance, the British Geological Survey (BGS), within the NDA-supported EC project FORGE, has carried out a number of laboratory tests that reacted a candidate cement backfill (i.e. Nirex Reference Vault Backfill; NRVB) with carbon dioxide under different conditions [58]. Also, the National Nuclear Laboratory, in work for RWM, has performed long-term, low-pressure carbonation tests on larger concrete samples [59].

This work shows that carbonation of the outer surfaces of the cement is initially rapid, with uptake of carbon dioxide into the cement creating a denser, lower permeability zone. Carbonation appears more extensive with free-phase carbon dioxide (because it can access / enter the cement pores more easily), but dissolved carbon dioxide produces a far lower permeability alteration zone. Laboratory carbonation tests involving flow through the matrix of intact NRVB showed that the samples retained some permeability, even after complete carbonation. This indicated that carbon dioxide would still be able to migrate through the carbonated zone to un-reacted NRVB, and the backfill could dissipate excess gas pressure emanating from the vents in waste packages (i.e. mechanical disruption of the NRVB, and consequently the potential for gas transport along newly formed cracks would appear to be unlikely). However, there is a concern that if there is a network of cracks these could become armoured as a result of reduction in permeability.

Figure 9  Partially carbonated cement sample showing zones having different degrees of carbonation together with associated reaction fronts (from [58]; © NERC 2013)

Evidence for carbonation is provided by work from a natural analogue at the Maqarin site in northern Jordan [60, 61, 62]. At this site, the groundwater flowing into the Analogue Cement Zone (ACZ) contains bicarbonate ions (HCO_3^-; or dissolved CO_2), which are replaced with hydroxide ions (OH^-) in the groundwater flowing out. This means that all of the carbon dioxide in the groundwater that flows into the ACZ is removed as a result of carbonation reactions that occur in the ACZ.

The ‘carbonation capacities’ of the various cement materials that might be present in a GDF have been determined. Measurements of the carbonation capacity of NRVB are typically in the range from 5,000 to 6,000 mol m^-3 (e.g. [59]), while theoretical estimates suggest that the carbonation capacities of 3:1 BFS / OPC grout and 3:1 PFA / OPC grout are about double and about half that of NRVB respectively [42].

These carbonation capacities can be compared with the ‘reference case’ calculation of the total amount of carbon dioxide that will be generated by 100,000 A.D.:

- The seventeen vaults of Legacy UILW / ULLW will generate 1.4 \times 10^6 m^3 at STP (or 6.2 \times 10^7 mol); and
- The five vaults of Legacy SILW / SLLW will generate 4.7 \times 10^3 m^3 at STP (or 2.1 \times 10^5 mol).
Considering the illustrative designs for a GDF in either a higher-strength rock or a lower-strength sedimentary rock [44], it follows that only 1% of the total volume of NRVB (i.e. about 1.3 x 10^6 m^3; [44]) would be sufficient to react with all of this carbon dioxide. The quantities of carbon dioxide listed above come from the possible microbial degradation of cellulose, and not from the wastes that are of especial interest to this project. Focusing on the latter wastes (i.e. graphite, steels and reactive metals), it is possible to refine the argument that the carbonation reactions in a GDF will immobilise any carbon dioxide (including carbon-14 bearing carbon dioxide) that is generated.

First, based on the understanding of the mechanisms by which carbon will be released from graphite (see Reference [12]), there will be a small release of carbon dioxide from the graphite surfaces. The only other source of gas that will be associated with a package of graphite wastes is slow corrosion of its steel container. Therefore, the gas phase inside the package will migrate only slowly, and there will be sufficient time for any carbon dioxide to react with the encapsulation grout.

Next, any steels present in the GDF will contain some carbon. Carbon will be released (congruently) from these steels as they corrode. Because steels corrode slowly under the alkaline, anaerobic conditions that will prevail in the GDF, only a small fraction of their carbon will be released before the carbon-14 decays. In a similar way to graphite, the flows of gas out of a package containing irradiated steel wastes will be very slow, and therefore, even if any carbon dioxide were to form, it should have time to react with the encapsulation grout.

Lastly, the reactive metals of interest to this project are Magnox alloy and uranium metal. These metals would have contained only trace amounts of stable carbon at the time of their manufacture. Afterwards, some carbon-14 could have been formed in the metals as a result of thermal neutron activation of nitrogen-14 impurities. Carbonation reactions in the encapsulation grout should be able to remove the small amounts of carbon dioxide that might be released from the reactive metals.

In conclusion, it seems reasonable to assume that the carbonation reactions will occur for the above types of waste, and therefore any carbon-14 bearing carbon dioxide that is generated will be immobilised as solid carbonate minerals.

4.4 Microbes in the EBS

A number of the gases that are generated have the potential to take part in microbially mediated reactions. However, the evidence suggests that these do not occur at very high pH, and so microbially mediated reactions will be restricted to niches in the EBS where the pH is lower. Carbon-14 is not associated with wastes (e.g. cellulose) where such niches would be found.

The gaseous species of interest fall into two groups: firstly carbon-14 bearing gases such as 14CH4, 14CO and 14CO2, and secondly non-radioactive (bulk) gases (H2, CH4 and CO2) which may have an impact on gaseous transport. These gases have the ability to take part in a range of microbially mediated redox reactions. Whether or not these processes are active depends on the prevailing physical/geochemical environment (e.g. pH, Eh, and the activity of water).

The expected evolution of the near field, and the associated alkaline disturbed zone generated by the ingress of groundwater, will have a profound impact on the associated

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15 Carbonation could reduce the pH buffering capacity of the cement. This would make it more likely that niches could form with a relatively “low” pH, which would be more favourable for microbial activity.
microbial activity. The predicted pH (>12.4 for about 100,000 years [63]) is above that normally associated with even the most extreme alkaliphiles. Although the upper pH limit for microbial activity is a topic of debate [64], generally pH 12.0 is regarded as an upper limit (see Figure 10) due to the inability of bacteria to maintain the required internal pH of 10.0.

Figure 10 Relationship of growth rate and pH for three alkaliphilic sulphate reducing bacteria isolates [65]

Under the anaerobic conditions likely to be prevalent in a GDF, many of the bacteria present may be able to reduce the pH of their immediate environment. (This behaviour is commonly seen in high pH microbiological experiments [66, 67, 68], where the pH is not actively maintained.)

The potential for microbial activity in the near field to influence the transport of carbon-14 bearing gases was reviewed [15], and it was concluded that the conditions likely to be prevalent in a homogeneous near field would appear to be too aggressive for widespread microbial activity, primarily due to the ambient pH. A more credible scenario is a mainly homogenous near field, with pockets of microbial activity arising from un-grouted wastes and other areas of lower pH. The wastes which are most likely to support microbial activity (such as, for example, PCM wastes containing cellulose) will not be important sources of carbon-14.

Therefore, microbial activity:

- Is unlikely to affect the rate of generation of carbon-14 bearing gases; but
- Could contribute to the generation of bulk gas (e.g. methane and carbon dioxide) from the degradation of organic material in the GDF.
5 Gas in the Geosphere

Gases that migrate through the EBS may enter the surrounding geological environment (the geosphere).

Gas migration is site-specific, depending both on the host rock and the features of any overlying strata. Specific features may have the ability to trap or dissolve some or all of the gas generated, affecting whether or not it is able to reach the biosphere.

The geological environment also affects the flow of water into a GDF; which could limit the rate of gas generation at longer times.

This section links back to the fifth point in our AND approach (i.e. the gases must migrate through the overlying geological environment; see Figure 2).

The process of gas migration is described in Section 5.1, and then is illustrated using generic geological environments in Section 5.2. Modelling approaches are outlined in Section 5.3. The potential significance of microbes in the geosphere is discussed in Section 5.4, and gas dissolution is considered in Section 5.5. The final element to be addressed is the release of any carbon-14 to the biosphere (either as a gas or in solution), and this is found in Section 5.6.

5.1 Gas migration

Gas migration is a site-specific issue. There are a number of different processes that are relevant to gas migration, and there are a number of features that may be present at a site that could affect the way gases migrate or is trapped or dissolved. The properties of the host rock and overlying geological strata may be significant, as may be the properties of the seals used in vaults, access tunnels and shafts.

5.1.1 Processes affecting gas migration

Gas that is formed in a GDF may dissolve in water, undergo chemical reactions or form a free gas phase. The amount of free gas and its migration through the EBS and the geosphere depend strongly on site-specific conditions. Two important aspects are the amount of water available to dissolve the gas and the permeability and porosity of the host rock. Dissolved gas will undergo advection along with the groundwater and diffusion due to concentration gradients in the groundwater. If the solubility limit of any gas were exceeded, a separate gas phase would form. This gas phase would displace groundwater in the pores under the influence of capillary, gravitational and viscous forces [6].

The principal flow and transport mechanisms which will determine how the carbon-14 bearing gases migrate are:

- Fluid (i.e. both gas and groundwater) flow in response to pressure gradients;
- Buoyancy-driven flow;
- Dissolution into the groundwater;
- Diffusion; and
- Dispersion, and fingering\(^\text{16}\), caused by heterogeneities in the formation.

\(^{16}\) Fingering can also be caused by the contrast in mobility between the gas and the groundwater. This ‘viscous’ fingering will occur when the surface tension acting across the interface between the gas phase and the groundwater (i.e. the capillary pressure) is small compared to the viscous forces, and therefore is more likely to be observed in porous media with fracture-dominated permeability. However, because the gas phase will migrate relatively easily through a host rock with fractures, the precise details of how the gas migrates through the fractures are unimportant.
Once a distinct gas phase has formed, any further gas generation within a GDF will increase the pressure there, creating a pressure gradient that will drive fluid flow away from the GDF (potentially reducing the amount of water available for further gas generation). This would be an important mechanism in a lower-strength sedimentary rock (e.g. clay), because clays have low permeability and very small pores, and therefore, from the Young-Laplace equation [52], a large capillary pressure\(^{17}\) will be needed before the gas phase can migrate away from the vault into the surrounding host rock.

Buoyancy-driven flow occurs when the lower density of a gas phase compared to the groundwater causes the gas to migrate upwards until either it reaches the surface or it encounters a low-permeability formation, where it would accumulate at high points.

If gases come into contact with water that is undersaturated with respect to dissolved gas, then the gases will dissolve. The significance of this mechanism depends on the solubility of the gas, the velocity of the gas phase, and the contact area between the gas phase and the water.

If fluid flow away from the GDF is small, then diffusion will be the main transport mechanism for a gas. Diffusion through the groundwater could be an important transport mechanism in settings (e.g. a lower-strength sedimentary rock) where the permeability of the host rock is very low.

Heterogeneities within the permeable geosphere could cause a gas plume to spread out (disperse) as it migrates upwards.

### 5.1.2 Pathways

Gas will migrate through:

- The rock matrix;
- Fractures and faults; or
- Man-made features, such as the EDZ around a GDF or unsealed boreholes.

As discussed above, gas migration depends on the porosity and permeability of the rock. Gas migration through the low-permeability rock matrix is likely to be very slow.

In some types of rocks, fractures will affect the flow of gas through the geosphere significantly, particularly if they are found in low-permeability layers which otherwise would act as seals. For example, in the Tommeliten area of the North Sea, cracks in buried (low-permeability) marl allow methane to migrate to overlying higher-permeability sediments and eventually into the sea [69]. The ability of fractures and faults to transmit gas depends on the geology, and whether the discontinuities are sealed or allow fluid flow.

Gas migration through fault systems has been reported in the natural world at sites such as CO\(_2\) seeps at Latera in Italy [70], CO\(_2\) seeps at Pantelleria Island, Sicily, Italy [71] and submarine methane seepage on the Hikurangi subduction zone in New Zealand [72]. These particular locations, where gas migration up faults has been observed, are in tectonically active regions, and so may not provide a good analogue to faults in the UK. The oil and gas fields of the North Sea are a closer analogue to the onshore geology of the UK, and here about 70% of reservoirs are found in fault block traps, where oil and / or gas has accumulated against impermeable faults [73].

In addition, a range of onshore geological settings have been considered for natural gas storage [74, 75]. Faulting is present in many of the localities discussed, with some faults having indistinguishable hydraulic properties from the surrounding rock (e.g. the Cheshire Basin), but other fault systems are thought to seal less well (e.g. the Wessex Basin). Many

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\(^{17}\) Capillary pressure is the difference in pressure across the interface between two immiscible fluids. In this context, it is the difference in pressure between the gas phase and the liquid phase.
of the fault systems either do not reach the ground surface, or juxtapose clay against clay, sealing the fault. In both cases, the faults may provide a preferential pathway for gas through some of the geosphere, but not through the whole of the geosphere. Thus not all faulted systems will result in rapid migration of gas to the biosphere.

In the environment surrounding a GDF it will also be necessary to consider whether any of the features introduced by the facility, such as the engineered disturbed zone and access tunnels, could affect gas migration.

For natural gas storage (as well as for CO₂ sequestration), boreholes have been identified as a possible route for gases to leave the store and migrate towards the ground surface [75]. The leakage could be due to poor sealing of the borehole, seal degradation or failure, casing failure, the presence of unidentified boreholes with poor sealing or inadvertent drilling into the gas storage complex. Gas migrating up a borehole might reach the ground surface as a localised release, or could leave the borehole and disperse within any transmissive formations that are intercepted by the borehole.

In the case of radioactive waste disposal in a lower-strength sedimentary rock, managing gas pressures in the GDF may be important, because of the high gas entry pressure (e.g. [55]). In particular, research is considering the use of sand / bentonite seals, which would allow the passage of gas, but not of water. While such seals would allow gas to migrate upwards along the access tunnels, and thereby mitigate pressurisation of the GDF, they might introduce challenges for managing the release of carbon-14 bearing gases. However, models of gas migrating away from an underground disposal facility for the Canadian waste management organisation (NWMO) have shown that if a gas phase were to migrate up along the access shaft, the gas would leave the shaft at a shallower, permeable formation [76].

5.1.3 Barriers

In some geological environments, there may be features, such as cap rocks or gas traps, that could trap gases migrating through the geosphere, and thereby delay or prevent their release to the biosphere.

Several trapping mechanisms are simply the result of the geometry of the geological sequence (as shown in Figure 11), and a common way to search for natural gas in the subsurface is to use seismic exploration to identify the geological features that are known to trap gas. In the CO₂ storage industry, the security of the trapping mechanism will be under close scrutiny, and so a CO₂ storage project is unlikely to rely on a single trapping mechanism, rather using arguments about a range of mechanisms (which might include both geological structures and processes that could slow the transport or fix CO₂ in the subsurface).

(a) Cap rock

For natural gas reservoirs, the cap rock (or seal) typically is a thick and laterally continuous layer of very low permeability rock, which has a very high gas entry pressure. If the gas entry pressure is sufficiently high, gas cannot enter the pore space and is trapped beneath the low permeability rock. The most common cap rock lithologies over commercial petroleum reservoirs are shales and evaporites (mainly halite) [74].

In reality, cap rocks are unlikely to act as perfect seals, some failing due to capillary leakage (i.e. some gas gets into the pore space) and others failing due to fracturing [77]. For this reason, in CO₂ storage, multiple layers of low permeability are sought, and the thicker the layers, the slower the progress of the gas through the layers, giving more time for dissolution (and, in the case of radionuclides, radioactive decay). While cap rocks may not be perfect seals, many have been good enough to enable large accumulations of gas (and oil) to build up over millions of years.
A good cap rock is not sufficient to prevent the migration of buoyant gas, as the gas could migrate laterally along the base of the cap rock. The gas could migrate over kilometres, until it encounters more transmissive structures that allow vertical migration. Therefore, successful gas traps usually include a structural component that focuses the gas flow to one location.

**Figure 11 Schematic showing the three basic examples of structural trap (i.e. the anticline trap and the fault trap) and a stratigraphic trap**

**(b) Structural traps**

Structural traps are key features that can be mapped using reflection seismology and used to identify possible hydrocarbon reserves. Structural traps are formed by processes such as faulting and folding, forming geometries into which gas can flow, but from which the gas is unlikely to leave. Examples include anticlines and fault traps, (see Figure 11). Fault traps may prevent gas migration because the fault itself is very impermeable, or because the reservoir layer is juxtaposed against a low-permeability layer (as in Figure 11).

In the North Sea, about 70% of reservoirs are found in faulted traps [73], and anticline traps are also common (e.g. the anticlinal domes of the Forbes and Esmond fields [78, 79]. The flank of a salt dome can also form a structural trap; they are common places to find gas in the USA (e.g. the Louisiana Salt Domes [80]).

**(c) Stratigraphic traps**

Stratigraphic traps arise from the geometry of the original deposition of the sediments, instead of from later movement, as in the case of structural traps. Stratigraphic traps can be caused by high permeability units pinching out, or eroding to form an unconformity.

**(d) Residual and chemical trapping**

As gas migrates through the pores in a rock, a small amount of gas may be trapped due to capillary forces. This is known as residual trapping [81, 82]. Once the gas is immobilised in the pore space, there is more time for the gas to dissolve in the formation water. While
the degree of residual trapping is formation specific, Holtz [83] has demonstrated that residual gas (CO$_2$) saturations may be as high as 15-25%.

Hydrogen will be the major constituent of the gases released from a GDF. There may be a small amount of CO$_2$ present, and over long timescales, if the correct chemistry is present, CO$_2$ could be taken up into minerals that precipitate in the pore space. However, because hydrogen is much less reactive than CO$_2$, mineral precipitation will not be a significant process for the migration of the bulk gas.

5.2 Illustrative geological environments

The programme to develop a GDF is in a generic phase; currently no sites have been identified or selected.

Gas migration will be influenced by both the host rock and the overlying geological environment. Three broad classes of rock that potentially could host a GDF are being considered, and can be used to illustrate the range of behaviours that the gas could exhibit as it migrates.

For the time being, given the absence of a site, and because the way in which gas will migrate through the geosphere is site specific, it is helpful to consider generic geological environments. These can be used to illustrate the range of behaviours that the gas could exhibit as it migrates.

Host rocks that are being considered for disposal of radioactive waste include:

- Higher-strength rocks;
- Lower-strength sedimentary rocks; and
- Evaporites.

Each of these host rocks could be combined with various overlying rock strata.

Previous work [84] has considered gas migration in a number of generic geological environments. Adaptations of these environments are described below, and are used to explain the characteristics of gas migration.

5.2.1 Higher-strength rock

Examples of this environment include basement rocks, which could be granite or high-grade meta-sediments (i.e. sedimentary rocks that have been altered by relatively high temperatures and pressures). Higher-strength rocks tend to be fractured and the majority of gas migration is through fractures. Gas will migrate upwards on a timescale that is short in comparison with the half-life of carbon-14.

Depending on features in the host rock and overlying formations:

- If there are no features that delay or trap the gas, then buoyancy and dispersion will be the key processes affecting the migration.
- If the higher-strength rock is overlain by a low permeability sedimentary rock, then the gas will accumulate beneath this formation, and may spread out. If the low permeability formation acts as a cap rock, then the gas could be trapped for a long time (i.e. sufficient for the carbon-14 to decay).
- If a transmissive feature (e.g. an open fault, which allows more vertical movement) is present, then that could provide a more focused pathway for the gas up to the ground surface.
- If a near-surface aquifer is present, where there is a relatively large flow of groundwater, then all of the gas could dissolve in its groundwater.
5.2.2 Lower-strength sedimentary rock

Differences from the case of a higher-strength host rock include:

- The hydraulic conductivity of the host rock. The hydraulic conductivity will be low in a lower-strength sedimentary rock, and therefore larger pressures would be needed for the same flow.

- The size of the pores in the host rock [6]. In a lower-strength sedimentary rock, the pores will be very small, and so a large capillary pressure will be needed before the gas phase can start to migrate into the surrounding host rock.

- The porosity of the host rock [6]. The porosity will be higher in a lower-strength sedimentary rock, and therefore there will be more groundwater present into which gases can dissolve.

- The resaturation time. This time may be considerable and water ingress may be further reduced or prevented because of pressurisation within the GDF.

As a consequence of these differences, much higher pressures will be required before a gas phase from the GDF can migrate into the surrounding rock, and then the gas will move only slowly through the host rock. Predictions of the time to cross the host rock are typically several thousand years [54, 55].

Because of the high gas entry pressure, if all the gas generated is unable to dissolve in groundwater, it may not be possible for a free gas phase to migrate from a GDF sufficiently quickly to relieve the build up of pressure. Gas pressure could be relieved by micro-fissuring which may then self-seal [85]; however, it may be appropriate to actively manage gas pressures in the GDF [54, 55]. For example, Nagra is researching the use of gas-permeable seals (manufactured from sand / bentonite, which is relatively permeable to gas, but not water, when partially saturated). The use of such seals would allow some of the gas to migrate away from the vaults along the access tunnels, but might introduce challenges for managing the release of carbon-14 bearing gases. For example, the GDF would have to be designed so that the radioactive gases either remain trapped within the access tunnels for a long time, or dissolve into the groundwater of an overlying aquifer. Gas might also migrate through the more permeable EDZ surrounding the excavation, and this would have to be considered in developing the conceptual design.

5.2.3 Evaporite

The illustrative design for an evaporite [44] assumes that the waste packages will be emplaced in open vaults.

As discussed in Section 4.2, the rock salt will be gas-tight, because of high gas entry pressures. The wastes (which will contain some pore water at the time of their emplacement) will generate gas, and therefore the gas pressure within a vault will increase. Using the modelling basis adopted in this report, the cumulative amount of gas formed is calculated\(^{18}\) to be 2.6 \(10^7\) m\(^3\) at STP at 50,000 A.D. Converting this to a volume at the \textit{in situ} pressure, assumed to be about 65 bar [44], the physical volume of gas generated will be 4.0 \(10^5\) m\(^3\). This volume of gas would be comparable to the initial void volume within the vaults at the time of facility closure. The actual volume of gas generated in an evaporate environment could be significantly less than this because only water present within waste packages will be available for gas generation and some packages may have dried out.

Concurrently with gas production, rock convergence (creep) will occur. The pressures required for gas entry to the host rock may be relatively high, for example Evans [74] notes that typical bedded evaporites of monomineralic composition have entry pressures greater

\(^{18}\) The cumulative amount of gas was computed by integrating the rates of gas generation shown in Figure 3, Figure 4 and Figure 5 up to 50,000 A.D., and then summing the results.
than 3000 psi and impure evaporite beds have typical entry pressures greater than 1000 psi (equivalent to approximately >20 MPa and >7 MPa respectively). These values are similar or greater than entry pressures of 4 to 5 MPa for undisturbed Callovo-Oxfordian argillites [54] and 5 MPa for Opalinus clay [53] and gas migration in evaporites may have some similarities to that in clay. Because of the high entry pressures, salt caverns can be used for natural gas storage [74].

Understanding from the German radioactive waste management programme [56] is that if the gas pressure within a vault were to approach the minimum principal stress in the host rock (i.e. approximately twice the hydrostatic pressure), then either the salt would become permeable or the void space within the GDF would increase [56]. The first process (‘gas infiltration’) is considered to be the more likely to occur, and would result in a limited flow of gas into the salt.

Based on this understanding, gas generated in a GDF within an evaporite host rock would be expected to be confined to the host rock immediately surrounding the GDF and would not be expected to reach the biosphere. However, this would depend on the details of the actual geological environment and the efficacy of the sealing of access routes.

5.3 Modelling gas migration

There is a substantial track record of modelling multi-phase flow through geological environments in a number of industries. Modelling is used in the hydrocarbon industry to understand oil and gas resources. It has also been used in support of the development of GDFs and in the development of underground disposal caverns.

The models are based on an understanding of the relevant physical processes and on observations from natural systems, complemented by laboratory experiments.

The hydrocarbon industry has been simulating multiphase flow in porous media for many years in order to evaluate reserves and optimize the recovery of oil and gas. Sophisticated software (e.g. the reservoir simulator ECLIPSE [86]) has been developed, and is used to predict the behaviour of oil and gas reservoirs. Whereas the simulations for the hydrocarbon industry may involve three phases (i.e. oil, gas and water), gas migration from a GDF would involve only two phases (i.e. gas and water).

In addition to reservoir simulators, a number of other computer programs are available to model two-phase flow in porous media. For example, TOUGH2 [87] has been applied widely in studies of gas migration from geological repositories for radioactive wastes [34, 35]. This particular computer program discretises the continuity equations onto a finite-volume grid. The result is a large set of simultaneous, non-linear algebraic equations, which are solved using standard iterative methods.

The use of such simulators makes it possible to account for a number of processes in a properly coupled manner, and to represent geological and geometric features in reasonable detail. Thus, pressure rise in a GDF and gas flux from the GDF are coupled, and it is possible to represent both the spatial variation of geological properties, such as might be associated with rock strata, and the geometry of a GDF within a 2D or 3D model.

Figure 12 shows a simulation of the gas phase migrating from a GDF situated at depth in a higher-strength rock under a sedimentary cover [88]. The gas saturation (i.e. the fraction of the pore space in the rock that is occupied by gas) is shaded in colour. The different types of rock are demarcated by the black lines. In this simulation, the gas moves upward through the host rock and overlying rocks until it comes to a low-permeability formation with a high gas entry pressure (a barrier layer, or ‘cap rock’). The barrier layer forces the gas to move upwards and towards the right. Eventually the gas finds a place where a major fault breaks the continuity of the barrier layer, and then it is able to move upwards into the more permeable, near-surface rocks.
Conventional porous-medium flow models have some known shortcomings. They describe fluid flow at a moderate scale using effective properties. Although the effective properties are intended to account for processes that are happening on smaller scales, this is not always practicable. For example, instability in the flow and heterogeneity in the pore structure may occur on smaller length scales, and these would be a challenge for the model to represent. In the light of this a number of alternative approaches have been developed [15].

The models are based on an understanding of the relevant physical processes and on observations from natural systems, complemented by laboratory experiments. These include:

- **Field-scale experiments in fractured rock.** Gas injection tests at Reskajeage Farm in Cornwall [89, 90] demonstrate some of the challenges in predicting gas migration in the field. Helium was injected from a borehole into fractured rock at a depth of about 54m. A key conclusion of these experiments was ‘that gas localisation at the surface can occur in fractured geology and that gas release can continue for a significant time after the initial injection has ceased’ [90].

- **Field-scale experiments in mudrock.** The EC FORGE project [91] also included two *in situ* experiments:
  - Andra performed a gas experiment (named PGZ-1) at its Bure site, to understand gas migration through undisturbed clay; and
  - Nagra investigated the mechanisms of gas migration at different gas pressures in the HG-C / HG-D experiment at the Mont Terri URL.

These experiments show that it would be difficult for free gas to flow into an intact mudrock. The importance of the hydro-mechanical coupling for gas migration is still being debated. The disturbed rock around the excavations is likely to act as a preferential pathway for the gas.

- **Natural systems.** A review [92] has considered evidence from the hydrocarbon industry on natural gas migration in the geosphere. The review examined references about:
  - The migration of petroleum hydrocarbons (liquid and gaseous) from source rocks, through carrier beds, to reservoir traps;
  - The leakage of hydrocarbons, particularly gases, from reservoirs and their migration to the surface, where they appear as surface seeps;
  - The analysis of surface seeps to identify gas sources; and
The modelling techniques used within the hydrocarbon industry to simulate gas migration.

The review concluded that the available data were insufficiently quantitative to provide definitive evidence for particular gas migration mechanisms, or to be used in detailed modelling. Nevertheless, the review concluded that natural gas migrates from a subsurface accumulation or trap through the geosphere to the surface as a separate phase driven by buoyancy. In addition, the majority of evidence of natural gas migration in the form of macro-seeps indicates that the gas flows mainly through fractures and faults. The distribution of these features determines the location and nature of the surface expression of gas migration.

5.4 Microbes in the geosphere

Microbes may exist in the geological environment through which the gases are migrating. There is the possibility that such microbes could consume hydrogen, which would provide a ‘sink’ for migrating hydrogen gas. Scoping calculations suggest that although some hydrogen may be consumed, there will be insufficient electron acceptors to affect the amount of migrating gas significantly.

Hydrogen will be a major constituent of the gas phase migrating away from a GDF, and also plays a crucial role in biology, supporting anabolic processes such as carbon and nitrogen fixation (e.g. linked to reductive processes, with hydrogen as the electron donor) and catabolic process (linked directly to energy metabolism, with hydrogen acting as an electron donor for the respiration of a broad range of electron acceptors). The latter processes can support life in a range of subsurface environments, including some of those associated with GDFs.

Because of the high pH, $^{14}$CO and $^{14}$CH$_4$ will be the most important carbon-14 bearing gases leaving the near field (any $^{14}$CO$_2$ will be retained within the near field by carbonation). These gases will be accompanied by hydrogen. As the alkaline plume extends out into the far field, there will be a point where the ambient pH drops to a value that allows microbiology to proceed.

Once a favourable ambient pH is established sulphate reduction and methanogenesis both have the potential to oxidise this hydrogen source. The sulphate content of UK deep groundwaters would indicate sulphate to be the dominant terminal electron acceptor.

Sulphate reduction coupled to hydrogen oxidation has been described in both microcosms and pure cultures up to pH 10 [65, 93, 94, 95], suggesting that below this pH there can be confidence that sulphate reduction will proceed.

The sulphate reduction reaction is:

$$4H_2 + SO_4^{2-} + 2H^+ \rightleftharpoons H_2S + 4H_2O$$

A cautious calculation, which is based on multiplying together:

- An upper-bound specific discharge in a higher-strength rock, about $10^{-11}$ m s$^{-1}$ (see Section 4.1.2);
• An upper-bound estimate of the cross-sectional area of contact between the groundwater and hydrogen, about $10^5 \text{ m}^2$ (corresponding to the approximate width of the ILW / LLW modules, i.e. 1,000m, multiplied by a representative height of rock, i.e. 100m); and

• The concentration of sulphate in seawater, 0.0282 M (to put this number into context, this is about double the concentration of sulphate that was measured in borehole RCF3 DET5 at Sellafield [96], and is above the concentration that would correspond to saturation with CaSO_4, about 0.015 M [49]); suggests that the flow of SO_4^{2-} through the plume of hydrogen will be (much) less than 900 moles per year.

If all of this sulphate were to be utilised in sulphate reduction, then that would correspond to consuming 3,600 moles (or about 80 m^3 at STP) per year of hydrogen. In practice, only a fraction of this sulphate will be utilised, mostly around pockets of trapped gas, where some of the hydrogen will be able to dissolve in the groundwater. The implication is that the microbial metabolism of hydrogen will be limited by the quantities of electron acceptors (e.g. sulphate) present in the groundwater, and therefore this process is unlikely to affect the migration of the gas phase significantly.

This is consistent with ‘analogue’ observations of free hydrogen in nature. The main natural occurrences of hydrogen are gas seepages associated with the serpentinization of ultramafic rocks in ophiolite complexes (e.g. Oman, Troodos, Philippines, etc.). The largest known on-shore hydrogen-rich seeps of this type are encountered in the Zambales Ophiolite in the Philippines and at Chimaera in Turkey. At Chimaera, in excess of 50 tons of gas is discharged per year, of which approximately 10% (by volume) is hydrogen. The gas migrates upwards along fracture pathways through fractured carbonate cover rocks to the surface. Because free hydrogen is observed to reach the surface at these sites, not all of the hydrogen can be consumed by microbes in the rocks.

5.5 Dissolution of gas in the geosphere

Gas may migrate away from the GDF and through the host rock. However, when the gas migrates into overlying sequences there may be sufficient groundwater to allow the gas to dissolve. Such dissolved gas would then be transported with the groundwater and might discharge to the biosphere. The quantity of gas that dissolves is site specific.

As the gas migrates upwards, it might encounter a more permeable formation with a higher flow of groundwater (an aquifer), in which some or all of the gas will dissolve\(^21\).

Properties of the aquifer that would control the dissolution of the bulk gas include:

- The presence of clay or silt lenses, and their size and depth;
- The (square root of the) specific discharge in the aquifer; and
- The (square root of the) porosity and tortuosity of the aquifer.

A calculation based on a conceptual model for the movement of non-aqueous phase liquids is presented in Box 1 below and in an underlying report [15] and shows that the flow of gas into the groundwater from a single pocket of trapped gas is relatively small. An alternative approach is to consider gas migrating from the GDF across a low-permeability sedimentary rock, and then to ask what release area would be needed to dissolve the bulk gas that is generated at around 10,000 years after closure (410 m^3 at STP yr\(^{-1}\) assuming water is

\(^{21}\) Dissolution in the EBS has already been discussed in Section 4.1.3.
available at the same rate as in a higher-strength rock). The release area that would be needed is 1.5 \(10^6\) m\(^2\), which is comparable to the footprint of the ILW / LLW modules.

Although it is a site specific result, the conclusions are that:

- the gas phase might not dissolve in the groundwater, as it moves through an overlying aquifer, until several hundred years following closure (when the rate of gas generation will have decreased to 100's m\(^3\) at STP yr\(^{-1}\)); and

- the gas phase will be more likely to dissolve in the groundwater of an overlying aquifer in those geological environments where the gas flux to the aquifer is distributed over a larger area.

### 5.6 Release of gas to the biosphere

Gas could migrate to the biosphere. The implications of any such release will depend on the area over which the gas is released (see Section 6.2), and in particular whether it is focused and released over a restricted area, or whether it is released over the footprint of the GDF (or of the vaults that produce carbon-14 bearing gases), or whether it is dispersed and released over an even larger area.

An important factor affecting the calculated consequence of any radiological release to the biosphere is the area over which that gas is released. The release area will depend on the geological environment and the migration processes occurring and will be site specific. In the absence of a site, a range of cases can be used to illustrate the range of behaviour that might be observed.

- In many geological environments (for example in an evaporite, or where there is an overlying cap rock) there would be no release to the biosphere.

- In many instances, buoyancy would mean that gas migration would be predominately vertical and therefore the release area would be similar to the footprint of the ILW / LLW modules in the GDF (i.e. about \(10^6\) m\(^2\)). A similar release area could also apply in a lower strength sedimentary rock; although in this case the gas migration would be slower.

- There may be features in a higher-strength host rock that focus the release of gas to an area much less than the footprint of the GDF. \(10^5\) m\(^2\) is deemed to be the smallest area sufficient to support the relevant potentially exposed group, and therefore a case with this release area is considered.

In all cases, an aquifer might be present; further discussion of the consequences of dissolved gas is presented in Section 6. The expected release area for gas dissolved in an aquifer depends on whether the gas pathway has been focused or distributed. These release areas are estimated on the basis of possible plume dimensions (see Box 2 below):

- If the gas pathway has been focused (e.g. by migrating up an open fault or along an access shaft), the gases would be released from solution to the biosphere over an area of the order of \(10^5\) m\(^2\);

- Otherwise, the gases would be released to the biosphere over an area of the order of \(10^7\) m\(^2\)  \(^{22}\)

\(^{22}\) \(10^7\) m\(^2\) is the central value of the release area for the groundwater pathway in the 2010 post-closure safety assessment [46].
Box 1 Could the gas dissolve in an overlying aquifer?

A considerable body of work (e.g. [97, 98, 99]) has developed conceptual models for the movement of non-aqueous phase liquids (NAPL) in the subsurface, and although the analogy has limitations (e.g. the specific gravity of a gas phase will be different from that of a NAPL), it is helpful to be aware of this work. Based on these conceptual models, we assume that gas migrating upwards through an aquifer might be trapped either as residual gas in the pore space or below low-permeability strata (i.e. clay or silt lenses), where it could dissolve into flowing groundwater. Thus the source zone would be composed of multiple subzones (where the gas phase resides), which would have the architecture of thin horizontal gas pockets interconnected by vertical fingers of gas.

This conceptual picture has been used to answer the following question: Could the gas dissolve in an overlying aquifer? Clearly this is a site-specific question, but the following expression identifies the main controls on gas dissolution.

The maximum rate of dissolution of the bulk gas (mostly hydrogen) from pockets of gas trapped beneath low-permeability strata, such as clay or silt lenses, into the groundwater, $J$ (m$^3$ at STP s$^{-1}$), can be estimated from [15]:

$$J = N w \sqrt{\frac{4 \phi \tau D l}{q \pi C}}$$

where $N$ is the number of clay or silt lenses beneath which the gas will be trapped; $w$ is the width of a lens (normal to the groundwater flow), taken to be about 30m; $\phi$ is the aquifer’s porosity, assumed to be 0.2; $\tau$ is the tortuosity$^{23}$ of the pore structure (which describes whether the pathways through the porous medium are tortuous), here assumed to be 0.1; $D$ is the molecular diffusion coefficient of hydrogen in free water, 4.5 $10^{-9}$ m$^2$s$^{-1}$; $l$ is the length of a pocket of trapped gas (where the concentration of hydrogen is equal to its solubility), also taken to be about 30m; $q$ is the specific discharge in the aquifer$^{24}$, which might be up to about 10$^{-7}$ m s$^{-1}$; and $C$ is the equilibrium concentration of hydrogen dissolved in the groundwater at the relevant depth in the aquifer (e.g. the solubility of hydrogen gas at a depth of about 50m would be 0.087 m$^3$ at STP m$^{-3}$).

Evaluating the final answer, the flow of bulk gas into the groundwater from a single pocket of gas trapped beneath a low-permeability stratum, with dimensions of 30m, would be about 1.5 m$^3$ at STP yr$^{-1}$. This is small in comparison with the calculated rates of bulk gas generation (see Section 4.1.1), except perhaps at late times. Hence only a small fraction of the bulk gas would dissolve in such an overlying aquifer.

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$^{23}$ Note that alternative definitions of the ‘tortuosity’ are used in the literature.

$^{24}$ This value is based on multiplying the effective hydraulic conductivity of the aquifer, assumed to be $10^{-5}$ m s$^{-1}$, by a typical regional head gradient, 0.01 m m$^{-1}$.
Box 2 Over what area would the gases from a dissolved plume be released?

If we assume that bulk gas is injected (at a constant rate) into the groundwater at a point (i.e. the origin of the coordinate system), then the steady-state concentration of bulk gas in the plume (m$^3$ at STP m$^{-3}$) can be calculated [100]. The shape of the plume is a function of the depth of injection, and the dispersion lengths in the aquifer.

Defining the release area of the plume as comprising those points at the ground surface where the concentration is greater than ten percent of its maximum concentration at the surface, and assuming that:

- The source is at a depth of 50m below the ground surface; and
- The longitudinal dispersion length is $\alpha_x = 30$m, and the transverse dispersion lengths are one-tenth of this value, $\alpha_y = \alpha_z = 0.1 \, \alpha_x$;

Then (see reference [15]):

- The release area of the plume will be $1.5 \times 10^6$ m$^2$;
- The length of the plume aligned with the flow will be 6,100m; and
- The maximum width of the plume will be 320m.

Based on this result, if the carbon-14 bearing gases go into solution effectively at a single point, then a release area of about $10^6$ m$^2$ is proposed.

If the gases go into solution at a number of points distributed across the width of the ILW / LLW modules, a release area that is several times larger (because the width of the modules will be larger than the width of each plume) is appropriate. A release area of $10^7$ m$^2$ is proposed, which is consistent with an assumption in the 2010 generic DSSC [46].

The travel time of the gases from their point of dissolution to the ground surface can be computed by dividing the path length (up to 6,100m) by the transport velocity (which will be equal to the specific discharge divided by the porosity of the aquifer, and here is assumed to be $5 \times 10^{-7}$ m s$^{-1}$). For these parameter values, the travel time is about 400 years, which is short compared to the half-life of carbon-14 (i.e. 5,730 years). The specific discharge (or, equivalently, the hydraulic conductivity) of the aquifer needs to be only an order of magnitude smaller for the travel time to start to become significant, but in that case the gas phase would be less likely to dissolve in the groundwater.
6 Biosphere

To evaluate the consequences of any release of carbon-14 bearing gases we need a methodology to relate a release of carbon-14 to potential doses to future generations. The approach depends on the timing of the release: principally whether it is before or after the closure of the GDF.

Different approaches to evaluate the consequences of carbon-14 release to the biosphere are used depending on the timing and the nature of the release.

The three main aspects to be considered are:

- Release of carbon-14 bearing gases up a ventilation stack during operations;
- Release of carbon-14 bearing gases to the deep soil zone following closure;
- Discharge of carbon-14 bearing gases dissolved in groundwater following closure – such gas might have migrated part of the way to the surface as a gas, which has dissolved once exposed to larger volumes of groundwater in, for example, an aquifer.

These are discussed in turn in the remainder of this section25. The consequences of any such releases have to be considered in the context of regulatory guidance by the environment agencies [10].

6.1 Pre-closure releases of gas

The approach to operational discharges in Phase 1 of this project was to use an initial assessment methodology adopted in the 2010 generic DSSC. In the light of those results an updated methodology has been developed. This methodology addresses some of the assumptions in the initial methodology that are not well tailored to the particular nature of the release being considered. This enables a better founded assessment to be undertaken of the significance of any gas released during the operational period.

In the Carbon-14 Project Phase 1 report [2], the results of an operational assessment to estimate effective dose rates from carbon-14 bearing gases discharged from an underground GDF were presented. These results were based on an approach set out in the 2010 generic Operational Environmental Safety Assessment (OESA) [101], but using updated gas generation rates developed within the Phase 1 project [2]. Effective dose rates to members of exposed groups were calculated using the Environment Agency’s Initial Assessment Methodology as detailed in [102, 103], since this was regarded as an appropriate basis for an initial scoping assessment that could subsequently be refined in key areas determined by the results obtained.

The Environment Agency’s approach to the assessment of aerial discharges is based on a general application of PC-CREAM that is not tailored to the particular nature of the release being considered. Specifically, the PC-CREAM approach is primarily relevant to aerosol releases, rather than to the release of gases such as carbon dioxide, carbon monoxide and methane that are utilised by higher plants and by microbial communities in soils.

The main pathway for aerial discharges from the underground facilities will be through the GDF ventilation system and into the atmosphere through a discharge stack. The discharge stack height and location will be designed to meet the requirements specified in [104]. In the Phase 1 report, effective dose rates were calculated using the average and peak gas

25 Any releases of radioactive gas into the operating GDF would be managed as part of the operation of the GDF. These aspects are considered as part of the Operational Safety Case.
release rates for discharges from a 15m stack height for the operational period to the local resident family receptor group [101], which is cautiously assumed:

- to be located 100 metres from a discharge point of a GDF; and
- to consume food grown at 500 metres from a GDF.

As part of Phase 2 of the carbon-14 project, a methodology was developed to provide a more realistic representation of the discharge pathway applicable to releases of carbon-14 bearing gases from the GDF during operations [17]. This more specific methodology considers carbon-14 bearing carbon dioxide, carbon monoxide and methane, as these have been identified as the three main carbon-14 bearing gases that could be released (see for example Section 8).

The approach adopted is to calculate effective dose rates for continuous releases of these carbon-14 bearing gases from an operational GDF, for the external irradiation, inhalation and ingestion exposure pathways. These values are then compared with those that were applied in the OESA.

The atmospheric dispersion of the three carbon-14 bearing gases subsequent to their release from a GDF is discussed. This allows specification of appropriate atmospheric dispersion factors for both a ground-level release and a more realistic release height of 15 m, as might arise from a stack. The exposure pathways considered are:

- external irradiation from radionuclides in the effluent plume;
- inhalation of radionuclides in the effluent plume;
- consumption of terrestrial food incorporating radionuclides deposited on the ground, including both plant and animal products;
- external irradiation from radionuclides in the plume deposited on the ground.

A significant difference between the current study and the approach in the OESA is that more realistic and up-to-date data are used in the calculations reported here. In particular, more realistic dose-per-unit-intake values for the individual gases are adopted, and the latest understanding of methane and carbon monoxide behaviour in soil-plant systems is applied (as discussed in more detail in Section 6.2).

Based on the analysis presented in this study, updated effective dose factors for unit release rate have been derived. These are listed in Table 11, where they are compared with the values given in the Environment Agency (EA) Initial Assessment Methodology and used in the OESA.

26 Design tasks are in hand that are giving further consideration to the appropriate stack height to adopt. The 15 m value was selected for the OESA and has been retained here for consistency, but the height to be adopted will be reassessed in the future and may be changed.

27 The OESA gives only values for infants, as these are the age group found to have the highest doses. These values were taken from the user report on the EA Initial Assessment Methodology. However, values for other age groups can be obtained from the tables in the methods and data report for the EA Initial Assessment Methodology. It is these values that are reported here. In this report, the normal practice adopted in prospective assessments is followed in which radiation dose rates for a unit release rate are calculated for infants (one year old), children (ten years old) and adults. The most highly exposed group can then be determined by calculating the dose rates to each of these age groups for any source term, which may include not only these three gases but also aerosol and gaseous releases of other radionuclides.
Table 11 Effective dose factors (Sv yr\(^{-1}\) per Bq yr\(^{-1}\) for a release at a height of 15 m)

<table>
<thead>
<tr>
<th>Age Group</th>
<th>External All gases</th>
<th>External Carbon dioxide</th>
<th>External Carbon monoxide</th>
<th>External Methane</th>
<th>Ingestion Carbon dioxide</th>
<th>Ingestion Carbon monoxide</th>
<th>Ingestion Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infant</td>
<td>2.1 10(^{-23})</td>
<td>9.2 10(^{-21})</td>
<td>2.8 10(^{-21})</td>
<td>2.1 10(^{-22})</td>
<td>9.0 10(^{-18})</td>
<td>1.2 10(^{-16})</td>
<td>2.7 10(^{-21}) to 7.8 10(^{-20})</td>
</tr>
<tr>
<td>Child</td>
<td>2.1 10(^{-23})</td>
<td>1.3 10(^{-20})</td>
<td>2.4 10(^{-21})</td>
<td>2.7 10(^{-22})</td>
<td>5.5 10(^{-18})</td>
<td>7.1 10(^{-17})</td>
<td>1.6 10(^{-21}) to 4.7 10(^{-20})</td>
</tr>
<tr>
<td>Adult</td>
<td>2.1 10(^{-23})</td>
<td>1.3 10(^{-20})</td>
<td>1.4 10(^{-21})</td>
<td>2.0 10(^{-22})</td>
<td>5.5 10(^{-18})</td>
<td>7.2 10(^{-17})</td>
<td>1.7 10(^{-21}) to 4.8 10(^{-20})</td>
</tr>
<tr>
<td>EA (Infant)</td>
<td>5.8 10(^{-24})</td>
<td>3.2 10(^{-18})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.5 10(^{-17})</td>
</tr>
<tr>
<td>EA (Child)</td>
<td>7.4 10(^{-24})</td>
<td>4.0 10(^{-18})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.5 10(^{-18})</td>
</tr>
<tr>
<td>EA (Adult)</td>
<td>5.8 10(^{-24})</td>
<td>4.1 10(^{-18})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.7 10(^{-18})</td>
</tr>
</tbody>
</table>

Summing the individual contributions listed in Table 11 and using the geometric mean of the range of ingestion values given for methane, the overall effective dose factors listed in Table 12 are recommended for assessment purposes. In each case, ingestion is the dominant exposure pathway.

Table 12 Recommended effective dose factors (Sv yr\(^{-1}\) per Bq yr\(^{-1}\) for a release at a height of 15m)

<table>
<thead>
<tr>
<th>Age Group</th>
<th>Carbon dioxide</th>
<th>Carbon monoxide</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infant</td>
<td>9.0 10(^{-18})</td>
<td>1.2 10(^{-16})</td>
<td>1.5 10(^{-20})</td>
</tr>
<tr>
<td>Child</td>
<td>5.5 10(^{-18})</td>
<td>7.1 10(^{-17})</td>
<td>8.7 10(^{-21})</td>
</tr>
<tr>
<td>Adult</td>
<td>5.5 10(^{-18})</td>
<td>7.2 10(^{-17})</td>
<td>9.0 10(^{-21})</td>
</tr>
</tbody>
</table>

The effective dose factors for carbon dioxide, carbon monoxide and methane listed in Table 12 exhibit approximate ratios of 1:13:0.003. Thus, if even a small fraction of the release of carbon-14 bearing gas is as carbon dioxide or carbon monoxide, rather than as methane, this fraction will determine the radiological impact of the release. However, it is emphasised that this result arises from a cautious assumption concerning the assimilation of carbon monoxide by plants at low atmospheric concentrations of the gas. The values given in Table 12 are for the case that the carbon-14 discharge is entirely one or other of the three carbon-14 bearing gases. In practice, carbon monoxide is likely to comprise at most a small fraction of the discharge, so the larger effective dose rates given for carbon-14 bearing carbon monoxide in Table 12 are likely to be of limited radiological significance.

For the operational period, the calculated doses are compared with the radiological protection criteria for normal conditions of operation. The effective dose rates for a member of the public should be below the source-related dose constraint for members of the public for a new facility of 0.15 mSv yr\(^{-1}\) (Requirement R5 in [10]). If this constraint is met than the requirement that the effective dose rate for a member of the public should be below the legal dose limit of 1 mSv yr\(^{-1}\) will also be met.
6.2 Post-closure releases of gas

Any carbon-14 bearing gases that reach the biosphere following closure would be released to the deep soil. Recently a combined experimental and modelling programme has been completed, which focused on whether the methane released would be oxidised to carbon dioxide. In the light of the results of this programme a revised assessment model has been developed. This quantifies the potential dose per unit release of carbon-14 bearing methane, and updates the values used in previous assessments. The revised model gives separate consideration to:

- methane oxidation in the soil zone – the assumption that methane is oxidised to carbon dioxide is now well underpinned by experimental evidence and literature reviews;
- uptake through the root system; and
- the important processes that take place in the plant canopy and above the canopy – these processes play an important role in uptake of carbon-14 by plants.

These models are consistent with those used by Low Level Waste Repository (LLWR).

The gas most likely to be released from the near field of the GDF and reach the biosphere is carbon-14 bearing methane (\(^{14}\text{CH}_4\)) (since carbon-14 bearing carbon dioxide (\(^{14}\text{CO}_2\)), which is also predicted to form, is expected to react with cementitious backfill in the GDF) (see Section 4.3). There is also the possibility that carbon-14 bearing carbon monoxide (\(^{14}\text{CO}\)) will be released.

There are three aspects of the assessment of post-closure release of gas to the deep soil after closure of the GDF. These concern processes in the soil zone, processes in the canopy and above-canopy zone, and finally the pathways whereby the carbon-14 leads to doses to future populations. These aspects are represented in Figure 13.

In recent years, a number of models have been developed to represent these aspects and then to assess the implications of the release of carbon-14 bearing methane following closure of a GDF (for example RIMERS [105], which was used in Nirex 97 [106] and GPA (03) [107], Enhanced RIMERS [108], which was used in the GPA (03) Update assessment [109], and finally an approach used in assessments undertaken by LLWR [110]). In the light of recent work, a new model has been developed [24]. The potential implications of release of carbon-14 bearing carbon monoxide are also considered in Reference [24].

In some respects, the representation in the assessment models has become simpler (e.g. the representation of the soil components); in others it has become more complex (e.g. the treatment of canopy and above-canopy processes). It has been recognised more recently that a key process controlling the uptake of carbon-14 is transport through the canopy atmosphere. A specific activity model is generally used to represent plant uptake, and the importance of turbulence in determining the loss of carbon-14 from the canopy is now incorporated into the models.

The three aspects of the current assessments model [24] are discussed in the rest of this section. As part of this presentation, recent experimental and modelling work on the oxidation of methane in the soil zone is described.
6.2.1 Modelling soil processes

The potential flux of radioactive methane from a deep repository can be treated as being at quasi-steady state (i.e. the timescale over which the flux of methane varies is much longer than the timescale for methane to diffuse across the near-surface soil). This means that it is appropriate to use a simple, steady-state diffusion-reaction equation to describe the transport of methane, and its product carbon dioxide, through the soil. In particular, this model depends on two input parameters:

- the effective diffusion coefficient of a gas through the soil, which in turn depends on the porosity and the gas-occupied pore volume in the soil; and
- the rate of methane oxidation.

This model, for a given flux of radioactive methane, provides predictions of:

- the concentration of radioactive carbon dioxide through the soil; and
- the flux of radioactive carbon dioxide from the soil (likely to correspond to almost complete conversion of the methane – discussed below).
It is considered that much of the radioactive carbon dioxide will migrate upwards from the soil, through the canopy of any overlying vegetation, and into the free atmosphere.

6.2.2 Methane oxidation in the soil zone

(a) Laboratory and field experiments

Despite much work in recent years on the behaviour of both CH₄ and CO₂ in soils, uncertainty remained over the potential rate of transport of carbon-14 as ^14CH₄ in the soil, its oxidation to ^14CO₂ and subsequent root and foliar uptake by plants.

In view of these uncertainties, a series of laboratory and field experiments were commissioned to investigate the transport and retention of ^13CH₄ (as a stable analogue for the radioactive ^14CH₄) in agricultural soil. These experiments have been undertaken at the University of Nottingham. The results of these experiments have been modelled to support the parameterisation of the model. The work programme is summarised in Reference [25].

Antecedent measurements were taken before methane injection, including various soil properties and soil methane concentrations at a number of depths. Methane fluxes into or out of the soil were estimated using a fixed volume head space chamber in which the air was continuously stirred. Then methane labelled with ^13C was injected at a depth of about 50 cm, and samples were taken throughout the soil profile a number of times following injection. Head space measurements were again taken at a number of times after injection to estimate fluxes of methane and carbon dioxide. The set-up of these experiments is illustrated in Figure 14. Details of the experiments can be found in References [22, 111, 112].

(b) Wider context

In many soil systems methane is being consumed in soils; in such systems many of the same processes are taking place in the soils. To complement the experiments, a review of wider in situ studies of methane fluxes across the soil-atmosphere interface in different eco-systems has been undertaken [16]. Geometric mean methane oxidation fluxes from the atmosphere into soils are:

- 1.01 mg m⁻² d⁻¹ for forests (excluding tropical forests) – mean taken over 39 measurements;
- 0.58 mg m⁻² d⁻¹ for grasslands (excluding tropical grasslands) – mean taken over 7 measurements;
- 0.25 mg m⁻² d⁻¹ for arable or agricultural systems – mean taken over 22 measurements.

The methane oxidation fluxes found in the Nottingham laboratory and field experiments are consistent with the values for arable or agricultural systems given above. In contrast, in wetland environments there is net methane production in near-surface soil, and thus there is a net flux of methane out of these soils into the free atmosphere. The uncertainties in these fluxes and the significance of the differences are discussed in more detail in reference [16].
Figure 14 Field and Laboratory Experiments Results on the oxidation of methane

(c) Modelling the experiments
The experimental data, mainly the profiles of gas concentrations (i.e. $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$) through the soil, but also the effluxes of gases from the soil, provide a consistent picture. Methane ($^{12}\text{CH}_4$ and $^{13}\text{CH}_4$) diffuses away from the point of injection. As it diffuses, specialist microbes in the soil (methanotrophs) oxidise the methane to carbon dioxide. In the experiments, the majority of the methane was converted to carbon dioxide. The carbon dioxide ($^{12}\text{CO}_2$ and $^{13}\text{CO}_2$) then diffuses upwards through the partially saturated soil and into the overlying atmosphere. A small volume of methane was injected so as not to stimulate the microbial populations. As a result, the uptake of labelled carbon dioxide by the plants was below the detection limit. However, the experiments allowed the key processes in the soils to be examined. It follows that the key processes are:

- diffusion of gases through partially saturated soil;
- microbial oxidation of methane; and
- soil respiration, which is the degradation of soil organic matter to produce carbon dioxide; this affects the background concentration profile of CO$_2$ in the soil.

A computational model has been developed that accounts for all of these processes. The model accounts also for isotopic effects; that is, the fact that different isotopic forms of a gas will have slightly different rates for each process. The model has been applied to interpret the experimental data [23].

This model has been complemented by simpler analytical models that were used to analyse the antecedent head space and soil profile measurements, based on assuming a soil column with homogeneous properties and steady-state conditions. They were also used to estimate the proportion of $^{14}\text{CH}_4$ that left the system, and the characteristic length scale (m) over which methane will be oxidised.

Although this characteristic length scale will be specific to the site and ecosystem under consideration, it seems generally to be of the order of tens of centimetres in agricultural or arable environments. The implication is that most of the radioactive methane migrating from a deep repository is likely to be converted to radioactive carbon dioxide in the soil. There is then the potential for the uptake of radioactive carbon dioxide by plants. This is the key conclusion from the experimental and modelling programme.
6.2.3 Modelling canopy and above-canopy processes and plant uptake

The assessment model uses an atmospheric dispersion model to calculate the concentration of radioactive carbon dioxide in the atmosphere above the vegetation. Next, the concentration of radioactive carbon dioxide in the canopy of the vegetation is estimated using the concept of an aerodynamic resistance (the difference in the concentration of radioactive carbon dioxide between the plant canopy and the atmosphere is equal to the flux of the gas multiplied by the aerodynamic resistance). Although the aerodynamic resistance has some dependence on plant morphology (e.g. height of plant and density of leaves) and wind category, it is not unduly cautious to use a generic formulation for this quantity. Finally the concentration of radioactive carbon dioxide in the canopy of the vegetation can be used to determine the specific activity of the canopy atmosphere.

As a result of photosynthesis, the plant will fix carbon dioxide from its canopy atmosphere during daylight hours. Photosynthesis discriminates very slightly (at a level of a few percent) between $^{12}$CO$_2$ and $^{14}$CO$_2$. This is not considered to be an important effect, and so the specific activity of the plant will be equal to the specific activity of its canopy atmosphere.

An additional uptake pathway allows for the possibility of carbon-14 being taken up by the plant’s roots in the transpiration stream. In this pathway, the concentration of $^{14}$CO$_2$ in the soil is multiplied by a scaling of the transpiration ratio (i.e. the amount of water taken up by a plant per unit mass of the plant), to calculate an additional source of carbon-14 in the plant. The scaling accounts for the possibility that root uptake of carbon-14 is an active process, and also that carbon-14 will be respired.

6.2.4 Dose calculations

The assessment model assumes that grazing animals will derive most of their food from contaminated vegetation, but humans will derive only part of their diet from the local area (in particular, much of the dietary cereals and sugars would be sourced from elsewhere). It is assumed, cautiously, that at most 30% of carbon in the diet of humans could come from the local area, and so the specific activity of carbon in humans would be diluted from the specific activity of the plants by this fraction.

Finally, a standard calculation can be used to relate the specific activity of carbon-14 in humans to the effective dose rate.

6.2.5 Comparison with other work

Models have been developed for both RWM and LLWR; there is the possibility of carbon-14 bearing gases being generated in the facilities being designed or used by the two organisations. The two models are now very similar. The area of greatest difference is in the choice of a potentially exposed group and the diet of that group. This is justified because the group for the existing LLWR facility is better defined, whereas the group for the GDF at this generic stage is less well defined.

The work has also been presented as part of the international BIOPROTA project [113]. It is in line with international developments in this area.

6.2.6 Overall assessment

All the models result in a calculation of dose in the form

$$H = \Phi \frac{Q}{A},$$

where $H$ is dose-rate (Sv yr$^{-1}$), $\Phi$ is the factor derived from the model, $Q$ is the release rate of $^{14}$CH$_4$ (Bq s$^{-1}$) at the bottom of the vadose zone\textsuperscript{28}, and $A$ is the release area (m$^2$).

---

\textsuperscript{28} The vadose zone is also known as the unsaturated zone.
equation, a key parameter is the release area. If the area is smaller than $10^4$ m$^2$, then the dose would not increase, because $10^4$ m$^2$ is deemed to be the smallest area sufficient to support the relevant potentially exposed group. If a larger area could be justified, then the doses would fall as the area increased.

The value of the flux to dose conversion factor derived in the current work is compared with the values used in previous assessments [2, 106, 109] in Table 13 below. In particular the value should be compared with the value used in the last formal assessment (the GPA (03) Update). It can be seen that the value recommended from this work is over an order of magnitude lower than the value used in that assessment. The flux to dose conversion factors have changed significantly over the years as the understanding of these systems has developed. These changes have included the dependence on the release area.

Table 13 also shows the limiting flux of $^{14}$CH$_4$ ($Q$ in the equation above) that would comply with the regulatory risk guidance level. Reference [24] concludes that the same approach can be used for release of carbon monoxide to the deep soil as is used for methane, i.e. the release rates for methane and carbon monoxide can be summed.

In the remainder of this report, quantities described as ‘risks’ are calculated. It is recognised that this term is a simplification. These quantities are really assessed ‘conditional risks’ in which the occurrence of the scenario and exposure has been assumed to occur with a probability of 1.0. In addition the assessed ‘risk’ is just from carbon-14. There may be risks from other radionuclides, e.g. $^3$H and $^{222}$Rn. In a full assessment it would be necessary to take account of any contributions to risk from other radionuclides.

### Table 13 Comparison Flux to Dose Conversion Factors in Recent Assessments

<table>
<thead>
<tr>
<th>Assessment</th>
<th>Nirex 97 / GPA (03)</th>
<th>GPA (03) Update</th>
<th>C14 IPT Ph 1</th>
<th>New Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux to Dose Conversion Factor (Sv yr$^{-1}$) per (Bq m$^{-2}$s$^{-1}$)</td>
<td>$2.21 \times 10^{-5} A^{0.5}$†</td>
<td>0.628</td>
<td>0.009</td>
<td>0.0225</td>
</tr>
<tr>
<td>Limiting flux (TBq yr$^{-1}$)</td>
<td>Area $10^4$ m$^2$</td>
<td>$2.4 \times 10^3$</td>
<td>$8.4 \times 10^6$</td>
<td>$5.8 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>Area $10^6$ m$^2$</td>
<td>$2.4 \times 10^2$</td>
<td>$8.4 \times 10^4$</td>
<td>$5.8 \times 10^2$</td>
</tr>
</tbody>
</table>

† In Nirex 97 and GPA (03), the flux to dose conversion factor depended on the release area, $A$.

### 6.3 Dissolution in an aquifer

It is possible that some of the migrating gas dissolves in an overlying aquifer before it reaches the biosphere. The dissolved gas then returns to the biosphere with the groundwater. The dissolved gas that reaches the biosphere is expected to come out of solution, and then a similar approach can be used as for carbon-14 that reaches the biosphere as a gas.

In Section 6.2 above, the consequences of the release of gaseous carbon-14 bearing methane to the deep soil is considered. This is based on the approach in Reference [24], which also briefly considers the release of carbon-14 bearing carbon monoxide. Carbon-14 bearing carbon dioxide is not expected to migrate as a gas, as it is expected to react with the cementitious materials in the EBS (see Section 4.3).

There remains the possibility that carbon-14 bearing species dissolve in groundwater in some part of the geological system, possibly in an aquifer where there is more groundwater available, and then migrate with the groundwater to the biosphere.
The groundwater pathway has been much studied; the most recent assessments are described in Reference [46], where a number of parameters are described. These include:

- The groundwater travel time (see Sections 4.5.2 and 5.2 of Reference [46])
- The groundwater mixing flux (see Sections 4.5.2 and 5.2 of Reference [46])
- The discharge area for the groundwater pathway (see Sections 4.5.2 and 5.2 of Reference [46])
- The sorption coefficient for carbon-14 for the relevant geological materials (see Section 5.1.2 and Appendix A4 of Reference [46])
- The biosphere dose conversion factors for the groundwater and well pathways for carbon-14 (see Section 5.1.3 and Appendix A5 of Reference [46]).

There are, however, a number of important differences for the treatment of carbon-14 in a dissolved gas and carbon-14 migrating with the groundwater as other species, as normally considered in the groundwater pathway.

These differences are discussed in Table 14; the considerations are different for methane, carbon monoxide and carbon dioxide.

**Table 14 Comparison of the treatment of dissolved gas with the normal treatment of the groundwater pathway**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Methane</th>
<th>Carbon monoxide</th>
<th>Carbon dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater travel time</td>
<td>Consider whether the travel time as dissolved species would allow significant decay when compared to the half-life of carbon-14.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Groundwater mixing flux</td>
<td>The mixing flux and the release area for the groundwater pathway that is used in the generic post-closure safety assessment (PCSA) should be used. Consideration given to whether a smaller release area might be appropriate than for the groundwater pathway.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge area</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorption coefficient</td>
<td>Dissolved methane and carbon monoxide are different to the forms of carbon considered in the groundwater pathway. This suggests we take no credit for sorption (set $K_d = 0$)</td>
<td>Expect the carbon-14 to be present as bicarbonate – use the values in Reference [46] for these parameters</td>
<td></td>
</tr>
<tr>
<td>Biosphere factor</td>
<td>The model described in Section 6.2 above is the appropriate one to use for release to the deep soil.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biosphere factor for wells</td>
<td>Dissolved methane and carbon monoxide would be expected to come out of solution if the water is used for irrigation or other purposes between abstraction and use. Thus this pathway can be ignored.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In summary:

- The approach to assessing the implications of dissolved carbon-14 bearing methane and carbon monoxide should be the same as for migration to the biosphere in the gas phase. Additional consideration should be given to decay of carbon-14 as the dissolved gas migrates, although no credit should be taken for retardation arising from sorption. Consideration should also be given to whether the same release area is appropriate.
- The approach for dissolved carbon-14 bearing carbon dioxide should be the same as for the groundwater pathway. Credit can be taken for retardation arising from sorption.

---

29 In this context, the relevant groundwater travel time is that for the dissolved species, probably in the overlying aquifer, rather than the overall groundwater travel time from the GDF.
30 The flux of groundwater into which the gas dissolves and then mixes.
Migration and Release Scenarios

A limited number of release and migration scenarios have been developed to describe:

- Discharge during operation of the GDF;
- Discharge after closure, taking into account any delay time before the gas reaches the surface and the area over which it is released;
- Discharge after closure where the gas has migrated part of the way in solution.

The methodology allows the gas generation rates to be converted to doses or risks to enable the radiological consequences of carbon-14 bearing gases to be assessed.

In this section, the understanding described in Sections 4 to 6 is used to define a set of cases for which radiological consequences can be evaluated using the calculated generation rates of carbon-14 bearing gases. This covers the operational and the post-closure periods.

For calculations of doses during the operational period of the GDF, a similar approach is used for all geological environments.

In the absence of (i) a site for geological disposal of radioactive wastes and (ii) detailed information on GDF design, it is not possible to develop a single conceptual model for how carbon-14 bearing gases might migrate from a GDF to the biosphere. Rather, at this generic stage of the process for implementing geological disposal, it is appropriate to consider a range of behaviours following closure of the GDF, which will depend on hydrogeological details of the selected site.

This section summarises the range of behaviours, and then defines a set of cases that can be used to link the generation rates of carbon-14 bearing gases to an effective dose rate in the different stages of the evolution of the GDF.

7.1 Stages in the evolution of the GDF

The stages in the evolution of the GDF are described in Table 15, along with a summary of the expected temperature, water and oxygen availability, as identified in the modelling basis for this report.

The important aspects of the evolution of the environments for different wastes may be different. For example:

- the corrosion rate of Magnox is dependent on the availability of chloride;
- the corrosion rates of steels and uranium are dependent on whether the environmental conditions are aerobic or anaerobic; and
- water availability may be different in the various environments; this has been discussed in Section 3.3.

Moreover, the local environments in different wastes may develop on slightly different timescales (for example, the timescales on which anaerobic conditions are established around the waste materials).

The approach to the evaluation of doses and risks in these stages is discussed in turn in the remainder of this section.
Table 15  Timing of stages, temperature, water and oxygen availability

<table>
<thead>
<tr>
<th>Stage</th>
<th>Time (AD)</th>
<th>Temperature</th>
<th>Water availability</th>
<th>Oxygen availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emplacement</td>
<td>In the reference case for legacy vaults: 2040 – 2190  For NNB vaults: 2100 – 2190</td>
<td>35°C</td>
<td>Water within waste packages available</td>
<td>Aerobic (from dissolved oxygen within the water inside the waste packages) – except for uranium wastes</td>
</tr>
<tr>
<td>Backfilling and closure</td>
<td>In the reference case 2190 – 2200</td>
<td>45°C</td>
<td>As for Emplacement</td>
<td>As for Emplacement</td>
</tr>
<tr>
<td>Post-closure (resaturation)</td>
<td>Depends on the geological environment</td>
<td>45°C</td>
<td>Water in backfill available</td>
<td>Oxygen present at closure is consumed over a period of a few years</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pore space resaturates over a period dependent on the geological environment For HSR, resaturation modelled as being 5 years after closure</td>
<td></td>
</tr>
<tr>
<td>Post-closure (following saturation)</td>
<td>Depends on the geological environment</td>
<td>35°C</td>
<td>Essentials unlimited</td>
<td>Anaerobic</td>
</tr>
</tbody>
</table>

7.2 Waste emplacement

As wastes are emplaced, the vaults and tunnels will be ventilated, and it is appropriate to apply the updated OESA methodology developed in Section 6.1.

7.3 Backfilling and closure

The reference case is that backfilling will occur in a concerted campaign shortly before closure, and the crown space will be backfilled. In this case there may be some releases to the operating areas of the GDF, and the updated OESA methodology developed in Section 6.1 can be applied. However, if vaults have been sealed, releases may be to the surrounding geological environment, in which case the post-closure methodology may be more applicable.

It is possible that consideration will be given to backfilling vaults and tunnels once they have been filled with waste. If a crown space is then left open and the vaults are not sealed, then releases may be captured by the operational ventilation system. In this case the updated OESA methodology developed in Section 6.1 is applicable. On the other hand, the gas generated may be retained within the system and released after closure.

Given the uncertainties in this stage, it is considered appropriate to apply both the OESA and post-closure methodologies.

7.4 Post-closure

Gas that is formed in a GDF may dissolve in water, undergo chemical reactions or form a free gas phase. The amount of free gas and its migration through the EBS and the

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31 These timings correspond to the current baseline programme.
geosphere depend strongly on site-specific conditions, and may also depend on the design of the GDF. Two important aspects of the geological environment are the amount of water available to dissolve the gas and the permeability and porosity of the host rock.

A small amount of gas could dissolve in groundwater in the EBS. This dissolved gas will undergo advection along with the groundwater and diffusion due to concentration gradients in the groundwater. The majority of the gas is expected to form a free gas phase (although this may not be retained at longer times in certain environments). To avoid pressurisation, the EBS will be designed to allow migration of gases out of the vented waste packages and through any backfill. Carbon dioxide is expected to react with cement-based materials that are likely to be used in the ILW and LLW vaults, and thus will be retained in the EBS.

The three generic host rock environments have been considered, along with the important features that may be found in the overlying rocks.

In a **higher-strength host rock**, the gas will migrate through fractures in the host rock. Other site specific features (e.g. a cap rock, an open fault, a gas trap, an aquifer) could be present in the overlying geological environment and these features could delay or prevent gas reaching the biosphere and affect the area over which any gas would be released.

Because a **lower-strength sedimentary host rock** would have low permeability and very small pores, it will be more difficult for the gas to migrate across the host rock than in a higher-strength rock. Gas would also migrate across the host rock more slowly. Resaturation will be slower in this environment and water ingress may be reduced or prevented by pressurisation of the GDF. In a lower strength sedimentary rock, it may be appropriate to manage gas pressure in the GDF through the use of gas permeable seals and backfill materials, but these requirements would be site specific. However, it may well not be desirable for the pressure to be released by allowing the gas to return directly to the surface via an access shaft.

In the case of an **evaporite**, the gas phase would be expected to be confined to the host rock immediately surrounding the GDF and would not be expected to reach the biosphere. This would depend on the details of the actual geological environment and the efficacy of the sealing of access routes.

The calculated post-closure consequences are dependent on the migration time relative to the half-life of carbon-14 and the area over which the carbon-14 is released to the deep soil. Six illustrative cases have been developed to enable the implications of the release of carbon-14 to be assessed; they include a case where there is no release of carbon-14. These cases are not exhaustive, but they span the geological environments that may be considered in the future to host a GDF. The development of the cases is discussed in one of the companion reports [15]. They are listed in Table 16. Given that there is no specific site currently being investigated, none of these cases is given more weight than any other.

The environment agencies’ GRA [10] has two requirements that are particularly relevant to the post-closure period:

- If there is a period of institutional control after closure, then the source-related dose constraint for members of the public for a new facility of 0.15 mSv yr\(^{-1}\) applies (Requirement R5 – see Section 6.1 above);
- After any period of institutional control, risks should be consistent with the risk guidance level of 10\(^{-6}\) (Requirement R6 [10]), using the dose to risk conversion factor of 0.06 Sv\(^{-1}\).

At this generic stage of the programme, there is uncertainty over the period of institutional control, and so for simplicity the risk guidance level is applied; this is more stringent than the source-related dose constraint.
Table 16  Post-closure cases considered

<table>
<thead>
<tr>
<th>ID</th>
<th>Description</th>
<th>Delay Time ($^{14}$C ½-lives)</th>
<th>Release Area ($m^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Higher-strength host rock where gas is released over an area similar to the footprint of the GDF ILW/LLW vaults</td>
<td>0</td>
<td>$10^6$</td>
</tr>
<tr>
<td>B</td>
<td>Environments where there is a low permeability formation limiting gas migration</td>
<td>No release</td>
<td>No release</td>
</tr>
<tr>
<td>C</td>
<td>Higher-strength host rock where there are features that focus the release of gas to an area much less than the footprint of the GDF ILW/LLW vaults</td>
<td>0</td>
<td>$10^4$</td>
</tr>
<tr>
<td>D</td>
<td>Higher-strength host rock where there are features that distribute the release of gas to an area greater than the footprint of the GDF, e.g. as a result of dissolution</td>
<td>0</td>
<td>$10^7$</td>
</tr>
<tr>
<td>E</td>
<td>Lower-strength host rock where gas migrates slowly across the lower strength sedimentary host rock and is released over the footprint of the GDF ILW/LLW vaults</td>
<td>1</td>
<td>$10^6$</td>
</tr>
<tr>
<td>F</td>
<td>Lower-strength host rock where gas migrates slowly across the lower strength sedimentary host rock and there are features that distribute the release of gas to an area greater than the footprint of the GDF, e.g. as a result of dissolution</td>
<td>1</td>
<td>$10^7$</td>
</tr>
</tbody>
</table>

7.5 Species and pathways
There are a number of ways whereby carbon-14 species could potentially return to the biosphere. These are:

- Gaseous carbon-14 bearing methane;
- Gaseous carbon-14 bearing carbon monoxide;
- Dissolved carbon-14 bearing methane or carbon monoxide;
- Carbon-14 bearing carbon dioxide
- Inorganic aqueous species
- Small organic molecules

These species are based on those found in, for example, the graphite leaching experiments [19]. These are discussed in Table 17, where the assessment approaches for the migration pathways for the different species are considered.
Table 17 Species and pathways considered

<table>
<thead>
<tr>
<th>Species</th>
<th>Migration Pathway</th>
<th>Assessment Approach</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaseous $^{14}$CH$_4$</td>
<td>As a gas</td>
<td>Release as a gas in the operational and post-closure periods</td>
<td>Released up the stack during the operational period; released to the sub-soil during the post-closure period. This is the focus of the assessments. Leads to the highest post-closure radiological consequences.</td>
</tr>
<tr>
<td>Gaseous $^{14}$CO</td>
<td>As a gas</td>
<td>As gaseous $^{14}$CH$_4$</td>
<td>There is uncertainty in the quantity of CO produced. It is assessed in the same way as CH$_4$, i.e. it is assumed to be oxidised in the sub-soil zone in the same way as methane. CO can react with transition metals to form metal carbonyl compounds and complexes [114]$^{32}$, but there is uncertainty over the extent of reactions in the EBS and geosphere.</td>
</tr>
<tr>
<td>Dissolved $^{14}$CH$_4$ or $^{14}$CO</td>
<td>At least part of the pathway as a dissolved species</td>
<td>Any releases would be after closure – Cases D and F in Table 16</td>
<td>Assessed in the same way as the gaseous species, i.e. assumed to outgas in the sub-soil zone and be oxidised in the same way as the gaseous species. Dissolution is expected to contribute to a larger release area, and may contribute to a delay.</td>
</tr>
<tr>
<td>$^{14}$CO$_2$</td>
<td>Expected to react with cementitious materials in the GDF</td>
<td>No release</td>
<td>There may be an associated aqueous species (e.g. CO$_3^{2-}$) – this would be considered as part of inorganic aqueous species below.</td>
</tr>
<tr>
<td>Inorganic aqueous species</td>
<td>Groundwater</td>
<td>Not assessed here – see comment</td>
<td>These species will migrate and are considered in the PCSA [46]. They may be solubility limited and they may sorb. As their migration time is significantly longer than the $^{14}$C half-life, the calculated risks are negligible – $^{14}$C is not one of the radionuclides shown in Figure 15 of the PCSA$^{33}$.</td>
</tr>
<tr>
<td>Small organic molecules</td>
<td>Groundwater</td>
<td>Not assessed quantitatively – see comment</td>
<td>Not received much attention to date, although they were considered in reference [115]. Potential significance has been considered in Section 5.7 of [15]. May not be solubility limited or sorbed – would then migrate with the groundwater. May be degraded in the geosphere by microbes to form CO$_2$ and CH$_4$ (see Section 5.4)$^{34}$. This degradation will not coincide with a bulk gas phase, and resulting gases would be in solution. Impact will be bounded by the post-closure risks for Cases D and F (Section 7.4). Potentially more $^{14}$C released as small molecules from graphite than as CH$_4$ directly – see Section 8.5.2.</td>
</tr>
</tbody>
</table>

$^{32}$ Reference [114] states, ‘only for nickel and iron is direct reaction of metal with carbon monoxide feasible’. Finely divided nickel will react at room temperature, whereas reaction with iron requires elevated temperatures and pressures. Other transition metals require more extreme conditions and different starting compounds (e.g. cobalt carbonyl species are prepared from cobalt carbonate at 250-300 atm pressure and 120-200°C. The metal carbonyl products can be solid, e.g. V(CO)$_6$, or volatile liquids, e.g. Cr(CO)$_6$, Mo(CO)$_6$, Fe(CO)$_5$, and Ni(CO)$_4$, the latter reported as decomposing readily to metal. They can also form anionic complexes (carbonylate ions) under alkaline conditions, e.g. Mn(CO)$_5^-$, Fe(CO)$_5^{2-}$, Co(CO)$_5^-$; Mn(CO)$_5^-$, but complexation with other ligands, such as amines, may provide competition for complex formation.

$^{33}$ The low risks found are also illustrated in Figure 29 of the viability report [3] – groundwater pathway risks are over 7 orders of magnitude lower than for gas.

$^{34}$ This would occur in the geosphere as the microbial activity will be suppressed by the high pH of the near field (see Section 4.4).
7.6 Summary of calculations undertaken

The calculation cases considered in the modelling described in subsequent sections are summarised in Table 18. The periods listed broadly correspond to those identified in Table 15.

Any releases during the operational phase would be via a stack, and so the OESA methodology (Table 11) has been applied. Releases during the backfilling period could be either up the stack, or they could be delayed and released in the post-closure period. Therefore, cautiously, both the OESA (Table 11) and post-closure methodology (Table 12) have been applied. The post-closure methodology (Table 12) was applied to releases after closure.

Table 18 Summary of cases considered

<table>
<thead>
<tr>
<th>Stage</th>
<th>OESA (from Table 12)</th>
<th>Post-closure (from Table 13)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emplacement</td>
<td>Yes</td>
<td>No</td>
<td>Any gas generated would be released through the ventilation system.</td>
</tr>
<tr>
<td>Backfilling</td>
<td>Yes</td>
<td>Yes</td>
<td>Gas may be released during operations through the ventilation system or it may be retained within the system and released following closure. Therefore consider both and post-closure implications.</td>
</tr>
<tr>
<td>Early Post-closure</td>
<td>No</td>
<td>Yes</td>
<td>Corresponds to the period of about 30 years after backfilling. The implications are generally considered qualitatively. There will be no release during this period in Cases E and F (Table 16).</td>
</tr>
<tr>
<td>Medium-term Post-closure</td>
<td>No</td>
<td>Yes</td>
<td>Corresponds to the period over which Magnox corrodes (about 1000 years) – consider Cases A to D in Table 16. There will be no release during this period in Cases E and F.</td>
</tr>
<tr>
<td>Long-term Post-closure</td>
<td>No</td>
<td>Yes</td>
<td>Corresponds to the period after the reactive metals have corroded – consider Cases A to F in Table 16.</td>
</tr>
</tbody>
</table>
8 Irradiated Graphite Wastes

Irradiated graphite wastes were a significant contributor to calculated releases of carbon-14 in the Phase 1 work. As a consequence work in Phase 2 has examined the various components of the AND approach for these wastes, to enable an improved assessment for these wastes to be developed.

The Phase 1 work of the project concluded that, ignoring any potential benefits from the geosphere in retarding or preventing gas from reaching the surface, the calculated release rates of carbon-14 from irradiated graphite exceed the risk guidance level in the post-closure period.

The approach to addressing the ‘AND’ approach for graphite wastes (see Section 1.4) has been to seek new evidence, to improve the available data, and to develop a new model for the release of carbon-14 from irradiated graphite wastes. In particular the available inventory data have been reviewed and refined (Section 8.1). The experimental evidence for the release of carbon-14 from irradiated graphite is summarised (Section 8.2); the resultant improved understanding has been incorporated into a revised model (Section 8.3). The results of the revised model are discussed in Section 8.4, and in Section 8.5 they are set in the context of the scenarios that have been developed as part of the work on the geosphere and biosphere; these scenarios have been selected to be appropriate given that the GDF programme is at a generic stage and no specific geological environment has been selected. Possible alternative approaches to the management of irradiated graphite wastes are considered in Section 8.6. The potential availability of additional samples of graphite for future experimental programmes is described in Section 8.7. The current position on irradiated graphite wastes is summarised in Section 8.8.

Further details are provided in the separate report on irradiated graphite wastes that has been written as part of the project [12].

8.1 Inventory

The inventory of carbon-14 associated with graphite wastes that was used in Phase 1 of the project has been reviewed as the 2013 Derived Inventory has been developed. This has resulted in a modest reduction in the inventory (from 7190 TBq to 6930 TBq). This revised inventory has been incorporated into the Phase 2 work.

The wastes streams contributing to carbon-14 in graphite are grouped as follows:

- Magnox ILW core graphite;
- AGR ILW core graphite;
- Magnox and AGR LLW core graphite;
- Other core graphite;
- AGR fuel assembly graphite; and
- Magnox fuel element graphite.

The approach to evaluating the inventory for these waste groups has been examined and reviewed. The knowledge gained is summarised in Table 19. Further details can be found in reference [11].

The revised inventory of carbon-14 in the graphite waste streams is given in Table 20. The changes from the previous Derived Inventory are also summarised in the table. Further details can be found in Appendix A of reference [11]. It can be seen that, although there
has been an increased understanding of the inventory of carbon-14 associated with graphite wastes, the overall inventory is little changed from the previous inventory.

Table 19 Summary of knowledge gained for legacy graphite wastes

<table>
<thead>
<tr>
<th>Waste stream group</th>
<th>Remaining knowledge gap at the end of Phase 1</th>
<th>Knowledge gained during Phase 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILW core graphite</td>
<td>How representative are the calculations, as there is a wide range in graphite elemental compositions?</td>
<td>Based on carbon-14 measurements of a PGA moderator, Magnox Ltd has used a nitrogen precursor concentration of 25 ppm for PGA(^1) and PGB across reactors.</td>
</tr>
<tr>
<td></td>
<td>Nitrogen impurity levels used in the AGR core graphite calculations.</td>
<td>There are different nitrogen precursor concentrations of 15 ppm and 2.5 ppm for the stations. It is understood that values of 15 ppm were determined by mass spectrometry.</td>
</tr>
<tr>
<td></td>
<td>Whether the loss of carbon-14 to the coolant has been included in calculations, and whether or not possible additional nitrogen from the adsorption of nitrogen from additives to coolant gases onto graphite surfaces are accounted for.</td>
<td>No account has been taken of potential losses in carbon-14 activity or the potential adsorption (with the exception of Windscale Piles).</td>
</tr>
<tr>
<td>ILW AGR fuel element graphite</td>
<td>Nitrogen impurity levels.</td>
<td>No further information was obtained.</td>
</tr>
<tr>
<td>ILW Magnox fuel element graphite</td>
<td>Nitrogen impurity levels.</td>
<td>No further information was obtained.</td>
</tr>
</tbody>
</table>

Note:
1. PGA and PGB are Pile grade A and Pile grade B.

Table 20 Summary of the carbon-14 activity in graphite in the 2013 Derived Inventory and the change from the 2010 Derived Inventory

<table>
<thead>
<tr>
<th>Waste Category</th>
<th>Carbon-14 activity (TBq) (^{(1)})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2010 Derived Inventory (^{(2)})</td>
</tr>
<tr>
<td>Graphite – ILW core graphite</td>
<td>7,090</td>
</tr>
<tr>
<td>Graphite – ILW AGR fuel assembly graphite</td>
<td>45.0</td>
</tr>
<tr>
<td>Graphite – ILW Magnox fuel element graphite</td>
<td>6.15</td>
</tr>
<tr>
<td>Graphite – LLW core graphite</td>
<td>5.74</td>
</tr>
<tr>
<td>Total</td>
<td>7,150</td>
</tr>
</tbody>
</table>

Note:
1. All numbers are reported with up to 3 significant figures. This can mean that the change in activity does not exactly equal the difference between the 2010 Derived Inventory and the 2013 Derived Inventory.
8.2 Experimental evidence on the release of carbon-14 from irradiated graphite

Experiments on the release of carbon-14 from irradiated graphite have been undertaken as part of a number of programmes. These provide a good understanding of the proportion of carbon-14 that is released, the rate at which it is released, and its speciation following release. The evidence shows:

- A substantial fraction of the carbon-14 in graphite is not releasable;
- Some carbon-14 will initially be released rapidly, and some will be released more slowly at a rate reducing over time (i.e. the release cannot be defined by a single rate constant);
- Carbon-14 can be released to both the gas and aqueous phases. Carbon-14 released to the gas phase may exist as a number of different species with potentially different consequences, including organic species (e.g. CH₄), CO₂ and CO;
- Release rates and speciation of the released carbon-14 may change depending on the conditions (e.g. pH and presence of oxygen).

A review of the then current understanding of carbon-14 releases from graphite wastes was included in Section 4.1 of the Phase 1 Report [2]. As part of the Phase 2 work, this earlier review has been brought up to date to include the results of more recent work undertaken under the NDA RWMD [19] and EU CARBOWASTE programmes [e.g. 116, 117]. This section summarises the description provided in the supporting report on graphite [12].

The understanding that has been gained has been used as the basis for developing and parameterising a revised model for carbon-14 release from irradiated graphite. Three main inputs are required for the development of that model:

- information on the extent to which the carbon-14 content of irradiated graphite is potentially releasable;
- information on the potential carbon-14 release rates to both solution and the gas phase; and
- information on the speciation of any carbon-14 that is released and, in particular, its distribution between inorganic and organic species.

These aspects are discussed in turn.

8.2.1 The releasability of carbon-14 from irradiated graphite

New information on whether the carbon-14 can be released from irradiated graphite has emerged from the CARBOWASTE programme. A major focus of CARBOWASTE was on potential chemical and thermal treatments of irradiated graphite to reduce the inventory of releasable radionuclides, including carbon-14, prior to disposal in a GDF. The results of these studies are providing an insight into the location and nature of carbon-14 in irradiated graphite, the mechanisms of its release and the extent to which it is releasable, although only a limited amount of information has yet been published and made available in the public domain [e.g. 118, 119].

A recent study on chemical leaching of UK irradiated graphite was undertaken as part of the CARBOWASTE programme [116]. The principal objective of this work was to investigate the potential chemical treatment of irradiated graphite to remove labile carbon-14 and tritium prior to disposal. This work has provided insight into the releasability of the carbon-14 content of irradiated graphites.

This study concluded that only a small fraction of the total carbon-14 inventory (up to about 1%) is released on leaching over timescales of up to 3 years. Some illustrative results are
shown in Figure 15 for some samples from the BEP0 reactor. Even when harsh acidic conditions are applied, less than 30% of the carbon-14 inventory is released over the experimental timescales. These experiments support the conclusion that there are two forms of carbon-14 in irradiated graphite: a leachable form and an unleachable form. This is taken into account in the revised graphite model described in Section 8.3.

**Figure 15** Comparison of fractional carbon-14 releases from powdered and monolithic samples of BEP0 channel 16 graphite [116]

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### 8.2.2 Carbon-14 release rates from irradiated graphite under disposal conditions

Information on carbon-14 release rates from irradiated graphite under disposal conditions has been gained from the results of leaching experiments. Published release rate data from graphite leaching experiments up to 2002 (with one exception [120]) were reviewed by Marsden [121]. Most of these experiments were conducted at near-neutral pH and under oxic conditions, rather than under the anoxic and high-pH conditions of a cement-based GDF. In addition, none of these studies made measurements of gas phase releases or of the speciation of the carbon-14 released to solution.

To address these data gaps, new leaching studies more relevant to anoxic and high-pH disposal conditions were performed under the CARBOWASTE programme [116, 117] and as part of the UK programme. Following the demonstration that only a small fraction of the carbon-14 inventory of irradiated WAGR graphite was released to the gas phase [122], the focus of work on this topic became the discrimination and measurement of gas-phase carbon-14 (and tritium) releases [123, 124, 125].

The most recent study, on Magnox carrier graphite from Oldbury, has investigated a wider range of experimental conditions [19]. A number of effects on the rates and speciation of gaseous carbon-14 releases have been investigated, namely:

- anaerobic compared to aerobic conditions;
- pH;
- temperature; and
- the form of the graphite (powder or monolith).
The experiments included periodic sampling with leaching times of up to one year. In addition, the experimental design has been extended to discriminate between inorganic gas phase releases as $^{14}\text{CO}_2$ or $^{14}\text{CO}$. In common with a previous BEP0 study [124], measurements of carbon-14 releases to the solution phase were only made at the end of the experiments. However, one additional experiment was run under anaerobic high-pH conditions with periodic sampling to measure solution-phase releases only. An important feature of the results is that continued release of carbon-14 was observed to both gas and solution phases during the sampling period from 3 to 12 months, i.e. carbon-14 releases continued, albeit at a slow rate. A further sampling period is now underway to confirm whether this release continues.

The results of all six Oldbury graphite experiments in terms of the total gaseous phase carbon-14 releases as a fraction of the sample inventory are compared in Figure 16 where they are also compared to the BEP0 [124] and WAGR [122] results. In all cases, after an initial period of faster release, the rate of carbon-14 release decreases and is continuing at a slower rate at the end of the experiments.

Figure 16 Comparison of total gas phase carbon-14 releases from Oldbury (Magnox), WAGR and BEP0 graphites in leaching experiments under a range of experimental conditions (in the case of the pH 7 experiment with Oldbury graphite, the total comprises $^{14}\text{CO}_2$ and $^{14}\text{C}$-organic releases only); lines joining the points are included to aid the eye: oxic conditions - full lines, anoxic - dashed lines

The highest initial rate of gaseous carbon-14 release from Magnox graphite was measured in the experiment at 50°C, but this release rate decreased more rapidly over time (up to 94 days). In the experiment at pH 7 the gas phase releases were dominated by $^{14}\text{CO}_2$ due to lower solubility of CO$_2$ as carbonate at lower pH. The gas phase releases of $^{14}\text{CO}_2$ in this
case were about 15 times higher than those of $^{14}$CO and $^{14}$C organics combined, both of which were released at similar rates and in a similar ratio as at pH 13.

8.2.3 Speciation of carbon-14 released from irradiated graphite

One of the key aims of the experiments described above is to discriminate the speciation of the carbon-14 released, including whether the release is to the gas phase or to the solution phase. Work to discriminate between inorganic and organic carbon-14 releases to solution has also been undertaken in Japan [126–132] and more recently in France [117]; the French study also included measurements of gas phase carbon-14 releases.

Results from the Oldbury study [19] have confirmed that under both aerobic and anaerobic conditions the principal gas-phase inorganic species is $^{14}$CO (the majority of $^{14}$CO$_2$ release is retained as carbonate in solution). Figure 17 shows the gas-phase releases measured from an intact sample of Magnox graphite under anaerobic conditions at pH 13 and ambient temperature. The results of duplicate experiments under these conditions at pH 13 were similar. The line shown as ‘organics’ represents methane and other low molecular weight organics. Higher molecular weight organics would be expected to partition into solution.

Figure 17 Speciation of carbon-14 gaseous releases from Oldbury graphite under anaerobic conditions, pH 13 solution; total carbon-14 inventory of graphite sample is 2.8 MBq [19]

Releases to both solution and gas phases under anaerobic high-pH conditions show an initial rapid release followed by a slower release over longer timescales. The ratio of solution phase to gaseous release was of the order of 100:1 at most sampling points, but had increased to between 200-300:1 for the final samples after one year. This compares with a lower ratio of about 20:1 measured on termination of the BEP0 experiment after 431 days [124].

In summary, experimental evidence has shown that not all of the carbon-14 is releasable; graphite is a very stable material and it is thought that this unreleasable carbon-14 is associated with the graphite matrix. A small fraction of the carbon-14 is releasable on
leaching, but not all of it is released as gas. It is thought that this fraction is associated with carbonaceous surface deposits and this deposit reacts on leaching to produce species that are released into the aqueous or gaseous phase. Measurements show release in the form of carbon dioxide (which is mostly released in the aqueous phase, particularly in high pH environments), aqueous organic species and smaller amounts of gaseous carbon monoxide and methane or other hydrocarbons. These features have been represented in a revised model, which is described below.

8.3 Modelling the release of carbon-14 from irradiated graphite

The enhanced understanding of the release of carbon-14 has enabled a revised model of the release of carbon-14 to be developed and parameterised. This incorporates the understanding that only a proportion of carbon-14 is considered to be releasable. The experimental evidence has also been used to assess the uncertainties in the identified parameters.

8.3.1 Original model

Recent calculations of gas generation from ILW in a GDF, including those reported in Phase 1, have been performed with SMOGG v 5.1 [37, 38]. This includes a very simple empirical model for the release of carbon-14 from graphite into the gas phase. The model assumes that all the carbon-14 inventory in the graphite is available for release and it is released at a rate proportional to the remaining inventory. It assumes that all the carbon-14 released potentially forms gaseous molecules, but that CO2 molecules are likely to exist as carbonate in solution and the carbon-14 is likely to be immobilised by carbonation of the surrounding grout. Thus only a small fraction of the carbon-14 released is normally modelled as being released as a free gas. This level of detail is consistent with the information that was available to parameterise the model at the time it was developed. The conceptual model is illustrated in Figure 18.

Figure 18 Conceptual model for carbon-14 release from graphite on which the modelling in Phase 1 was based.

8.3.2 Revised model

The evidence base discussed in Section 8.2 indicates that the previous simple modelling approach could be improved. An improved conceptual model for the release of carbon-14 from graphite has been developed; the main features are shown schematically in Figure 19. In particular, the evidence shows:

- A substantial fraction of the carbon-14 in graphite is not releasable;
• Some carbon-14 will initially be released rapidly, and some will be released more slowly at a rate reducing over time (i.e. the release cannot be defined by a single rate constant);
• Carbon-14 can be released to both the gas and aqueous phases. Carbon-14 released to the gas phase may exist as a number of different species with potentially different consequences, including organic species (e.g. CH₄), CO₂ and CO;
• Release rates and speciation of the released carbon-14 may change depending on the conditions (e.g. pH, presence of oxygen).

Figure 19 Improved conceptual model for carbon-14 release from graphite used in Phase 2.

So that these behaviours can be accounted for in the Phase 2 calculations, the following improved mathematical model has been developed from the conceptual model for the release rate of carbon-14 from graphite, and has been implemented in SMOGG v7.0 [37, 38]

\[
q_c = [k_{ca} A'_c(0)e^{-k_{ca}t} + k_{cc} A'_c(0)e^{-k_{cc}t}]e^{-\lambda t}
\]

where:
- \(k_{ca}\) is a rate constant for the rapid release of carbon-14 from the graphite (yr⁻¹);
- \(k_{cc}\) is a rate constant for the slower release of carbon-14 from the graphite (yr⁻¹);
- \(A'_c(0)\) is the initial rapidly releasable activity of the carbon-14 in the graphite (TBq);
- \(A'_c(0)\) is the initial slowly releasable activity of the carbon-14 in the graphite (TBq).

The model also divides the carbon-14 release, allowing it to be released as a combination of CO, CO₂ and organic species (nominally represented as CH₄), with the same option as used in the Phase 1 model (see Section 8.3.1) for CO₂ to be retained as carbonate in cementitious grouts or backfill (so that it is not released as a gas). In addition, the model allows rate constants and speciation of released carbon-14 to differ for different sets of conditions.

The model includes two terms, so that it can represent both rapid initial and slower long-term releases; initially the first term will normally dominate, whereas at sufficiently large times the second term will dominate. Each term includes an activity factor (the sum of which must be less than the total activity), so that only the relevant fractions of the total activity can be released at each of the two rates, and any remaining activity fraction will not be released. Otherwise each term is similar to the model used in Phase 1, so that each component of the release rate reduces over time.

8.3.3 Model parameterisation

The inputs required for this model will be:
• The initial total activity of carbon-14 in the graphite;
• The fractions of the carbon-14 activity in the graphite that are available for rapid and slower releases (any remaining fraction will not be releasable);
• Rate constants for the rapid release of carbon-14 under each set of conditions;
• Rate constants for the slower release of carbon-14 under each set of conditions;
• The fractions of carbon-14 released as CH₄ and CO under each set of conditions (the fraction not released as CH₄ or CO is assumed to be released as CO₂).

For consistency with the current options available for gas generation modelling in SMOGG, three sets of conditions are considered for which input values can be specified. These are:
• Aerobic, neutral pH: expected to be applicable to waste packaged without grouting;
• Aerobic, high pH: expected to be applicable to grouted waste during GDF operations and early post-closure;
• Anaerobic, high pH: expected to be applicable in the post-closure period, usually after resaturation.

Clearly, the improved model is still empirical. Although some information regarding the potential mechanisms of release of carbon-14 from graphite has been obtained, the mechanisms are not currently fully understood. Therefore, it is appropriate for the model to represent the important features of the release behaviour observed across the various types of experiments. The limitation of this approach is that there will be uncertainty in the release calculated by the model on timescales that are substantially longer than those for which experimental data are available.

In the light of the experimental evidence summarised in Section 8.2 above (and discussed in more detail in references [12, 19], the following parameterisation has been adopted; the release model parameters are shown in Table 21, and the speciation parameters in Table 22. This parameterisation is cautious, taking into account the long timescales over which leaching may occur and the partial variability of the graphite used in different reactors. When longer-term measurements are available it may be possible to reduce the release rates and release fractions.

Table 21 Parameter values for carbon-14 release recommended for use with the revised model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lower bound</th>
<th>Best estimate</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constant for the rapid release of carbon-14 from graphite (kᵣ)</td>
<td>10 yr⁻¹</td>
<td>30 yr⁻¹</td>
<td>100 yr⁻¹</td>
</tr>
<tr>
<td>Rate constant for the slower release of carbon-14 from graphite (kₛ)</td>
<td>1 10⁻³ yr⁻¹</td>
<td>1 10⁻² yr⁻¹</td>
<td>1 10⁻¹ yr⁻¹</td>
</tr>
<tr>
<td>Fraction of the carbon-14 activity in the graphite that is available for rapid release</td>
<td>0</td>
<td>2 10⁻⁴</td>
<td>2 10⁻³</td>
</tr>
<tr>
<td>Fraction of the carbon-14 activity in the graphite that is available for slower release</td>
<td>1 10⁻²</td>
<td>5 10⁻²</td>
<td>3 10⁻¹</td>
</tr>
</tbody>
</table>
Table 22  Parameter values for speciation of released carbon-14 recommended for use with the revised model.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Fraction released as CO$_2$</th>
<th>Fraction released as CO</th>
<th>Fraction released as CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic, neutral pH</td>
<td>0.99</td>
<td>0.0050</td>
<td>0.0050</td>
</tr>
<tr>
<td>Aerobic, high pH</td>
<td>0.99</td>
<td>0.0050</td>
<td>0.0050</td>
</tr>
<tr>
<td>Anaerobic, high pH</td>
<td>0.99</td>
<td>0.0033</td>
<td>0.0066</td>
</tr>
</tbody>
</table>

8.4  Application of the revised model

The original model for the release of carbon-14 from graphite was used in the Phase 1 report [2]. The revised model allows the rates of release from graphite to be re-assessed. The implications for the identified uncertainties have also been considered. The improved understanding has shown that not all the carbon-14 is released and not all that is released is released as a gas. The gases generated include methane and carbon monoxide.

The revised model results in lower generation rates of carbon-14 bearing gases in the post-closure period. The rates also fall off more rapidly than in the Phase 1 calculations.

In this section, the results of the revised model are first discussed, and the sensitivities explored (Section 8.4.1); then the Phase 2 results for graphite are summarised (Section 8.4.2).

8.4.1  Comparison with Phase 1

The results of the revised model are shown in Figure 20, where the release from the graphite component of SILW is shown. To show the development from Phase 1 of the project, the results correspond to the Phase 1 inventory.

The Figure shows:

- The results of the Phase 1 calculation;
- The results from the revised model using the best-estimate parameters in Table 21 and Table 22;
- Three variants based on the lower and upper bounds in Table 21.
  - **Variant 1**: Slowly releasable fraction reduced to lower bound value of 1% (as given in Table 21), and rate constant for slower release increased accordingly to $5 \times 10^{-2}$ yr$^{-1}$.
  - **Variant 2**: Slowly releasable fraction increased to upper bound value of 30% (as given in Table 21), and rate constant for slower release decreased accordingly to $1.67 \times 10^{-3}$ yr$^{-1}$.
  - **Variant 3**: Slowly releasable fraction increased to upper bound value of 30% (as given in Table 21), and rate constant for slower release increased to upper bound value of $1 \times 10^{-1}$ yr$^{-1}$.

35 The carbon-14 released as CO$_2$ is assumed to be the sum of the $^{14}$CO$_2$ measured in the gas phase (this is only significant for neutral pH conditions) and the total carbon-14 in solution. For high pH conditions, the proportion released as gaseous carbon dioxide is small in comparison to the fractions released as carbon monoxide and methane.
The main change in the case with the best estimates of the parameters is that the release rate in the longer term is reduced. This arises because of the different rate constant in the longer term. In the revised model the rate constant is larger, so the release occurs over a shorter period. This means that the release rate becomes insignificant after a few hundred years, compared with ten thousand in the Phase 1 calculation.

The Figure shows that changing the slowly releasable fraction, and rescaling the rate constant accordingly, essentially affects the rate of reduction of the release rate, so that a smaller releasable fraction results in the release rate reducing more quickly (Variant 1), and the opposite is true for a larger releasable fraction (Variant 2). The extent of this change is such that if only 1% of the carbon-14 inventory in graphite is releasable, its release is a potential issue only for a few decades post-closure. Further, if an upper bound value for the rate constant for the slower release is assumed, the potential issue will still only exist for a relatively short period, even if the releasable fraction is larger (Variant 3). This is because in this case the release mainly occurs in the operational period, and occurs at a much higher rate in this period than calculated previously (this may mean that the operational release rate requires further consideration). It should be noted other possible variant calculations (i.e. with smaller values for both releasable fraction and the rate constant for the slower release) would indicate that there is no issue at any time.

**Figure 20 Calculations of carbon-14 containing gas generation rate for the graphite component of the waste for SILW/LLW using the previous model and revised model (including variant sets of parameter values)**

8.4.2 Phase 2 results

The results for the reference-case SMOGG calculation in the Phase 2 calculations with the revised model are shown in Table 29. Five time periods are shown:

- the emplacement period (the conditions are aerobic and the temperature is assumed to be 35°C);
- the backfilling period (the conditions are aerobic and the temperature is assumed to be 45°C);
the early post-closure period (taken to be around 30 years – during which the conditions in the GDF become anaerobic; initially the temperature is assumed to be 45°C, and then is assumed to fall to 35°C);

- the medium-term post-closure period (taken to be around a thousand years – the conditions are anaerobic and the temperature is assumed to be 35°C); and

- the long-term post-closure period (the conditions are anaerobic and the temperature is assumed to be 35°C).

The results are shown for $^{14}$CH$_4$ and $^{14}$CO. $^{14}$CO$_2$ is not shown, as it is assumed that it reacts with the cementitious backfill.

**Table 23** Generation rates of carbon-14 (TBq yr$^{-1}$) from irradiated graphite, for the different phases of the GDF, before and after closure

<table>
<thead>
<tr>
<th>Graphite</th>
<th>Emplacement period</th>
<th>Backfilling period</th>
<th>Early post-closure</th>
<th>Medium-term post-closure</th>
<th>Long-term post-closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>$1.23 \times 10^{-2}$</td>
<td>$6.56 \times 10^{-3}$</td>
<td>$6.56 \times 10^{-3}$</td>
<td>$4.92 \times 10^{-3}$</td>
<td>$7.45 \times 10^{-7}$</td>
</tr>
<tr>
<td>CO</td>
<td>$1.23 \times 10^{-2}$</td>
<td>$5.61 \times 10^{-3}$</td>
<td>$5.61 \times 10^{-3}$</td>
<td>$2.46 \times 10^{-3}$</td>
<td>$3.72 \times 10^{-7}$</td>
</tr>
<tr>
<td>CH$_4$ + CO</td>
<td>$2.46 \times 10^{-2}$</td>
<td>$1.12 \times 10^{-2}$</td>
<td>$1.12 \times 10^{-2}$</td>
<td>$7.37 \times 10^{-3}$</td>
<td>$1.12 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

The comparison with Phase 1 is shown in Figure 21. The generation rates during the operating and backfilling periods are similar to or slightly lower in Phase 2. This is partly due to the modest decrease in the inventory of carbon-14 associated with graphite, although the main change arises from the improved model, which recognises that there is a proportion of carbon-14 that will not be released. The generation rate is over three orders of magnitude lower in the long-term post-closure than in the medium-term post-closure.

**Figure 21** Comparison of the maximum generation rates (TBq yr$^{-1}$) in Phase 1 and Phase 2 for irradiated graphite wastes
8.5 Implications for release of carbon-14 from irradiated graphite

Having calculated the generation rates in the different phases of the GDF evolution, these can be set in context by combining them with the migration scenarios and biosphere factors developed in the earlier sections of this report.

Effective doses during the operational phase arising from methane and carbon monoxide are below the source-related dose constraint for members of the public for a new facility. Post-closure risks are below the risk guidance level for all but one of the migration scenarios. They are above the risk guidance level for the case of a focused discharge to the smallest area of $10^4 \text{ m}^2$.

To set the generation rates in context, the reference-case generation rates (summarised in Table 23) have been combined with the biosphere and migration cases developed in Sections 6 and 7. The operational and post-closure cases are discussed in turn.

8.5.1 Operational period

The updated OESA methodology described in Section 6.1 is applied to the operational and backfilling stages (Sections 7.2 and 7.3).

The pathway considered for release from the GDF is for the gases to be ventilated out of a 15m high stack. The effective doses during the operational phase can be calculated by combining the generation rate with the recommended effective dose factors given in Table 12. The effective doses are shown in Table 24. The values for carbon dioxide are not included in the Table, as it would be expected to react with the cementitious grout in the packages.

Table 24 Calculated effective doses (mSv yr$^{-1}$) from off-site discharge of carbon-14 to the local resident family receptor group for irradiated graphite wastes

<table>
<thead>
<tr>
<th>Graphite</th>
<th>Gas</th>
<th>Operational period</th>
<th>Backfilling period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Maximum discharge (TBq yr$^{-1}$)</td>
<td>Dose rate (mSv yr$^{-1}$)</td>
</tr>
<tr>
<td>UILW</td>
<td>$^{14}\text{CH}_4$</td>
<td>$1.32 \times 10^{-3}$</td>
<td>$1.99 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$^{14}\text{CO}$</td>
<td>$1.32 \times 10^{-3}$</td>
<td>$1.59 \times 10^{-4}$</td>
</tr>
<tr>
<td>SILW</td>
<td>$^{14}\text{CH}_4$</td>
<td>$1.11 \times 10^{-2}$</td>
<td>$1.66 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>$^{14}\text{CO}$</td>
<td>$1.11 \times 10^{-2}$</td>
<td>$1.33 \times 10^{-3}$</td>
</tr>
<tr>
<td>Total</td>
<td>$^{14}\text{CH}_4$</td>
<td>$1.23 \times 10^{-2}$</td>
<td>$1.85 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>$^{14}\text{CO}$</td>
<td>$1.23 \times 10^{-2}$</td>
<td>$1.48 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The contribution to effective dose rate from carbon-14 bearing gases during the operational period is below the maximum effective dose rate constraint to members of the public from a new facility of $0.15 \text{ mSv yr}^{-1}$ (see Section 6.1).

8.5.2 Post-closure period

The early and medium-term post-closure risks arising from the corrosion of irradiated graphite are shown in Table 25. These are obtained by combining:

- The reference-case generation rate given in Table 23;
- The migration cases described in Section 7;
The biosphere factors given in Table 13; and

- The dose to risk conversion factor of 0.06 Sv⁻¹ [10].

The environment agencies’ risk guidance level is 10⁻⁶ [10], and risks above this guidance level are shown in **Bold**. Only Case C (Focused Release) is above the risk guidance level in the early post-closure and medium-term post-closure periods. In three of the cases (Cases B, E and F), there is no release during this period. Risks in the long-term post-closure period are negligible.

**Table 25 Post-closure risks for the graphite wastes for the different migration cases**

<table>
<thead>
<tr>
<th>Geosphere case</th>
<th>Annual risk</th>
<th>Early post-closure (2200 to 2230 AD)</th>
<th>Medium-term post-closure (2230 to 3000 AD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID</td>
<td>Release area (m²)</td>
<td>Delay time (¹⁴C half-lives)</td>
<td>4.80 10⁻⁷</td>
</tr>
<tr>
<td>A</td>
<td>10⁶</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>No release</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>10⁴</td>
<td>0</td>
<td>4.80 10⁻⁵</td>
</tr>
<tr>
<td>D</td>
<td>10⁷</td>
<td>0</td>
<td>4.80 10⁻⁸</td>
</tr>
<tr>
<td>E</td>
<td>10⁶</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>10⁷</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Some of the carbon-14 identified for release as carbon dioxide in Table 22 could be released as small organic molecules. These have not received much attention to date, although they were considered in reference [115]. The potential significance has been considered as part of this project, and this is discussed in Section 5.7 of [15]. They are potentially not solubility limited and they may or may not be sorbed, and will initially migrate with the groundwater. They will potentially be degraded by microbes to form carbon dioxide and methane (see Section 5.4). This would occur in the geosphere as the microbial activity will be suppressed by the high pH of the near field (see Section 4.4). Therefore this degradation will not be expected to coincide with the bulk gas phase, and resulting gases would be expected to be in solution. The impact from such methane is expected to be bounded by the medium-term post-closure risks for Cases D and F above. There is sufficient margin in the risks calculated for graphite (Table 25) for the risks from methane generated from small molecules to be below the risk guidance level.

The improved understanding also has implications for the assessment of the groundwater pathway in terms of the inventory available for release and the speciation of carbon-14 in the aqueous phase. Account could be taken of the significant proportion of carbon-14 in graphite that would not be released on relevant timescales.

### 8.6 Alternative approaches for the management of graphite wastes

Graphite wastes constitute a distinct waste group, which could be considered for disposal in distinct vaults in a separate part of the GDF. As part of the work of the project, this alternative approach has been explored to examine the potential benefits.

It has been concluded that, although disposal in separate vaults is feasible, it is not necessary for the management of carbon-14.

It has been proposed that graphite could be disposed of in separate vaults. It is recognised that, although graphite is potentially a substantial source of gaseous carbon-14 generation, graphite itself does not generate any bulk gas. Without a source of bulk gas there will be
no significant consequences from the generation of carbon-14 post-closure, since the carbon-14 containing gases alone will not be able to form a gas phase that can migrate through the geosphere\textsuperscript{36}. In the reference case calculations it is assumed that bulk gas generated from other sources provides the required gas phase. In particular, since most graphite waste is expected to be packaged in stainless steel containers these will provide a bulk gas source local to the graphite as they corrode under anaerobic conditions.

Given that graphite waste itself does not generate bulk gas, there is potential to restrict bulk gas generation in the vicinity of the graphite wastes, and therefore to prevent migration of carbon-14 generated from graphite post-closure. On this basis the following alternative options were identified in Phase 1 \cite{2} as being potentially beneficial:

- Segregation of core graphite wastes from other wastes;
- Emplacement of core graphite wastes in the GDF with minimal packaging.

Alternative options involving disposal in shallower vaults and with no cement were also identified in Phase 1 as potentially of interest. However, these options were seen as opportunities to simplify the disposal of these wastes, rather than options to reduce the consequences relating to the generation of gaseous carbon-14. A cementitious backfill may be required to limit the generation of gaseous $^{14}$CO$_2$.

The benefits of some alternative options for the packaging and disposal of graphite wastes have also been considered in previous modelling studies. In particular, one study \cite{133} has considered segregation of graphite wastes and use of an alternative backfilling material (sand-bentonite) for both a higher-strength host rock and a lower strength sedimentary host rock. This study concluded that segregation was desirable, and that use of an alternative backfill (that provides a more substantial physical barrier) may also be an advantage for segregated graphite waste.

If packages containing other waste are emplaced in the same vault as graphite waste, it is difficult to determine how bulk gas generated from the other waste will affect the transport of carbon-14 containing gas generated from the graphite. Given this, the option of minimal packaging identified in Phase 1 is not considered alone, but in combination with segregation of graphite waste.

A further option between simple segregation of graphite waste and segregation with minimal packaging is also possible, namely segregation and use of packages with low metal content. It should, however, be noted that if concrete containers are used, there would still be some metal in them due to the reinforcements. If these comprised a modest amount of steel, then there might be insufficient for a free gas phase to form.

The option of shallower vaults affects only the bulk gas generation rate required for a gas phase to form. At shallower depths the solubility of gas in the groundwater will reduce, but the flow rate of the groundwater may be higher. However, the potential for a gas phase to form will still be bounded by the analysis presented in Section 4.1. Therefore, in terms of the consequences of gaseous carbon-14 post-closure, it can be concluded that the depth of the vaults is not expected to be a significant factor. The option of no cement is expected to increase corrosion rates of any metals present. Therefore, for this to be viable it must also be considered in combination with segregation of graphite waste.

Taking the above into account, the following four alternative options have been selected for further analysis:

\begin{itemize}
  \item Segregation of core graphite wastes from other wastes;
  \item Emplacement of core graphite wastes in the GDF with minimal packaging.
  \item Segregation of core graphite wastes and use of an alternative backfilling material (sand-bentonite) for both a higher-strength host rock and a lower strength sedimentary host rock.
  \item Segregation and use of packages with low metal content.
\end{itemize}

\textsuperscript{36} Carbon-14 migrating from the GDF to the biosphere in solution is not expected to lead to significant radiological consequences. There may nevertheless be other significant radionuclides in the waste, such as chlorine-36. The potential radiological consequences of transport of such radionuclides in groundwater are not considered further in this report.
Segregation of graphite waste from all other wastes;
• Packaging of graphite wastes in concrete containers and segregation from all other wastes;
• Segregation of unpackaged graphite wastes from all other wastes;
• Packaging of graphite wastes without grouting and segregation from all other wastes in unbackfilled vaults.

The benefit of these options has the potential to be significant only if applied to the majority of the graphite waste. Considering the graphite waste streams in the 2013 DI, most of them contain only graphite and no other waste materials, and the majority are Legacy SILW. Therefore the alternative options are most relevant to the Legacy SILW / SLLW group. Any benefit for this waste group is likely to be proportionately smaller for other waste groups. Calculations of gas generation and the associated consequences for each of the four alternative options have been undertaken and are reported in reference [12]. The conclusions are summarised in Table 26.
Table 26  Summary of the conclusions from the study of alternative options for graphite

<table>
<thead>
<tr>
<th>Option</th>
<th>Summary of Results</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Segregation</td>
<td>Bulk gas generation rate is much lower for the first few hundred years following closure, but is only a factor of 3 lower at longer times.</td>
<td>The implications are site dependent. Increases the range of host rocks for which the groundwater flow would be high enough to prevent a gas phase from forming compared with the gas generation for the reference case, but is still sufficient that a gas phase would form in a GDF in many locations.</td>
</tr>
<tr>
<td>Segregation with concrete containers</td>
<td>Bulk gas generation rate is much lower for the first few hundred years following closure, but is only a factor of 3 lower at longer times. There is less steel in the packaging, but this is balanced by the higher corrosion rate of the mild steel reinforcements in the concrete container.</td>
<td>The implications are site dependent. Increases the range of host rocks for which the groundwater flow would be high enough to prevent a gas phase from forming compared with the gas generation for the reference case, but is still sufficient that a gas phase would form for a GDF in many locations.</td>
</tr>
<tr>
<td>Segregation with no packaging</td>
<td>Much lower gas generation rates throughout the post-closure period.</td>
<td>The implications are site dependent. This option substantially increases the range of host rocks for which the groundwater flow would be high enough to prevent a gas phase from forming compared with the gas generation for the reference case. There is a realistic possibility that there will be no gas phase for much of the likely range of properties for higher-strength host rocks, but is less likely for other potential rock types. Certain aspects of practicability, such as of handling, contamination control, retrievability and dose control, would need further consideration to confirm the viability of this option.</td>
</tr>
<tr>
<td>Segregation with normal containers but no cement</td>
<td>Much higher gas generation rates. Potentially a substantial increase in the gaseous carbon-14 generation rate post-closure.</td>
<td>It is not recommended that disposal in a non-cementitious environment is considered as a suitable option for segregated graphite waste. It may still be viable if implemented alongside other modifications to the management of the waste (e.g. disposal without containers), or if a non-cementitious backfill that may provide alternative benefits was used, such as sand-bentonite as considered in a previous modelling study [133].</td>
</tr>
</tbody>
</table>

Of the options, the third option (segregation with no packaging) offers the clearest benefit if the potential consequences arising from carbon-14 generation from graphite are a concern. The practicality of this option has not been considered here; this would be required as a next step before this option could be taken forward.

However, the conclusion of this study on alternative approaches for the management of graphite is that, although disposal in separate vaults is feasible, it is not necessary for the management of carbon-14 (except potentially in environments where the gaseous release is focused over a very small area).
8.7 Additional graphite samples

As part of the work of the project, the availability of additional graphite samples has been investigated that could support consideration of further experiments. Such experiments would complement the experiments already undertaken in support of the UK disposal programme, and the programmes of overseas waste management organisations. However, allowing the current experiments to run for a long period of time appears to be the most attractive option.

The types of graphite of most relevance to radioactive waste disposal in the UK are Magnox core graphite, which totals around 48,000 tonnes, and AGR core graphite, at 23,000 tonnes. Other sources, including Windscale Piles and Experimental Test reactors, contribute to a total of 76,000 tonnes of nuclear graphite waste.

Magnox reactors used PGA (Pile grade A) graphite. It was produced from a petroleum coke, which is a by-product of the oil refining industry. The PGA coke has needle-shaped coke particles, which tended to align. Significant quantities of irradiated graphite from Oldbury have been handled by Amec Foster Wheeler in its active laboratory at Birchwood [19]. These samples are currently held by NNL but, subject to agreement with Magnox Ltd, this material could potentially be used in experiments to augment the data already available. In particular, access to additional samples would help to improve understanding of the variability of carbon-14 releases from irradiated graphite from different locations and irradiation histories. Amec Foster Wheeler has also investigated the procurement of samples of additional irradiated Magnox graphite. These samples are being made available primarily for studies of changes in physical properties in the reactor, but a fraction may be made available for measurements of radionuclide release.

The AGR reactors used Gilsocarbon graphite. In comparison to PGA, Gilsocarbon is a more robust graphite that has a polycrystalline microstructure. It has a higher density and strength compared to PGA and a lower porosity, which gives a lower radiolytic oxidation rate. The AGR graphite contains higher quantities of impurities, which gives rise to higher concentrations of activation products. The higher radiation levels make handling of AGR graphite in standard radiochemical laboratory experiments difficult and at present no samples have been sought for leaching experiments.

The CARBOWASTE programme has carried out leaching tests to investigate chemical decontamination by acid treatment, liquid decontamination agents and aggressive leaching. The materials used consist of Magnox graphite, materials test reactor graphite (MTR) and EDF (Pechiney) graphite. Potentially, some samples of these graphites could be made available for investigation of the behaviour under disposal facility conditions.

Experiments with new samples would complement the experiments already undertaken in support of the UK disposal programme, and the programmes of overseas waste management organisations. However, allowing the current experiments to run for a long period of time appears to be the most attractive option, as it would enable the improved understanding to be extended to longer timescales. At the end of these projects, it would be appropriate to review the remaining knowledge gaps and consider whether further experiments are required.

8.8 Summary and next steps

There are about 7,000 TBq of carbon-14 associated with graphite. Experimental evidence has shown that not all of the carbon-14 is releasable; graphite is a very stable material and it is thought that this unreleasable carbon-14 is associated with the graphite matrix. A small fraction of the carbon-14 is releasable on leaching, but not all of it is released as gas. It is thought that this fraction is associated with carbonaceous surface deposits and this deposit reacts on leaching to produce species that are released into the aqueous or
gaseous phase. Measurements show release in the form of carbon dioxide (which is mostly released in the aqueous phase, particularly in high pH environments), aqueous organic species and smaller amounts of gaseous carbon monoxide and methane or other hydrocarbons.

In the operational period, if the graphite is packaged in a cement-based encapsulation grout or in a container with a cement annulus, then any carbon dioxide generated in the aqueous or gas phase would react with the cement and be immobilised. Smaller amounts of methane and carbon monoxide would also be generated, but the resulting doses would be below the source-related dose constraint for members of the public for a new facility.

In the post-closure period, the radiological impact of any release of gaseous carbon-14 from graphite would be site specific. Some carbon-14 would be released by leaching of the releasable fraction. Any carbon dioxide released would be retained in the cement grout and or backfill. Smaller amounts of carbon monoxide and methane could be released in the gas phase and there will also be some aqueous organic release. In the first thousand years following closure, risks would be below the risk guidance level except in environments where features focus the gas and it is released to an area which is considerably smaller than the repository footprint. Therefore it will be important to understand the gas migration characteristics of any site proposed for the disposal of these wastes.

It has been proposed that graphite could be disposed of in separate vaults. This could have the advantage that it might be possible to package the waste in such a way as to limit the amount of metal and thus avoid the production of a bulk gas phase. A number of alternative packaging options have been investigated as part of this project and it has been concluded that, although disposal in separate vaults is feasible, it is not necessary for the management of carbon-14 (except potentially in environments where the gaseous release is focused over a very small area).

There is ongoing work on carbon-14 release from graphite. Leaching experiments on Oldbury graphite have been extended to longer times to determine whether the release slows further or stops. The implications of these results will be considered once they are available. If, for example, they show that the release stops after a period of a year or two, then it would be possible to revise the parameter values in Table 21 to be less cautious. This would mean that the release rate would be more like that shown for variant 1 in Figure 20 and that releases would reduce rapidly over a shorter period.

A remaining knowledge gap concerns leaching from a wider range of graphites, and in particular from AGR graphite. The formation of the carbonaceous deposit depends on the reactor coolant and on the reactor core temperature. Some further information will become available as part of the C-14 BIG project37 (and see [134, 135]) and through the international EC funded CAST project. At the end of these projects, it would be appropriate to review the remaining knowledge gaps and consider whether further experiments are required. For example, it might be appropriate to use the experimental approach to measuring the release of carbon-14 from irradiated stainless steel (which is being carried out as part of CAST), to carry out similar measurements on AGR graphite samples, as these will also require a shielded facility.

A summary of the current position is provided in Table 27. The status is described in the context of the AND questions identified in Section 1.4 and shows that graphite wastes would be disposable in geological environments where the gas migration characteristics lead to either no release, or a release that is not focused to a restricted area. Therefore

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37 The C14-BIG project is a collaborative programme involving the Universities of Huddersfield, Bristol and Central Lancashire and is jointly funded by the RWM and the Research Councils UK Energy programme.
these wastes should continue to be packaged through the disposability assessment process.

Table 27  Summary of the current position on irradiated graphite wastes

<table>
<thead>
<tr>
<th>‘AND’ Question</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Is there a significant inventory?</td>
<td>Yes. There is a significant inventory of carbon-14 (about 7,000 TBq) in irradiated graphite (mostly in SILW).</td>
</tr>
<tr>
<td>Does the waste stream generate carbon-14 bearing gas?</td>
<td>Yes. However, improved understanding has shown that not all of the carbon-14 is released and not all of it is released as gas. Gases generated include $^{14}$CH$_4$ and $^{14}$CO. $^{14}$CO$_2$ is more soluble and most will react with any cementitious materials in the waste packages.</td>
</tr>
<tr>
<td>Is there a bulk gas phase to entrain the carbon-14 bearing gas?</td>
<td>There is no significant bulk gas phase generated from the graphite. Any bulk gas would arise from container corrosion. Release is not expected to be limited by water availability.</td>
</tr>
<tr>
<td>Do these gases migrate through the near field in significant quantities?</td>
<td>$^{14}$CO$_2$ is expected to be retained in the EBS, but $^{14}$CH$_4$ and $^{14}$CO would migrate through the near field in most concepts if there is a bulk gas phase present.</td>
</tr>
<tr>
<td>Do these gases migrate through the geological environment in significant quantities?</td>
<td>This is a site-specific question. Some geological environments (e.g. LSSR and evaporite) would provide a significant barrier to gas migration or may allow the gas time to dissolve in groundwater or to decay. Important factors are the time taken for the carbon-14 to migrate to the biosphere and the area of any release.</td>
</tr>
<tr>
<td>Do these gases lead to significant doses in the operational phase?</td>
<td>No.</td>
</tr>
<tr>
<td>Do these gases lead to significant risks to potentially exposed groups in the post-closure phase?</td>
<td>Impact is site specific. Risks are assessed to be below the risk guidance level provided that the release is not focused over a small area.</td>
</tr>
</tbody>
</table>
9 Irradiated Steel Wastes

Irradiated steel wastes were identified as a significant contributor to calculated releases of carbon-14 in the Phase 1 work. As a consequence, work in Phase 2 has examined the various components of the AND approach for these wastes, to enable an improved assessment to be developed.

The Phase 1 work of the project concluded that, ignoring any potential benefits from the geosphere in retarding or preventing gas from reaching the surface, the calculated release rates of carbon-14 from the corrosion of irradiated stainless steels exceed the risk guidance level in the post-closure period.

The approach to addressing the ‘AND’ approach for stainless steels (see Section 1.4) has been to seek new evidence and to improve the available data, rather than to develop new models for the release of carbon-14 from irradiated stainless steels.

In particular the available inventory data have been reviewed and refined (Section 9.1) and the data on corrosion rates have been reviewed as part of the international CAST project (Section 9.2). The nature of the releases of carbon-14 – whether they are to the groundwater or gaseous phase – is considered in Section 9.3. The improved data have been incorporated into the existing model for steel corrosion (Section 9.4) to provide release rates for carbon-14. These release rates are incorporated into the scenarios that have been developed as part of the work on the geosphere and biosphere (Section 9.5); these scenarios have been selected to be appropriate given that the GDF programme is at a generic stage and no specific geological environment has been selected. Possible alternative approaches to the management of irradiated steel wastes are discussed in Section 9.6. The current position on irradiated steel wastes is summarised in Section 9.7, where there is also a discussion of the implications once the results of ongoing work become available.

Further details are provided in the separate report on irradiated steel wastes that has been written as part of the project [13].

9.1 Inventory

The treatment of the inventory for steel wastes in the Phase 1 report was intentionally quite broad and not detailed. That treatment enabled more detailed questions to be asked about which wastes were potentially important; this has been explored, and the inventory information has been refined. In addition some new waste streams have been incorporated into the 2013 Derived Inventory, and these have been incorporated into the Phase 2 work.

Carbon-14 is produced in reactor steels by the interaction of thermal neutrons with nitrogen impurities in the steel via the $^{14}\text{N}(n,p)^{14}\text{C}$ reaction. Owing to the low natural abundance and thermal neutron cross-section of carbon-13, the $^{13}\text{C}(n,\gamma)^{14}\text{C}$ reaction is not a significant source of carbon-14 in the low-carbon content stainless and mild steels that are used in reactor applications.

In Phase 1 of the project [2], contributions to the generation rates of carbon-14 containing gas and bulk gas from different types of waste were analysed by processing the results from the then most recent 2012 gas generation assessment [136]. This was done to identify the most important contributions to carbon-14 gas generation. The 2012 gas generation assessment was based on the carbon-14 and bulk materials inventories developed as part of the 2007 Derived Inventory [29, 30, 31]. During Phase 2 of the carbon-14 project, the carbon-14 disposal inventory has been progressively updated and improved as new and updated information has become available [11].
The legacy waste streams were grouped as follows:

- ILW AGR stainless steel fuel cladding;
- ILW AGR stainless steel fuel assembly components;
- ILW AGR fuel stringer debris;
- ILW stainless steels from reactor decommissioning;
- ILW other stainless steel reactor wastes;
- ILW other ferrous metal decommissioning wastes;
- ILW other ferrous metal reactor wastes.

As a result of work early in Phase 2, Encapsulated AGR Cladding (2F03/C) and AGR Stainless Steel Fuel Assembly Components (2F08) were identified as key legacy waste streams. The inventory and shape data for these wastes have been examined, and the data refined. In particular the inventory of carbon-14 in these waste streams has been reduced by a factor of over five. The data for the other legacy wastes have also been examined, and the progress made as part of Phase 2 is summarised in Table 28.

Wastes and spent fuel from a 16 GW(e) nuclear new build programme are included in the 2013 Derived Inventory. The decommissioning wastes from such a programme make a significant contribution to the inventory of carbon-14 in steels. Indeed, these wastes lead to a substantial increase in the overall inventory. The changes from the previous Derived Inventory are summarised in Table 29. There is considerable uncertainty in the programme, and therefore also in the extent of wastes that will arise from it.

It can be seen that as a result of the work on the Derived Inventory, the inventory of carbon-14 in legacy ILW steel wastes has been reduced substantially. However, the inventory of carbon-14 in the NNB wastes is considerably greater, so the overall inventory associated with steels has increased by a factor of over seven. The inventory of NNB wastes may be refined in the future.

In addition, the data on the geometry (whether the wastes should be modelled as plates or spheres, and the corresponding thicknesses and diameters) have been revised, and the modelling has taken these changes into account.
Table 28  Summary of knowledge gained for legacy steel wastes

<table>
<thead>
<tr>
<th>Waste stream group</th>
<th>Remaining knowledge gap at the end of Phase 1</th>
<th>Knowledge gained during Phase 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILW AGR stainless steel fuel cladding</td>
<td>Details of metal thicknesses, surface area, size and shape (geometry).</td>
<td>Average metal thicknesses are known.</td>
</tr>
<tr>
<td></td>
<td>Nitrogen impurity levels in the cladding.</td>
<td>Information from Springfields Fuels Ltd (SFL) supports 100 ppm basis of existing calculation, so previous enhancement of the carbon-14 inventory can be discounted. Propose that historic measurements are investigated to confirm 100 ppm level.</td>
</tr>
<tr>
<td>ILW AGR stainless steel fuel assembly components</td>
<td>Details of metal thicknesses, surface area, size and shape (geometry).</td>
<td>Information has been obtained from SFL.</td>
</tr>
<tr>
<td></td>
<td>Nitrogen impurity levels in the grids and braces.</td>
<td>Information has been obtained from SFL.</td>
</tr>
<tr>
<td>ILW stainless steels from reactor decommissioning</td>
<td>Details of metal thicknesses, surface area, size and shape (geometry).</td>
<td>Some thickness, surface area and geometry data have been obtained for three Magnox stations. Information for PWR decommissioning ILW stainless steel typical thicknesses has been obtained.</td>
</tr>
<tr>
<td></td>
<td>The stainless steel compositions/grades used in reactors and associated data on nitrogen concentration.</td>
<td>A nitrogen precursor value of 500 ppm has been taken for all stainless steel decommissioning waste from Sizewell B PWR. No further information on grades for AGR/PWR stainless steels has been obtained.</td>
</tr>
<tr>
<td>ILW other ferrous metal decommissioning wastes</td>
<td>Details of metal thicknesses, surface area, size and shape (geometry).</td>
<td>Some thickness, surface area and geometry data have been obtained for three Magnox stations.</td>
</tr>
<tr>
<td></td>
<td>The steel compositions/grades used in reactors and associated data on nitrogen concentration.</td>
<td>No further information has been collected.</td>
</tr>
<tr>
<td>ILW other ferrous metal reactor wastes</td>
<td>Details of the metal compositions/grades.</td>
<td>All Magnox reactor decommissioning mild steels have an assumed nitrogen precursor value of 200 ppm in calculations.</td>
</tr>
</tbody>
</table>
### Table 29  Summary of the carbon-14 activity in steels in the 2013 Derived Inventory and the change from the 2010 Derived Inventory

<table>
<thead>
<tr>
<th>Waste Category (1)</th>
<th>Carbon-14 activity (TBq) (2)</th>
<th>2010 DI (3)</th>
<th>2013 DI</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILW AGR stainless steel fuel cladding</td>
<td>171</td>
<td>29.4</td>
<td>-141</td>
<td></td>
</tr>
<tr>
<td>ILW AGR stainless steel fuel assembly components</td>
<td>235</td>
<td>38.3</td>
<td>-196</td>
<td></td>
</tr>
<tr>
<td>ILW AGR Fuel stringer debris</td>
<td>122</td>
<td>99.5</td>
<td>-22.0</td>
<td></td>
</tr>
<tr>
<td>ILW stainless steels from legacy reactor decommissioning</td>
<td>225</td>
<td>104</td>
<td>-121</td>
<td></td>
</tr>
<tr>
<td>ILW stainless steels from NNB reactor decommissioning</td>
<td>0</td>
<td>6,660</td>
<td>6,660</td>
<td></td>
</tr>
<tr>
<td>ILW stainless steel reactor wastes(4)</td>
<td>4.45</td>
<td>7.78</td>
<td>+3.34</td>
<td></td>
</tr>
<tr>
<td>ILW other ferrous metal decommissioning wastes</td>
<td>198</td>
<td>124</td>
<td>-73.8</td>
<td></td>
</tr>
<tr>
<td>ILW other ferrous metal reactor wastes</td>
<td>41.0</td>
<td>29.4</td>
<td>-11.6</td>
<td></td>
</tr>
<tr>
<td><strong>Total Carbon-14</strong></td>
<td><strong>996</strong></td>
<td><strong>7,090</strong></td>
<td><strong>6,110</strong></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
1. The groups used here are similar to, but not identical to, the groups in Table 28. The main difference arises from the inclusion of new build wastes. The grouping of waste streams follows that adopted in the inventory report – see Appendix A of [11].
2. All numbers are reported with up to 3 significant figures. This can mean that the change in activity does not exactly equal the difference between the 2010 Derived Inventory and the 2013 Derived Inventory.
3. Enhancements carried forward from the 2007 Derived Inventory are included.
4. 2013 Derived Inventory contains both legacy and NNB wastes.

#### 9.2 Steel corrosion rates

As part of the international CAST project, a detailed review of corrosion rates has been undertaken. Although much of the information collected has supported the corrosion rates used in earlier work, additional data have become available on the anaerobic corrosion of stainless steel, and the corrosion rate has been reduced by over an order of magnitude. This has implications for the rates of generation of bulk gas and for the rates of release of carbon-14 from activated steels.

Data on the corrosion rates of mild steels and stainless steels under disposal conditions were reviewed in 2007 [137]. Based on these reviews, recommendations were made regarding the corrosion rates to be used in SMOGG. The same values were used in the 2012 gas assessment [136] and the Phase 1 work of this project [2].

The review of steel corrosion rates has been updated as a task during the first year of the CAST project (see Section 1.4) – this review is reported in reference [20]. This review has largely supported the corrosion rates used in previous modelling.

Anaerobic corrosion rates of stainless steel in alkaline solutions are very low and have proved difficult to measure in the past. On the basis of UK measurements in anaerobic alkaline conditions [138] (which provided only an upper limit for the corrosion rate) and comparable, independent Japanese work [139], a corrosion rate of 0.01 µm yr⁻¹ was selected as being representative in a previous review [137]. It was also concluded that there is no initial high corrosion-rate phase and that the corrosion rate is likely to remain constant in the long term.
Recently, RWMC in Japan have reported some experimental measurements [140, 141] on the corrosion rate of 18Cr-8Ni stainless steel under anoxic conditions in pH 12.5 solutions at 30 to 80°C over test periods up to 720 days (Figure 22). The corrosion rate was measured using the hydrogen generation technique (the amount of gas released was measured using gas chromatography (GC)). The measured corrosion rates for 720 days exposure at 30, 50, 80°C were 0.00077 μm yr⁻¹, 0.0026 μm yr⁻¹, and 0.0075 μm yr⁻¹ respectively (i.e. the corrosion rate increases with temperature). The new data indicate a mean anaerobic corrosion rate of 0.0008 μm yr⁻¹ for 18/8 stainless steel at 30°C after two years exposure, about one order of magnitude lower than the value used in the 2012 gas assessment [136]. The Japanese data also show a decrease of the anaerobic corrosion rate under alkaline conditions with time, and a temperature dependence, neither of which could be discriminated previously.

These data have been used to justify taking a lower corrosion rate for stainless steel in anaerobic conditions, leading to the values shown in **Bold** in the table below. There are insufficient data to justify using an Arrhenius relationship; instead linear interpolation is used between the measurements at 30 and 50°C. By analogy with findings for mild steels, it is considered to be unlikely that chloride will affect the corrosion rate under alkaline anaerobic conditions.

The data used in this project are shown in Table 30.

**Table 30  Corrosion rate of steels and other ferrous metals**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Conditions</th>
<th>Timescale ¹</th>
<th>Corrosion rate at different temperatures (μm yr⁻¹)</th>
<th>Characteristic time (yr) ²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>35°C</td>
<td>45°C</td>
</tr>
<tr>
<td>Stainless</td>
<td>Aerobic, high pH</td>
<td>Chronic</td>
<td>0.054</td>
<td>0.10</td>
</tr>
<tr>
<td>steel</td>
<td>Anaerobic, high pH</td>
<td>Chronic</td>
<td><strong>0.00123</strong></td>
<td><strong>0.0021</strong></td>
</tr>
<tr>
<td>Mild</td>
<td>Aerobic, high pH</td>
<td>Acute</td>
<td>290</td>
<td>370</td>
</tr>
<tr>
<td>steel</td>
<td></td>
<td>Chronic</td>
<td>0.15</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Anaerobic, high pH</td>
<td>Chronic</td>
<td>0.005</td>
<td>0.005</td>
</tr>
</tbody>
</table>

**Notes:**

1. Acute corrosion refers to a short period of rapid corrosion of an initially uncorroded surface, which results in the formation of a passivating oxide layer on the steel surface. The chronic corrosion rate applies in the long term.

2. Acute corrosion rates are assumed to reduce exponentially from the rates given on a time scale defined by the characteristic time. It is assumed that at time t the initial corrosion rate is multiplied by exp(-t/t_c) where t_c is the characteristic time.

The Japanese experiments, discussed above, investigate the corrosion of unirradiated stainless steel. There is a question as to whether the corrosion rate might be affected by the sensitisation of steels that have been irradiated. It is considered that sensitisation might affect the location of some of the carbon-14 in the steel, and it might also affect the corrosion rate locally. To address this possibility, a variant is considered in which the corrosion rate of irradiated steels is increased by factors of 3 and 10. The corrosion rate of unirradiated steels is not increased. The results of these variants are discussed briefly in Section 12.3, and more fully in reference [13]. The medium and long-term post-closure generation rates approximately scale with the corrosion rate.
Figure 22 Anaerobic corrosion of 304 (18-8) stainless steel in pH 12.5 solution at 30 to 80°C: a) equivalent corrosion thickness; and b) average corrosion rate with time; a simple power law of the form $\Delta W = a \times t^b$ was used to fit the data where $\Delta W$ is the equivalent corrosion thickness (μm), $a$ is the initial corrosion rate (μm day$^{-1}$), $t$ is time (day) and $b$ is an exponent to account for the decrease in corrosion rate with time (from reference [140] with permission from RWMC).
9.3 The release of carbon-14 from irradiated steels

As the steels corrode, carbon-14 will be released. This could be retained in solid phases, or released in dissolved species, or released in gaseous form. There has been limited work in this area to date. Experiments are currently underway to measure how much is released as gaseous species.

In the absence of the results from the experiments, the post-closure reference case assumes 10% of the carbon is released as methane gas, with variant cases assuming 100% and 1% is released as methane gas. When further information is obtained from the experimental programme, the assessments will be updated.

Carbon and nitrogen are present as alloy components in steels. The chemical forms of carbon and nitrogen in steels depend upon the steel composition and its production process. Both elements are soluble to some extent as interstitial carbides and nitrides in the iron phases that comprise the bulk of steels. Nitrogen may also be present as distinct nitride phases of iron or other alloying metals (e.g. manganese, niobium); carbon may be present as metal carbides. Carbonitrides may also form with iron and many alloying elements.

The reactivity of the different carbon species that may be present in steel on contact with water varies considerably [142]. Some metals (e.g. niobium, titanium) form very stable interstitial carbide phases that react only slowly with acids, releasing methane and hydrogen. In contrast, the electropositive metals (e.g. aluminium) form reactive carbides that are essentially ionic in character, rapidly releasing hydrocarbons related to the nature of the carbide ion present (methane in the case of aluminium carbide, Al₄C₃) on contact with water. The smaller-sized transition metal elements (e.g. iron, manganese) form so-called intermediate carbides in which carbon atoms may form chains through a distorted metal lattice; multiple carbide stoichiometries are possible and these carbides may be hydrolysed by water and dilute acids, releasing a range of hydrocarbon species and hydrogen. In general, carbonitride phases tend to be more resistant to hydrolysis than the equivalent carbide phase.

There is considerable uncertainty over whether carbon-14 produced by activation of nitrogen-14 will be present in the same chemical forms in irradiated steels as the carbon present in the steels at the time of their production; radiation-induced segregation of alloying components of steel may also contribute to a redistribution of the carbon species.

On the basis of the known information on the reactions of metal carbides and carbonitrides with water, the following carbon-14 release behaviour might be expected on leaching irradiated steel.

- As the steel slowly corrodes, the carbon-14 in its different chemical forms will be exposed to the waste disposal environment; different forms of carbon-14 may be expected to be released in different ways.
- Dispersed ionic and intermediate carbide phases and interstitial carbon present in the iron phase may be hydrolysed over relatively short time periods to form methane and other hydrocarbons.
- Intermediate carbonitrides may be hydrolysed at a much slower rate than the equivalent carbides to yield a range of products that may include hydrocarbons and compounds containing C-N bonds such as amines and cyanides.
- Stable carbides and carbonitride phases may react only very slowly (if at all) and may be released in particulate form.
Experiments by Deng et al. [143] on inactive iron-water systems have shown clear evidence for the release of carbon as hydrocarbon species as a result of the hydrolysis of carbide species in the iron. A variety of species ranging from C1 to C5 hydrocarbons have been identified in the gas phase in separate studies, and quantitative conversion of carbide carbon to hydrocarbons has been reported. The mechanism of hydrocarbon formation is proposed to occur through processes similar to those occurring in Fischer-Tropsch (FT) synthesis (hydrocarbon formation from CO/H₂ mixtures over a metal catalyst). It is suggested that the carbide species exposed at the iron surface may be similar to the intermediates formed on the surfaces of metal catalysts in the FT synthesis.

Experiments are currently underway to measure the speciation of carbon-14 released from the corrosion of activated steels under the international CAST project. One approach being adopted builds on the successful measurement techniques used in measurements of the carbon-14 release from graphite [19].

Until the results of those experiments are available, it is assumed in the post-closure calculations that 10% of the carbon-14 is released as methane, with variants where 100% and 1% are released as a gas. Once the experiments are complete, the modelling will be reviewed and revised in the light of the results.

9.4 Modelling

The model for the release of carbon-14 is a simple congruent release model. In the light of additional information provided on the inventory, a more detailed analysis of the release of carbon-14 from irradiated steels has been undertaken. This understanding is captured in some simple scoping models and in the more detailed modelling undertaken with SMOGG. The generation rate of carbon-14 bearing gases is similar to the Phase 1 results in the operational and early post-closure periods, in the medium and long-term post-closure phases they are much reduced.

The mathematical model for the release of carbon-14 from steel wastes is a simple congruent source-term model. The overall inventory in the steels wastes is divided amongst a number of waste groups, as discussed in Section 9.1 above. The typical shapes of the steel wastes have been considered, and the inventory assigned as either ‘plates’ or ‘spheres’ as appropriate.

The rate of release of carbon-14 bearing methane, \( R_{14CH_4} \), is given by:

\[
R_{14CH_4} = \sum_{i} \frac{X_{i} r_{i} F_{i} I_{i}(t)}{s_{i}}
\]

where

- \( I_{i}(t) \) is the inventory of carbon-14 in waste group \( i \) (TBq);
- \( s_{i} \) is the mean (plate) thickness of waste type \( i \) (m) – for wastes classified as spheres it is the radius;
- \( F_{i} \) is a dimensionless shape factor for waste group \( i \). It is 2 for plates (recognising they corrode from both sides). It is initially 3 for spheres, and decreases with time as the spheres corrode;

---

38 Were it released as carbon monoxide, it would be assessed in the same way as methane (see Section 7.5). Were it released as carbon dioxide, it would be expected to react with the backfill (see Section 4.3).
is the corrosion rate of the type of steel in waste group \( i \) (m yr\(^{-1}\)), taken from Table 30, which depends on the corrosion conditions and temperature of the wastes; and

\[ \chi_i \]

is the fraction of carbon-14 released as \(^{14}\)CH\(_4\) in waste group \( i \) (-).

The same formula can be used for other gaseous releases, using appropriate values of \( \chi_i \).

This is the model included in SMOGG [37, 38]. It assumes the carbon-14 is uniformly distributed throughout the steel. There is no information provided on this in the inventory. This may be a better approximation for certain waste streams than for others. For relatively thin wastes that have been subjected to a relatively high radiation fields (which is the case for the important waste streams here), it is expected to be a reasonable approximation. For thicker materials that have been subjected to higher radiation fields on one side, it may well be a less satisfactory approximation (e.g. reactor pressure vessels). Further consideration could be given to this as the inventory is refined further or through disposability assessments of specific waste streams.

There are currently no data on the proportion of carbon-14 released as carbon-14 bearing methane or carbon monoxide, and so cases are presented later in which \( \chi_i \) are set to 1.0, 0.1 and 0.01 (see Section 9.3 above) to cover all gases that might be released and reach the biosphere. Experiments to provide such information are underway. When the data from the experiments are available, the assessment results below will be updated.

### 9.4.1 Scoping calculations

In the medium-term and long-term post-closure the above model can be readily applied to examine the releases from the steel wastes using the anaerobic corrosion rates. The results from the simple application of the model are in excellent agreement with the full SMOGG results.

The medium-term post-closure results are given for the identified waste groups in Table 31, based on the division of the inventory by material type, i.e. this included the carbon-14 associated with stainless steel. Groups with an overall inventory of less than 1 TBq are omitted, as they make a negligible contribution. The rates in the table apply after a few decades once anaerobic conditions have been established.

Four waste streams (or groups of waste streams) give a maximum generation rate above \( 10^{-4} \) TBq yr\(^{-1}\) (taken to indicate those streams generating most carbon-14). These are:

- 2F03/C (Encapsulated AGR Cladding);
- 2F08 (AGR Stainless Steel Fuel Assembly Components);
- Legacy mild steel shielded ILW; and
- AP301 (a new build decommissioning stream).

The first two of these are unshielded ILW. The last is a waste stream arising from the decommissioning of reactors that have not yet been built, and there is significant uncertainty over the characteristics of this stream.
### Table 31 Medium-term post-closure carbon-14 generation rates for the different waste groups for steels

<table>
<thead>
<tr>
<th>Waste Stream Group</th>
<th>Material Mass (t)</th>
<th>Activity (TBq)</th>
<th>Plate Thickness (m)</th>
<th>Corrosion Rate (m yr⁻¹)</th>
<th>Maximum Generation Rate (TBq yr⁻¹)</th>
<th>Corrosion Time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UILW Encapsulated AGR Cladding (2F03/C)</td>
<td>934</td>
<td>29.4</td>
<td>4.00 × 10⁻⁴</td>
<td>1.23 × 10⁻⁹</td>
<td>1.80 × 10⁻⁴</td>
<td>1.63 × 10⁵</td>
</tr>
<tr>
<td>UILW AGR Stainless Steel Fuel Assembly Components (2F08)</td>
<td>235</td>
<td>38.3</td>
<td>8.00 × 10⁻⁴</td>
<td>1.23 × 10⁻⁹</td>
<td>1.18 × 10⁻⁴</td>
<td>3.26 × 10⁵</td>
</tr>
<tr>
<td>UILW Other Stainless Steel</td>
<td>2,430</td>
<td>83.6</td>
<td>1.60 × 10⁻²</td>
<td>1.23 × 10⁻⁹</td>
<td>1.28 × 10⁻⁵</td>
<td>6.52 × 10⁶</td>
</tr>
<tr>
<td>SILW Stainless Steel</td>
<td>2,280</td>
<td>58.9</td>
<td>1.00 × 10⁻²</td>
<td>1.23 × 10⁻⁹</td>
<td>1.45 × 10⁻⁵</td>
<td>4.07 × 10⁵</td>
</tr>
<tr>
<td>UILW Mild Steel</td>
<td>8,350</td>
<td>42.0</td>
<td>1.34 × 10⁻²</td>
<td>5.00 × 10⁻⁹</td>
<td>3.13 × 10⁻⁵</td>
<td>1.34 × 10⁶</td>
</tr>
<tr>
<td>SILW Mild Steel</td>
<td>10,800</td>
<td>137</td>
<td>1.25 × 10⁻²</td>
<td>5.00 × 10⁻⁹</td>
<td>1.10 × 10⁻⁴</td>
<td>1.25 × 10⁶</td>
</tr>
<tr>
<td>NNB – AP301</td>
<td>867</td>
<td>1,180</td>
<td>1.00 × 10⁻²</td>
<td>1.23 × 10⁻⁹</td>
<td>2.90 × 10⁻⁴</td>
<td>4.07 × 10⁵</td>
</tr>
<tr>
<td>NNB – EP302, EP303</td>
<td>1290</td>
<td>5,480</td>
<td>1.79 × 10⁻¹</td>
<td>1.23 × 10⁻⁹</td>
<td>7.52 × 10⁻⁵</td>
<td>7.29 × 10⁷</td>
</tr>
<tr>
<td>NNB – AP302</td>
<td>1840</td>
<td>1.14</td>
<td>2.00 × 10⁻¹</td>
<td>5.00 × 10⁻⁹</td>
<td>5.70 × 10⁻⁸</td>
<td>2.00 × 10⁷</td>
</tr>
<tr>
<td>NNB – EP02, EP03</td>
<td>33</td>
<td>0.07</td>
<td>5.00 × 10⁻³</td>
<td>1.23 × 10⁻⁹</td>
<td>3.25 × 10⁻⁸</td>
<td>2.04 × 10⁶</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>29,500</td>
<td>7,050</td>
<td></td>
<td>8.31 × 10⁻⁴</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes**

1. Inventory values are rounded to three significant figures, including Totals.
2. The material masses are for the waste streams that contribute to the carbon-14 inventory.
3. Values of generation rate greater than 10⁻⁴ TBq yr⁻¹ are highlighted in Bold.

**9.4.2 Results using SMOGG**

As well as the scoping calculations described above, SMOGG calculations have been undertaken; these incorporate a more detailed treatment of the timing of waste emplacement and vault backfilling. The results in the medium-term and long-term post-closure from the scoping model are in excellent agreement with the SMOGG results. However, in the earlier time periods for the GDF, the agreement is not as good, because of the simpler treatment of the timing of waste emplacement and vault backfilling. The full application of the SMOGG model and the associated results are described in Section 13. Key features relevant to steel wastes are summarised here to complete the discussion of irradiated steel wastes.

The results for the reference-case SMOGG calculation are shown in Table 32. The values presented are for the total release of carbon-14. Five time periods are shown:

- the emplacement period (the conditions are aerobic and the temperature is assumed to be 35°C);
- the backfilling period (the conditions are aerobic and the temperature is assumed to be 45°C);
• the early post-closure period (taken to be around 30 years – during which the conditions in the GDF become anaerobic, initially the temperature is assumed to be 45°C, and then is assumed to fall to 35°C);
• the medium-term post-closure period (taken to be around a thousand years – the conditions are anaerobic and the temperature is assumed to be 35°C); and
• the long-term post-closure period (the conditions are anaerobic and the temperature is assumed to be 35°C).

The rates are highest when the conditions in the GDF are aerobic and the temperature is 45°C. The long-term rates are slightly lower than the medium-term rates, as the decay that takes place over 1,000 years is taken into account.

Table 32 Maximum generation rates of carbon-14 (TBq yr⁻¹) from irradiated steels for the different phases of the GDF, before and after closure

<table>
<thead>
<tr>
<th>Steel</th>
<th>Emplacement period</th>
<th>Backfilling period</th>
<th>Early post-closure</th>
<th>Medium-term post-closure¹</th>
<th>Long-term post-closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generation rate</td>
<td>3.52 10⁻²</td>
<td>6.22 10⁻²</td>
<td>6.22 10⁻²</td>
<td>8.35 10⁻⁴</td>
<td>7.52 10⁻⁴</td>
</tr>
</tbody>
</table>

Note:
¹ The medium-term post-closure rate can be compared with the value of 8.31 10⁻⁴ TBq yr⁻¹ in Table 31. This illustrates the good agreement between the scoping model and the SMOGG model.

The comparison with Phase 1 is shown in Figure 23. The generation rates during the emplacement and backfilling periods are similar to or slightly higher in Phase 2. There has been an increase in the inventory of carbon-14 associated with steels, and this would be expected to lead to an increase in generation rates. However, this is offset by the more detailed treatment of important waste streams and the geometrical data that describes them. Thereafter the generation rates are lower. This arises because of the lower value for the stainless steel corrosion rate under anaerobic conditions that is used in the Phase 2 work.

Figure 23 Comparison of the maximum generation rates (TBq yr⁻¹) in Phase 1 and Phase 2 for irradiated steel wastes
9.5 Implications for release of carbon-14 from irradiated steels

Having calculated the generation rates in the different phases of the GDF, these can be set in context by combining them with the migration scenarios and biosphere factors developed in the earlier sections of this report.

Effective doses during the operational phase arising from all gases are below the source-related dose constraint for members of the public for a new facility.

Post-closure risks in the medium and long-term are below the risk guidance level for all but one of the migration scenarios. They are above the risk guidance level for the case of a discharge to the worst-case area of $10^4$ m$^2$ if all the carbon-14 is released as methane.

To set the generation rates in context, the generation rates from Table 32 have been combined with the biosphere and migration cases developed in Sections 6 and 7. The operational and post-closure cases are discussed in turn.

9.5.1 Operational period

The updated OESA methodology described in Section 6.1 was applied to the emplacement and backfilling stages (Sections 7.2 and 7.3).

From Table 32, the highest generation rates for irradiated steel wastes during the operational period occur after backfilling and while the temperature is $45^\circ$C. The pathway considered for release from the GDF is for the gases to be ventilated out of a 15m high stack. The effective off-site doses during the operational phase can be calculated by combining the generation rate with the recommended effective dose factors given in Table 12. The effective doses are shown in Table 33. This Table has to be read with care. The values given assume 100% generation of each of carbon monoxide and methane. Clearly they cannot both be 100%. The values for carbon dioxide are not included in the Table, as it would be expected to react with the cementitious grout in the packages.

<table>
<thead>
<tr>
<th>Age Group</th>
<th>Carbon monoxide</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infant</td>
<td>$7.5 \times 10^{-6}$</td>
<td>$9.3 \times 10^{-10}$</td>
</tr>
<tr>
<td>Child</td>
<td>$4.4 \times 10^{-6}$</td>
<td>$5.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>Adult</td>
<td>$4.5 \times 10^{-6}$</td>
<td>$5.6 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

The highest possible contribution to effective dose rate to members of the public from carbon-14 containing gas generation for the operational period is calculated to be that for carbon monoxide, namely $7.5 \times 10^{3}$ mSv yr$^{-1}$. This is below the maximum effective dose rate constraint to members of the public from a new facility of 0.15 mSv yr$^{-1}$ (see Section 6.1).

9.5.2 Post-closure period

The medium-term post-closure risks arising from the corrosion of irradiated steels are shown in Table 34. These are obtained by combining:

- The reference-case generation rate given in Table 31;
- The migration cases described in Section 7;

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39 As discussed in Section 4.3, the small amount of $^{14}$CO$_2$ from steel wastes is expected to carbonate.
• The biosphere factors given in Table 13;
• The cases for the proportion of carbon-14 released as methane or carbon monoxide discussed in Section 9.3; and
• The dose to risk conversion factor of 0.06 Sv\(^{-1}\) [10].

The environment agencies’ risk guidance level is 10\(^{-6}\) [10], and risks above this guidance level are shown in **Bold**. The reference case for the proportion released as methane or Carbon monoxide is shown in Plain text and the variants are shown in Grey in the Table.

Only one of the cases in the Table is above the risk guidance level. This is for the variant case of 100% of the carbon-14 being released as methane with a focused release to an area of 10\(^4\) m\(^2\) (Case C). Even with a focused release, the two cases, where 10% (the reference case) or 1% is released as carbon-14 bearing methane, are below the risk guidance level.

Risks in the **long-term post-closure period** (Table 35) are very similar to the medium-term post-closure risks, but decrease progressively with time due to radioactive decay. There are releases in Cases E and F in the long-term post-closure period, but these are lower than those calculated for Cases A and C, because no carbon-14 is released until one half-life has elapsed.

The generation rates are highest in the **early post-closure period** (Table 32). These will occur in the short period while the conditions in the GDF remain aerobic. However, the releases are over a very short period (5 years after closure, corresponding to the period of elevated temperature), and the generation rates are lower than for Magnox in the same period.

**Table 34 Medium-term post-closure risks for the different steels release cases – combining the migration cases with the cases for the proportion of carbon-14 released as methane**

<table>
<thead>
<tr>
<th>ID</th>
<th>Delay Time (^{14}\text{C} \text{half-lives})</th>
<th>Release Area ((\text{m}^2))</th>
<th>100% Methane</th>
<th>10% Methane</th>
<th>1% Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>10(^6)</td>
<td>3.6 10(^{9})</td>
<td>3.6 10(^{10})</td>
<td>3.6 10(^{10})</td>
</tr>
<tr>
<td>B</td>
<td>No release</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>10(^6)</td>
<td>3.6 10(^{9})</td>
<td>3.6 10(^{10})</td>
<td>3.6 10(^{10})</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>10(^7)</td>
<td>3.6 10(^{9})</td>
<td>3.6 10(^{10})</td>
<td>3.6 10(^{11})</td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>10(^6)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>10(^7)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 35  Long-term post-closure risks for the different steels release cases – combining the migration cases with the cases for the proportion of carbon-14 released as methane

<table>
<thead>
<tr>
<th>ID</th>
<th>Delay Time (14C half-lives)</th>
<th>Release Area (m²)</th>
<th>100% Methane</th>
<th>10% Methane</th>
<th>1% Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>10⁶</td>
<td>3.2 × 10⁻⁸</td>
<td>3.2 × 10⁻⁹</td>
<td>3.2 × 10⁻¹⁰</td>
</tr>
<tr>
<td>B</td>
<td>No release</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>10⁶</td>
<td>3.2 × 10⁻⁶</td>
<td>3.2 × 10⁻⁷</td>
<td>3.2 × 10⁻⁸</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>10⁷</td>
<td>3.2 × 10⁻⁹</td>
<td>3.2 × 10⁻¹⁰</td>
<td>3.2 × 10⁻¹¹</td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>10⁶</td>
<td>1.8 × 10⁻⁸</td>
<td>1.8 × 10⁻⁹</td>
<td>1.8 × 10⁻¹⁰</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>10⁷</td>
<td>1.8 × 10⁻⁹</td>
<td>1.8 × 10⁻¹⁰</td>
<td>1.8 × 10⁻¹¹</td>
</tr>
</tbody>
</table>

Our improved understanding also has implications for the assessment of the groundwater pathway in terms of the inventory available for release and the speciation of carbon-14 in the aqueous phase. The long timescales over which carbon-14 would be released from steels could be taken into account.

9.6 Alternative approaches

Steel wastes constitute a distinct waste group, and consideration could be given to alternative management approaches, by way of treatment, packaging, design and disposal options. However, as a whole, steel wastes are reasonably ubiquitous, and as a consequence alternative management options for all such wastes may not be an attractive option. Alternative approaches may be considered for particular waste streams, in the future, should they prove to be problematic.

In the Phase 1 report [2], consideration was given to whether alternative treatment, packaging, design or disposal options would be practicable for the management of irradiated steel wastes. The options considered were:

- Segregation of the steel wastes from other wastes;
- Spread the steel wastes over many vaults;
- Surface treatments of the wastes;
- Melting or thermal treatment;
- Disposal of the wastes in a long-lived container.

Some of these may be practicable for certain wastes; some of these may be beneficial for certain wastes.

Considering the waste groups that lead to the highest generation rates in Table 31, some of them have very large masses and volumes (e.g. SILW Mild Steel), and alternative approaches may well not be appropriate for such large volume waste streams. Some have already been packaged (e.g. 2F03/C), and so an alternative approach may be less appropriate. However, other waste groups leading to the highest generation rates (e.g. 2F08 and AP301) have lower masses and volumes, and so an alternative approach may be practicable if required.

However, on the basis of the results presented in Section 9.5, irradiated steels are not the highest priority for such consideration on the basis of the current understanding.
9.7 Summary and next steps

There are about 7,000 TBq of carbon-14 associated with irradiated steel wastes. The overall inventory has increased in the 2013 Derived Inventory, because wastes associated with new build reactors are now included, but the inventory of certain key waste streams has decreased as a result of the improved understanding of the nitrogen impurity concentrations in the wastes. The inventory of carbon-14 in legacy steel wastes has been reduced by over 50%.

Post-closure release of carbon-14 depends particularly on the anaerobic corrosion rate of the stainless steel. As part of the international CAST project, a detailed review of corrosion rates has been undertaken, and as a consequence the anaerobic corrosion rate of stainless steel under alkaline conditions has been reduced by over an order of magnitude. The overall gas generation rate is also dependent on the geometry of the steel wastes, particularly on the thickness of the steel plates and the ‘diameter’ of more bulky items. The understanding and data for these have been improved for some of the important waste streams.

Not all of the carbon-14 may be released to the gas phase; some of it may remain in the aqueous or in solid phases. Experimental measurements are planned to measure this.

In the operational period, effective doses from gases released from the stainless steels are assessed to be below the source-related dose constraint for members of the public for a new facility.

In the post-closure period, the radiological impact of any release of carbon-14 from steels will be site specific. Steel wastes are the major contributor to the risks at times greater than a thousand years post-closure. However, it is not expected that risks arising from steel wastes will be above the risk guidance level, providing the planned experimental measurements confirm that a significant proportion of the carbon-14 is retained in aqueous or solid phases and is not released as a gas.

Alternative treatment, packaging, design and disposal options are not particularly beneficial for these wastes, but could be considered in future for specific waste streams, should they prove to be problematic.

For irradiated steel wastes, consideration should be given to the following aspects:

- Whether the distribution of carbon-14 might not be uniform for any particular waste streams (as is assumed in the model).
- Whether a different corrosion rate might be applicable to specific waste streams (taking into account the possible effects of irradiation and sensitisation of stainless steel wastes)
- Whether the carbon-14 inventory could be overestimated, or particularly for new build wastes, whether material specifications could be chosen to reduce the expected inventory.
- Whether there could be additional surface precipitation of carbon-14 from coolant gas and whether this could persist following packaging.

Possible future work includes:

- Experiments are under way\(^{40}\) to measure the speciation from irradiated stainless steel in anaerobic environments. Consideration could be given to the applicability of these measurements to the aerobic period and to other steels (although this is not currently a priority);

\(^{40}\) Task 201 in the Science & Technology Plan [9].
* Work on the corrosion rates for irradiated stainless steel, and in particular to what extent sensitisation of the steel affects the metal and the general corrosion of the bulk material. However, given the difficulties associated with testing of irradiated materials, this process may be better studied using 'what-if' calculations, as done in this work.

The current assessments will be updated when further information on carbon-14 speciation is available.

A summary of the current position is provided in Table 36. The status is described in the context of the ‘AND’ questions identified in Section 1.4. Certain next steps are also identified in the Table.

**Table 36 Summary of the current position on irradiated steel wastes**

<table>
<thead>
<tr>
<th>‘AND’ Question</th>
<th>Current Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Is there a significant carbon-14 inventory?</td>
<td>Yes. There is a significant carbon-14 inventory in irradiated steels (about 7,000 TBq, of which 6,660 TBq is associated with NNB). The focus has been on a few legacy waste streams where a significant inventory is in irradiated steels that have relatively small thickness.</td>
</tr>
<tr>
<td>Does the waste stream generate carbon-14 bearing gas?</td>
<td>Yes, but it is not certain what proportion of the carbon-14 is released as gas. It is likely that there is some $^{14}$CH$_4$ released as the metal corrodes; some carbon-14 may be released as other species, some of which may partition into solution. Experiments are starting to examine how much is released as a gas, and the assessments will be updated when these are complete.</td>
</tr>
<tr>
<td>Is there a bulk gas phase to entrain the carbon-14 bearing gas?</td>
<td>These wastes generate hydrogen very slowly, when they corrode anaerobically. Corrosion is not expected to be limited by water availability. Hydrogen will also be generated from corrosion of inactive steel waste containers. In the longest time-frame there may not be a bulk gas phase.</td>
</tr>
<tr>
<td>Do these gases migrate through the near field in significant quantities?</td>
<td>Any trace $^{14}$CO$_2$ in the gas phase is expected to react with cementitious materials (in package grout or surrounding backfill) – there is no bulk CO$_2$ from these wastes. $^{14}$CH$_4$ and $^{14}$CO would migrate through the near field in most concepts.</td>
</tr>
<tr>
<td>Do these gases migrate through the geological environment in significant quantities?</td>
<td>This is a site-specific question. Some geological environments (e.g. LSSR and evaporite) would provide a significant barrier to gas migration or may allow the gas time to dissolve in groundwater or to decay. Important factors are the time taken for the carbon-14 to migrate to the biosphere and the area over which any release is spread.</td>
</tr>
<tr>
<td>Do these gases lead to significant doses in the operational phase?</td>
<td>No.</td>
</tr>
<tr>
<td>Do these gases lead to significant risks to potentially exposed groups in the post-closure phase?</td>
<td>Impact is site specific. The radiological risk is expected to be tolerable in most environments. Even where there is a focused release, provided that 10% or less of the carbon-14 from these wastes is released in gaseous form, then the release is expected to be acceptable.</td>
</tr>
</tbody>
</table>
10 Irradiated Reactive Metal Wastes

Irradiated reactive metal wastes were the most significant contributor to the calculated releases of carbon-14 in the Phase 1 work, even though the inventory of carbon-14 associated with reactive metals is modest when compared with that associated with other wastes. As a consequence, work in Phase 2 has examined the various components of the AND approach for these wastes, to enable an improved assessment for these wastes to be developed.

The Phase 1 work of the project concluded that, ignoring any potential benefits from the geosphere in retarding or preventing gas from reaching the surface, the calculated release rate of carbon-14 is dominated by corrosion of reactive metals in the operational and early post-closure time frame.

The approach to addressing the ‘AND’ approach for reactive metals (see Section 1.4) has been to seek new evidence and to substantiate the data for inventory and corrosion rates for reactive metals. More detailed descriptions of the evolution of the wastes have been developed, supported by some modelling of the evolution of individual packages (vault-scale and package-scale modelling).

The available inventory data have been reviewed (Section 10.1). The presentation of the overview of the work on reactive metals is split so the carbon-14 associated with Magnox (Section 10.2), uranium (Section 10.3) and aluminium (Section 10.4) are considered separately. Possible alternative approaches to the management of irradiated reactive metal wastes are discussed in Section 10.5. The current position on irradiated reactive metal wastes is summarised in Section 10.6.

Further details are provided in the separate report on irradiated reactive metal wastes that has been written as part of the project [14].

10.1 Inventory

The inventory of carbon-14 associated with reactive metals has been re-examined. Although the inventory has changed little, there is a better understanding of the nature of the material with which the carbon-14 is associated, in particular about a quarter of the Magnox and a third of the uranium has already corroded at the time of encapsulation, and therefore is not available for gaseous release. There is also the prospect of further information becoming available from Sellafield Ltd in the future.

Most of the carbon-14 activity in reactive metals is associated with waste streams at Sellafield that can be broken down into untreated wastes from Legacy Ponds and Silos (LP&S) and encapsulated Magnox cladding wastes from the Magnox Encapsulation Plant (MEP). The main waste streams contributing to carbon-14 associated with reactive metals are shown in Table 37 [11]. In the Table, the waste streams are colour-coded to indicate the status of their packaging: some are packaged already, some are being packaged and some have packaging plans in place.

The main strands of work on the inventory are outlined in Table 38, where the progress that has been made is also summarised. The work has focused on:

- Reactive metal sampling;
- Nitrogen levels in uranium fuel; and
- Analysis of carbon-14 in mixed reactive metal waste streams.

The work is described in detail in reference [11].
### Table 37  Waste stream contributors to carbon-14 in reactive metals (Magnox and uranium)

<table>
<thead>
<tr>
<th>Waste stream identifier</th>
<th>Waste package category</th>
<th>Waste stream name</th>
<th>Packaged volume (m³)</th>
<th>C-14 activity (TBq)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D07 UILW</td>
<td>Pile Fuel Cladding and Miscellaneous Solid Waste</td>
<td>8,160</td>
<td>14.6</td>
<td></td>
<td>23.9% Magnox, 3.6% uranium metal, 6.5% aluminium, 2.4% lead, 22.5% steel, stainless steel scrap</td>
</tr>
<tr>
<td>2D08 UILW</td>
<td>Magnox Cladding and Miscellaneous Solid Waste</td>
<td>12,700</td>
<td>11.0</td>
<td></td>
<td>3% Magnox, &lt;1% uranium metal, 5% stainless steel and &lt;1% mild steel</td>
</tr>
<tr>
<td>2D09 UILW</td>
<td>Magnox Cladding and Miscellaneous Solid Waste</td>
<td>10,500</td>
<td>15.6</td>
<td></td>
<td>~6% Magnox, &lt;2% uranium metal, &lt;10% stainless steel and &lt;1% mild steel</td>
</tr>
<tr>
<td>2D22 UILW</td>
<td>Magnox Cladding and Miscellaneous Solid Waste</td>
<td>3,830</td>
<td>7.78</td>
<td></td>
<td>~21% Magnox and ~4% uranium metal</td>
</tr>
<tr>
<td>2D24 UILW</td>
<td>Magnox Cladding and Miscellaneous Solid Waste</td>
<td>5,040</td>
<td>10.8</td>
<td></td>
<td>~25% Magnox and ~8% uranium metal</td>
</tr>
<tr>
<td>2D35 UILW</td>
<td>Magnox Cladding and Miscellaneous Solid Waste</td>
<td>2,720</td>
<td>10.6</td>
<td></td>
<td>79% Magnox and ~3% uranium metal</td>
</tr>
<tr>
<td>2D35/C UILW</td>
<td>Encapsulated Retrieved Magnox Cladding</td>
<td>1,410</td>
<td>4.76</td>
<td></td>
<td>16% Magnox and 1% uranium metal</td>
</tr>
<tr>
<td>2D38/C UILW</td>
<td>Encapsulated Magnox Cladding</td>
<td>11,700</td>
<td>36.7</td>
<td></td>
<td>15% Magnox and 1% uranium metal</td>
</tr>
<tr>
<td>2D45 UILW</td>
<td>Magnox Fuel End Crops</td>
<td>55.2</td>
<td>0.79</td>
<td></td>
<td>25% Magnox, 60% uranium metal and 8% zirconium</td>
</tr>
<tr>
<td>2D96.2 UILW (formerly 2D17)</td>
<td>FGMSP Pond Solid Waste to BEP</td>
<td>2,610</td>
<td>1.52</td>
<td></td>
<td>5% Magnox, 3.5% uranium</td>
</tr>
<tr>
<td>2S304 UILW</td>
<td>Windscale Piles Fuel and Isotopes</td>
<td>144</td>
<td>0.46</td>
<td></td>
<td>79% uranium fuel</td>
</tr>
<tr>
<td>9A39 DCIC</td>
<td>FED Magnox</td>
<td>34.8</td>
<td>0.0016</td>
<td></td>
<td>&gt;99% Magnox (AL80) metal</td>
</tr>
<tr>
<td>9A40 DCIC</td>
<td>FED Magnox</td>
<td>52.2</td>
<td>0.0023</td>
<td></td>
<td>&gt;99% Magnox (AL80) metal</td>
</tr>
<tr>
<td>9A41 DCIC</td>
<td>FED Magnox</td>
<td>60.9</td>
<td>0.0027</td>
<td></td>
<td>&gt;99% Magnox (AL80) metal</td>
</tr>
<tr>
<td>9A42 DCIC</td>
<td>FED Magnox</td>
<td>37.0</td>
<td>0.0033</td>
<td></td>
<td>&gt;99% Magnox (AL80) metal</td>
</tr>
<tr>
<td>9A43 DCIC</td>
<td>FED Magnox</td>
<td>15.2</td>
<td>0.0014</td>
<td></td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9E24 UILW</td>
<td>FED Magnox</td>
<td>101</td>
<td>0.0080</td>
<td></td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9E25 UILW</td>
<td>FED Magnox</td>
<td>101</td>
<td>0.0080</td>
<td></td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9E26 UILW</td>
<td>FED Magnox</td>
<td>105</td>
<td>0.42</td>
<td></td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9E27 UILW</td>
<td>FED Magnox</td>
<td>105</td>
<td>0.017</td>
<td></td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9E28 UILW</td>
<td>FED Magnox</td>
<td>105</td>
<td>0.0083</td>
<td></td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9G15 UILW</td>
<td>FED Drummed Magnox</td>
<td>64.8</td>
<td>0.0007</td>
<td></td>
<td>&gt;99% Magnox metal</td>
</tr>
<tr>
<td>9G34 UILW</td>
<td>FED Magnox</td>
<td>127</td>
<td>0.022</td>
<td></td>
<td>94.5% Magnox metal</td>
</tr>
<tr>
<td>9G35 UILW</td>
<td>FED Magnox</td>
<td>189</td>
<td>0.086</td>
<td></td>
<td>94.5% Magnox metal</td>
</tr>
<tr>
<td>Total DCIC</td>
<td></td>
<td>200</td>
<td>0.011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total UILW</td>
<td></td>
<td>59,700</td>
<td>115</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Key:**
- Wastes that have already been packaged are highlighted in Blue.
- Wastes that are currently being packaged are highlighted in Green.
- Wastes with plans reported in the UK RWI for packaging are highlighted in Yellow.
Magnox Cladding and Miscellaneous Solid Waste (waste streams 2D08, 2D09, 2D22, 2D24 and 2D35) are associated with the Sellafield site Magnox Swarf Storage Silos (MSSS) – one of the LP&S facilities. Wastes from MEP comprise encapsulated Magnox cladding wastes in 500 litre drums. Since 1992, Magnox swarf has been routed directly from the Fuel Handling Plant for packaging in the MEP (waste stream 2D38/C). In addition, some Magnox swarf was retrieved from MSSS compartments during the 1990s and the wastes packaged in the MEP (waste stream 2D35/C).

From Table 37, it can be seen that all the major streams are associated with Sellafield (the stream identifier starts with ‘2’); there are only minor contributions from the FED (Fuel Element Debris) from the Magnox stations (the stream identifier starts with ‘9’).

Table 38 Summary of knowledge gained for legacy reactive metal wastes

<table>
<thead>
<tr>
<th>Waste stream group</th>
<th>Remaining knowledge gap at the end of Phase 1</th>
<th>Knowledge gained during Phase 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILW reactive metals (Magnox and uranium)</td>
<td>Carbon-14 split between materials for mixed waste streams.</td>
<td>Nitrogen concentrations used in the calculation have been updated.</td>
</tr>
<tr>
<td></td>
<td>Degree of pre-packaging corrosion.</td>
<td>No further information has been collected. However, an analysis of carbon-14 split for mixed uranium / Magnox streams has been carried out.</td>
</tr>
<tr>
<td></td>
<td>Nitrogen impurity levels in Magnox alloys and uranium.</td>
<td>Pile Fuel Cladding and Miscellaneous Solid Waste (stream 2D07). The underpinning material composition data indicate that activation calculations include a nitrogen impurity concentration in Magnox cladding of 28 ppm.</td>
</tr>
<tr>
<td></td>
<td>Magnox alloy specifications.</td>
<td>No further information was available.</td>
</tr>
</tbody>
</table>

Current estimates of uranium metal and Magnox metal masses in MSSS, waste streams are likely to be overestimates as they are based on historic data. However, a characterisation study from Sellafield Ltd is awaited, and this should provide greater confidence in the quantities of reactive metals for disposal to a GDF and their carbon-14 content.

No new information has been obtained for wastes from MEP, Magnox fuel end-crops or Pile fuel cladding.

A number of carbon-14 data enhancements for LP&S and MEP wastes have been carried forward to the 2013 Derived Inventory from earlier derived inventories. Nitrogen concentrations for Magnox uranium fuel have been provided by SFL, and are lower than assumed in the enhancement calculations. However, no adjustments will be made until further assessment of the contribution of uranium to these enhancements has been undertaken.

An analysis of the carbon-14 activity by material type was completed as part of the 2013 Derived Inventory.

There has been essentially no change to the carbon-14 inventory associated with reactive metals from that used in Phase 1 of the work of project. The inventory is summarised in Table 39. Where the percentage by weight of metal and sludge (metal oxide/hydroxide) is reported in the 2013 UK RWI, it has been used in the Phase 2 work to split the waste streams into metal (uncorroded) and oxide/hydroxide (corroded) fractions [2]. This division is reproduced in the Table. The inventory associated with the uncorroded metal is used in the calculations reported elsewhere in the report.
Currently there is no inventory declared as being associated with aluminium. The total carbon-14 activity associated with aluminium is not thought to be significant relative to those in Magnox and uranium. There is a programme in place to measure whether any meaningful quantities of carbon-14 are associated with irradiated aluminium [11]. The results of this programme will determine whether any changes are made to assumptions underpinning future Derived Inventories.

Table 39 Summary of the carbon-14 activity in reactive metals in the 2013 Derived Inventory and the change from the 2010 Derived Inventory

<table>
<thead>
<tr>
<th>Material category – Waste stream group</th>
<th>Carbon-14 activity (TBq) (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2010 DI</td>
</tr>
<tr>
<td>Magnox</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranium</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Total –ILW Reactive Metals</td>
<td>117</td>
</tr>
</tbody>
</table>

Note:
1 All numbers are reported with up to 3 significant figures. This can mean that the change in activity does not exactly equal the difference between the 2010 Derived Inventory and the 2013 Derived Inventory.

10.2 Magnox

In the Phase 1 work, Magnox wastes were important contributors to the release of carbon-14 at very early times – before and shortly after closure of the GDF. The assumed corrosion rate increases substantially in the presence of chloride. It is important therefore to understand how quickly chloride will reach the Magnox wastes. Package-scale and vault-scale models have been developed to help understand which processes are the most important, and these models have informed the assessments that have been undertaken.

The approach to refining the assessment approach for Magnox wastes is as follows:

- The data on corrosion rates are considered (Sections 10.2.1) and corresponding corrosion times are evaluated (Section 10.2.2);
- Package-scale and vault-scale modelling (Section 10.2.3) has been undertaken, examining the availability of water and chloride to the waste materials; these are key determinants of how quickly the Magnox corrodes, and this has enabled a clearer picture of the timescales on which these wastes evolve to be developed;
- The data on the speciation of carbon-14 released are considered (Section 10.2.4).
- In the light of the understanding developed, the life cycle of Magnox wastes is described (Section 10.2.5);
- Calculations have been undertaken to describe the generation rates in the different phases of the life cycle of Magnox wastes using simple scoping models and more detailed calculations using SMOGG (Section 10.2.6);

41 Task 204 in the Science & Technology Plan [9].
The resulting calculated generation rates are incorporated into the scenarios that have been developed as part of the work on the geosphere and biosphere; these scenarios have been selected to be appropriate given that the GDF programme is at a generic stage and no specific geological environment has been selected (Section 10.2.7).

Further details are provided in the separate report on irradiated reactive metal wastes that has been written as part of the project [14].

### 10.2.1 Magnox corrosion rates

One of the fundamental quantities in the generation of carbon-14 gases from Magnox wastes is the corrosion rate, and the understanding of what it is sensitive to. There is some dependence on temperature in the range of interest, but it is crucially dependent on the chloride concentration local to the wastes in the waste packages.

New evidence has been sought to examine whether the rates should be updated. No evidence has been found to suggest they should be adjusted.

Data on the corrosion rates of the reactive metals under disposal conditions were reviewed in 2007 [144]. The review drew heavily on a previous international review [145]. Recommendations were made regarding the corrosion rates to be used in SMOGG. The recommended corrosion rates are summarised in Table 40.

#### Table 40 Magnox corrosion rates [144]

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Timescale</th>
<th>Corrosion Rate (µm yr⁻¹)</th>
<th>Characteristic time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>35°C</td>
<td>50°C</td>
</tr>
<tr>
<td>High pH Low Cl⁻</td>
<td>Acute</td>
<td>10</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Chronic</td>
<td>0.78</td>
<td>4.3</td>
</tr>
<tr>
<td>High pH High Cl⁻</td>
<td>Acute</td>
<td>1000</td>
<td>3500</td>
</tr>
<tr>
<td></td>
<td>Chronic</td>
<td>78</td>
<td>430</td>
</tr>
</tbody>
</table>

A further review of metal corrosion rates related to the encapsulation of waste metals (including Magnox, uranium and aluminium) in cementitious grout was undertaken by NNL in 2010 [146]. This review included data from extensive trials undertaken by BNFL that were not available for the 2007 review [144].

In the case of Magnox, the rate of corrosion is independent of the oxygen concentration, so there is no distinction between aerobic and anaerobic conditions, but continuing corrosion is determined by the availability of water. There was found to be a good accord between the corrosion rates derived for Magnox for use in SMOGG, and the findings of the NNL review. Thus, in general, the Magnox corrosion parameters used in the assessments are considered to be well-founded.

One possible exception concerns the effect of salinity on the chronic corrosion rate of Magnox. A value two orders of magnitude higher than the chronic corrosion rate is used in SMOGG for saline conditions, based on results from Winfrith Product Evaluation Task Force (PETF) tests to which salt was added [147, 148], as shown in Figure 24. A review has been undertaken by NNL [149] to examine whether further data are available. They do not recommend any reduction in the enhancement factor to take account of the effect of chloride. NNL consider that higher corrosion rates could apply if the wasteform is extremely cracked.
There remains the question as to whether the groundwaters at a site will be sufficiently saline for the corrosion rates to be enhanced. The review [144] suggests that a threshold of 100 ppm should be used. This is considerably less than the concentration of chloride in seawater (20,000 ppm) and the concentration of chloride in many deep groundwaters [15]. As a consequence, although the composition of groundwater will be site dependent, it appears likely that the composition of the groundwaters at many sites will be above the threshold at which the rate of corrosion of Magnox will increase.

Figure 24 Corrosion rates for Magnox encapsulated in grout in 500 litre scale experiments [147] (reproduced from [144])

10.2.2 Corrosion times

To understand the evolution of the Magnox as it corrodes, it is helpful to calculate illustrative corrosion times corresponding to the range of corrosion rates. This supports the description of the state of the wastes in the different periods of operation of the GDF.

The corrosion times calculated are around 1,300 years at 35°C with low chloride values (relevant to the operational period), and 13 years at 35°C with high chloride values (relevant to the post-closure period once chloride reaches the waste).

To illustrate how long it takes the Magnox to corrode, indicative times for the total corrosion of 0.002m thick Magnox plates are presented in Table 41. The values are quoted for the low and high chloride corrosion rates from the SMOGG review [144] given in Table 40. It can be seen that the high chloride corrosion times are relatively short, particularly at the elevated temperatures expected on backfilling. Consequently it is of prime importance to understand when the chloride reaches the Magnox wastes, once the vaults have been backfilled.
Table 41  Indicative corrosion times for 0.002m plates of Magnox, using the low and high chloride chronic corrosion rates from the SMOGG review [144]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Low Chloride Corrosion Time (yr)</th>
<th>High Chloride Corrosion Time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>16,000</td>
<td>160</td>
</tr>
<tr>
<td>25</td>
<td>4,400</td>
<td>44</td>
</tr>
<tr>
<td>35</td>
<td>1,300</td>
<td>13</td>
</tr>
<tr>
<td>45</td>
<td>400</td>
<td>4</td>
</tr>
</tbody>
</table>

10.2.3 Vault-scale and package-scale modelling of the corrosion of Magnox wastes

To support the development of the understanding of the time it takes for chloride from local groundwater to reach the waste, modelling has been undertaken at the package scale and at the vault scale. The time it takes could be determined by:

- Processes at the vault scale;
- Processes in the ullage space at the top of packages; or
- Processes in the encapsulation grout (the wasteform).

The analyses suggest that processes at the vault scale are more important than processes in the wasteform. There are uncertainties around the role played by the ullage space; it may act as a barrier, but this cannot be assumed with confidence. The possibility of cracking in the vault backfill is taken into account. The analysis builds confidence that it will take at least until a thousand years after closure before chloride reaches all the wastes, and this is consistent with wider evidence.

For chloride from local groundwaters to reach the waste, it has to migrate across the vault and into the package. The time it takes could be determined by:

- Processes at the vault scale;
- Processes in the ullage space at the top of packages; or
- Processes in the encapsulation grout (the waste form).

These are considered below. As the treatment of the ullage space is part of the package-scale modelling, this is discussed after processes in the encapsulation grout.

(a) Processes at the vault scale

The first process by which chloride will migrate into a vault is advection by the flow of groundwater into the vault during resaturation (Figure 25(a)). Once a vault has been closed, groundwater will flow into its gas-occupied porosity until the pressure inside the vault approaches the in situ hydrostatic pressure. This flow could transport chloride into the vault relatively quickly. However, the gas-occupied volume is likely to be a small fraction of the total pore volume, and therefore on average the chloride front will move only a small distance into the vault during resaturation [15]. The water that reaches the waste package will have been the water present in the backfill on emplacement.

After the vault has resaturated, a regional groundwater flow could continue to transport chloride through the backfill surrounding the waste packages (Figure 25(b)). This process would be significant only for the case of a higher-strength host rock, because it is likely that the hydraulic conductivity, and therefore the groundwater flow, would be much smaller in other potential host rocks.
Simple analytical models have been developed [14] to estimate the length of time it takes for chloride to migrate across a vault. These take into account:

- Typical hydraulic conductivities and head gradients of the host rock [45];
- Typical hydraulic conductivities of the backfill [51] and the focusing of flow through the vaults [15, 47];
- The sorption of chloride onto the backfill [150, 151]; an effect of the sorption will be to increase the travel time for the chloride by a retardation factor [50];
- The implications of cracks in the backfill [14, 152], leading to flow being preferentially along the cracks, with diffusion of chloride into the intact backfill between the cracks [153, 154].

These simple analytical models show that the arrival of chloride at the waste packages in a vault will be spread over a considerable time [14]. Even in a relatively permeable host rock chloride will come into contact with the Magnox wastes gradually, with first contact occurring perhaps a hundred years post-closure and the last contact of the order of a thousand years later. For a lower-permeability host rock the arrival times will be spread over a longer time.

This means that the enhancement of the Magnox corrosion rate due to chloride will happen after the temperature excursion due to the backfill curing exotherm (the duration of the latter temperature rise will be less than ten years [15]).

(b) Processes in the wasteform in the package

It might be expected that there would be little advection of chloride inside the waste packages, at least at early times (i.e. up to about a thousand years) post-closure. The reasons for this include:

- Most of the metal containers of the waste will still be intact, and therefore there will be no flow pathways through the waste packages. (Although the waste packages might have vents, they would have no other penetrations.)
- The encapsulating grout inside the waste packages is expected to have a much lower hydraulic conductivity than the surrounding backfill, unless it is cracked [51].

If this were the case, then chloride would have to diffuse from the backfill, migrate through the ullage space, and then diffuse through the grout before it could come into contact with the Magnox wastes. However, the results obtained from package-scale numerical models [14] suggest that the corrosion of Magnox alloy, which will consume water and produce hydrogen, will set up a system of flows both around and inside the waste packages. The flow of porewater will transport chloride downwards through the wasteform inside a waste package.

The pathways by which chloride will migrate from the groundwater into the waste packages could be influenced by the presence of cracks in the backfill and / or the grout.

The package-scale numerical models [14] showed that if fluids are mobile in the ullage, then the surrounding backfill can supply water at approximately the rate it is consumed by corroding Magnox alloy inside the package. After chloride migrates into the waste package, the rate of Magnox corrosion, and therefore the rate of water consumption, will increase locally by a factor of about a hundred. As a consequence, the flow of water into the package will grow, and the chloride will be transported at an increasing rate down through the wasteform (Figure 25(c)).

At the chloride-enhanced rate of corrosion it will take only about 20 years for all of the Magnox at a point to be consumed. This is less than the time for the chloride to migrate to the bottom of the wasteform, and therefore a narrow region of Magnox corroding at an accelerated rate (some centimetres high) will form behind the chloride front as the chloride
moves downwards through the wasteform. It will take tens or a few hundreds of years for
the chloride to be transported down the height of the wasteform. This is less than the time
estimated earlier for the spread arising from flow across the vault.

(c) Processes in the ullage space

The ullage is the unfilled space above the encapsulated waste at the top of the waste
package. The behaviour of the ullage is a complicating factor in the analysis of chloride
migration in the system.

Corrosion of the Magnox alloy will generate hydrogen, which will migrate upwards through
the encapsulation grout. This gas will accumulate in the ullage until the gas pressure there
exceeds the sum of the pressure and the ‘gas entry pressure’ in the overlying backfill, and
then it will flow out into the backfill. Within the ullage, the pressure of the gas phase will be
equal to the pressure that would be associated with a liquid phase, but within the backfill,
the pressure of the gas phase will be larger than the pressure of the liquid phase.

Therefore, for the whole period that gas is migrating away from the waste package, the
pressure of an incipient liquid phase in the ullage will exceed the pressure of the liquid
phase in the backfill. This circumstance will oppose the flow of liquid water into the waste
package, and might stop the ingress of chloride.

The package-scale models were parameterised to represent a range of behaviours of
migration across the ullage space. These included three variants:

- The ullage allows water to flow into the package, and gas to flow out;
- The ullage pressurises with gas before chloride can get into the waste package. In
  this variant, the rate of Magnox corrosion is not enhanced;
- Chloride enters the waste package, and then the ullage pressurises with gas. In
  this variant, the ullage also restricts the supply of water to the Magnox wastes, and
  so the package dries out. Thereafter, corrosion continues at a lower rate
determined by the transport of water through the ullage into the waste package.

Clearly the ullage is an important feature, affecting how the Magnox alloy in a waste
package might corrode. There is evidence that the ullage might act as a barrier to water
flow [155], but it is difficult to know with certainty how the ullage will behave in a real GDF
over the long timescales involved. Therefore, although the presence of the ullage is
recognised as being potentially beneficial, no credit has been taken for it when assessing
the release of carbon-14 from packages containing Magnox wastes.

(d) Summary

Once chloride has entered a waste package, it will take about a few hundreds of years for
the chloride to migrate down through the wasteform. Thus, the transport of chloride within
a waste package is not the factor controlling the spread in times when the Magnox wastes
will be corroding at the chloride-enhanced rate, but rather it is the transport of chloride
through the backfill to the vicinity of the waste package that controls the arrival of chloride.
This is likely to be an extremely slow process. Even in the case of a higher-strength rock, it
is expected to take over a thousand years.

The performance of the ullage space remains an uncertainty. It may act to limit the ingress
of chloride further, but currently this is neglected, which is cautious.
Figure 25 Schematic representation of chloride transport into the vault and packages in a higher-strength rock

(a) During initial resaturation

(b) Longer term advection by the regional flow

(c) Advection into the waste package, arising from corrosion of Magnox wastes
10.2.4 Speciation of carbon-14 released from Magnox wastes

As the Magnox corrodes, carbon-14 will be released. This could be retained in solid phases, or released in dissolved species, or released in gaseous form. There has been limited work in this area to date. Experiments are currently underway to measure how much is released as gaseous species; initial results are becoming available.

In the light of the limited results available, the reference case assumes 30% of the carbon is released as methane, with variant cases assuming 100% and 10%.

Experiments are underway to examine the speciation of carbon-14 released from Magnox wastes. These experiments use a similar approach to the experiments with graphite [19] to separate and analyse the different species released. The experiments are in their early days, and it is not yet possible to draw definitive conclusions. However, the preliminary results show:

- the Magnox corrodes;
- carbon-14 is seen in both the solution phase and the gas phase;
- the carbon-14 in the gas phase appears to be mainly either methane or other low molecular weight hydrocarbon.

In the light of this, and given the preliminary nature of the measurements, the reference case for the post-closure modelling is taken to be 30% release as carbon-14 bearing methane, with variants where the proportion of carbon-14 bearing methane is taken to be 100% and 10% (approximately half an order of magnitude lower and higher than the reference case).

10.2.5 Life cycle for Magnox wastes

The corrosion rate for Magnox is dependent on the local environment, and in particular whether there is chloride present and the temperature. In the light of the estimated corrosion times, the life cycle of typical Magnox waste packages can be evaluated. After emplacement the wastes will corrode at the rate appropriate to the vault temperature, but with no chloride enhancement. After backfilling the corrosion rate will increase, because of the temperature pulse. Once this has passed, the corrosion rate will decrease. The rate will increase once chloride reaches the waste in question. This rate will persist until the Magnox is all corroded.

As discussed above, the corrosion rate for Magnox is dependent on the local environment, and in particular whether there is chloride present and the temperature. After packaging, there are a number of stages in the life cycle of Magnox wastes, namely:

- They will be held in a surface store. We do not expect there to be chloride present in the packaged wastes;
- Once the GDF is ready, they will be taken underground and emplaced in the disposal areas (vaults or tunnels). The underground temperature is expected to be significantly higher than in the surface store;

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42 Task 204 in the Science & Technology Plan [9].
43 Were it released as carbon monoxide, it would be assessed in the same way as methane (see Section 7.5). Were it released as carbon dioxide, it would be expected to react with the backfill (see Section 4.3).
• Depending on the GDF concept, the disposal areas will be backfilled. In certain concepts, the backfill will be cementitious, and it is expected that there will be a short-term temperature excursion associated with backfill curing;
• After this the backfilled vaults will start to re-saturate, but it will take time for local groundwater to reach the packages;
• After the temperature excursion, the temperature will return to a value appropriate to the underground conditions (recognising the packages will generate a modest amount of heat);
• At some point, the GDF will be closed;
• Local groundwaters are expected to have sufficiently high chloride levels [15] to result in elevated corrosion rates. These groundwaters will not reach the waste until the temperature excursion has passed. They will not reach all the packages at the same time. Having reached a package, it will take time for the chloride to migrate through the package. In the light of the calculations reported in Section 10.2.3 above, it is assumed the chloride reaches the Magnox wastes over the period from 100 to 1,000 years after backfilling. Variants are considered where period is taken to be 100 to 300 years and 100 to 3,000 years instead.

These stages are illustrated in Table 42. An important feature of the evolution is that the package-scale modelling has built confidence that the peak temperature of 45°C does not coincide with high chloride concentrations. This picture of the evolution has been developed to enable simple calculations to be undertaken that illustrate the more detailed calculations reported in Section 13 and in reference [18]. The programme times are an update on those provided in the 2010 DSSC [44, 156]. The assumed temperature evolution is discussed in more detail in reference [15].

Table 42 Illustrative stages in the evolution of a package containing Magnox

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature (°C)</th>
<th>Environmental Conditions</th>
<th>Illustrative Programme Timing</th>
<th>Illustrative Duration (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface store</td>
<td>15</td>
<td>No chloride</td>
<td>Until emplacement</td>
<td>50</td>
</tr>
<tr>
<td>Underground emplacement before backfilling</td>
<td>35</td>
<td>No chloride</td>
<td>2040 – 2106</td>
<td>84 (2106 to 2190) or 160 (2040 to 2200)</td>
</tr>
<tr>
<td>Shortly after backfilling</td>
<td>45</td>
<td>No chloride</td>
<td>Backfilling from 2190 – 2200</td>
<td>5 (1)</td>
</tr>
<tr>
<td>After the temperature excursion</td>
<td>35</td>
<td>No chloride</td>
<td></td>
<td>95</td>
</tr>
<tr>
<td>Chloride gradually reaches the wastes</td>
<td>35</td>
<td>Chloride present for a proportion of the wastes – there is no chloride available for the other uncorroded wastes</td>
<td>From 2290</td>
<td>Until the Magnox is consumed</td>
</tr>
</tbody>
</table>

Note:
1 The temperature pulse is estimated to be 5 years.
10.2.6 Modelling the release of carbon-14 from Magnox wastes

The model for the release of carbon-14 is a simple congruent release model. In the light of additional information provided on the inventory a more detailed analysis of the release of carbon-14 from Magnox has been undertaken. This understanding is captured in some simple scoping models and in the more detailed modelling undertaken with SMOGG.

The generation rate of carbon-14 bearing gases is slightly lower than the Phase 1 results in the emplacement and backfilling periods. It is much less during the early post-closure period, but this rate persists into the medium-term post-closure period because of the spread of arrival times of chloride at the wastes.

Two approaches have been adopted to model the generation rates of carbon-14 bearing gases from Magnox. First some simple scoping calculations are presented, and then some more detailed calculations using SMOGG.

(a) Scoping calculations

A simple spreadsheet model has been developed to provide estimates of the generation rates of carbon-14 during the different phases of package evolution. The model is based on:

- A congruent release model based on the inventory and shape data summarised in Section 10.1 and provided in detail in reference [11];
- The corrosion rates given in Table 40; and
- The phases in the evolution of waste packages from Table 42 (taking the shorter time for storage underground).

The approach is similar to the model in SMOGG. However, it assumes all the packages are emplaced at the same time and are backfilled at the same time. Thus the results should be similar to the SMOGG results, but are not exactly comparable. In particular the releases rates will be higher, as peak generation rates for packages in SMOGG will occur at different times. An averaged corrosion rate is used based on the proportion of the waste that has a high chloride concentration.

The results from this simple model are shown in Table 43 and Figure 26. It can be seen that:

- In all but one of the cases, the maximum generation rate occurs during the temperature excursion – later, the proportion of the waste that is experiencing high chloride concentrations is not sufficient for the generation rate to be greater.
- In the case where the chloride reaches all the waste after 300 years, the maximum rate occurs after chloride has entered the waste packages, and the generation rate is about twice that during the temperature excursion.
- If the time for chloride to enter all the packages increases beyond 1,000 years, the average corrosion rate approaches the value with no chloride.
- The generation rates are not particularly dependent on when backfilling takes place.
Table 43  Maximum generation rates during different phases of package evolution

<table>
<thead>
<tr>
<th>Phase of Evolution of Waste Packages</th>
<th>Maximum Generation Rate (TBq yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reference Case</td>
</tr>
<tr>
<td>Cl⁻ accesses waste from</td>
<td>100 to 1,000 years</td>
</tr>
<tr>
<td>Backfilling after</td>
<td>84 years</td>
</tr>
<tr>
<td>Surface store (15°C)</td>
<td>4.1 10⁻³</td>
</tr>
<tr>
<td>Underground emplacement before backfilling (35°C)</td>
<td>5.2 10⁻²</td>
</tr>
<tr>
<td>Shortly after backfilling (45°C)</td>
<td>1.6 10⁻¹</td>
</tr>
<tr>
<td>After the temperature excursion (35°C)</td>
<td>5.2 10⁻²</td>
</tr>
<tr>
<td>Chloride gradually reaches the wastes</td>
<td>1.1 10⁻¹</td>
</tr>
</tbody>
</table>

Figure 26  Maximum generation rates (TBq yr⁻¹) from irradiated Magnox during different phases of package evolution
(b) Results using SMOGG

As well as the scoping calculations described above, SMOGG calculations have been undertaken; these incorporate a more detailed treatment of the timing of waste emplacement and vault backfilling. The results in the medium-term and long-term post-closure from the scoping model are in excellent agreement with the SMOGG results. However, in the earlier time periods for the GDF, the agreement is not as good, because of the simpler treatment of the timing of waste emplacement and vault backfilling. The full application of the SMOGG model and the associated results are described in Section 13. Key features relevant to Magnox wastes are summarised here to complete the discussion.

The results for the reference-case SMOGG calculation are shown in Table 44. The values presented are for the total release of carbon-14. Five time periods are shown:

- the emplacement period;
- the backfilling period;
- the early post-closure period (taken to be around 30 years – this is the period over which Magnox was assumed to corrode in Phase 1);
- the medium-term post-closure period (taken to be around a thousand years – the period over which Magnox corrodes in Phase 2);
- the long-term post-closure period.

The rates are fairly similar for first 1000 years. They are highest when the temperature is 45°C.

Table 44 Maximum generation rates of carbon-14 (TBq yr⁻¹) from irradiated Magnox for the different phases of the GDF, before and after closure

<table>
<thead>
<tr>
<th>Magnox Generation rate</th>
<th>Emplacement period</th>
<th>Backfilling period</th>
<th>Early post-closure</th>
<th>Medium-term post-closure (ᵀ)</th>
<th>Long-term post-closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.03 × 10⁻²</td>
<td>2.23 × 10⁻¹</td>
<td>2.23 × 10⁻¹</td>
<td>1.21 × 10⁻¹</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Note:  
1 The medium-term post-closure rate can be compared with the value of 1.1 × 10⁻¹ TBq yr⁻¹ in Table 43. This illustrates the good agreement between the Scoping model and the SMOGG model.

The comparison with Phase 1 is shown in Figure 27. It is seen that the generation rates during the operating and backfilling periods are slightly lower in Phase 2. The main contribution to this is that some of the Magnox has been identified in Phase 2 as already having been corroded. The generation rate during the early post-closure periods is much lower in Phase 2, but then extends into the medium-term post-closure period. This is because it is now assessed that it will take considerably longer for the chloride to access all the wastes. In both the Phase 1 and Phase 2 work, all the Magnox has corroded by the end of this period, so there is no carbon-14 bearing gas generated in the long-term post-closure period.
10.2.7 Implications for release of carbon-14 from Magnox

Having calculated the generation rates in the different phases of the GDF, these can be set in context by combining with the migration scenarios and biosphere factors developed in the earlier sections of this report.

Because there is limited information on which gases are formed, effective doses in the operational phase have been calculated on the assumption of 100% formation of each gas. Effective doses arising from methane and carbon dioxide are below the source-related dose constraint for members of the public for a new facility.

The post-closure risks from Magnox will be site specific. Taking the best estimate of the fraction of carbon-14 released as a gas, the calculated risk is below the risk guidance level in four of the six illustrative cases. It is less than a factor of two above the risk guidance level in one of the illustrative cases. In the remaining illustrative case, corresponding to a focused release to an area which is considerably smaller than the repository footprint, risks are expected to be substantially above the risk guidance level.

To set the generation rates in context, the reference-case generation rates from Table 43 have been combined with the biosphere and migration cases developed in Sections 6 and 7. The operational and post-closure cases are discussed in turn.

(a) Operational period

From Table 43, the highest release rates for Magnox wastes during the operational phases of the GDF life cycle occur shortly after backfilling, when the temperature is 45°C. The pathway considered for release from the GDF is for the gases to be ventilated out of a 15m high stack. The effective doses during the operational phase can be calculated by combining the generation rate with the recommended effective dose factors given in Table 12. The effective doses are shown in Table 45. This Table has to be read with care. The values given assume 100% generation of each of carbon dioxide, carbon monoxide and methane. Clearly they cannot all be 100%. In practice the proportion released as carbon monoxide is expected to be at most modest. The values for carbon dioxide are not
included in the Table, as it would be expected to react with the cementitious grout in the packages\textsuperscript{44}.

Table 45 Calculated effective doses (Sv yr\textsuperscript{-1}) corresponding to generation rates during the temperature peak for Magnox wastes, assuming 100\% generation of each of carbon monoxide and methane

<table>
<thead>
<tr>
<th>Age Group</th>
<th>Carbon monoxide</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infant</td>
<td>$2.7 \times 10^{-5}$</td>
<td>$3.3 \times 10^{-9}$</td>
</tr>
<tr>
<td>Child</td>
<td>$1.6 \times 10^{-5}$</td>
<td>$1.9 \times 10^{-9}$</td>
</tr>
<tr>
<td>Adult</td>
<td>$1.6 \times 10^{-5}$</td>
<td>$2.0 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

The highest possible contribution to effective dose rate to members of the public from carbon-14 containing gas generation for the operational period is calculated to be that for carbon monoxide, namely $2.7 \times 10^{-2}$ mSv yr\textsuperscript{-1}. The contribution to effective dose rate from carbon-14 during the operational period is below the maximum effective dose rate constraint to members of the public from a new facility of 0.15 mSv yr\textsuperscript{-1} (see Section 6.1), even if all the carbon-14 is released as carbon monoxide. In practice not all will be released in this form.

(b) Post-closure period

The medium-term post-closure risks arising from the corrosion of Magnox are shown in Table 46. These are obtained by combining:

- The reference-case generation rate given in Table 43 once chloride has reached the waste;
- The migration cases described in Section 7;
- The biosphere factors given in Table 13;
- The cases for the proportion of carbon-14 released as methane or carbon monoxide discussed in Section 10.2.6; and
- The dose to risk conversion factor of 0.06 Sv\textsuperscript{-1} [10].

The environment agencies’ risk guidance level is $10^{-6}$ [10], and risks above this guidance level are shown in Bold. The reference case for the proportion released as methane or Carbon monoxide is shown in Plain text and the variants are shown in Grey in the Table.

- For a release area of $10^6$ m\textsuperscript{2} and no delay (Case A), provided that the proportion of carbon-14 released as methane or carbon monoxide is limited (less than around 30\%), the risks will be below the risk guidance level.
- For a release area of $10^7$ m\textsuperscript{2} (Case D), the risks are below the guidance level.
- For a focused release to an area of $10^4$ m\textsuperscript{2} (Case C), neither the reference case nor the variants considered are below the risk guidance level;
- For Cases B, D and F, there is no release.

\textsuperscript{44} As discussed in Section 4.3, there is no source of bulk carbon dioxide from reactive metal wastes, and so the small amount of $^{14}$CO\textsubscript{2} is expected to carbonate.
Table 46  Medium-term post-closure risks for the different Magnox release cases – combining the migration cases with the cases for the proportion of carbon-14 released as methane

<table>
<thead>
<tr>
<th>ID</th>
<th>Delay Time (14C half-lives)</th>
<th>Release Area (m²)</th>
<th>100% Methane</th>
<th>30% Methane</th>
<th>10% Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>10⁶</td>
<td>5.2 10⁻⁶</td>
<td>1.6 10⁻⁶</td>
<td>5.2 10⁻⁷</td>
</tr>
<tr>
<td>B</td>
<td>No release</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>10⁴</td>
<td>5.2 10⁻⁴</td>
<td>1.6 10⁻⁴</td>
<td>5.2 10⁻⁵</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>10⁷</td>
<td>5.2 10⁻⁷</td>
<td>1.6 10⁻⁷</td>
<td>5.2 10⁻⁸</td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>10⁶</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>10⁷</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The early post-closure risks are slightly higher (by a factor of less than 2 – see Table 43). The broad conclusions are the same as for the medium-term post-closure period, although the risk for Case A with 10% of the release being methane is only just below 10⁻⁶. However, the releases are over a very short period (5 years after closure, corresponding to the period of elevated temperature). Were this gas to be released, it is expected that it would be spread in time, and give a release rate no higher than in the medium-term post-closure period.

There is no Magnox remaining in the long-term post-closure period for the reference case, and therefore there are no risks to calculate.

10.3 Uranium

In Phase 1, metallic uranium wastes were important contributors at very early times – before and shortly after closure of the GDF. The assumed corrosion rate is dependent on whether the conditions are aerobic or anaerobic. The assumption has been re-examined and scenarios for the evolution of packages containing uranium wastes have been developed. This has enabled the sensitivities of the overall modelling to be better understood. This in turn informs the potential benefits of alternative management approaches.

The approach to refining the assessment approach for metallic uranium wastes is as follows:

- The data on corrosion rates are considered (Sections 10.3.1), and corresponding corrosion times are evaluated (Section 10.3.2);
- The data on the speciation of carbon-14 released are considered (Section 10.3.3);
- In the light of the understanding developed, the life cycle of uranium wastes is described (Section 10.3.4);
- Calculations have been undertaken to describe the generation rates in the different phases of the life cycle of uranium wastes using simple scoping models and more detailed calculations using SMOGG (Section 10.3.5);
- The resulting calculated generation rates are incorporated into the scenarios that have been developed as part of the work on the geosphere and biosphere; these scenarios have been selected to be appropriate given that the GDF programme is

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45 In this discussion uranium wastes are restricted to metallic uranium wastes,
at a generic stage and no specific geological environment has been selected (Section 10.3.6).

Further details are provided in the separate report on irradiated reactive metal wastes that has been written as part of the project [14].

10.3.1 Uranium corrosion rates

One of the fundamental parameters in the determination of the generation of carbon-14 gases from uranium wastes is the corrosion rate, and the understanding of what it is sensitive to. There is some dependence on temperature, but it is crucially dependent on whether the conditions are aerobic or anaerobic in the waste packages.

New evidence has been sought to examine whether the rates should be updated. Evidence from laboratory experiments suggests that the rates of corrosion are close to the anaerobic values, and that anaerobic conditions are established quickly if Blast Furnace Slag (BFS) is used in the encapsulation grout. In the light of this, the reference case assumes anaerobic conditions are established by the time of waste emplacement.

Data on the corrosion rates of the uranium metal under disposal conditions were reviewed for use in SMOGG in 2007 [144]. The review drew heavily on a previous international review [145]. The selected corrosion rates depend crucially on whether the conditions are aerobic or anaerobic; anaerobic corrosion is significantly higher than aerobic corrosion [145]. They also depend on temperature; the higher the temperature, the faster the corrosion and an Arrhenius relationship is used. The corrosion rates are given in Table 47.

Further review of metal corrosion rates related to the encapsulation of waste metals (including Magnox, uranium and aluminium) in cementitious grout was undertaken by NNL in 2010 [146, 157]. These reviews include data from extensive trials undertaken by BNFL and Sellafield Ltd that were not available for the 2007 review [144].

The data available for the earlier of these two reviews [Error! Bookmark not defined.] are shown in Figure 28, where the correlations proposed in [144] are also shown. Two Arrhenius fits to the data are shown in the Figure – one for wastes with a fractional water content below 0.24 and one for water content above 0.24. The data with high water content cover a wider temperature range than those with low water content.

This Figure shows that the SMOGG anaerobic rate overestimates the rate of corrosion of uranium, whereas the aerobic rate significantly underestimates it. The implication is that, even though the wastes are in environments similar to above surface stores, rather than those relevant to a closed GDF, a significant proportion of the uranium is corroding anaerobically, i.e. the uranium consumes oxygen sufficiently rapidly for the establishment of anaerobic microenvironments within waste packages.
Figure 28 Arrhenius plot of the ln(U corrosion rate) against inverse of temperature with the SMOGG model data [144] overlayed – reproduced from [146]

Table 47 Modelled uranium corrosion rates [144, Error! Bookmark not defined.]

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Temp (K)</th>
<th>Corrosion Rate (µm yr⁻¹)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SMOGG Review [144]</td>
<td>NNL Review [146]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aerobic</td>
<td>Anaerobic</td>
<td>High water content (&gt;0.24)</td>
</tr>
<tr>
<td>15</td>
<td>288.15</td>
<td>9.14 x10⁻¹</td>
<td>4.25 x10⁻¹</td>
<td>1.45 x10⁻¹</td>
</tr>
<tr>
<td>20</td>
<td>293.15</td>
<td>1.58 x10⁰</td>
<td>6.82 x10⁻¹</td>
<td>2.39 x10⁻¹</td>
</tr>
<tr>
<td>25</td>
<td>298.15</td>
<td>2.68 x10⁰</td>
<td>1.08 x10¹</td>
<td>3.88 x10⁻¹</td>
</tr>
<tr>
<td>30</td>
<td>303.15</td>
<td>4.47 x10⁰</td>
<td>1.68 x10²</td>
<td>6.20 x10⁻¹</td>
</tr>
<tr>
<td>35</td>
<td>308.15</td>
<td>7.34 x10³</td>
<td>2.57 x10²</td>
<td>9.76 x10⁻¹</td>
</tr>
<tr>
<td>40</td>
<td>313.15</td>
<td>1.19 x10⁻¹</td>
<td>3.89 x10²</td>
<td>1.51 x10⁻²</td>
</tr>
<tr>
<td>45</td>
<td>318.15</td>
<td>1.89 x10¹</td>
<td>5.80 x10²</td>
<td>2.32 x10⁻²</td>
</tr>
<tr>
<td>50</td>
<td>323.15</td>
<td>2.96 x10¹</td>
<td>8.55 x10²</td>
<td>3.50 x10⁻²</td>
</tr>
</tbody>
</table>

The NNL experiments have included BFS/OPC and PFA/OPC matrices46 [146]. They note that in some of the experiments with PFA/OPC there was a delayed start, which suggests that there was a delay in the establishment of anaerobic conditions. The authors comment that BFS/OPC is a more reducing system than PFA/OPC. In the experiments, once anaerobic corrosion is established, the corrosion rates are comparable to those measured in BFS/OPC and water only systems.

This is in line with the understanding from other authors. Glasser [158] comments that 'Portland cement is normally made under oxidising conditions and has a measured potential of +100 to +200 mV, i.e. it is slightly oxidising. However, cements lack poising capacity (the Eh equivalent of buffering) with the result that added electroactive substances

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46 BFS is Blast Furnace Slag, OPC is Ordinary Portland Cement and PFA is Pulverised Fuel Ash.
affect the Eh. Blast furnace slag, which typically contains ~1% sulphide, markedly lowers the Eh to negative -300 mV and provides a poising reserve'. These comments are endorsed in other publications [159, 160, 161].

If it is considered preferable for the uranium to corrode as early as possible, then the use of BFS rather than PFA may be preferable. Examination of the data sheets for the 2013 inventory [162] suggest that the conditioning matrices for many streams have yet to be determined; a number of the sheets say the conditioning matrix is likely to be BFS/OPC or PFA/OPC. For certain streams, e.g. 2D35/C and 2D38/C, the data sheets state that BFS/OPC has been used, and this is understood to be the likely choice in the future for this type of waste.

10.3.2 Corrosion times

To understand the evolution of the uranium as it corrodes, it is helpful to calculate illustrative corrosion times corresponding to the range of corrosion rates. This supports the description of the state of the wastes in the different periods of operation of the GDF.

The corrosion times calculated are around 680 years for 35°C with aerobic conditions (possibly relevant to the operational period), and 9 years for 45°C with anaerobic conditions (relevant during the temperature spike following backfilling).

To illustrate how long it takes the uranium to corrode, indicative times for the complete corrosion of 0.01m plates or spheres of uranium are presented in Table 48. The values are quoted for the aerobic and anaerobic corrosion rates from the SMOGG review [144]. It can be seen that the anaerobic corrosion times are relatively short, particularly at the elevated temperatures expected in the GDF.

Table 48  Indicative corrosion times for 0.01m plates or spheres of uranium, using the aerobic and anaerobic corrosion rates from the SMOGG review [144]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Aerobic Corrosion Time (yr)</th>
<th>Anaerobic Corrosion Time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>5500</td>
<td>120</td>
</tr>
<tr>
<td>25</td>
<td>1900</td>
<td>46</td>
</tr>
<tr>
<td>35</td>
<td>680</td>
<td>19</td>
</tr>
<tr>
<td>45</td>
<td>270</td>
<td>9</td>
</tr>
</tbody>
</table>

10.3.3 Speciation of carbon-14 released from uranium wastes

As the uranium corrodes, carbon-14 will be released. This could be retained in solid phases, or released in dissolved species, or released in gaseous form. There has been no experimental measurements of carbon-14 release.

There are currently no published data on the speciation of carbon-14 releases from the corrosion of uranium to either gas or solution phases. RWM has considered undertaking experimental work on this topic. However, there are considerable challenges in setting up such experiments, as the samples generate a significant dose rate.

Where appropriate, for example in variant calculations, the approach to considering the speciation of carbon-14 released from uranium is to have a small number of scenarios based on the understanding gained from other waste materials, such as Magnox.
10.3.4 Life cycle for uranium wastes

The corrosion rate for uranium is dependent on the local environment and, in particular, on whether conditions are aerobic or anaerobic and on the temperature. In the light of the estimated corrosion times, the life cycle of typical uranium waste packages can be evaluated. After emplacement the wastes will corrode at the rate appropriate to the vault temperature, with the conditions either anaerobic or aerobic. After backfilling the corrosion rate will increase, because of the temperature pulse, and by the end of this conditions are certainly expected to be anaerobic. Once this has past, the corrosion rate will decrease, as the temperature decreases. Any remaining uranium will then corrode more slowly.

As discussed above, the corrosion rate for uranium is dependent on the local environment, and in particular whether the conditions are aerobic or anaerobic and the temperature. After packaging, there are a number of stages in the life cycle of uranium wastes, namely:

- They will be held in a surface store (typically at temperatures in the range of 10-20°C). The environment external to the packages will be aerobic. As discussed above, there is uncertainty whether the environment within the package will be aerobic or anaerobic, although the evidence from the NNL experiments suggests that there is a significant contribution from anaerobic corrosion;

- Once the GDF is ready, they will be taken underground and emplaced in the disposal areas – typically at temperatures in the range of 30-40°C. The underground temperature is expected to be significantly higher than in the surface store;

- Depending on the GDF concept, the emplacement areas will be backfilled. In certain concepts, the backfill will be cementitious, and it is expected that there will be a short-term temperature excursion associated with backfill curing – typically at a temperature of 45°C;

- Shortly after this any remaining oxygen in the packages will be consumed, and the environment will become anaerobic. During this period the backfilled vaults will start to re-saturate;

- After the temperature excursion, the temperature will return to a value appropriate to the underground conditions (recognising the packages will generate a modest amount of heat);

- The GDF will be closed.

These stages are illustrated in Table 49. This has been developed to enable simple calculations to be undertaken that illustrate the more detailed calculations reported in Section 13 and in reference [18]. The programme times are an update on those provided in the 2010 DSSC [44, 156]. The assumed temperature evolution is discussed in more detail in reference [15].
Table 49 Illustrative stages in the evolution of a package containing uranium

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature (°C)</th>
<th>Environmental Conditions</th>
<th>Illustrative Programme Timing</th>
<th>Illustrative Duration (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface store</td>
<td>15</td>
<td>Possibly mixture of aerobic and anaerobic</td>
<td>Until emplacement</td>
<td>50</td>
</tr>
<tr>
<td>Underground emplacement before backfilling</td>
<td>35</td>
<td>Probably essentially anaerobic</td>
<td>2040 – 2106</td>
<td>84 or 160</td>
</tr>
<tr>
<td>Very shortly after backfilling</td>
<td>45</td>
<td>Probably essentially anaerobic</td>
<td>Backfilling from 2190 – 2200</td>
<td>2 (1)</td>
</tr>
<tr>
<td>Shortly after backfilling</td>
<td>45</td>
<td>Anaerobic</td>
<td></td>
<td>3 (2)</td>
</tr>
<tr>
<td>Later backfilled</td>
<td>35</td>
<td>Anaerobic</td>
<td>Thereafter</td>
<td></td>
</tr>
</tbody>
</table>

Notes:
1. The estimate that all oxygen will be used up within 2 years of backfilling comes from the SMOGG calculations [18].
2. The temperature pulse is estimated to be 5 years – 3 years is derived as 2 years less than 5 years.

10.3.5 Modelling the release of carbon-14 from uranium wastes

The model for the release of carbon-14 is a simple congruent release model. In the light of additional information provided on the inventory a more detailed analysis of the release of carbon-14 from uranium has been undertaken. This understanding is captured in some simple scoping models and in the more detailed modelling undertaken with SMOGG described later.

A revised reference case has been defined, in which uranium is taken be under anaerobic conditions by the time the waste is emplaced in the GDF. Even if this were not the case, only a small quantity of uncorroded uranium would remain at the time of closure.

Two approaches have been adopted to model the generation rates of carbon-14 bearing gases from Magnox. First, some simple scoping calculations are presented, and then some more detailed calculations using SMOGG.

(a) Scoping calculations

A simple spreadsheet model has been developed to provide estimates of the generation rates of carbon-14 during the different phases of package evolution, based on different corrosion rate datasets. The model is based on:

- A congruent release model utilising the inventory and shape data summarised in Section 10.1 and provided in detail in reference [11];
- The corrosion rates given in Table 47; and
- The phases in the evolution of waste packages from Table 49 (taking the shorter time for emplacement underground).

The approach is similar to the model in SMOGG. However, it assumes all the packages are emplaced at the same time and are backfilled at the same time. Thus the results should be similar to the SMOGG results, but are not exactly comparable. In particular the
releases rates will be higher, as peak generation rates for packages in SMOGG will occur at different times.

The results from this simple model are shown in Table 50 and Figure 29; the same results are shown in the Table and the Figure. It can be seen that the maximum rate occurs in different phases, depending on the corrosion dataset used. In particular, in three cases most of the uranium has corroded before the highest temperatures are reached, and therefore the highest corrosion rates experienced. However, for each dataset, there will be a relatively high generation rate in at least one phase.

With three of the datasets, much of the uranium corrodes before backfilling. In these cases any gas generated would be expected to be released during GDF operations.

Table 50 Maximum generation rates during different phases of package evolution, based on different corrosion rate datasets

<table>
<thead>
<tr>
<th>Phase of Evolution of Waste Packages</th>
<th>Duration (years)</th>
<th>Maximum Generation Rate (TBq yr^-1)</th>
<th>SMOGG Review [144]</th>
<th>NNL Review [146]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anaerobic</td>
<td>Aerobic then Anaerobic</td>
<td>High water content</td>
</tr>
<tr>
<td>Surface store</td>
<td>50</td>
<td>7.0 \times 10^1</td>
<td>1.5 \times 10^2</td>
<td>2.4 \times 10^1</td>
</tr>
<tr>
<td>Underground emplacement before backfilling</td>
<td>84</td>
<td>6.1 \times 10^1</td>
<td>1.2 \times 10^1</td>
<td>4.1 \times 10^1</td>
</tr>
<tr>
<td>Backfilled possibly aerobic (1)</td>
<td>2</td>
<td>1.2 \times 10^4</td>
<td>8.1 \times 10^2</td>
<td>7.6 \times 10^3</td>
</tr>
<tr>
<td>Backfilled – oxygen exhausted</td>
<td>3</td>
<td>1.4 \times 10^{-6}</td>
<td>2.5 \times 10^9</td>
<td>7.2 \times 10^3</td>
</tr>
<tr>
<td>Backfilled – heat pulse finished</td>
<td></td>
<td>0.0</td>
<td>5.3 \times 10^1</td>
<td>2.8 \times 10^3</td>
</tr>
</tbody>
</table>

Note:
1 The difference between this phase and the next is only significant for the column labelled ‘Aerobic then Anaerobic’, where different corrosion rates are used for the aerobic and anaerobic phases.
To explore an alternative backfill strategy in which vaults are backfilled shortly after they are filled with emplaced waste, some variant calculations have been undertaken. These are discussed in reference [14].

(b) Results using SMOGG

As well as the scoping calculations described above, SMOGG calculations have been undertaken; these incorporate a more detailed treatment of the timing of waste emplacement and vault backfilling. The full application of the SMOGG model and the associated results are described in Section 13. Key features relevant to uranium wastes are summarised here to complete the discussion.

The results for the reference-case SMOGG calculation are shown in Table 51. The values presented are for the total release of carbon-14. Five time periods are shown:

- the emplacement period;
- the backfilling period;
- the early post-closure period (taken to be around 30 years);
- the medium-term post-closure period (taken to be around a thousand years);
- the long-term post-closure period.
Table 51  Maximum generation rates of carbon-14 (TBq yr\(^{-1}\)) from irradiated uranium for the different phases of the GDF, before and after closure

<table>
<thead>
<tr>
<th>Uranium</th>
<th>Emplacement period</th>
<th>Backfilling period</th>
<th>Early post-closure</th>
<th>Medium-term post-closure (^{(1)})</th>
<th>Long-term post-closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generation rate</td>
<td>(3.66 \times 10^{-1})</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Note:

1  The values for the backfilling period and early post-closure period can be compared with the values in Table 50. This illustrates the reasonable agreement between the scoping model and the SMOGG model even in the early periods when the modelling approach is least comparable.

The results are shown in Figure 30. It is seen that the generation rate is slightly higher during the emplacement period in Phase 2, but is entirely corroded by the end of that period.

**Figure 30** Comparison of the maximum generation rates (TBq yr\(^{-1}\)) in Phase 1 and Phase 2 for uranium wastes
10.3.6 Implications for release of carbon-14 from uranium

Having calculated the generation rates in the different stages of the GDF life cycle, these can be set in context by combining them with the migration scenarios and biosphere factors developed in the earlier sections of this report.

A revised reference case has been identified, in which uranium is taken be under anaerobic conditions by the time the waste is emplaced in the GDF.

Because there is limited information on which gases are formed, effective doses in the operational phase have been calculated on the assumption of 100% formation of each gas. Effective doses are below the source-related dose constraint for members of the public for a new facility.

The uranium is expected to have corroded before closure, and therefore the post-closure risks are negligible.

To set the generation rates in context, the reference-case generation rates from Table 50 have been combined with the biosphere and migration cases developed in Sections 6 and 7. The operational and post-closure cases are discussed in turn.

(a) Operational period

From Table 51, the highest release rates for uranium wastes during the operational wastes occur shortly after backfilling, when the temperature is 45°C. The pathway considered for release from the GDF is for the gases to be ventilated out of a 15m high stack. The effective doses during the operational phase can be calculated by combining the generation rate with the recommended effective dose factors given in Table 12. The effective doses are shown in Table 52. This table has to be read with care. The values given assume 100% generation of each of carbon dioxide, carbon monoxide and methane. Clearly they cannot all be 100%. In practice the proportion released as carbon monoxide is expected to be at most modest. The values for carbon dioxide are not included in the Table, as it would be expected to react with the cementitious grout in the packages47.

<table>
<thead>
<tr>
<th>Age Group</th>
<th>Carbon monoxide</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infant</td>
<td>$4.4 \times 10^{-5}$</td>
<td>$5.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>Child</td>
<td>$2.6 \times 10^{-5}$</td>
<td>$3.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Adult</td>
<td>$2.6 \times 10^{-5}$</td>
<td>$3.3 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

The highest possible contribution to effective dose rate to members of the public from carbon-14 containing gas generation for the operational period is calculated to be that for carbon monoxide, namely $4.4 \times 10^{-2}$ mSv yr$^{-1}$. The contribution to effective dose rate from carbon-14 during the operational period is below the maximum effective dose rate constraint to members of the public from a new facility of 0.15 mSv yr$^{-1}$ (see Section 6.1), even if all the carbon-14 is released as carbon monoxide. In practice not all will be released in this form.

47 As discussed in Section 4.3, there is no source of bulk carbon dioxide from reactive metal wastes, and so the small amount of $^{14}$CO$_2$ is expected to carbonate.
(b) Post-closure period
In the SMOGG reference case, there is no uranium remaining at closure, and therefore there are no risks to calculate.

A variant case has been undertaken in SMOGG in which the uranium wastes are taken to be aerobic until just after closure [14]. In this case a small amount of uranium remains to be corroded at around closure. The maximum generation rate in the early post-closure period is a factor of 5.5 higher than the reference case for Magnox in the medium-term post-closure period for the reference case. As there is only a little uranium remaining at this time, the release occurs over a very short period. It is not expected that release to the surface would occur over such a short period, and so this release is judged not to be of concern.

10.4 Aluminium
Aluminium wastes are currently judged to have no carbon-14 associated with them, and they are therefore unimportant from the point of view of direct contributions to radiological consequences. They do, however, contribute to bulk gas generation.

As stated in Section 10.1, there is currently no inventory declared as being associated with aluminium. The total carbon-14 activity associated with aluminium is not thought to be significant relative to activities in Magnox and uranium. There is, however, an experimental programme in place to measure whether any meaningful quantities of carbon-14 are associated with irradiated aluminium [11].

The corrosion rates of aluminium in high pH conditions were reviewed in reference [144]. These have not been further reviewed in the current work. Were a significant inventory to be identified in the future, the data would be reviewed to see if further information had become available. The data are given in Table 53, and the table shows a short-term acute phase (with characteristic time of 0.001 yr), followed by a long-term chronic rate, which is not dependent on the temperature.

Table 53 Aluminium corrosion rates ($\mu$m yr$^{-1}$) in high pH conditions [144]

<table>
<thead>
<tr>
<th>Phase</th>
<th>35°C</th>
<th>50°C</th>
<th>80°C</th>
<th>Characteristic time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acute</td>
<td>15,300</td>
<td>15,300</td>
<td>15,300</td>
<td>0.001</td>
</tr>
<tr>
<td>Chronic</td>
<td>24.5</td>
<td>24.5</td>
<td>24.5</td>
<td></td>
</tr>
</tbody>
</table>

10.5 Alternative approaches
There are alternative approaches for the management of reactive metal wastes. However, many are already packaged or are being packaged. Whether an alternative approach is recommended should be considered as a better understanding of the behaviour is developed and once the characteristics of a site for the GDF become available.

Much of the waste containing reactive metals originates from Sellafield. As shown in Table 37, many of the streams have either already been packaged or are currently being packaged in a cementitious wasteform in 500 litre drums. They arise from high hazard facilities at Sellafield [163]. All of the reactive metals containing a significant inventory of carbon-14 are UILW.

As part of Phase 1 [2], a number of possible alternative options for treatment, packaging, design and disposal options for reactive metal wastes were identified. These included:
- A container that limits water inflow;
- A wasteform that limits water availability e.g. polymer;
- The use of a lower pH cement;
- Treatment e.g. oxidise/dissolve FED;
- Gas capture during backfilling; or
- Alternative backfilling strategy.

These are discussed in turn:

- **A container that limits water inflow.** The analysis undertaken as part of Phase 2 suggests:
  - With the current packaging proposals, there is sufficient water in the grout already for a significant amount of corrosion to take place. The package would probably be required to allow this gas to be released.
  - Although in principle it could be envisaged that a vent could be designed to allow gas to escape, but not allow water ingress, it is not easy in practice to be confident that this can be demonstrated in modelling over the long timescales involved\(^{48}\).

- **Conditioning to limit water access.** This would be expected to reduce the corrosion rates of the reactive metals over the modelled period, which would reduce both the carbon-14 containing and bulk gas generation rates. It is anticipated that this could be achieved by using a polymer, and this option is already being used for certain waste streams.

- **The use of a lower pH cement** has been suggested as an alternative. However, this would only be attractive if there was assurance that the corrosion rate of Magnox would be reduced.

- **Treatment e.g. oxidise/dissolve FED.** Treatment of the waste before disposal to convert it to a form from which the carbon-14 could not easily be released, or from which the carbon-14 is released during the treatment process, would effectively remove the corresponding fraction of the carbon-14 (as well as the bulk gas) from the gas generated. This is already the baseline for certain waste streams containing reactive metals.

- **Gas capture during backfilling.** Essentially this manages gas release during the operational phase of a GDF, complementing the work undertaken on assessing doses for the OESA. This would be a way of mitigating consequences during the operational phase.

- **Alternative backfilling strategy.** As commented above the releases from uranium wastes may be dependent on the approach adopted for the operation of the GDF. The reference case at the moment is that the vaults would be backfilled shortly before closure. It is not currently clear that there are any benefits were the vaults backfilled earlier.

### 10.6 Summary and next steps

There are about 100 TBq of carbon-14 associated with reactive metal wastes. This inventory is small compared with the inventories of carbon-14 in graphite and steels.

\[^{48}\text{The possibility of inverting packages could be considered, but this would have to take into account the possibility of contaminated water being flushed from the package.}\]
However, it is potentially significant as the carbon-14 could be released over a shorter period of time. Although the inventory has changed little, there is a better understanding of the nature of the material with which the carbon-14 is associated. In particular about a quarter of the Magnox and a third of the uranium is declared in the 2013 Derived Inventory as already corroded, and is therefore not available for gaseous release of carbon-14.

The releases are sensitive to the corrosion rates of Magnox and uranium. The Magnox rate is sensitive to the presence of chloride (the corrosion rate is higher in the presence of chloride), and the uranium rate is sensitive to whether the conditions are aerobic or anaerobic (the corrosion rate is higher under anaerobic conditions). Reviews have been undertaken and support the corrosion rates used. However, as a result of these reviews, it is expected that the uranium will be corroding under anaerobic conditions by the time the waste is emplaced in the GDF. Most of the uranium is expected to have corroded before the vaults are backfilled.

On the basis of vault-scale and package-scale modelling of the migration of chloride, it is assessed that the times at which chloride reaches the Magnox waste will be spread over at least a thousand years. Thus Magnox will corrode at an enhanced rate resulting from the presence of chloride at different times in different parts of the GDF. As a consequence the ‘effective’ or ‘average’ corrosion rate is only slightly higher than the rate without chloride. This reduces the rate at which Magnox corrodes in the post-closure period compared to the rate if chloride reached all the waste at the same time, and thus reduces the gas generation rates.

The releases from reactive metals are higher than those from any of the other wastes during the operational and backfilling periods and during the first thousand years following closure:

- Effective doses during the operational period will be below the source-related dose constraint for members of the public for a new facility.
- The post-closure risks from Magnox are substantially lower than in earlier work, arising from the spreading of the times that chloride affects the corrosion of the wastes; however, these risks persist for much longer.
- The post-closure risks from Magnox will be site specific. Taking the best estimate of the fraction of carbon-14 released as a gas, the calculated risk is below the risk guidance level in four of the six illustrative cases. It is less than a factor of two above the risk guidance level in one of the illustrative cases. In the remaining illustrative case, corresponding to a focused release to an area which is considerably smaller than the repository footprint, risks are expected to be substantially above the risk guidance level. Therefore it will be important to understand the gas migration characteristics of any site proposed for the disposal of these wastes.
- In the longer term, after a thousand years, the wastes will have corroded and there are no calculated risks.

There remain some uncertainties, which could make a difference to the calculated consequence from these wastes. For example: the inventory may be overestimated and more of the Magnox waste may have corroded before emplacement; the corrosion rate for partially corroded metal in the absence of chloride may be lower than the value used here [149], or if the wasteform is highly cracked, may be somewhat higher. However, the most important factors affecting the calculated consequences are the speciation of the release and the site-specific migration behaviour.

In some circumstances, an alternative approach to the management of these wastes, such as pre-treatment, may be appropriate. However, it is recognised that for a substantial proportion of these wastes (including a substantial proportion of the inventory) either are already packaged or packaging plans are in place. As a consequence, pre-treatment could
only be considered as part of option studies for wastes that are neither currently packaged
nor being packaged.

The results presented here will be updated once the current experiments measuring the
speciation of carbon-14 release from irradiated Magnox are completed.

Consideration should be given to developing a better understanding of the rate and extent
of corrosion of reactive metal wastes prior to closure of a GDF. Sellafield is working
towards measuring gas release form active waste packages, but these data will take
several years to obtain. Such data would be valuable for comparison with the assessed
releases.

A summary of the current position is provided in Table 54. The status is described in the
context of the ‘AND’ questions identified in Section 1.4.
Table 54  Summary of the current position on irradiated reactive metals

<table>
<thead>
<tr>
<th>‘AND’ Question</th>
<th>Irradiated Magnox</th>
<th>Irradiated uranium</th>
<th>Irradiated aluminium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Is there a significant inventory?</td>
<td>The inventory associated with uncorroded Magnox is modest (about 70 TBq), but has a large potential impact. Inventory may decrease in future, based on updated understanding of precursor concentrations and extent of corrosion.</td>
<td>The inventory is modest (about 20 TBq). Inventory may decrease in future based on the extent of corrosion prior to disposal. Remaining uranium is expected to corrode before closure of the GDF.</td>
<td>No carbon-14 currently declared as being associated with aluminium wastes.</td>
</tr>
<tr>
<td>Does the waste stream generate carbon-14 bearing gas?</td>
<td>Yes. Carbon-14 in the gas phase is either $^{14}$CH$_4$ or low molecular weight hydrocarbon. Some is released to the aqueous phase, so not all would be released as gas. The rate of generation depends on the availability of chloride.</td>
<td>Uncertain – but likely to, based on comparison with Magnox.</td>
<td></td>
</tr>
<tr>
<td>Is there a bulk gas phase to entrain the carbon-14 bearing gas?</td>
<td>Yes – these wastes also generate hydrogen as they corrode. Once water initially available in the containers is used up, continuing corrosion will depend on water from resaturation. Resaturation times will depend on the geological environment.</td>
<td>Yes – these wastes also generate hydrogen as they corrode.</td>
<td></td>
</tr>
<tr>
<td>Do these gases migrate through the near field in significant quantities?</td>
<td>Any trace $^{14}$CO$_2$ in the gas phase is expected to react with cementitious materials (in package grout or surrounding backfill) – there is no bulk CO$_2$ from these wastes.</td>
<td>Any trace $^{14}$CO$_2$ in the gas phase may react with cementitious materials (in package grout) – there is no bulk CO$_2$ from these wastes.</td>
<td></td>
</tr>
<tr>
<td>Do these gases migrate through the geological environment in significant quantities?</td>
<td>This is a site-specific question. Some geological environments (e.g. LSSR and evaporite) would provide a significant barrier to gas migration or may allow the gas time to dissolve in groundwater. Important factors are the time taken for the carbon-14 to migrate to the biosphere and the area of any release.</td>
<td>Provided uranium corrodes anaerobically after emplacement, it will all have corroded before closure.</td>
<td></td>
</tr>
<tr>
<td>Do these gases lead to significant doses in the operational phase?</td>
<td>No.</td>
<td>No.</td>
<td></td>
</tr>
<tr>
<td>Do these gases lead to significant risks to potentially exposed groups in the post-closure phase?</td>
<td>Impact is site specific. Risks are expected to be tolerable provided releases are to an area comparable to the GDF footprint and the proportion of the carbon-14 released as $^{14}$CH$_4$ or $^{14}$CO is limited, or there is a significant hold-up of gas in the geosphere.</td>
<td>Provided uranium corrodes anaerobically after emplacement, it will all have corroded before closure.</td>
<td></td>
</tr>
</tbody>
</table>
11 Spent fuel

A significant inventory of carbon-14 is associated with spent fuels. The container design adopted will be expected to provide containment for times substantially longer than the half-life of carbon-14.

11.1 Inventory

There are 3,290 TBq of carbon-14 in spent fuel. Much of this arises from neutron irradiation of impurities such as nitrogen in the metal cladding. The split of the inventory amongst different fuel types is shown in Table 55, where the material type of the fuel is also given. It can be seen that:

- 3240 TBq is associated with oxide fuels and, in particular, their stainless steel or Zircaloy cladding material. This is further divided into:
  - 826 TBq in legacy spent oxide fuel;
  - 2150 TBq in Nuclear New Build (NNB) spent fuel;
  - 262 TBq in spent MOX fuel.

- 47.3 TBq is associated with legacy metal fuel and their cladding material.

Table 55 Inventory of carbon-14 in spent fuel streams

<table>
<thead>
<tr>
<th>Waste stream identifier</th>
<th>Waste stream name</th>
<th>Packaged volume (m³)</th>
<th>C-14 activity (TBq)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2D100</td>
<td>Spent AGR fuel</td>
<td>9,160</td>
<td>599</td>
<td>Fuel – 83% UO$_2$; Cladding -17% stainless steel Type 20/25/Nb</td>
</tr>
<tr>
<td>M2D300</td>
<td>Legacy ponds fuel</td>
<td>3,390</td>
<td>47.3</td>
<td>Fuel – 62% uranium metal; cladding – 11%; Magnox AL80 27%</td>
</tr>
<tr>
<td>M3S100</td>
<td>Spent PWR fuel</td>
<td>2,160</td>
<td>221</td>
<td>Fuel – 62% UO$_2$; cladding –11%; Zircaloy 4 (stocks) or Zircaloy M5 (arisings); 27% stainless steel 304</td>
</tr>
<tr>
<td>M5B100</td>
<td>Spent PFR fuel</td>
<td>48.7</td>
<td>6.42</td>
<td>Fuel - 49% UO$_2$ /PuO$_2$ Cladding – 38% stainless steel Type 309, 13% Nimonic</td>
</tr>
<tr>
<td>MAP100</td>
<td>Spent AP1000 fuel</td>
<td>16,400</td>
<td>942</td>
<td>Fuel – 78% UO$_2$ Cladding -20% Zirlo; 2% stainless steel type AISI 304L SS</td>
</tr>
<tr>
<td>MEP100</td>
<td>Spent EPR fuel</td>
<td>23,000</td>
<td>1,210</td>
<td>Fuel – 77% UO$_2$ Cladding – 20% Zircaloy M5, 2% stainless steel type AISI 304L SS</td>
</tr>
<tr>
<td>MOX100</td>
<td>Spent MOX fuel</td>
<td>11,900</td>
<td>262</td>
<td>Fuel – 77% UO$_2$/PuO$_2$ Cladding – 20% Zircaloy M5, 2% stainless steel</td>
</tr>
<tr>
<td>Total</td>
<td>Legacy SF</td>
<td>14,800</td>
<td>873</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NNB SF</td>
<td>39,400</td>
<td>2,150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MOX SF</td>
<td>11,900</td>
<td>262</td>
<td></td>
</tr>
</tbody>
</table>
The 2013 Derived Inventory includes the waste and spent fuel from a 16 GW(e) nuclear new build programme. There is considerable uncertainty in the programme, and therefore also in the extent of wastes that will arise from it.

11.2 Potential for release of carbon-14

Illustrative disposal concepts for spent fuel are summarised in Section 1.2; all the illustrative concepts for spent fuel include a high integrity container, which would remain intact for a period of time that is long in comparison with the half-life of carbon-14.

Dual shell copper containers are currently considered for the disposal of spent fuel in Sweden, Finland, Canada and, as an alternative option, in Switzerland, Japan and Korea. Copper containers are likely to provide long durability because of the chemical stability of copper in the absence of oxygen and its tendency to undergo slow, uniform corrosion.

In the KBS-3 concept design adopted in Sweden for the disposal of spent fuel in higher-strength rock, the copper containers would be expected to remain intact for periods considerably in excess of 100,000 years, which would allow the carbon-14 to decay before the containers were breached. This would prevent the carbon-14 from ever migrating out of the container.

Carbon steel has been considered as a container material for spent fuel in Belgium, France, Japan and Switzerland. The primary reasons for using carbon steel are a good understanding of its corrosion resistance in a range of geological environments, so that containers can be designed with a suitable corrosion allowance. Thus containers would be designed to maintain their integrity for timescales of the order of several tens of thousands of years, by which time most of the carbon-14 would have decayed.

If a container were to be breached while a significant amount of carbon-14 remained, potential releases would differ for the two main material types of fuel. In the case of AGR and PWR fuel, the cladding and other fuel assembly components are made of corrosion-resistant metals (Zircaloy, stainless steel or nickel alloys) and therefore the release of gaseous species containing carbon-14 would be spread in time.

Some scoping calculations have been carried out to look at the impact of an early breach of a container containing spent AGR or PWR fuel [164]. These show that if, following an early container breach, carbon-14 were released at the rate of the corroding cladding material, the calculated release rate would be low (i.e. even if released directly to the biosphere the calculated risk would be below the risk guidance level).

In the case of metallic fuel, corrosion of both the cladding and the uranium metal fuel is expected to be rapid once in contact with water, leading to the generation of hydrogen as well as gaseous carbon-14. The quantity of carbon-14 associated with metallic fuels is 47 TBq, which is slightly smaller than the quantity in the ILW reactive metal wastes (see Section 10). These fuels have not been investigated in detail in RWM’s research programme, but although the chemical conditions in this part of the GDF would be different to those in the ILW vaults, as there are no cementitious materials, the corrosion rates of uranium are not very sensitive to the pH. Scoping calculations to look at the impact of an early breach of a container containing metallic fuel [164] showed that if water availability were unlimited and any carbon-14 were released over a focused area directly to the biosphere then the calculated radiological consequence could be significant. However, the containers will be designed to minimise the possibility of such a breach.

The concepts in higher-strength rock and lower-strength sedimentary rock include a pelleted bentonite buffer (Table 3). Bentonite that is fulfilling its safety functions will limit the rate at which groundwater can reach the metallic spent fuel and would restrict the rates of corrosion and the generation rates of hydrogen and gaseous carbon-14.
The ‘AND’ approach was discussed in Section 1.4, and has been used to structure the work of the project. The conclusions of the Phase 2 work for spent fuel are presented at the end of Section 12 in Table 60.
12 Other Wastes

Carbon-14 is also found in a number of other wastes not discussed in previous sections. The impact of the carbon-14 from these wastes is small or negligible in comparison to the impacts from irradiated graphite, irradiated steel and irradiated reactive metals.

12.1 Inventory of other wastes

The first step is to understand which waste streams contain carbon-14, and then to understand the characteristics of the materials in the waste streams and whether they are a potential source of carbon-14 bearing gases. The inventory is tabulated here and the material characteristics are discussed in the subsequent sections.

The 2013 Derived Inventory lists a number of other waste streams containing carbon-14 and these are summarised in Table 56, which shows the waste stream, its packaged volume and the activity of carbon-14 [11]. Each group is discussed in turn in the remainder of this Section.

Table 56 Other Waste Streams with an Inventory of Carbon-14

<table>
<thead>
<tr>
<th>Waste stream identifier</th>
<th>Waste package category</th>
<th>Waste stream name</th>
<th>Packaged volume (m³)</th>
<th>C-14 activity (TBq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILW Organics from GE Healthcare</td>
<td></td>
<td>ILW Organics from GE Healthcare</td>
<td>200</td>
<td>204</td>
</tr>
<tr>
<td>1A07, 1B05, 1B07, 1B10</td>
<td>UILW</td>
<td>Encapsulated LWR Cladding</td>
<td>2,000</td>
<td>28</td>
</tr>
<tr>
<td>Zircaloy Wastes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2F04/C</td>
<td>UILW</td>
<td>Encapsulated Barium Carbonate Slurry/MEB Crud</td>
<td>640</td>
<td>33.4</td>
</tr>
<tr>
<td>Barium Carbonate Wastes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2F06/C</td>
<td>UILW</td>
<td>Encapsulated Floc from Effluent Treatment</td>
<td>14,200</td>
<td>3.82</td>
</tr>
<tr>
<td>Other Legacy ILW with Low Inventories of Carbon-14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2D27/C</td>
<td>UILW</td>
<td>Miscellaneous Activated Components - Spalled Oxide &amp; Dust</td>
<td>28.7</td>
<td>1.3</td>
</tr>
<tr>
<td>3K24</td>
<td>SILW</td>
<td>CVCS Resins and Spent Resins (ILW)</td>
<td>198</td>
<td>2.77</td>
</tr>
<tr>
<td>3S12</td>
<td>SILW</td>
<td>ILW Submarine Ion Exchange Resin</td>
<td>60</td>
<td>2.22</td>
</tr>
<tr>
<td>Other ILW from NNB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP01, EP04, EP05</td>
<td>SILW</td>
<td>Other ILW from NNB - EPR</td>
<td>9,360</td>
<td>1.90</td>
</tr>
<tr>
<td>EP01, EP04, EP05</td>
<td>SILW</td>
<td>Other ILW from NNB - AP1000</td>
<td>19,000</td>
<td>3.1</td>
</tr>
<tr>
<td>AP02, AP03</td>
<td>UILW</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
12.2 ILW organics from GE Healthcare

The largest inventory of carbon-14 in other wastes is associated with the ILW organic waste streams from GE Healthcare. RWM have been informed that GE Healthcare has been given permission to incinerate their organic wastes and they are therefore not planned for disposal in a GDF. Thus they have not been considered further in the work of the project.

These wastes are intermediate level wastes that have been produced by GE Healthcare and its predecessor during the manufacture of compounds labelled with carbon-14. The wastes are mixed wastes, described as containing glass, cellulosics, paper, absorbed liquid, metals, water, oils, ion exchange resins, rubber, plastics and vermiculite/silica.

In 2012 GE Healthcare advised NDA RWMD (the predecessor organisation to RWM) that the Environment Agency had given them permission to incinerate their organic wastes. In the 2010 Baseline Inventory, the carbon-14 activity in these wastes was 560 TBq, but in the 2013 derived inventory, this has been considerably reduced to 204 TBq.

Since these waste are in the process of being incinerated, and are not planned for disposal in a GDF, they have not been considered further in the work of the project and are not included in modelling calculations.

12.3 Encapsulated LWR cladding (Zircaloy)

Zircaloy cladding contains carbon-14. These wastes share many characteristics in common with steel wastes in the way they corrode and potentially release carbon-14. A similar scoping approach has been adopted to that used for steel wastes. The Zircaloy wastes are included in the full SMOGG calculations, and the results are discussed in Section 13. The radiological consequences are less than for other wastes, and in particular those for irradiated steels.

Data on the corrosion rates of Zircaloy under disposal conditions were reviewed in 2007 [137]. Based on these reviews, recommendations were made regarding the corrosion rates to be used in SMOGG. The same values were used in the 2012 gas assessment [136] and the Phase 1 work of this project [2]. These values are used in the current assessments. They are summarised in Table 57.

Table 57 Corrosion Rate Data for Zircaloy

<table>
<thead>
<tr>
<th>Stage in SMOGG model</th>
<th>Zircaloy Corrosion Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic, high pH</td>
<td>Assumed to be zero</td>
</tr>
<tr>
<td>Acute</td>
<td>$k_a = 0.02 \mu m \ \text{yr}^{-1}$ at 30°C</td>
</tr>
<tr>
<td></td>
<td>$k_a = 0.06 \mu m \ \text{yr}^{-1}$ at 45°C</td>
</tr>
<tr>
<td></td>
<td>$t_a = 0.1 \text{ years}$</td>
</tr>
<tr>
<td>Chronic</td>
<td>$k_c = 0.001 \mu m \ \text{yr}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$t_c = \infty$</td>
</tr>
<tr>
<td></td>
<td>No temperature dependence</td>
</tr>
</tbody>
</table>

The same model has been used as was used for steels (see Section 9.4). The results for the maximum generation rate once anaerobic conditions are established and once the acute phase has passed, are tabulated in Table 58.
### Table 58 Rates of release of carbon-14 for the different waste groups for Zircaloy

<table>
<thead>
<tr>
<th>Waste Stream Group</th>
<th>Material Mass (t)</th>
<th>Activity (TBq)</th>
<th>Plate Thickness (m)</th>
<th>Corrosion Rate (m yr(^{-1}))</th>
<th>Maximum Generation Rate (TBq yr(^{-1}))</th>
<th>Corrosion Time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircaloy UILW</td>
<td>1,240</td>
<td>28</td>
<td>6.00 (10^4)</td>
<td>1.00 (10^{-9})</td>
<td>9.33 (10^{-5})</td>
<td>3.00 (10^5)</td>
</tr>
<tr>
<td>Zircaloy SILW</td>
<td>45.5</td>
<td>1.19</td>
<td>6.00 (10^4)</td>
<td>1.00 (10^{-9})</td>
<td>3.97 (10^{-6})</td>
<td>3.00 (10^5)</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1,290</strong></td>
<td><strong>29.2</strong></td>
<td></td>
<td></td>
<td><strong>9.73 (10^{-5})</strong></td>
<td></td>
</tr>
</tbody>
</table>

**Note:**
1. Inventory values are rounded to three significant figures, including totals.

These rates are nearly an order of magnitude lower than the medium-term post-closure rates for irradiated steels (see Table 31), where a total of \(8.59 \times 10^{-4}\) TBq yr\(^{-1}\) is given.

Post-closure risks arising from the corrosion of Zircaloy are shown in Table 59. These are obtained by combining:

- The reference-case generation rate given in Table 58;
- The migration cases described in Section 7;
- The biosphere factors given in Table 13;
- The cases for the proportion of carbon-14 released as methane or carbon monoxide discussed in Section 9.3 (the same ones are taken for Zircaloy as steels to illustrate the effects); and
- The dose to risk conversion factor of 0.06 Sv\(^{-1}\) [10].

The environment agencies' risk guidance level is \(10^{-6}\) [10]. All the eighteen cases in the Table are below the risk guidance level; all are below the corresponding values for irradiated steels.

### Table 59 Post-closure risks for the different Zircaloy release cases – combining the migration cases with the cases for the proportion of carbon-14 released as methane

<table>
<thead>
<tr>
<th>ID</th>
<th>Delay Time ((^{14})C half-lives)</th>
<th>Release Area (m(^2))</th>
<th>100% Methane</th>
<th>10% Methane</th>
<th>1% Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>10(^6)</td>
<td>4.1 (10^{-9})</td>
<td>4.1 (10^{-10})</td>
<td>4.1 (10^{-11})</td>
</tr>
<tr>
<td>B</td>
<td>No release</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>10(^4)</td>
<td>4.1 (10^{-7})</td>
<td>4.1 (10^{-8})</td>
<td>4.1 (10^{-9})</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>10(^7)</td>
<td>4.1 (10^{-10})</td>
<td>4.1 (10^{-11})</td>
<td>4.1 (10^{-12})</td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>10(^6)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>10(^7)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

These wastes are included in the full SMOGG calculations, and the results are discussed in Section 13.
12.4 Encapsulated barium carbonate slurry/multi-element bottle crud

There is a modest quantity of carbon-14 associated with encapsulated barium carbonate slurry/ multi-element bottle (MEB) crud (33.4 TBq). This is a stable wasteform, and carbon-14 bearing gases are not expected to be generated from these wastes.

Radioactive barium carbonate, $\text{Ba}^{14}\text{CO}_3$, arises as a result of reprocessing operations. It is an ILW waste stream described as containing concrete, water, barium carbonate, $\text{NaNO}_2/\text{NaNO}_3$, $\text{NaOH}$, $\text{Ba(NO}_3)_2$, $\text{Ba(OH)}_2$, $\text{BaI}_2$ and $\text{Ba(IO}_3)_2$ [11]. The carbon-14 inventory is 33 TBq, which is small in comparison to the amount of carbon-14 in other waste types discussed in detail above; however, it cannot be regarded as being negligible.

In a high pH environment, barium carbonate is a stable material with very low solubility. The solubility will be especially low because of the high concentrations of CO$_3^{2-}$ already present in the backfill porewater. Therefore the carbon-14 in this waste is likely to be in the form of insoluble carbonate and will not generate gaseous carbon-14. The one possible route for formation of gaseous carbon-14 from these wastes would be through microbial reactions, which could act on soluble forms of inorganic oxidised carbon to form methane. This biogenesis of methane from barium carbonate was considered unlikely in [165], because of the low solubility of barium carbonate and because microbial activity would also be limited at high pH (which was also discussed in Section 4). Therefore this inventory of carbon-14 is not included in the gas generation calculations.

12.5 Other ILW containing carbon-14

There are a number of other waste streams that contain a modest quantity of carbon-14. These are discussed briefly in turn, and the reasons are presented as to why they are not a significant source.

Other legacy ILW waste streams that contain carbon-14 include:

- Encapsulated Enhanced Actinide Removal Plant (EARP) floc, arising from reprocessing at Sellafield. This is a high volume waste stream, with a low inventory of carbon-14 and the carbon-14 is likely to be in the form of carbonate (either dissolved or precipitated). It is unlikely to be a source term for gaseous carbon-14 release.

- Spalled oxide and dust, which may include spalled metal oxide and graphite dust. This is a small volume waste stream, where the carbon-14 content is likely to be an estimate and may be associated with corroded metal (and therefore unlikely to be a source term for gaseous carbon-14 release) or with graphite (where it would contribute a small additional source of gaseous carbon-14 release).

- Spent resins arising from reactor coolant purification. Carbon-14 in the coolant may have been associated with dissolved or spalled corrosion product and would be absorbed on the resin beads in trace quantities. The carbon-14 in this waste stream is unlikely to be a source term for gaseous carbon-14 release. A state-of-the-art review on releases from spent ion-exchange resins has been prepared as part of the CAST project [166].

Also listed in this category is a small amount of carbon-14 (5 TBq) associated with ‘other ILW from nuclear new build’. As discussed in the section on stainless steel, the inventory of carbon-14 associated with nuclear new build will be better defined in the future; the dominant contribution to the carbon-14 inventory from these wastes is in spent fuel and in the decommissioning wastes and this small amount in ‘other ILW’ has not been considered.
further in this project, but would be considered as part of future disposability assessments for these wastes.

There are a number of other ILW waste streams in reference [11] with a total inventory of carbon-14 of 0.58 TBq and a packaged volume of 31.5 m$^3$. These are streams 9A52, 9A53, 9A55, 9A56, 9C47, 9D44, 9E40, 9E41, 9E43, 9F43, 9G41. They are declared as being primarily Zircaloy or Nimonic. As the inventory is so small they are not considered further in this study.

12.6 Aluminium nitride cartridges

An additional source of carbon-14 is some aluminium nitride isotope cartridges that were irradiated in the Calder Hall and Windscale Pile reactors. They contain carbon-14 formed on irradiation of the target material. These wastes have the potential to release the carbon-14 in the form of methane, by alkaline hydrolysis. The inventory in these wastes is not yet included in the 2013 DI and is somewhat uncertain. Packaging and treatment options for these wastes are the subject of ongoing discussions and include the possibility of chemically converting the carbon-14 to carbonate.

12.7 Summary position for the other waste groups

The ‘AND’ approach was discussed in Section 1.4, and has been used to structure the work of the project. The conclusions of the Phase 2 work for the other waste groups are presented in Table 60 as answers to the questions in the ‘AND’ approach. Where an answer essentially closes the issue for a waste group, subsequent questions are not answered, and the boxes are shaded grey.
Table 60  Current position on the status of the ‘AND’ approach for the principal other waste groups

The grey boxes indicate the issue for these wastes is closed by an earlier question

<table>
<thead>
<tr>
<th>‘AND’ Question</th>
<th>GE Healthcare</th>
<th>Zircaloy</th>
<th>Barium carbonate</th>
<th>Spent fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Is there a significant inventory?</td>
<td>Not destined for the GDF.</td>
<td>There is a moderate inventory of carbon-14 (about 30 TBq).</td>
<td>There is a moderate inventory of carbon-14 (about 30 TBq).</td>
<td>There is a substantial inventory of carbon-14 associated with spent fuel (over 3,000 TBq).</td>
</tr>
<tr>
<td>Does the waste stream generate carbon-14 bearing gas?</td>
<td></td>
<td>There is the possibility of some carbon-14 bearing gas, but the levels are assessed to be lower than the main waste streams.</td>
<td>BaCO$_3$ is a stable material with very low solubility. It will not be a significant source of $^{14}$CH$_4$.</td>
<td>Provided the wastes are disposed in a high integrity container, these wastes are not expected to be a significant source of carbon-14 bearing gases.</td>
</tr>
<tr>
<td>Is there a bulk gas phase to entrain the carbon-14 bearing gas?</td>
<td></td>
<td>Other materials are expected to lead to a bulk gas in most environments.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Do these gases migrate through the near field in significant quantities?</td>
<td></td>
<td>Any $^{14}$CO$_2$ would be retained in the EBS, but $^{14}$CH$_4$ and $^{14}$CO would migrate through the near field in most concepts.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Do these gases migrate through the geological environment in significant quantities?</td>
<td></td>
<td>This is a site-specific question. Some geological environments would provide a significant barrier to gas migration or may allow the gas time to dissolve in groundwater or to decay.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Do these gases lead to significant doses in the operational phase?</td>
<td></td>
<td>No.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Do these gases lead to significant risks to potentially exposed groups in the post-closure phase?</td>
<td></td>
<td>Expected to be less significant than other wastes, e.g. steel wastes.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
13 Summary and Conclusions

The summary and conclusions of the work are presented in three ways:

- An overview is presented of the modelling;
- The overall summary conclusions are presented, along with any next steps that have been identified; and
- The ‘AND’ approach is used to present the conclusions for the different waste groups. The questions in the ‘AND’ approach are answered for the waste groups to illustrate the progress that has been made as part of Phase 2.

13.1 Overview of the modelling results

The results for the individual waste groups have been discussed in Sections 8 to 12. In this section, an overview of the results is presented.

13.1.1 Improvements since Phase 1

A number of improvements to the modelling of carbon-14 containing gas generation and its potential consequences have been made between the results presented in Phase 1 [2] and the results presented in this report. The main improvements and their effects are:

- The inventory is now based on the 2013 Derived Inventory. There have been a number of improvements in the inventory as a result of improvements in understanding – see Section 2. There has been a substantial increase in the carbon-14 inventory in stainless steel due to inclusion of nuclear new build wastes in the current calculations. Certain organic wastes containing carbon-14 are now excluded from the calculations (as these are not expected to be disposed in their current form).
- An improved model for the generation of carbon-14 from the degradation of graphite. The recognition that only a small fraction of the carbon-14 contained in graphite is expected to be released as gas has reduced the carbon-14 generation rate and risk from this source in the long-term post-closure period – see Section 8.3.
- A reduction in the anaerobic corrosion rate of stainless steel. This has reduced the carbon-14 generation rate and risk from this source during the post-closure period; this is particularly important for the long-term post-closure period – see Section 9.2.
- A better representation of the shape and geometry data for the stainless steel wastes with high carbon-14 contents. This has increased the carbon-14 generation rate from these wastes, but reduced it from other wastes – see Section 9.4.
- A better representation of the corrosion of Magnox post-closure, as affected by the availability of chloride. This has substantially reduced the peak carbon-14 generation rate and risk in the early post-closure period, but extended the time over which Magnox corrodes post-closure, so increasing the peak carbon-14 generation rate and risk (due to this additional source) in the medium-term post-closure period – see Section 10.2.
- Following a review of the corrosion of uranium, it is now considered to be corroding anaerobically by the time of emplacement. This leads to higher corrosion rates during the operational period, and as a result most of the uranium will have corroded by closure of the GDF – see Section 10.3.
- A set of migration cases representing the range of possible release and migration cases that may be relevant to the geological environments being considered at this generic stage of the programme to develop a GDF.
• An improved methodology of the conversion of carbon-14 release rate to dose rate for the operational period. A single factor has been replaced with different factors for each carbon-14 containing gas. The consequences of carbon-14 as carbon monoxide has become more important in the operational period, whereas the consequences of carbon-14 as methane is now insignificant in that period – see Section 6.1.

• An updated factor for the conversion of carbon-14 flux at the surface to dose rate for the post-closure period. This factor has increased by a factor of 2.5 compared with Phase 1 [2], although the current factor is much smaller than the factor used previously [109]). This difference is masked in the post-closure risks by the other changes noted above.

• An improved understanding has been developed on the availability of water. There are a number of sources of water in a GDF, and a number of processes that consume water. Corrosion of certain wastes consumes water. Encapsulated wastes contain a significant quantity of water in the grout. Resaturation may provide additional water depending on the geological environment. Gas generation may be less in environments with longer resaturation times once the initial water in the encapsulation grout is consumed, but this qualitative understanding is not captured in the calculations – see Section 3.3.

13.1.2 Generation rates for carbon-14 bearing gases

To illustrate the results, Figure 31 shows the generation rates from legacy UILW/ULLW during the operational and early post-closure periods; Figure 32 shows the same generation rates during the late post-closure period.

A summary of the maximum generation rates in the different periods is presented in Table 61. The generation rates presented are for the total quantity of carbon-14 generated, excepting $^{14}$CO$_2$, which is excluded, as it is expected to react with cementitious materials present in the GDF. The two major contributors are also shown. This table shows the waste streams that are potentially most important in the various periods. Each of the major waste streams appears in at least one of the time periods.

Table 61 Summary of the maximum generation rates (TBq yr$^{-1}$) in the different time periods for the GDF

<table>
<thead>
<tr>
<th>Period</th>
<th>Maximum Generation Rate (TBq yr$^{-1}$)</th>
<th>Major Contributor</th>
<th>%age of Max$^{1,2}$</th>
<th>Next Contributor</th>
<th>%age of Max$^{1,2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emplacement period (2040-2190 AD)</td>
<td>$4.32 \times 10^{-1}$</td>
<td>Uranium (Legacy UILW)</td>
<td>85%</td>
<td>Magnox (Legacy UILW)</td>
<td>19%</td>
</tr>
<tr>
<td>Backfilling and early post-closure period (2190-2230 AD)</td>
<td>$2.96 \times 10^{-1}$</td>
<td>Magnox (Legacy UILW)</td>
<td>75%</td>
<td>Various Steels (Legacy UILW &amp; SILW, NNB)</td>
<td>21%</td>
</tr>
<tr>
<td>Medium-term post-closure period (2230-3000 AD)</td>
<td>$1.25 \times 10^{-1}$</td>
<td>Magnox (Legacy UILW)</td>
<td>96%</td>
<td>Graphite (Legacy UILW &amp; SILW)</td>
<td>65%</td>
</tr>
<tr>
<td>Long-term post-closure period (From 3000 AD)</td>
<td>$8.39 \times 10^{-4}$</td>
<td>Various Steels (Legacy UILW &amp; SILW, NNB)</td>
<td>90%</td>
<td>Zircaloy (Legacy UILW)</td>
<td>10%</td>
</tr>
</tbody>
</table>

Note:
1. The percentage of the maximum generation rate given in the second column.
2. The percentages can add up to more than 100% of the maxima occur at different times in the period.
Figure 31 Breakdown by waste group of calculated generation rates for carbon-14 containing gases from Legacy UILW / ULLW during GDF operations and early post-closure
Figure 32 Breakdown by waste group of calculated generation rates for carbon-14 containing gases from Legacy UILW / ULLW in the long term
13.1.3 Implications for the emplacement period

The highest release rates during the emplacement period are those for uranium wastes. The contribution to effective dose rate from carbon-14 during the emplacement period is below the maximum effective dose rate constraint to members of the public from a new facility of 0.15 mSv yr\(^{-1}\).

13.1.4 Implications for the backfilling and early post-closure period

The highest generation rate arises from Magnox wastes, but they are lower than the generation rates in the emplacement period (see Table 61). Releases during this period could be either through a stack or through the rock.

For releases up a stack, the contribution to effective dose rate from carbon-14 is below the maximum effective dose rate constraint to members of the public from a new facility of 0.15 mSv yr\(^{-1}\).

In the early post-closure period the risks in a number of the migration cases are above the risk guidance level. However, this release is over a very short period and the release to the biosphere may be spread in time as the gas migrates through the EBS or through the geosphere, which would reduce the maximum release rate to no more than that in the medium-term post-closure period.

13.1.5 Implications for the medium-term post-closure period

The highest generation rate arises from Magnox wastes (see Table 61).

Post-closure risks arising from the release of carbon-14 bearing gases are given in Table 62 (medium-term post-closure period). These are obtained by combining the reference-case generation rate given in for example in Figure 31 (and summarised in Table 61), the migration cases described in Section 7, the biosphere factors given in Table 13, and the cases for the proportion of carbon-14 released as methane or carbon monoxide discussed in the respective sections.

The environment agencies’ risk guidance level is \(10^{-6}\) [10], and risks above this guidance level are shown in **Bold**. The reference case for the values proportion of carbon-14 released as methane or carbon monoxide are in Black – other values are shaded Grey. As the risks are dominated by Magnox, the reference case corresponds to a release of 30% as methane or carbon monoxide.
Table 62 Calculated peak risks from carbon-14 containing gas for the medium-term post-closure period for a range of scenarios

<table>
<thead>
<tr>
<th>Geosphere case</th>
<th>Fraction of carbon-14 released as gas from metals$^{1,2,3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID</td>
<td>Release area (m²)</td>
</tr>
<tr>
<td>A</td>
<td>10⁶</td>
</tr>
<tr>
<td>B</td>
<td>No release</td>
</tr>
<tr>
<td>C</td>
<td>10⁴</td>
</tr>
<tr>
<td>D</td>
<td>10⁷</td>
</tr>
<tr>
<td>E</td>
<td>10⁶</td>
</tr>
<tr>
<td>F</td>
<td>10⁷</td>
</tr>
</tbody>
</table>

Notes:
1. The fractions for graphite are taken from the parameterisation of the revised graphite model. In this Table the same value is used for the fraction released as gas for each metal. In practice the fraction from the various metals will be different.
2. The reference case values are in black (dominated by Magnox) – other values are shaded grey.
3. Values below the risk guidance level of 10⁻⁶ are in plain text. Values above the risk guidance level are in Bold.

The risks in a number of the migration cases are above the risk guidance level. It is seen that:

- For a release area of 10⁶ m² and no delay (Case A), provided the proportion released as methane or carbon monoxide is less than around 30% the risks will be below the risk guidance level;
- For a focused release to an area of 10⁴ m² (Case C), neither the reference case nor the variants considered are below the risk guidance level;
- For Cases B, D and F, there is no release.

In environments where resaturation is slow, gas generation may be reduced because of a lack of water availability.

The results will be updated once there is more information on the release of carbon-14 bearing methane and carbon monoxide from Magnox as it corrodes. Once specific sites are identified and are being investigated, it will be important to understand the gas migration characteristics and whether a focused release may occur.

13.1.6 Implications for the long-term post-closure period

The highest generation rate arises from steel wastes (see Table 61). The generation rates during the long-term post-closure period are expected to be lower than in the medium-term post-closure period, and there may not be a gas phase present by that time.

Post-closure risks arising from the release of carbon-14 bearing gases are given in Table 59 (medium-term post-closure period). These are obtained by combining the reference-case generation rate given in for example in Figure 31 (and summarised in Table 61), the migration cases described in Section 7, the biosphere factors given in Table 13, and the cases for the proportion of carbon-14 released as methane or carbon monoxide discussed in the respective sections.

The environment agencies' risk guidance level is 10⁻⁶ [10], and risks above this guidance level are shown in Bold. The reference case for the values proportion of carbon-14
released as methane or carbon monoxide are in Black – other values are shaded Grey. As the risks are dominated by steel wastes, the reference case corresponds to a release of 10% as methane or carbon monoxide.

Table 63 Calculated peak risks from carbon-14 containing gas for the long-term post-closure period for a range of scenarios

<table>
<thead>
<tr>
<th>ID</th>
<th>Release area (m²)</th>
<th>Delay time (¹⁴C half-lives)</th>
<th>Geosphere case</th>
<th>Fraction of carbon-14 released as gas from metals¹²³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>100%</td>
<td>30%</td>
</tr>
<tr>
<td>A</td>
<td>10⁶</td>
<td>0</td>
<td>3.59 10⁻⁸</td>
<td>1.08 10⁻⁸</td>
</tr>
<tr>
<td>B</td>
<td>No release</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>10⁴</td>
<td>0</td>
<td>3.59 10⁻⁶</td>
<td>1.08 10⁻⁶</td>
</tr>
<tr>
<td>D</td>
<td>10⁷</td>
<td>0</td>
<td>3.59 10⁻⁹</td>
<td>1.08 10⁻⁹</td>
</tr>
<tr>
<td>E</td>
<td>10⁶</td>
<td>1</td>
<td>1.98 10⁻⁸</td>
<td>5.95 10⁻⁹</td>
</tr>
<tr>
<td>F</td>
<td>10⁷</td>
<td>1</td>
<td>1.98 10⁻⁹</td>
<td>5.95 10⁻¹⁰</td>
</tr>
</tbody>
</table>

Notes:
1. The fractions for graphite are taken from the parameterisation of the revised graphite model. In this Table the same value is used for fraction released as gas for each metal. In practice the fraction from the various metals will be different.
2. The reference case values are in black (dominated by steels) – other values are shaded grey.
3. Values below the risk guidance level of 10⁻⁶ are in plain text. Values above the risk guidance level are in Bold.

In the long-term post-closure period, only two of the cases are above the risk guidance level. These are for a focused release to an area of 10⁴ m² (Case C) where most of the carbon-14 is released as methane. Even with a focused release, the two variants, where 10% or 1% is released as carbon-14 bearing methane are below the risk guidance level.

In environments where resaturation is slow, there may not be a bulk gas phase in the long term.

The results will be updated once there is more information on the release of carbon-14 bearing methane and carbon monoxide from steel wastes as they corrode. Once specific sites are identified and are being investigated, it will be important to understand the gas migration characteristics and whether a focused release may occur.

13.2 Summary of the current position

The project has successfully updated the understanding of the key gas generation and migration processes that determine the potential impact of UK wastes containing carbon-14.

The integrated approach has covered a wide range of technical areas, gathering evidence to improve the knowledge base that supports our approach to management of these wastes.

A large number of knowledge gaps have been filled and the improved knowledge base has been captured in updated and new models. The calculated consequences have been reduced. The calculated impact is site specific and is dominated over the first thousand years following closure by the release of carbon-14 from irradiated reactive metals as they corrode.
In the first thousand years following closure, the calculated impact from gaseous carbon-14 will be below the risk guidance level, provided that:

- the proportion of carbon-14 released from reactive metals as methane or carbon monoxide is limited; and
- any gas that is released to the biosphere is released over an area roughly equivalent to the repository footprint or larger.

If there were a focused release of gas to a small area, risks may be above the risk guidance level. Therefore it will be important to understand the gas migration characteristics of any site proposed for the disposal of these wastes.

The inventory is based on the 2013 Derived Inventory. There are a number of waste streams where the inventory may be overestimated. The inventory is updated every three years.

The results presented here will be updated once experimental measurements on the speciation of carbon-14 released from irradiated Magnox and irradiated stainless steels become available.

Consideration should be given to developing a better understanding of the rate and extent of corrosion of reactive metal wastes prior to closure of a GDF. Sellafield is working towards measuring gas release form active waste packages, but these data will take several years to obtain. Such data would be valuable for comparison with the assessed releases.

Our improved understanding also has implications for the assessment of the groundwater pathway in terms of the inventory available for release and the speciation of carbon-14 in the aqueous phase. Account could be taken of the significant proportion of carbon-14 in graphite that would not be released on relevant timescales and the long timescales over which carbon-14 would be released from steels.

Carbon-14 remains a key radionuclide in the assessment of the safety of a GDF for radioactive waste because of the potential radiological impact of gaseous carbon-14 bearing species. As a result of this focused programme of work, we now have the knowledge base required to support packaging decisions for specific wastes and understand the envelope of conditions within which disposal of the UK’s wastes containing carbon-14 can be managed.

### 13.3 Integrated conclusions – the ‘AND’ approach

The ‘AND’ approach was introduced as a way of understanding which wastes might have a significant impact. The conclusions are presented here by the major waste groups to illustrate the progress that has been made as part of Phase 2.

The ‘AND’ approach was discussed in Section 1.4, and has been used to structure the work of the project.

In this section, the conclusions of the Phase 2 work are presented as answers to the questions in the ‘AND’ approach to describe the reasons the different waste groups could have a significant impact. This illustrates the progress that has been made as part of Phase 2.

The conclusions for the major waste groups are presented in Table 64.
Table 64  Current position on the status of the ‘AND’ approach for the main waste groups
The grey boxes indicate the issue for these wastes is closed by an earlier question

<table>
<thead>
<tr>
<th>‘AND’ Question</th>
<th>Graphite</th>
<th>Irradiated steel</th>
<th>Irradiated Magnox</th>
<th>Irradiated uranium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Is there a significant inventory?</td>
<td>Yes. There is a significant inventory of carbon-14 (about 7,000 TBq) in irradiated graphite (mostly in SILW).</td>
<td>Yes. There is a significant inventory of irradiated steels (about 7,000 TBq, of which 6,660 TBq is associated with NNB). The focus has been on a few legacy waste streams where a significant inventory is in irradiated steels that have relatively small thickness.</td>
<td>The inventory associated with uncorroded Magnox is modest (about 70 TBq), but has a large potential impact. Inventory may decrease in future, based on updated understanding of precursor concentrations and extent of corrosion.</td>
<td>The inventory associated with uncorroded uranium is modest (about 20 TBq). Inventory may decrease in future based on the extent of corrosion prior to disposal. The remaining uranium is expected to corrode before closure of the GDF.</td>
</tr>
<tr>
<td>Does the waste stream generate carbon-14 bearing gas?</td>
<td>Yes. However, improved understanding has shown that not all of the carbon-14 is released as gas. Gases generated include $^{14}$CH$_4$ and $^{14}$CO. $^{14}$CO$_2$ is more soluble and most will react with any cementitious materials in the waste packages.</td>
<td>Yes, but it is not certain what proportion of the carbon-14 is released as gas. Likely that there is some $^{14}$CH$_4$ released as the metal corrodes; some carbon-14 may be released as other species, some of which may partition into solution.</td>
<td>Yes. Carbon-14 in the gas phase is either $^{14}$CH$_4$ or low molecular weight hydrocarbon. Some is released to the aqueous phase, so not all would be released as gas. The rate of generation depends on the availability of chloride.</td>
<td>Uncertain – but likely to, based on comparison with Magnox.</td>
</tr>
<tr>
<td>Is there a bulk gas phase to entrain the carbon-14 bearing gas?</td>
<td>There is no significant bulk gas phase generated from the graphite. Any bulk gas would arise from container corrosion. Release is not expected to be limited by water availability.</td>
<td>These wastes generate hydrogen very slowly, when they corrode anaerobically. Corrosion is not expected to be limited by water availability.</td>
<td>Yes – these wastes also generate hydrogen as they corrode. Once water initially available in the containers is used up, continuing corrosion will depend on water from resaturation. Resaturation times will depend on the geological environment.</td>
<td>Yes – these wastes also generate hydrogen when they corrode anaerobically. Corrosion is not expected to be limited by water availability.</td>
</tr>
</tbody>
</table>
Table 64  Current position on the status of the ‘AND’ approach for the main waste groups (continued)

The grey boxes indicate the issue for these wastes is closed by an earlier question

<table>
<thead>
<tr>
<th>‘AND’ Question</th>
<th>Graphite</th>
<th>Irradiated steel</th>
<th>Irradiated Magnox</th>
<th>Irradiated uranium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Do these gases migrate through the near field in significant quantities?</td>
<td>$^{14}$CO$_2$ is expected to be retained in the EBS, but $^{14}$CH$_4$ and $^{14}$CO would migrate through the near field in most concepts if there is a bulk gas phase present.</td>
<td>Any trace $^{14}$CO$_2$ in the gas phase is expected to react with cementitious materials (in package grout or surrounding backfill) – there is no bulk CO$_2$ from these wastes.</td>
<td>Any trace $^{14}$CO$_2$ in the gas phase is expected to react with cementitious materials (in package grout or surrounding backfill) – there is no bulk CO$_2$ from these wastes.</td>
<td>Any trace $^{14}$CO$_2$ in the gas phase may react with cementitious materials (in package grout) – there is no bulk CO$_2$ from these wastes.</td>
</tr>
<tr>
<td>Do these gases migrate through the geological environment in significant quantities?</td>
<td>This is a site-specific question. Some geological environments (e.g. LSSR and evaporite) would provide a significant barrier to gas migration or may allow the gas time to dissolve in groundwater or to decay. Important factors are the time taken for the carbon-14 to migrate to the biosphere and the area of any release.</td>
<td></td>
<td>Provided uranium corrodes anaerobically after emplacement, it will all have corroded before closure.</td>
<td></td>
</tr>
<tr>
<td>Do these gases lead to significant doses in the operational phase?</td>
<td>No.</td>
<td>No.</td>
<td>No.</td>
<td>No.</td>
</tr>
<tr>
<td>Do these gases lead to significant risks to potentially exposed groups in the post-closure phase?</td>
<td>Risks are assessed to be below the risk guidance level provided that the release is not focused over a small area.</td>
<td>The radiological risk is expected to be tolerable in most environments. Even where there is a focused release, provided that 10% or less of the carbon-14 from these wastes is released in gaseous form, then the release is expected to be acceptable.</td>
<td>Risks are expected to be tolerable provided releases are to an area comparable to the GDF footprint and the proportion of the carbon-14 released as $^{14}$CH$_4$ or $^{14}$CO is limited, or there is a significant hold-up of gas in the geosphere.</td>
<td>Provided uranium corrodes anaerobically after emplacement, it will all have corroded before closure.</td>
</tr>
</tbody>
</table>
14 References


11 A. Adeogun and M. Plews, Carbon-14 Project Phase 2: Inventory, AMEC Report, AMEC 200047/003 Issue 1, 2016.


<table>
<thead>
<tr>
<th>Page</th>
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