Carbon-14 Project Phase 2
Irradiated Reactive Metal Wastes

To: Radioactive Waste Management Limited
Date: March 2016
From: Amec Foster Wheeler
Your Reference: RP50
Our Reference: AMEC/200047/006 Issue 1
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Prepared for  Radioactive Waste Management Limited

Your Reference  RP50

Our Reference  AMEC/200047/006 Issue 1

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Reviewed by  S. Vines

24 March 2016

Approved by  D.A. Lever

24 March 2016

1 Quintessa
2 Radioactive Waste Management

Transport Flask Photograph courtesy of Magnox Electric Ltd

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Preface

This report has been prepared by AMEC under contract to Radioactive Waste Management Limited (RWM) and forms part of an ongoing programme of research commissioned by RWM to underpin the long-term safety of a geological disposal facility for higher-activity radioactive wastes.

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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 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. This report is part of a suite of reports produced as part of the project.

This report summarises the work relating to irradiated reactive metal wastes. The focus of the work described in this report has been:

- To improve the understanding of the inventory of carbon-14 in reactive metal wastes;
- To improve the understanding of the rate and speciation of carbon-14 release from reactive metal wastes, based on experimental work that is being undertaken;
- To update the models used to assess gaseous carbon-14 generation from reactive metal wastes in line with the improved understanding of the release of carbon-14;
- To consider alternative options for management and disposal of reactive metal wastes.
Executive Summary

Background

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. In particular, the radiological impact of gaseous carbon-14 bearing species has been recognised as a potential issue. 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 (\(^{14}\text{CH}_4\)) likely to be the dominant carbon-14 species transported in the gas phase, potentially reaching the biosphere at low activity concentrations.

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.

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 in the Derived Inventory. 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;
  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 project has consisted of two phases. In Phase 1, the project team carried out a six month programme of work to summarise the current understanding and to set out a roadmap for Phase 2. This report is one of a suite of reports issued as part of Phase 2 of the project, and summarises the work relating to irradiated reactive metal wastes that has been completed as part of Phase 2 of the project.

Inventory

There are about 100 TBq of carbon-14 associated with reactive metal wastes (Magnox, uranium and aluminium). 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 as part of the Phase 2 work, there is a better understanding of the nature of the material with which the carbon-14 is associated.
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. Currently there is no inventory of carbon-14 declared as being associated with aluminium.

**Release of Carbon-14 through Corrosion**

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 packaged 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 overall gas generation rate from irradiated Magnox in a GDF.

**Assessment Implications**

The releases from reactive metals are higher than those from any of the other wastes during the emplacement 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.
- Post-closure risks arising from any uranium metal remaining 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 wastes 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 only be considered as part of option studies for wastes that are neither currently packaged nor being packaged.

**Possible future work**

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 from active waste packages, but these data will take several years to obtain. Such data would be valuable for comparison with the assessed releases. Consideration could also be given to further developments of the total system model.

- Summary of the Position on Reactive Metals

A summary of the current position is provided in Table ES.1. The status is described in the context of the ‘AND’ questions identified earlier.
<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 (66.3 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 (17.7 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>
<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 anaerobically. Corrosion is not expected to be limited by water availability.</td>
<td></td>
</tr>
<tr>
<td>Do these gases migrate through the near field in significant quantities?</td>
<td>After closure 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 very site specific. Risks are expected to be tolerable provided releases are not focused area and a significant proportion of the carbon-14 is not released as $^{14}$CH$_4$ or $^{14}$CO, 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>
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1 Introduction

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 [1]. 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 [2], in the 2010 generic Disposal System Safety Case (DSSC) [3], and in the issues register [4]. 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 (\(^{14}\)CH\(_4\)) likely to be the dominant carbon-14 species transported in the gas phase, potentially reaching the biosphere at low activity concentrations.

Radioactive Waste Management (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 [5], the 2010 radionuclide behaviour status report [6], the 2010 biosphere status report [7] and in the 2014 Science & Technology Plan [8]. However, following publication of the 2010 DSSC, it has been 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 GDF.

1.1 Carbon-14: Key Processes

The main sources of carbon-14 in waste materials that will be emplaced in a GDF 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. An overview of the key processes affecting the fate of carbon-14 in the geological disposal system is shown in Figure 1.1.

![Figure 1.1 Key generation and migration processes affecting the fate of carbon-14 in the disposal system](image)

At the same time, corrosion of metals, radiolysis and degradation of organic materials will generate ‘bulk gas’, mostly hydrogen. Intermediate-level waste (ILW) containers are generally vented and any gas generated will be released into the surrounding Engineered Barrier System (EBS). Depending on the amount of bulk gas generated, some species containing carbon-14 will dissolve in the near-field porewater and some will remain in the gas phase. Carbon dioxide is likely to be retained within the EBS due to carbonation of cementitious materials. 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 converted to carbon dioxide by microbes in the soil zone. This carbon dioxide could then be taken up by plants, and so enter the food chain, leading to a consequent dose to any exposed groups or potentially exposed groups.

1.2 Aims and Objectives of the Carbon-14 Project

The overall aim of the project is:

To support geological disposal of UK wastes containing carbon-14, by integrating 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, to 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 the 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; and
- To inform the requirements for site characterisation.

At the outset, it was established that a successful outcome from the project would be that:

RWM understands the envelope of conditions within which the disposal of the UK’s wastes containing carbon-14 can be managed.

1.3 The ‘AND’ 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 1.2 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.
Overview of the Project

The project has consisted of two phases. In Phase 1, the project team carried out a six month programme of work to summarise the current understanding and to set out a roadmap for Phase 2 [1]. The work concluded that the calculated release of carbon-14 from a GDF will 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. However, there was scope for improving the models used to calculate the radiological consequence for these wastes. The work 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.

The roadmap identified a number of specific tasks that combined desk-based, numerical modelling and experimental activities. The scope of some tasks was focused on particular groups of carbon-14 bearing wastes, such as graphite, irradiated steels and irradiated reactive metals; these tasks also included consideration of alternative treatment, packaging, design and disposal options for these wastes. Other tasks related to aspects of the disposal system that are not specific to particular wastes: these included migration through engineered barriers, the geosphere and release to the biosphere. Finally there were tasks in a number of overarching areas, such as modelling in support of safety assessments. Some tasks were already ongoing and were transferred into the project.

Phase 2 of the project has been completed. This report is one of a suite of reports issued by the project. An overview of all of the work undertaken, and the conclusions reached, is provided in Reference [9]. The main reports produced as part of the project are given in Table 1.1.

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.

Figure 1.2 The integrated technical approach (the ‘AND’ approach)
1.5 This Report

The focus of this report is the work undertaken on irradiated reactive metals, namely Magnox, uranium and aluminium [1].

Based on the work in the Phase 1, the calculated release from Magnox and uranium leads to an assessed risk that is significantly above the regulatory risk guidance level. However, this is based on a number of simplifications. The way forward for these wastes depends on understanding whether the carbon-14 from these materials is likely to be released in the operational and early post-closure period (in which case the peak release could be high, but could perhaps be mitigated by some means), or whether it is more likely to be spread out over a longer period. The proposed work for Phase 2 was to:

- Improve the quality for the inventory of carbon-14 in reactive metal wastes;
- Gather experimental data on the rate and speciation of the release of carbon-14 from these wastes;
- Consider how much of the carbon-14 may have been released before disposal;
- Consider the impact of water availability (or ways to limit access of water to the waste) and the impact of chloride;
- Update the modelling basis spreadsheet and scoping calculations;
- Develop a total system model adopting a structured approach to the treatment of uncertainty;
- Consider the potential benefits from alternative treatment, packaging, design and disposal options for these wastes.

This work is now broadly complete, and is reported here. The experimental work on the measurement of the rate and speciation of the release of carbon-14 from these wastes is still ongoing, and the results will be updated once that work is complete.
The structure of this report is as follows:

- The work on the inventory of reactive metal wastes is summarised in Section 2.
- The work on the corrosion of Magnox wastes is described in Section 3; this includes a discussion of the experimental evidence and the development of simple models.
- The work on the corrosion of uranium wastes is described in Section 4; this includes a discussion of the experimental evidence and the development of simple models.
- The position on aluminium wastes is summarised in Section 5.
- The revised assessment approach is summarised in Section 6. This enables the rate of generation of carbon-14 bearing gas from the various reactive metals to be set in the overall assessment context given the programme to develop a GDF is at a generic stage.
- The overall calculations of the implications from reactive metal wastes are presented in Section 7. These calculations are carried out using the Simple Model of Gas Generation (SMOGG) software tool [17, 18]. 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. The section also includes the results of the work on the initial development of a total system model.
- Alternative management approaches are considered in Section 8.
- The overall conclusions are summarised in Section 9.

A number of appendices present additional details on some of the modelling work undertaken.
2 Inventory of Carbon-14

One of the significant tasks of the project was to derive a reliable inventory for carbon-14 that could be used to underpin future decisions on carbon-14 management, specifically with regards to geological disposal. Previous estimations of the carbon-14 inventory were known to be subject to considerable uncertainties, and these uncertainties propagated through performance and safety assessment calculations. This section presents the currently projected carbon-14 inventory of reactive metal wastes that will be disposed in a UK GDF.

In Phase 1 of the project, 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 (the 2012) gas generation assessment [19]. 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 [20]. During Phase 1 [1] and 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 [10].

In Phase 1 of the project, a carbon-14 inventory for wastes destined for disposal in a UK GDF was developed based on information contained in RWM’s 2010 Derived Inventory [21]. A number of data enhancements were applied to address some limitations of the 2010 DI. The Phase 1 report [1] summarises the then current understanding of the carbon-14 inventory and presents detailed information on those waste streams that are the major contributors to the carbon-14 inventory. Knowledge gaps and key uncertainties in the carbon-14 inventory were also identified.

Since the inventory work under Phase 1 was completed, a Government White Paper on geological disposal [22] and the 2013 UK Radioactive Waste Inventory (RWI) [23] have been published, both of which have had an impact on the carbon-14 inventory for geological disposal. During Phase 2 of the project, the carbon-14 inventory has been updated to include the latest information available from the 2013 UK RWI and to address the changes in wastes to be included in the disposal inventory, as laid out in the White Paper. Further information about specific waste materials has been obtained through interactions with the key waste producers (Magnox, Sellafield and EDFE) and with Springfields Fuels Limited, the makers of the UK’s nuclear fuel, to address knowledge gaps identified during Phase 1. This has enabled a number of additional improvements to be made to the carbon-14 inventory [10].

2.1 2013 Derived Inventory

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 [24] differs in three significant ways from the 2010 Derived Inventory [21]:

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

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1 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 [25] in line with Government’s preferred policy for long term 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 [26].

At the same time as the carbon-14 project’s Phase 2 work, RWM has been undertaking a programme of work to develop a 2013 Derived Inventory. The 2013 Derived Inventory is a translation of the UK Government’s inventory for disposal (as defined in the ‘Implementing Geological Disposal’ White Paper [22] in terms of types of higher activity wastes and nuclear materials that could be declared as waste) into numerical information. The development of the 2013 Derived Inventory has been achieved through a review of RWM’s data requirements, and an analysis of the 2013 UK RWI data and other information sources. The results of the Phase 2 work have been integrated into the 2013 Derived Inventory.

The radionuclide content in the 2013 Derived Inventory is decayed to the expected GDF closure year of 2200\(^2\). 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 Carbon-14 Inventory in Reactive Metal Wastes

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 shape data for certain of the key waste streams. The key areas of progress are summarised below. Further details are provided in a supporting reference [10].

The neutron activation calculation methodology and assumed nitrogen precursor concentrations used for determining the carbon-14 activity for Magnox fuel (uranium metal), and information regarding calculation uncertainties associated with nitrogen precursor concentrations and other inputs for activation calculations was obtained.

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.

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 2.1 [10]\(^3\). 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. A number of the waste streams contain both Magnox and uranium.

\(^2\) The change from year 2150 used in the Phase 1 report is not significant given the long half-life of carbon-14.

\(^3\) Wastes are categorised as UILW (unshielded intermediate-level waste), SILW (shielded intermediate-level waste) or DCIC (waste packaged in Ductile Cast Iron Containers).
### Table 2.1  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></td>
<td>Pile Fuel Cladding and Miscellaneous Solid Waste</td>
<td>8,160</td>
<td>14.6</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></td>
<td>Magnox Cladding and Miscellaneous Solid Waste</td>
<td>12,700</td>
<td>11.0</td>
<td>3% Magnox, &lt;1% uranium metal, 5% stainless steel and &lt;1% mild steel</td>
</tr>
<tr>
<td>2D09 UILW</td>
<td></td>
<td>Magnox Cladding and Miscellaneous Solid Waste</td>
<td>10,500</td>
<td>15.6</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></td>
<td>Magnox Cladding and Miscellaneous Solid Waste</td>
<td>3,830</td>
<td>7.78</td>
<td>~21% Magnox and ~4% uranium metal</td>
</tr>
<tr>
<td>2D24 UILW</td>
<td></td>
<td>Magnox Cladding and Miscellaneous Solid Waste</td>
<td>5,040</td>
<td>10.8</td>
<td>~25% Magnox and ~8% uranium metal</td>
</tr>
<tr>
<td>2D35 UILW</td>
<td></td>
<td>Magnox Cladding and Miscellaneous Solid Waste</td>
<td>2,720</td>
<td>10.6</td>
<td>79% Magnox and ~3% uranium metal</td>
</tr>
<tr>
<td>2D35/C UILW</td>
<td></td>
<td>Encapsulated Retrieved Magnox Cladding</td>
<td>1,410</td>
<td>4.76</td>
<td>16% Magnox and 1% uranium metal</td>
</tr>
<tr>
<td>2D38/C UILW</td>
<td></td>
<td>Encapsulated Magnox Cladding</td>
<td>11,700</td>
<td>36.7</td>
<td>15% Magnox and 1% uranium metal</td>
</tr>
<tr>
<td>2D45 UILW</td>
<td></td>
<td>Magnox Fuel End Crops</td>
<td>55.2</td>
<td>0.79</td>
<td>25% Magnox, 60% uranium metal and 8% zirconium</td>
</tr>
<tr>
<td>2D96.2 (formerly 2D17) UILW</td>
<td></td>
<td>FGMSLP Pond Solid Waste to BEP</td>
<td>2,610</td>
<td>1.52</td>
<td>5% Magnox, 3.5% uranium</td>
</tr>
<tr>
<td>2S304 UILW</td>
<td></td>
<td>Windscale Piles Fuel and Isotopes</td>
<td>144</td>
<td>0.46</td>
<td>79% uranium fuel</td>
</tr>
<tr>
<td>9A39 DCIC</td>
<td>FED Magnox</td>
<td></td>
<td>34.8</td>
<td>0.0016</td>
<td>&gt;99% Magnox (AL80) metal</td>
</tr>
<tr>
<td>9A40 DCIC</td>
<td>FED Magnox</td>
<td></td>
<td>52.2</td>
<td>0.0023</td>
<td>&gt;99% Magnox (AL80) metal</td>
</tr>
<tr>
<td>9A41 DCIC</td>
<td>FED Magnox</td>
<td></td>
<td>60.9</td>
<td>0.0027</td>
<td>&gt;99% Magnox (AL80) metal</td>
</tr>
<tr>
<td>9A42 DCIC</td>
<td>FED Magnox</td>
<td></td>
<td>37.0</td>
<td>0.0033</td>
<td>&gt;99% Magnox (AL80) metal</td>
</tr>
<tr>
<td>9A43 DCIC</td>
<td>FED Magnox</td>
<td></td>
<td>15.2</td>
<td>0.0014</td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9E24 UILW</td>
<td>FED Magnox</td>
<td></td>
<td>101</td>
<td>0.0080</td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9E25 UILW</td>
<td>FED Magnox</td>
<td></td>
<td>101</td>
<td>0.0080</td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9E26 UILW</td>
<td>FED Magnox</td>
<td></td>
<td>105</td>
<td>0.42</td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9E27 UILW</td>
<td>FED Magnox</td>
<td></td>
<td>105</td>
<td>0.017</td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9E28 UILW</td>
<td>FED Magnox</td>
<td></td>
<td>105</td>
<td>0.0083</td>
<td>&gt;99.5% Magnox metal</td>
</tr>
<tr>
<td>9G15 UILW</td>
<td>FED Drummed Magnox</td>
<td></td>
<td>64.8</td>
<td>0.0007</td>
<td>&gt;99% Magnox metal</td>
</tr>
<tr>
<td>9G34 UILW</td>
<td>FED Magnox</td>
<td></td>
<td>127</td>
<td>0.022</td>
<td>94.5% Magnox metal</td>
</tr>
<tr>
<td>9G35 UILW</td>
<td>FED Magnox</td>
<td></td>
<td>189</td>
<td>0.086</td>
<td>94.5% Magnox metal</td>
</tr>
<tr>
<td>Total DCIC</td>
<td></td>
<td></td>
<td>200</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>Total UILW</td>
<td></td>
<td></td>
<td>59,700</td>
<td>115</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**.
The main strands of work on the inventory of reactive metals are outlined in Table 2.2, 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 [10]. 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 2.1, 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 2.2 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 for mixed material waste streams.</td>
<td>Nitrogen concentrations used in the calculation 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 and carbon-14 content of reactive metals for disposal to a GDF.

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 Springfields Fuels Ltd (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 is made.

An analysis of the carbon-14 activity by material type was completed as part of the 2013 Derived Inventory [23].

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 2.3. 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 [1]. 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 [10]. The results of this programme will determine whether any changes are made to assumptions underpinning future Derived Inventories.

Table 2.3 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></td>
<td>Category</td>
</tr>
<tr>
<td>Magnox</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranium</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>0</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.

2.3 Data on the Geometry of Reactive Metal Wastes

Later in this report, calculations are presented on the release of carbon-14 from the wastes in Table 2.3. First, scoping calculations are reported for Magnox wastes (Section 3.6) and uranium (Section 4.5). Then more comprehensive calculations are reported in Section 7 using SMOGG.

To estimate the generation rate of gas due to corrosion of the metals, information on the geometry of the various metal wastes is required. A simplification is adopted whereby the wastes are represented as either plates or spheres. This is a simplification but allows generation rates to be appropriately represented. The approximate geometry data of the metal wastes (i.e., whether they are plates or spheres, and their effective dimensions) are provided in the Inventory Report [10].

For the uncorroded Magnox wastes4, the carbon-14 inventory is associated with plates of various thicknesses. The inventories from different waste streams are grouped by thickness, as shown in Table 2.45.

---

4 All this waste is classified as UILW.

5 A small inventory (0.15 TBq) in uncorroded Magnox waste is not given a plate thickness. To ensure the correct total inventory, this is distributed amongst the other plate thicknesses.
Table 2.4  Inventory associated different plate thicknesses for uncorroded Magnox wastes

<table>
<thead>
<tr>
<th>Thickness (m)</th>
<th>Inventory (TBq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>55.7</td>
</tr>
<tr>
<td>0.00058</td>
<td>1.32</td>
</tr>
<tr>
<td>0.00028</td>
<td>0.49</td>
</tr>
<tr>
<td>0.00156</td>
<td>4.11</td>
</tr>
<tr>
<td>0.00148</td>
<td>2.60</td>
</tr>
</tbody>
</table>

Since over 85% of the inventory is associated with 0.002m thickness, this value is used in the scoping calculations for the inventory of all the Magnox wastes (see Section 3.6).

For the uncorroded uranium wastes, the carbon-14 inventory is associated with plates and spheres. The inventories grouped by thickness or diameter are shown in Table 2.5. This inventory is used in the scoping calculations for uranium metal wastes described in Section 4.5.

Table 2.5  Inventory associated different plate thicknesses and sphere diameters for uncorroded uranium wastes

<table>
<thead>
<tr>
<th>Plate or Sphere</th>
<th>Thickness/Diameter (m)</th>
<th>Inventory (TBq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate</td>
<td>0.01</td>
<td>3.89</td>
</tr>
<tr>
<td>Plate</td>
<td>0.001</td>
<td>5.45</td>
</tr>
<tr>
<td>Sphere</td>
<td>0.01</td>
<td>7.68</td>
</tr>
<tr>
<td>Sphere</td>
<td>0.05</td>
<td>0.66</td>
</tr>
</tbody>
</table>

For the overall modelling calculations reported in Section 7, which cover all wastes:

- all uncorroded Magnox wastes are treated as plates with an average thickness;
- uranium metal wastes are divided into plates of an average thickness and spheres of an average diameter.

The data are given in Table 2.6. The averages are different to those implied by Table 2.4 and Table 2.5 because of the inclusion of wastes with negligible carbon-14 associated with them. This is important for the bulk gas calculations; the scoping calculations do not estimate the contribution to bulk gas generation.

Table 2.6  Metal waste mass and geometry data for Legacy UILW / ULLW based on the 2013 Derived Inventory as used in the SMOGG calculations

<table>
<thead>
<tr>
<th>Waste stream group</th>
<th>Effective plate thickness (m)</th>
<th>C-14 Activity (TBq)</th>
<th>Effective sphere diameter (m)</th>
<th>C-14 Activity (TBq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnox</td>
<td>$1.48 \times 10^{-3}$</td>
<td>66.3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Uranium</td>
<td>$1.20 \times 10^{-3}$</td>
<td>9.08</td>
<td>$4.90 \times 10^{-3}$</td>
<td>8.59</td>
</tr>
</tbody>
</table>

---

6 All this waste is classified as UILW.
7 A small inventory (0.46 TBq) of uncorroded uranium waste is not given a dimension, and this is distributed amongst the other plate thicknesses.
8 The inventories in the inventory report [10] are decayed to 2200AD, for comparison that date is retained in this report. The inventory in the modelling report are decayed to 2040AD – the date of the start of waste emplacement.
3 Magnox Wastes

In the Phase 1 work, Magnox wastes were important contributors at very early times to the release of carbon-14 – 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 after the closure of the GDF. The corrosion rate is also sensitive to the temperature. 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 3.1), and corresponding corrosion times are evaluated (Section 3.2);
- Package-scale and vault-scale modelling (Section 3.3) 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 3.4).
- In the light of the understanding developed, the life cycle of Magnox wastes is described (Section 3.5);
- Calculations have been undertaken to describe the generation rates in the different phases of the life cycle of Magnox wastes (Section 3.6); more detailed modelling using SMOGG is reported in Section 7.
- A summary is provided in Section 3.7.

3.1 Magnox Corrosion Rates

A typical Magnox alloy has the following composition [27] (wt%): Al 0.80; Zn 0.005; Si 0.008; Cu 0.005; Mn 0.005; Fe 0.003; Sn 0.005; Ni 0.002; Ca 0.005; Pb 0.005; Be 0.005; with the balance being Mg. Studies have been made of the effect of alloying elements on the corrosion rate. Al, Zn, Pb, Sn, and Mn have little or no effect on the corrosion rate of magnesium and so Al and Zn are used as alloying elements.

The basic corrosion reaction is that the magnesium present in the Magnox alloy reacts with water to give magnesium hydroxide and hydrogen:

\[ \text{Mg} + 2\text{H}_2\text{O} \Rightarrow \text{Mg(OH)}_2 + \text{H}_2 \]

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 temperature range of interest (in the range of around 15°C to around 50°C), but it is crucially dependent on the chloride concentration local to the wastes in the waste packages.

Data on the corrosion rates of the reactive metals under disposal conditions were reviewed in 2007 [28]; this included the data on the corrosion of Magnox. The review drew heavily on a previous international review [29]. Recommendations were made regarding the corrosion rates to be used in the gas generation model SMOGG [17, 18]. The recommended corrosion rates are summarised in Table 3.1. 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.
Table 3.1  Magnox corrosion rates from the review of rates to be used in SMOGG [28]

<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>45°C</td>
</tr>
<tr>
<td>High pH Low Cl⁻</td>
<td>Acute</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Chronic</td>
<td>0.78</td>
<td>2.5</td>
</tr>
<tr>
<td>High pH High Cl⁻</td>
<td>Acute</td>
<td>1000</td>
<td>2300</td>
</tr>
<tr>
<td></td>
<td>Chronic</td>
<td>78</td>
<td>250</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 [30]. This review included data from extensive trials undertaken by BNFL that were not available for the 2007 review [28].

One important aspect is 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 [31, 32] as shown in Figure 3.1.

Figure 3.1  Corrosion rates for Magnox encapsulated in grout in 500 litre scale experiments [31] (reproduced from [28])

In the light of this, a further review has been undertaken by NNL [33]. The review did not find additional data that replicate the scenario of interest where chloride migrates into a wasteform in a GDF. This report summarised data that are available on the effects of chloride in water and grout mix water on Magnox corrosion and used these data to explore how the corrosion rate of Magnox in a resaturated repository may be enhanced. The results are summarised in Table 3.2.
Table 3.2  Magnox corrosion rates from the review by NNL [30]

<table>
<thead>
<tr>
<th></th>
<th>Corrosion Rate (μm yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35°C</td>
</tr>
<tr>
<td>Geometric mean Magnox corrosion rate</td>
<td></td>
</tr>
<tr>
<td>in grout</td>
<td>0.6</td>
</tr>
<tr>
<td>Arithmetic mean Magnox corrosion rate</td>
<td></td>
</tr>
<tr>
<td>in grout</td>
<td>0.9</td>
</tr>
<tr>
<td>Geometric mean converged Magnox</td>
<td></td>
</tr>
<tr>
<td>corrosion rate in water</td>
<td>30</td>
</tr>
<tr>
<td>Arithmetic mean converged Magnox</td>
<td></td>
</tr>
<tr>
<td>corrosion rate in water</td>
<td>39</td>
</tr>
<tr>
<td>Geometric mean corrosion rate in chlorinated water</td>
<td>3000</td>
</tr>
<tr>
<td>Arithmetic mean corrosion rate in chlorinated water</td>
<td>3900</td>
</tr>
<tr>
<td>Geometric mean corrosion rate in grout</td>
<td>0.6 – 3900</td>
</tr>
<tr>
<td>Arithmetic mean corrosion rate in grout</td>
<td>0.9 – 3900</td>
</tr>
</tbody>
</table>

The different datasets are in reasonable agreement. From Table 3.1 and Table 3.2 it is seen that different datasets show different degrees of dependence on temperature. The NNL review did 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 and the Magnox is essentially corroding in a free chloride solution.

It is concluded that the Magnox corrosion parameters used in the assessments are well-founded, and in the calculations reported here the SMOGG dataset [28] is used.

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 [28] 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 [13]. As a consequence, although the composition of groundwater will be site specific, 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.

The corrosion of Magnox is an exothermic reaction, and the corrosion rate increases with temperature. However, it is expected that the coupling between exothermic corrosion, the temperature and the corrosion rate will be relatively unimportant [34]. This is discussed further in Appendices 2 and 3.

### 3.2 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. Indicative times for the total corrosion of 0.002 m thick Magnox plates are presented in Table 3.3. The values are quoted for the low and high chloride corrosion rates from the SMOGG review [28] given in Table 3.1. 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 3.3  Indicative corrosion times for 0.002m plates of Magnox, using the low and high chloride chronic corrosion rates from the SMOGG review [28]

<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>

The availability of water is important for a number of gas generation processes, including the corrosion of Magnox. There are a number of sources of water in a GDF, and a number of processes that consume 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. In reactive metal wastes it is expected that there will be sufficient water in the encapsulation grouts in the package to allow a proportion of the wastes to corrode (estimated to be 23% for Magnox wastes [13]). Further corrosion would be dependent on further water becoming available from resaturation. This is discussed in more detail in reference [13].

3.3 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).

Detailed modelling has been undertaken to enable an understanding of the corrosion of Magnox wastes in a GDF to be developed; this is described in a number of Appendices to this report, as follows:

- The evolution of the chloride concentration in a GDF is discussed in Appendix 1. This work concerned the development of analytic models that are used to inform understanding of the time it takes for chloride in groundwater to reach all the Magnox wastes in a GDF. The Appendix considers:
  - Chloride migration through intact backfill;
  - Chloride migration through cracked backfill;
  - Chloride migration in the wasteform;

- Package-scale models have been developed to explore the ingress of water and chloride into waste packages and the migration of gas out of packages. These migration processes take place through the package vent. To build confidence in the approach, separate exercises have been conducted by Quintessa and AMEC. The work is described in Appendices 2 to 4, as follows:
  - Appendix 2 describes the data used in the modelling;
  - Appendix 3 describes the modelling undertaken by Quintessa; and
  - Appendix 4 describes the work undertaken by AMEC.
This modelling provides an understanding of the timescales over which Magnox corrodes within a package.

Processes at the vault scale and at the package scale are considered below; the discussion is informed by the work described in the appendices. As the treatment of the ullage space is part of the package-scale modelling, this is discussed after processes in the encapsulation grout. The discussion is informed by the key conclusions from the appendices.

3.3.1 Processes at the vault scale

The first process by which chloride will migrate into a vault after closure is advection by the flow of groundwater into the vault during resaturation (Figure 3.2 (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 [13]. The water that reaches the waste packages will have been the water present in the backfill on emplacement and this water will contain little chloride.

After the vault has resaturated, a regional groundwater flow could continue to transport chloride through the backfill surrounding the waste packages (Figure 3.2 (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 (see Appendix 1) to estimate the length of time it takes for chloride takes to migrate across a vault. These take into account:

- Typical hydraulic conductivities and head gradients of the host rock [35];
- Typical hydraulic conductivities of the backfill [36] and the focusing of flow through the vaults [13, 37];
- The sorption of chloride onto the backfill [38]; an effect of the sorption will be to increase the travel time for the chloride by a retardation factor [39];
- The implications of cracks in the backfill (see Appendix 1 and Reference [40]), leading to flow being preferentially along the cracks, with diffusion of chloride into the intact backfill between the cracks [41, 42].

These simple analytical models show that the arrival of chloride at the waste packages in a vault will be spread over a considerable time (see Appendix 1). 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 [13]).

---

9 The temperature profile is discussed in reference [13], and is summarised in Table 3.4 later in this Section.
(a) During initial resaturation

(b) Longer term advection by the regional flow

(c) Advection into the waste package, arising from corrosion of Magnox wastes

Figure 3.2 Schematic representation of chloride transport into the vault and packages in a higher-strength rock
3.3.2 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 most of the waste packages will have vents (including those of interest here), 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 [36].

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 (see Appendices 3 and 4) 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. This is illustrated in Figure 3.2(c). The flow of porewater will therefore transport chloride downwards through the wasteform inside a waste package. An example calculation is shown in Figure 3.3.

The pathways by which chloride will migrate from the groundwater into the waste packages could be influenced by the presence of cracks. The presence of cracks in the grout could shorten the timescale for chloride to migrate through the grout. However, from the analyses in Subsection A1.4, it is clear that it is the backfill, rather than the encapsulation grout, which will contribute most to the delay in chloride coming into contact with the Magnox alloy.

---

Figure 3.3 Gas pressure and gas saturation around and inside a waste package. The right-hand plot is an expansion of the top of the package on the left-hand plot; it includes the direction (but not magnitude) of the liquid velocity vectors.

---

10 The wasteform processes may be quite dynamic. Although the matrix grout will crack due to the expansive corrosion of Magnox and uranium metals once water enters the package, there is a possibility that the grout matrix would start to reform as a complex of hydrated magnesium oxide and calcium aluminium silicates deriving from the OPC and BFS. Although the new composite would not be homogenous it may tend to control the rate at which gases are released from the package.
The package-scale numerical models (see Appendices 3 and 4) show 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 3.2(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.

The package-scale modelling is illustrated in Figure 3.4, which shows the front where Magnox is corroding at an elevated rate because of the presence of chloride.

![Figure 3.4](image)

**Figure 3.4** Plot showing (left) the density of Magnox alloy (kg m\(^{-3}\)) in the wasteform, (middle) the liquid saturation, and (right) the concentration of chloride (ppm)

### 3.3.3 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. In reality the situation may be complicated by shrinkage cracks around the drum lid, which may affect the way the gas migrates into the backfill.

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 as the Magnox consumes the water. 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 [43], 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.

### 3.3.4 Summary and implementation

Once chloride has entered a waste package, it will take tens or 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 for the chloride to reach all the packages.

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.

A combination of different corrosion rates for different parts of the wastes cannot be directly modelled using SMOGG (see Sections 6.1 and 7.1), so a smaller enhancement of the corrosion rate has been applied in the calculations to approximate the ‘average’ behaviour. The ‘average’ enhanced corrosion rate is calculated as

\[
k_{\text{eff}} = k_0 + \frac{s_0}{2\Delta t} \frac{f - 1}{f}
\]

where

- \(k_{\text{eff}}\) is the ‘average’ enhanced corrosion rate \([\text{m yr}^{-1}]\);
- \(k_0\) is the corrosion rate in the absence of chloride \([\text{m yr}^{-1}]\);
- \(s_0\) is the thickness of the Magnox at the time chloride starts to enter the packages \([\text{m}]\);
- \(\Delta t\) is the range of times over which chloride reaches different packages \([\text{yr}]\);
- \(f\) is the chloride corrosion rate enhancement factor (i.e. 100) \([-\]).

This approach is also used in the scoping calculations discussed later in this Section.

On the basis of the above discussion, the ‘average’ enhanced corrosion rate used in the reference case calculations (Section 7.2) was calculated assuming chloride reaches the first packages 100
years after closure and reaches the last packages 1000 years after closure. Two variants on these
times are discussed in Section 7.3.

3.4 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 underway to examine the speciation of carbon-14 released from
Magnox wastes. These experiments use a similar approach to the experiments with graphite [11]
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; and
- The carbon-14 in the gas phase appears to be mainly either methane or other low molecular
  weight hydrocarbons.

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).

3.5 Life Cycle for Magnox Wastes

As discussed above, the corrosion rate for Magnox is dependent on the local environment, and in
particular on whether there is chloride present and on the temperature. In the light of the estimated
corrosion times, the life cycle of typical Magnox waste packages can be evaluated. 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, packages 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;
- 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 resaturate, 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 [13] to result in
  elevated corrosion rates. These groundwaters will not reach the waste until the temperature
  excursion has passed. The chloride 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 3.3 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 the period is taken to be 100 to 300 years and 100 to 3,000 years instead.

These stages are illustrated in Table 3.4. An important feature of the evolution is that the package-
scale modelling (see Section 3.3) 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 7 and in reference [16]. The programme times are an update on those provided in the 2010 DSSC [44, 45]. The assumed temperature evolution is discussed in more detail in reference [13].

Table 3.4  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 last 5 years.

3.6 Scoping Calculations for the Release of Carbon-14 from Magnox Wastes

The model for the release of carbon-14 is a simple congruent release model; as the metal corrodes, the carbon-14 is released.

The rate of release of carbon-14 bearing methane, $R_{^{14}CH_4}$, is given by:

$$ R_{^{14}CH_4} = \sum_i \frac{\chi_i r_i F_i I_i(t)}{s_i} $$

where

- $I_i(t)$ is the inventory of carbon-14 in waste group $i$ at time $t$ (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;
- $r_i$ is the corrosion rate of the type of Magnox in waste group $i$ (m yr$^{-1}$), 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 $i$ (·).

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. A simple spreadsheet model has been
developed to provide estimates of the release rates of carbon-14 during the different phases of package evolution. The model is based on:

- The above congruent release model, based on the inventory and shape data summarised in Section 2.2 (Table 2.4) and provided in detail in reference [10];
- The corrosion rates given in Table 3.1; and
- The stages in the evolution of waste packages from Table 3.4 (taking the shorter time for storage underground).

At this stage, no account is taken of the nature of the release; this is considered further in Section 7.2.

The approach is similar to the model in SMOGG (see Section 6.1). 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 (see Section 7.2), but are not exactly comparable. In particular the releases rates will be higher, as peak release rates for packages in SMOGG will occur at different times (depending on when they are emplaced). 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 3.5 and Figure 3.5. The result for the phase with the highest generation rate is shown in Bold. 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. The maximum generation rate is the same for all cases until chloride reaches the waste.

### Table 3.5 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 3.5  Maximum generation rates (TBq yr\(^{-1}\)) during different phases of package evolution – the cases are the same as in Table 3.5

This approach is compared with the more detailed SMOGG modelling in Section 7.

3.7  Summary of the Position on the Corrosion of Irradiated Magnox Wastes

The important areas where progress has been made in understanding the corrosion of Magnox wastes are:

- **Inventory.** The overall inventory is little changed compared with the one used in the Phase 1 work [1], but the quantity of carbon-14 that is associated with material that has already corroded is now understood, and is taken into account in the calculations. The inventory could be overstated, which could lead to a decrease in the calculated release rates.

- **Corrosion rates.** These have been reviewed, and the decision has been taken to leave them unchanged.

- **Time for chloride to reach the waste.** Detailed vault-scale and package-scale modelling has been undertaken to understand the controls on the time taken for chloride to migrate across the vaults and the expected spread in the time between the chloride reaching the first and the last containers containing Magnox waste. The transport of chloride through the backfill to the vicinity of the waste package controls the arrival of chloride; even in the case of a higher-strength rock, it is expected to take over a thousand years. This is judged to remain valid even if the backfill is cracked.
- **Package-scale modelling.** The ullage space plays a key role in allowing gas to escape from the containers, and potentially plays a key role in allowing or preventing water from entry into the containers. However, it is not possible to take credit with confidence for the possibility of water exclusion. Once chloride has entered a waste package, it will take tens or a few hundreds of years for the chloride to migrate down through the wasteform.

- **Maximum gas generation rate.** The spreading of the arrival of chloride spreads times at which Magnox corrodes. This reduces substantially the maximum generation rate of the release of carbon-14 bearing gases. However, once the chloride reaches the Magnox waste, the waste corrodes relatively rapidly.

- **Composition of carbon-14 bearing gases.** Experiments are underway to measure the composition of gases released as the Magnox corrodes. Early indications are that it may be reasonable to estimate the proportion released as methane or carbon monoxide as about 30%.

The implications for the various elements of the safety case are considered in Section 7.
4 Uranium Wastes

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\textsuperscript{11} is as follows:

- The data on corrosion rates are considered (Sections 4.1), and corresponding corrosion times are evaluated (Section 4.2);
- The data on the speciation of carbon-14 released are considered (Section 4.3);
- In the light of the understanding developed, the life cycle of uranium wastes is described (Section 4.4);
- Scoping 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 4.5); more detailed modelling using SMOGG is reported in Section 7;
- A summary is provided in Section 4.6.

4.1 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. The corrosion mechanism depends on whether conditions are aerobic or anaerobic. The reactions are:

\[ U + \frac{1}{2} (2+x) O_2 \rightarrow UO_{2+x} \quad \text{under aerobic conditions} \]

\[ U + (2+x) H_2O \rightarrow UO_{2+x} + (2+x) H_2 \quad \text{under anaerobic conditions} \]

Data on the corrosion rates of the uranium metal under disposal conditions were reviewed for use in SMOGG in 2007 [28]. The review drew heavily on a previous international review [29]. The selected corrosion rates depend crucially on whether the conditions are aerobic or anaerobic; anaerobic corrosion is significantly higher than aerobic corrosion. 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 4.1.

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 [30, 46]. These reviews include data from extensive trials undertaken by BNFL and Sellafield Ltd that were not available for the 2007 review [28].

The data available for the earlier of these two reviews [30] are shown in Figure 4.1, where the correlations proposed in [28] 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

\textsuperscript{11} In this discussion uranium wastes are restricted to metallic uranium wastes. Such metallic uranium is usually associated with Magnox cladding, and is therefore a component of some of the Magnox streams considered in Section 3.
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 4.1 Arrhenius plot of the ln(U corrosion rate) against inverse of temperature with the SMOGG model data [28] overlaid – reproduced from [30]

Table 4.1 Modelled uranium corrosion rates [28, 30]

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Corrosion Rate (µm yr⁻¹)</th>
<th>SMOGG Review [28]</th>
<th>NNL Review [30]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aerobic</td>
<td>Anaerobic</td>
<td>High water content (&gt;0.24)</td>
</tr>
<tr>
<td>15</td>
<td>9.14 10⁻¹</td>
<td>4.25 10⁻¹</td>
<td>1.45 10⁻¹</td>
</tr>
<tr>
<td>20</td>
<td>1.58 10⁰</td>
<td>6.82 10⁻¹</td>
<td>2.39 10⁻¹</td>
</tr>
<tr>
<td>25</td>
<td>2.68 10⁰</td>
<td>1.08 10⁻²</td>
<td>3.88 10⁻¹</td>
</tr>
<tr>
<td>30</td>
<td>4.47 10⁰</td>
<td>1.68 10⁻²</td>
<td>6.20 10⁻¹</td>
</tr>
<tr>
<td>35</td>
<td>7.34 10⁰</td>
<td>2.57 10⁻²</td>
<td>9.76 10⁻¹</td>
</tr>
<tr>
<td>40</td>
<td>1.19 10⁻¹</td>
<td>3.89 10⁻²</td>
<td>1.51 10⁻²</td>
</tr>
<tr>
<td>45</td>
<td>1.89 10⁻¹</td>
<td>5.80 10⁻²</td>
<td>2.32 10⁻²</td>
</tr>
<tr>
<td>50</td>
<td>2.96 10⁻¹</td>
<td>8.55 10⁻²</td>
<td>3.50 10⁻²</td>
</tr>
</tbody>
</table>

The NNL experiments have included BFS/OPC and PFA/OPC matrices [30]. 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

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12 BFS is Blast Furnace Slag, OPC is Ordinary Portland Cement and PFA is Pulverised Fuel Ash.
reducing system than PFA/OPC. In the experiments, once anaerobic corrosion is established, the corrosion rates in PFA/OPC systems are comparable to those measured in BFS/OPC and water only systems.

This is in line with the understanding from other authors. Glasser [47] comments ‘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 affect the Eh. Blast furnace slag, which typically contains ~1% sulphide, markedly lowers the Eh to -300 mV and provides a poising reserve’. These comments are endorsed in other publications [48, 49, 50].

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 [51] 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.

In the light of this understanding, the reference case is now taken to have anaerobic conditions established by the time the waste is emplaced. A variant case is considered in which aerobic conditions persist until shortly after the GDF is closed.

4.2 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. Indicative times for the complete corrosion of 0.01m plates or spheres of uranium are presented in Table 4.2. The values are quoted for the aerobic and anaerobic corrosion rates from the SMOGG review [28]. It can be seen that the anaerobic corrosion times are relatively short, particularly at the elevated temperatures expected in the GDF.

Table 4.2 Indicative corrosion times for 0.01m plates or spheres of uranium, using the aerobic and anaerobic corrosion rates from the SMOGG review [28]

<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>

4.3 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 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 currently to have a small number of scenarios based on the understanding gained from other waste materials, such as the Magnox results discussed in Section 3 above. The approach adopted is to use the same cases as taken for Magnox, with a
post-closure reference case for the modelling 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).

4.4 Life Cycle for Uranium Wastes

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 on the temperature. In the light of the estimated corrosion times, the life cycle of typical uranium waste packages can be evaluated. 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 (vaults or tunnels) – 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, if any oxygen remains in the packages, it will be consumed, and the environment will become anaerobic. During this period the backfilled vaults will start to resaturate;

- 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 4.3. This has been developed to enable simple calculations to be undertaken that illustrate the more detailed calculations reported in Section 7 and in reference [16]. The programme times are an update on those provided in the 2010 DSSC [44, 45]. The assumed temperature evolution is discussed in more detail in reference [13].
### Table 4.3 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 [16].
2. The temperature pulse is estimated to be 5 years – 3 years is derived as 2 years less than 5 years.

### 4.5 Scoping Calculations for the Release of Carbon-14 from Uranium Wastes

The same simple congruent-release spreadsheet model, as developed for Magnox (Section 3.6), has been used to provide estimates of the release rates of carbon-14 during the different phases of package evolution, based on different corrosion rate datasets. The model is based on:

- The congruent release model utilising the inventory and shape data summarised in Section 2.2 and provided in detail in reference [10];
- The corrosion rates given in Table 4.1 – the NNL datasets are used as listed, there is no attempt to relate the conditions in the experiments to the conditions in the GDF; and
- The phases in the evolution of waste packages from Table 4.3 (taking the shorter time for emplacement underground).

At this stage, no account is taken of the nature of the release; this is considered further in Section 7.2.

The approach is similar to the model in SMOGG (see Section 6.1). 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 (see Section 7.2), but are not exactly comparable. In particular the releases rates will be higher, as peak release rates for packages in SMOGG will occur at different times.

The results from this simple model are shown in Table 4.4 and Figure 4.2; the same results are shown in the Table and the Figure. The result for the phase with the highest generation rate is shown in **Bold**. 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. The exception being the case where the conditions remain aerobic until after backfilling.

In the cases where the peak occurs during underground emplacement before backfilling, there is a lower release after backfilling, because a small inventory is associated with bulky items.

Table 4.4 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 [28]</th>
<th>NNL Review [30]</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 10⁻¹</td>
<td>1.5 10⁻²</td>
<td>2.4 10⁻¹</td>
</tr>
<tr>
<td>Underground emplacement before backfilling</td>
<td>84</td>
<td>6.1 10⁻¹</td>
<td>1.2 10⁻¹</td>
<td>4.1 10⁻¹</td>
</tr>
<tr>
<td>Backfilled – aerobic (1)</td>
<td>2</td>
<td>1.2 10⁻⁴</td>
<td>8.1 10⁻²</td>
<td>7.6 10⁻³</td>
</tr>
<tr>
<td>Backfilled – oxygen exhausted</td>
<td>3</td>
<td>1.4 10⁻⁶</td>
<td>2.5 10⁰</td>
<td>7.2 10⁻³</td>
</tr>
<tr>
<td>Backfilled – heat pulse finished</td>
<td>0.0</td>
<td>5.3 10⁻¹</td>
<td>2.8 10⁻³</td>
<td>2.5 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.
Figure 4.2  Maximum generation rates during different phases of package evolution, based on different corrosion rate datasets

To explore an alternative backfill strategy in which vaults are backfilled shortly after they are filled with emplaced waste, similar scenarios are presented in Table 4.5. Two of the cases shown in Table 4.4 are used:

- The dataset from the SMOGG review with the anaerobic corrosion used at all times;
- The dataset from the SMOGG review where different corrosion rates are used for aerobic corrosion and anaerobic corrosion, and it is assumed that anaerobic conditions are not achieved until after backfilling.

These are combined with cases with shorter times before backfilling takes place. The result for the phase with the highest generation rate is shown in Bold.

More uranium survives at the time of backfilling and as a consequence there are higher generation rates following backfilling. However, in both cases considered, the amount of metallic uranium surviving to the time of closure of the GDF will be negligible. The results are made more complicated because of the nature of the uranium wastes (a mixture of plates and spheres). Some of the wastes are completely corroded in the earlier phases, and this affects the calculated maximum generation rates.

The results are shown graphically in Figure 4.3.
Table 4.5  Generation rates during different phases of package evolution – comparison of cases with backfilling just before closure and backfilling just after emplacement

<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 [28]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anaerobic</td>
<td>Aerobic then Anaerobic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Backfilling just before closure</td>
<td>Backfilling just after emplacement</td>
</tr>
<tr>
<td>Surface store</td>
<td>50</td>
<td>7.0 10⁻¹</td>
<td>7.0 10⁻¹</td>
</tr>
<tr>
<td>Underground emplacement before backfilling</td>
<td>84 or 2</td>
<td>6.1 10⁻¹</td>
<td>6.1 10⁻¹</td>
</tr>
<tr>
<td>Backfilled – aerobic (1)</td>
<td>2</td>
<td>1.2 10⁻⁴</td>
<td>1.1 10⁰</td>
</tr>
<tr>
<td>Backfilled – oxygen exhausted</td>
<td>3</td>
<td>1.4 10⁻⁶</td>
<td>6.4 10⁻¹</td>
</tr>
<tr>
<td>Backfilled – heat pulse finished</td>
<td></td>
<td>0</td>
<td>1.2 10⁻²</td>
</tr>
</tbody>
</table>

Note:

1  The difference between this phase and the next is only significant for the last two columns, where different corrosion rates are used for the aerobic and anaerobic phases.
4.6 Summary of the Position on Irradiated Uranium Wastes

The important areas where progress has been made on understanding the corrosion of uranium wastes are:

- **Inventory.** The overall inventory is little changed compared with the one used in the Phase 1 work [1], but the quantity of carbon-14 that is associated with material that has already corroded is now understood, and is taken into account in the calculations.

- **Corrosion rates.** These have been reviewed, and the decision has been taken to leave them unchanged.

- **Time for the wastes to become anaerobic.** In the light of NNL experiments, which suggest that experimental conditions quickly become anaerobic, the uranium is taken to experience anaerobic conditions by the time the waste is emplaced in the GDF. This leads to higher generation rates during the operation of the GDF, and lower generation rates post-closure. The case where the conditions change from aerobic to anaerobic shortly after closure of the GDF is retained as a variant.

- **Amount of uranium remaining at backfilling and closure.** If the uranium is anaerobic by the time it is emplaced, then the remainder will have corroded by the time of backfilling in the case of backfilling just before closure. Even if this were not the case, only a small quantity of uranium would remain at closure. In the case of early backfilling, some metallic uranium will
remain at the time of backfilling, but that corrodes shortly afterwards, and will have corroded by the time of GDF closure.

- **Composition of carbon-14 bearing gases.** The proportion of carbon-14 released as methane or carbon monoxide is taken to be the same as Magnox, based on the early indications from the experiments on Magnox.

The implications for the various elements of the safety case are considered in Section 7.
5 Aluminium Wastes

5.1 Carbon-14 Inventory in Aluminium Wastes

There is currently no inventory of carbon-14 declared as being associated with metallic aluminium. The total carbon-14 activity associated with aluminium is not thought to be significant relative to activities in Magnox and uranium. There is a programme in place to measure whether any meaningful quantities of carbon-14 are associated with irradiated aluminium [10].

5.2 Aluminium Corrosion

Although aluminium is a reactive metal, it can nevertheless be used for many practical applications because of the adherent, protective oxide and hydroxide films that develop on its surface. However, as the oxides are amphoteric, aluminium is not resistant to corrosion in acidic and alkaline conditions, because the protective films dissolve.

The corrosion of aluminium in high pH conditions has been reviewed in reference [28]. For the corrosion of aluminium both oxygen reduction and water reduction are possible cathodic reactions but the latter predominates at pHs greater than approximately 12.

The corrosion rates of aluminium in high pH conditions were also reviewed in reference [28]. These have not been further reviewed in the current work. Were a significant inventory identified in the future, the data would be reviewed to see if further information had become available. The data are given in Table 5.1, and the Table shows a short-term acute phase (with characteristic time of 0.001 yr), followed by a long-term chronic rate. The corrosion rate is not dependent on the temperature or the presence of chloride.

Table 5.1  Aluminium corrosion rates ($\mu$m yr$^{-1}$) in high pH conditions [28]

<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>

The corrosion of aluminium contributes significantly to the generation of bulk gases at early times (see Section 7.2.1). However, packages of aluminium are likely to dry out during storage, when approximately 10% – 20% of their aluminium inventories will have corroded. Further corrosion would depend on further water becoming available as the GDF resaturates. This is discussed further in reference [13].

5.3 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 (waste streams 2D12 and 2D14). They contain carbon-14 formed on irradiation of the target material. These wastes have the potential to undergo alkaline hydrolysis. The aluminium nitride could react with water to form aluminium hydroxide and ammonia [52]. Any carbon-14 present could potentially be released as $^{14}$CH$_4$.

The inventory in these wastes is not yet included in the 2013 DI and is somewhat uncertain, although it is estimated to be small compared with the overall inventory of carbon-14 in reactive metals, see Table 2.3. Were this to be released over a short period of time, it could potentially be significant.

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.
6 Revised Assessment Approach

To understand the potential consequences of the rates of release of carbon-14 containing gas from ILW vaults and tunnels, the same broad methodology is used as in Phase 1 of the project [1]. The methodology has been refined and updated. In this section the approaches to the overall gas generation calculations (Section 6.1), to assessing operational discharges (Section 6.2), and to assessing post-closure releases (Section 6.3) are described.

6.1 Modelling Gas Generation

The overall modelling of the generation of bulk gases and carbon-14 bearing gases was undertaken with SMOGG v7.0 [17, 18]. This version of SMOGG includes the most recent updates. SMOGG has been used for gas generation calculations over a number of years, most recently for the gas calculations based on the 2007 Derived Inventory [28] and the Phase 1 work of the Carbon-14 Project [1].

SMOGG takes into account:

- The generation of gas from a range of metals, present either as waste metal or packaging or other metals in the GDF (including the release of carbon-14 in 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;
- 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.

Carbon-14 is the focus of the current study, and so the release of tritium and radium are outwith the scope of this work.

SMOGG also takes into account the availability of water and oxygen, and the evolution of temperature. The approach to the operation of the GDF, including the waste emplacement strategy, provides further important inputs.

A full description of the modelling basis used in the SMOGG calculations is provided in the Modelling Report [16].

6.2 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 [15]. 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. In this improved methodology, $^{14}$CO$_2$, $^{14}$CO and $^{14}$CH$_4$ are treated differently.

The main pathway for aerial discharges from the underground facilities during operations would be through the GDF ventilation system and into the atmosphere through a discharge stack. In Phase 2 of the project, a methodology has been developed to calculate the effective dose rates...
arising from a continuous discharge of carbon-14 containing gases from a 15m high stack\textsuperscript{13} to a local resident family receptor group \cite{15}, which is assumed:

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

These values are chosen to be consistent with the Environment Agency guidance \cite{53,54} and the generic OESA \cite{55}.

This work has provided multiplying factors to convert releases of carbon-14 to dose, as shown in Table 6.1. In contrast to the factors used in the calculations presented in Phase 1, this work provides separate factors for carbon-14 as methane, carbon monoxide and carbon dioxide, because these have been identified as the three main carbon-14 bearing gases that could be released. Compared with the value of $1.8 \times 10^{-17} \text{Sv yr}^{-1}$ per Bq yr$^{-1}$ used in Phase 1 for all carbon-14 containing gases, the value for methane is substantially lower, but the value for carbon monoxide is significantly higher.

<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>$9.0 \times 10^{-18}$</td>
<td>$1.2 \times 10^{-16}$</td>
<td>$1.5 \times 10^{-20}$</td>
</tr>
<tr>
<td>Child</td>
<td>$5.5 \times 10^{-18}$</td>
<td>$7.1 \times 10^{-17}$</td>
<td>$8.7 \times 10^{-21}$</td>
</tr>
<tr>
<td>Adult</td>
<td>$5.5 \times 10^{-18}$</td>
<td>$7.2 \times 10^{-17}$</td>
<td>$9.0 \times 10^{-21}$</td>
</tr>
</tbody>
</table>

The effective dose factors for carbon dioxide, carbon monoxide and methane listed in Table 6.1 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, this result arises from a cautious assumption concerning the assimilation of carbon monoxide by plants at low atmospheric concentrations of the gas. 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 is likely to be of limited radiological significance.

In addition, it is not expected that carbon dioxide would be released from many waste packages during operations. Given the assumption that the wastes will be encapsulated in cementitious grout, it is expected that carbon dioxide will carbonate the grout, preventing carbon-14 in carbon dioxide from being released. However, there is the possibility that carbon-14 bearing carbon dioxide may be released from the waste packages that are not encapsulated in a cementitious grout.

The release rate to dose rate conversion factors given in Table 6.1 are combined with the gas generation rates calculated from SMOGG for the operational period. The calculated dose rates are compared with the radiological protection criteria for normal conditions of operation. The effective dose rate 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 \cite{56}). 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.

The methodology for assessing operational discharges is applied to the pre-backfilling period. For releases following backfilling, there is some uncertainty as to whether they will be discharged.

\textsuperscript{13} 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.
through the ventilation system or whether they will be retained within the engineered system until after closure (when the post-closure methodology would be applicable). Given the uncertainties in this stage, it is considered appropriate to apply both the OESA and post-closure methodologies (see Section 6.3).  

6.3 Assessing Post-closure Releases

Bulk gas that is formed in a GDF may dissolve in water, undergo chemical reactions or form a free gas phase. In the post-closure period, 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. The bulk gas could act as a carrier for carbon-14 bearing gases. 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 in the EBS (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.

One of the gases that will be generated within a GDF is carbon dioxide. However, the cementitious materials present in a GDF react with carbon dioxide. There is a substantial body of evidence supporting the view that this carbonation will occur [13]. 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 a GDF [13]. 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. This carbon-14 will not be released at the surface and is not included in the calculation of risk. Other gases such as CO and CH₄ have the potential to migrate into the geosphere, although this depends on site specific aspects of the host rock.

Three generic host rock environments have been considered, along with the important features that may be found in the overlying rocks [13].

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. These potentially have the shortest resaturation time, depending on the hydraulic conductivity of the host rock. Reference [13] estimates a resaturation time of 1 year for a hydraulic conductivity of 10⁻³ m s⁻¹ and 1,000 years for a hydraulic conductivity of 10⁻¹² m s⁻¹. The SMOGG calculations reported later use a resaturation time of 5 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. Reference [13] estimates a resaturation time of 10,000 years. 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.

---

14 A variant case of staged backfilling (backfilling shortly after emplacement) is considered in the companion modelling report [16]. In this case it is possible that releases occur during the operational period through the geosphere. The broad methodology in Section 6.3 is used to calculate dose rates during the operational period conditional on such a release taking place. The largest contributions to dose rates in this variant case arise from uranium wastes.
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. There will be little, if any, water available in these environments, apart from the water in the encapsulation grouts.

The calculated post-closure consequences are dependent on the initial 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 [13]. They are listed in Table 6.2. Given that there is no specific site currently being investigated, none of these cases is given more weight than any other.

### Table 6.2 Post-closure cases considered

<table>
<thead>
<tr>
<th>I.D.</th>
<th>Description</th>
<th>Delay Time (14C ½-lives)</th>
<th>Release Area (m²)</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</td>
<td>0</td>
<td>10⁶</td>
</tr>
<tr>
<td>B</td>
<td>Higher-strength and lower-strength host rock with an overlying low permeability formation limiting gas migration Evaporite host rock</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</td>
<td>0</td>
<td>10⁴</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>10⁷</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</td>
<td>1</td>
<td>10⁶</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>10⁷</td>
</tr>
</tbody>
</table>

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 [57]. This has been complemented by a wider review of the understanding of methane oxidation in soils from other fields [14]. 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 [58]. This model is consistent with those used by the Low Level Waste Repository (LLWR).

This revised model provides a single multiplying factor to be used to convert the flux of carbon-14 containing gases at the surface to the dose rate received by a local family receptor group. The conversion factor is given in Table 6.3; it is slightly higher than the value used in Phase 1 of the carbon-14 project [1]. The value for carbon-14 containing methane has been applied to the sum of the release rates of carbon-14 as methane and carbon monoxide; this is expected to be cautious.

The environment agencies’ GRA [56] 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 6.2 above);

- After any period of institutional control, risks should be consistent with the risk guidance level of 10\(^{-6}\) (Requirement R6 [56]), using the dose to risk conversion factor is 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 6.3  Carbon-14 flux at the surface to dose rate conversion factor for off-site discharge to the local resident family receptor group during the GDF post-closure period

<table>
<thead>
<tr>
<th>Carbon-14 containing gas</th>
<th>Conversion factor (Sv yr(^{-1}) per (Bq m(^{-2})s(^{-1})))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.0225</td>
</tr>
</tbody>
</table>

In the modelling section below, 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 have 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.
7 SMOGG Modelling

The main modelling has been undertaken with SMOGG (see Section 6.1). The different wastes groups have been discussed in the separate sections above. The overall calculations are presented in detail in reference [16]. The main results for reactive metals are presented here.

The approach adopted for the reference case and the modelling basis are summarised in Section 7.1. The results obtained for the reference case, using the best estimate of parameters, is outlined in Section 7.2. A number of variant cases are discussed in Section 7.3. An alternative approach, using a total system model, has been used for the first time for the gas pathway on this project; this allows a structured approach to uncertainty to be taken. The approach and results are summarised in Section 7.4.

7.1 The Reference Case and the Modelling Basis

The reference case uses the best estimates of the various parameter values, such as the corrosion rates. In particular it uses:

- The inventory described in Section 2 and in reference [10]. This provides the radionuclide inventory of carbon-14 and provides an estimate of the extent of pre-corrosion of the reactive metals, where there is evidence that it has occurred;
- The best estimates or reference values of the various parameters, such as corrosion rates, as discussed in the previous sections on graphite, steels, reactive metals and Zircaloy. Release from other wastes, such as spent fuel, is not included in the current analysis;
- A better representation of the corrosion of Magnox post-closure, as affected by the availability of chloride – see Section 3;
- An assumption that the environment for uranium wastes is taken to be anaerobic after waste emplacement – see Section 4.1;
- The post-closure reference case for reactive metal wastes that 30% is released as methane; however, alternatives are presented alongside the reference case with 100% and 10% released as methane;
- The waste emplacement and backfilling strategy summarised Table 7.1, whereby the emplacement of legacy wastes starts in 2040, with backfilling taking place in the final ten years before closure of the GDF in 2200;
- An assumption that resaturation of the GDF takes place reasonably quickly, as would be expected for a higher-strength rock; Table 7.1 describes the approach to modelling the availability of water and oxygen\(^\text{15}\);
- An improved methodology for 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 modelled – see Section 6.2;
- The migration and release scenarios described in Section 6.3; and
- An updated factor for the conversion of carbon-14 flux at the surface to dose rate for the post-closure period – see Section 6.3.

A full description of the data used can be found in the modelling report [16].

\(^{15}\) 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. This is discussed in more detail in reference [13].
Table 7.1  Timing of stages, temperature and 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</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></td>
<td>case for legacy vaults:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2040 – 2190</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>For NNB vaults:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2100 – 2190</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Backfilling and closure</td>
<td>In the reference case</td>
<td>45°C</td>
<td>As for Emplacement</td>
<td>As for Emplacement</td>
</tr>
<tr>
<td></td>
<td>2190 – 2200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post-closure (resaturation)</td>
<td>Depends on the</td>
<td>45°C (5 years)</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>geological environment</td>
<td></td>
<td>Pore space resaturates over a period dependent on the</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>geological environment</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>For HSR, resaturation modelled as being 5 years after</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>closure</td>
<td></td>
</tr>
<tr>
<td>Post-closure (following</td>
<td>Depends on the geological</td>
<td>35°C</td>
<td>Essentially unlimited</td>
<td>Anaerobic</td>
</tr>
<tr>
<td>saturation)</td>
<td>environment</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A full description of the modelling basis in SMOGG is provided in reference [16], where it is presented as a set of Tables. These update the similar tables presented in the Phase 1 report [1].

In the light of the work presented in Sections 3 and 4 above, the modelling bases for Magnox and uranium have been updated. These are presented in Table 7.2 and Table 7.3. The modelling basis for aluminium has not been changed; this is presented in Table 7.4. The important changes for Magnox and uranium are:

- The division of the inventory of carbon-14 between uncorroded and corroded metal; only the carbon-14 in uncorroded metal is available for release;
- The increase in the time taken for the chloride to reach the waste;
- The conditions that uranium experiences are anaerobic from the time of emplacement.
### Table 7.2  Modelling basis – gas generation from Magnox wastes

<table>
<thead>
<tr>
<th>Conceptual understanding</th>
<th>Model implementation</th>
<th>Data (including references)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Release of carbon-14</td>
<td>30% release as CH₄ (might be something else that is not CO₂), variants of 100% and 10%. Carbon-14 uniformly distributed throughout metal.</td>
<td>Carbon-14 data from 2013 DI [24] and project Inventory Report [10].</td>
<td></td>
</tr>
<tr>
<td>Bulk gas from Magnox</td>
<td>1 mole of metallic Mg generates 1 mole of H₂.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas generation – water availability</td>
<td>Some water is available initially. Further water enters subsequently as a result of resaturation.</td>
<td>Initial water availability comes from assumed conditioning factor of 4 and standard wasteform porosity (see Table A1.8 in reference [16]) and initial saturation.</td>
<td>If water enters slowly corrosion may be limited, and extended in time.</td>
</tr>
<tr>
<td>Gas generation – chloride availability</td>
<td>Assume zero during operations. Chloride is assumed to enter slowly some time after resaturation, reaching different containers over a period of time.</td>
<td>Average corrosion rate adopted based on the proportion of wastes where there is enhanced corrosion due to chloride (see Section 3.3).</td>
<td>Chloride does not reach any Magnox while there is elevated temperature.</td>
</tr>
</tbody>
</table>
Table 7.3  Modelling basis – gas generation from uranium wastes

<table>
<thead>
<tr>
<th>Conceptual understanding</th>
<th>Model implementation</th>
<th>Data (including references)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Release of carbon-14</td>
<td>30% release as CH$_4$ (might be something else that is not CO$_2$), variants of 100% and 10%. Carbon-14 uniformly distributed throughout metal.</td>
<td>Carbon-14 data from 2013 DI [24] and project Inventory Report [10].</td>
<td></td>
</tr>
<tr>
<td>Bulk gas from uranium</td>
<td>Aerobic gives UO$_{2+x}$ (no bulk gas). Anaerobic period: 1 mole of metallic uranium generates 2+x moles of H$_2$.</td>
<td>2013 DI [24] and project Inventory Report [10] give amounts of packaging and shape data. Corrosion rates from [59] and project Steels Report [12].</td>
<td></td>
</tr>
<tr>
<td>Bulk gas from corrosion of stainless steel containers</td>
<td>Aerobic chronic corrosion rate (non-gas generating). Anaerobic chronic corrosion rate. Rates are temperature dependent.</td>
<td></td>
<td>Not significant cf. bulk gas from waste.</td>
</tr>
</tbody>
</table>
# Table 7.4  Modelling basis – gas generation from aluminium wastes

<table>
<thead>
<tr>
<th>Conceptual understanding</th>
<th>Model implementation</th>
<th>Data (including references)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium corrosion</td>
<td>Acute and chronic corrosion rates. No temperature and no chloride dependence.</td>
<td>Quantities of aluminium metal and shape data from 2013 DI [24]. Corrosion rates from [28].</td>
<td>Assumes high pH. Aluminium corrodes until no water left during operational period, then stops until resaturation begins. Assume no additional corrosion until emplacement.</td>
</tr>
<tr>
<td>Bulk gas from aluminium</td>
<td>2 moles of metallic aluminium generates 3 moles of H₂.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas generation – water availability</td>
<td>Some water is available initially. Further water enters subsequently as a result of resaturation.</td>
<td>Initial water availability comes from assumed conditioning factor of 4 and standard wasteform porosity (see Table A1.8 in reference [16]) and initial saturation.</td>
<td>If water enters slowly corrosion may be limited, and extended in time.</td>
</tr>
</tbody>
</table>
7.2 Results for the Reference Case

7.2.1 Gas generation results

Figure 7.1 shows the generation rates of bulk gas from legacy UILW/ULLW\textsuperscript{16,17} during the operational and early post-closure periods; Figure 7.2 shows the same generation rates during the late post-closure period. The results for Magnox, uranium, aluminium and all other wastes are shown separately, along with the overall total. Much of the gas is hydrogen; the ‘other wastes’ category generates some methane.

The results show:

- During the emplacement period (2040 to 2105 AD), bulk hydrogen is generated predominantly due to corrosion of Magnox, uranium and aluminium wastes. The aluminium corrosion rate is high and therefore all the water in this waste is consumed at around 2110 AD, preventing further corrosion during the rest of the GDF operational period. The uranium corrosion rate is also high, corroding all the uranium soon after the end of emplacement. Bulk gas generation continues at a steady rate from the other sources through the operational period until 2190 AD.

- At 2190 AD the temperature increases from 35°C to 45°C. This increases the corrosion rate of Magnox, and results in a step increase in the bulk hydrogen generation rate from Magnox corrosion between 2190 and 2205 AD.

- The GDF is assumed to be closed at 2200 AD and to start to resaturate with groundwater. The resaturation process provides water to restart the corrosion of aluminium, which then provides most of the bulk hydrogen generation until the aluminium is consumed at around 2230 AD.

- Within a few years of closure the GDF becomes anaerobic as the oxygen has been consumed by corrosion and organic degradation or flushed out at full resaturation. Under anaerobic conditions, degradation of cellulose starts to generate bulk methane. After the aluminium is consumed Magnox corrosion is the dominant source of bulk hydrogen generation.

- At 2300 AD, chloride starts to reach some waste packages. This results in a slight increase in the bulk hydrogen generation rate from Magnox as a small fraction of the Magnox corrodes away rapidly. This continues for the next few hundred years as chloride reaches further waste packages, until all the Magnox has corroded.

- After the Magnox is consumed radiolysis becomes the main source of bulk gas generation, but this subsequently reduces due to decay. The rate of the bulk gas generation from the corrosion of steels remains steady until the end of the calculation.

---

\textsuperscript{16} Wastes are categorised as UILW (unshielded intermediate-level waste) or ULLW (unshielded low-level waste). SILW (shielded intermediate-level waste), SLLW (shielded low-level waste), NNB (nuclear new build wastes) and DCIC (waste packaged in Ductile Cast Iron Containers) do not have a significant inventory of carbon-14 associated with reactive metals.

\textsuperscript{17} Only the UILW has a significant inventory of carbon-14 (Table 2.3); therefore the results for SILW and NNB wastes are not presented in this report.
Figure 7.1 Breakdown of calculated generation rates for bulk gas from reactive metals from LegacyUILW / ULLW during GDF operations and early post-closure
Figure 7.2  Breakdown of calculated generation rates for bulk gas from reactive metals from Legacy UILW / ULLW in the long term

7.2.2 Results for the generation rates of carbon-14

Figure 7.3 shows the generation rates of carbon-14 from legacy UILW/ULLW during the operational and early post-closure periods; Figure 7.4 shows the same generation rates during the late post-closure period. The results for Magnox, uranium and all other wastes are shown separately, along with the overall total. The results are for the total amount of carbon-14 released; no account is taken at this stage for the proportion released as methane. The only exception to this is that the total line excludes carbon dioxide released from graphite.

There are no reactive metals present in the other major waste groups, namely SILW/SLLW and NNB, and so no results for these waste groups are shown in this report.

The results show:
- There is an initial rapid increase in the carbon-14 generation from uranium corrosion, reaching a constant value after a few years. This is due to a combination of rapid corrosion of emplaced uranium and emplacement of further uranium. At about 2065 AD the rate from uranium corrosion reduces as a result of the change in emplacement rate.
- At 2190 AD, the temperature increases from 35°C to 45°C. This increases the corrosion rates of the metals, resulting in a step increase in carbon-14 containing gas generated from corrosion processes, particularly Magnox.

- Within a few years of closure (at 2200 AD) the vaults become anaerobic as the oxygen has been consumed. At 2205 AD the temperature also reduces, so the carbon-14 containing gas generation rate from Magnox reduces.

- At 2300 AD, chloride starts to reach some waste packages. This results in a slight increase in the carbon-14 containing gas generation rate from Magnox as a small fraction of the Magnox corrodes away rapidly. This continues for the next few hundred years as chloride reaches further waste packages, until all the Magnox has corroded.

- From about 2700 AD carbon-14 containing gas generation continues at a relatively low rate due to corrosion of steels and Zircaloy, reducing as the carbon-14 decays.

Figure 7.3 Breakdown of calculated generation rates for carbon-14 containing gases from reactive metals from Legacy UILW / ULLW during GDF operations and early post-closure
7.2.3 Comparison with the scoping models and with the Phase 1 results

The SMOGG calculations incorporate a more detailed treatment of the timing of waste emplacement and vault backfilling than the simple scoping models discussed in Sections 3.6 and 4.5.

For the Magnox wastes, 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 results for the reference-case SMOGG calculation are shown in Table 7.5. At this stage, no account is taken of the nature of the release; this is considered later in this section.

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 corroded 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); and
- The long-term post-closure period.

**Table 7.5** 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</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>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>
</tr>
</tbody>
</table>

**Note:**
1. The medium-term post-closure rate can be compared with the value of \(1.1 \times 10^{-1}\) TBq yr\(^{-1}\) in Table 3.5. This illustrates the good agreement between the scoping model and the SMOGG model.

The comparison with Phase 1 is shown in Figure 7.5. 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 considered 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.

![Figure 7.5](image.png)

**Figure 7.5** Comparison of the maximum generation rates (TBq yr\(^{-1}\)) in Phase 1 and Phase 2 for Magnox wastes

The analogous results for uranium for the reference-case SMOGG calculation are shown in Table 7.6. The values presented are for the total release of carbon-14. The results are consistent with the scoping calculations in Section 4.5. In the SMOGG calculations all the uranium has corroded by the time of backfilling. In the scoping calculations a small amount associated with larger pieces of uranium remained. The SMOGG treatment is simpler in that there is only one size range. The difference is not important.
Table 7.6  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</th>
<th>Long-term post-closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generation rate</td>
<td>3.66 (10^{-1})</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The comparison with Phase 1 is shown in Figure 7.6. It is seen that the generation rate is slightly higher during the operating period in Phase 2, and lower thereafter. This because it is now assumed that the uranium is under anaerobic conditions, and therefore corrodes earlier.

![Graph comparing generation rates in Phase 1 and Phase 2](image)

Figure 7.6  Comparison of the maximum generation rates (TBq yr\(^{-1}\)) in Phase 1 and Phase 2 for uranium wastes

7.2.4 Operational period

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

The highest release rates for Magnox wastes during the operational period occur shortly after backfilling. Gas generated during this period may be released through the ventilation system; on the other hand, the gas generated may be retained within the system and released after closure. Given the uncertainties at this time it is considered appropriate to apply both the OESA and post-closure methodologies.

The pathway considered in the OESA methodology is for the gases to be ventilated out of a 15m high stack. Because there is only limited information on which gases are formed, effective doses in the operational phase are calculated on the assumption of 100% formation of each gas. Clearly they cannot all be 100%. In practice the proportion released as carbon monoxide is expected to be at most modest.

The effective doses during the operational phase can be calculated by combining the generation rate with the recommended effective dose factors given in Table 6.1. The results for Magnox wastes are shown in Table 7.7 and the results for uranium wastes are shown in Table 7.8. The
values for carbon dioxide are not included in the Tables, as it would be expected to react with the cementitious grout in the packages.

**Table 7.7**  Calculated effective doses (Sv yr\(^{-1}\)) 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 (10^5)</td>
<td>3.3 (10^3)</td>
</tr>
<tr>
<td>Child</td>
<td>1.6 (10^5)</td>
<td>1.9 (10^3)</td>
</tr>
<tr>
<td>Adult</td>
<td>1.6 (10^5)</td>
<td>2.0 (10^3)</td>
</tr>
</tbody>
</table>

**Table 7.8**  Calculated effective doses (Sv yr\(^{-1}\)) corresponding to generation rates during the operational period for uranium 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>4.4 (10^5)</td>
<td>5.5 (10^3)</td>
</tr>
<tr>
<td>Child</td>
<td>2.6 (10^5)</td>
<td>3.2 (10^3)</td>
</tr>
<tr>
<td>Adult</td>
<td>2.6 (10^5)</td>
<td>3.3 (10^3)</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 \(2.7 \times 10^5\) mSv yr\(^{-1}\) for Magnox and \(4.4 \times 10^5\) mSv yr\(^{-1}\) for uranium. These contributions to effective dose rate from carbon-14 during the operational period are below the maximum effective dose rate constraint to members of the public from a new facility of 0.15 mSv yr\(^{-1}\), even if all the carbon-14 is released as carbon monoxide. In practice not all will be released in this form.

### 7.2.5 Post-closure period

The post-closure risks are obtained by combining:

- The reference-case generation rates given in Table 7.5 (for Magnox) and Table 7.6 (for uranium);
- The migration cases and biosphere factors described in Section 6;
- The cases for the proportion of carbon-14 released as methane or carbon monoxide discussed in Section 3.6 – with the reference case using 30% and variants with 100% and 10%; and
- The dose to risk conversion factor of 0.06 Sv\(^{-1}\) [56].

The various post-closure periods in Table 7.5 and Table 7.6 are discussed separately.

The medium-term post-closure risks arising from the corrosion of Magnox are shown in Table 7.9. The environment agencies risk guidance level is \(10^{-6}\) [Error! Bookmark not defined.], 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.

It is seen that:

- For a release area of \(10^6\) m\(^2\) (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\(^2\) (Case D), the risks are below the guidance level.
- For a focused release to an area of \(10^4\) m\(^2\) (Case C), neither the reference case nor the variants considered are below the risk guidance level.
For Cases B, E and F, there is no release.

The post-closure risks from Magnox will be site specific. Given that in one of the cases the risks are substantially above the risk guidance level, it will be important to understand the gas migration characteristics of any site proposed for the disposal of these wastes.

For Magnox, the early post-closure risks are slightly higher (by a factor of less than 2 – see Table 7.5). 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.

In the SMOGG reference case, there is no uranium remaining at closure, and therefore there are no risks to calculate.

### Table 7.9 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>Relevant To Cases</th>
<th>Delay Time ($^{14}$C half-lives)</th>
<th>Release Area (m$^2$)</th>
<th>100% Methane</th>
<th>30% Methane</th>
<th>10% Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>HSR where gas is released over an area similar to the footprint of the GDF</td>
<td>0</td>
<td>$10^6$</td>
<td>$5.2 \times 10^6$</td>
<td>$1.6 \times 10^6$</td>
<td>$5.2 \times 10^7$</td>
</tr>
<tr>
<td>B</td>
<td>HSR and LSSR with an overlying low permeability formation limiting gas migration Evaporite host rock</td>
<td>No release</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>HSR where there are features that focus the release of gas to an area much less than the footprint of the GDF</td>
<td>0</td>
<td>$10^4$</td>
<td>$5.2 \times 10^4$</td>
<td>$1.6 \times 10^4$</td>
<td>$5.2 \times 10^5$</td>
</tr>
<tr>
<td>D</td>
<td>HSR where there are features that distribute the release of gas to an area greater than the footprint of the GDF</td>
<td>0</td>
<td>$10^7$</td>
<td>$5.2 \times 10^7$</td>
<td>$1.6 \times 10^7$</td>
<td>$5.2 \times 10^8$</td>
</tr>
<tr>
<td>E</td>
<td>LSSR where gas migrates slowly across the host rock and is released over the footprint of the GDF</td>
<td>1</td>
<td>$10^6$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>LSSR where gas migrates slowly across the host rock and there are features that distribute the release of gas to an area greater than the footprint of the GDF</td>
<td>1</td>
<td>$10^7$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Notes**
1. HSR is higher strength (host) rock and LSSR is lower strength sedimentary (host) rock.

### 7.3 Variant Cases

Three variants are considered. Two concern the time over which chloride accesses the Magnox wastes, and the third the timing of when the uranium wastes experience anaerobic conditions. These are discussed in turn.
The purpose of these variant calculations is to understand the potential implications of the assumptions made in the reference case. These are only relevant to wastes in the legacy UILW / ULLW. Therefore, the variant calculations have been performed only for this waste group.

7.3.1 Magnox – ingress of chloride occurs more rapidly

In the first variant considered, the chloride accesses the Magnox wastes more rapidly than in the reference case. Instead of being spread from 100 to 1,000 years, the ingress of chloride is spread between 100 and 300 years.

Varying the spread of times over which chloride reaches the Magnox only affects the carbon-14 generation after the time at which the chloride first reaches the Magnox (i.e. from 100 years post-closure) until all the Magnox is consumed. The majority of the carbon-14 containing gas generated during this time is from Magnox corrosion.

Figure 7.7 shows the generation rates of carbon-14 from legacy UILW/ULLW during the operational and early post-closure periods; Figure 7.8 shows the same generation rates during the late post-closure period. The results for Magnox, uranium and all other wastes are shown separately, along with the overall total. The results are for the total amount of carbon-14 released; no account is taken at this stage for the proportion released as methane. The results for uranium are unchanged from the reference case, and so the discussion is focused on Magnox.

The maximum generation rate of carbon-14 in the medium-term post-closure period is increased by a factor of about 2.5. This is because a larger fraction of the Magnox corrodes in the presence of chloride, which increases the ‘average’ enhanced Magnox corrosion rate. The more rapid corrosion exhausts the Magnox sooner than in the Reference Case calculation, so the Magnox completely corrodes about 260 years after closure rather than about 500 years after closure.

This change would propagate through to the calculated risks in the medium post-closure period (as shown in Table 7.9). For this scenario the peak rate of carbon-14 generation from Magnox corrosion is greater for the medium-term post-closure period than for the early post-closure period (when the rate is enhanced due to the increased temperature).
Figure 7.7  Calculated generation rates for carbon-14 containing gases from reactive metals from Legacy UILW / ULLW during GDF operations and early post-closure for Chloride Migration Variant Case (chloride reaches packages containing Magnox between 100 and 300 years after GDF closure)
Figure 7.8  Calculated generation rates for carbon-14 containing gases from reactive metals from Legacy UILW / ULLW in the long term for Chloride Migration Variant Case (chloride reaches packages containing Magnox between 100 and 300 years after GDF closure)

7.3.2 Magnox – ingress of chloride occurs more slowly

In the second variant considered, the chloride accesses the Magnox wastes more slowly than in the reference case. Instead of being spread from 100 to 1,000 years, the ingress of chloride is spread between 100 and 3,000 years.

Figure 7.9 shows the generation rates of carbon-14 from legacy UILW/ULLW during the operational and early post-closure periods; Figure 7.10 shows the same generation rates during the late post-closure period. The results for Magnox, uranium and all other wastes are shown separately, along with the overall total. The results are for the total amount of carbon-14 released; no account is taken at this stage for the proportion released as methane. The results for uranium are unchanged from the reference case, and so the discussion is focused on Magnox.

Increasing the spread of chloride migration times by about half an order of magnitude compared with the Reference Case calculation reduces the peak carbon-14 gas generation rate in the medium-term post-closure period by about 30%. This is because a smaller fraction of the Magnox corrodes in the presence of chloride, which decreases the ‘average’ enhanced Magnox corrosion rate. The slower corrosion exhausts the Magnox later than in the Reference Case calculation, so the Magnox completely corrodes about 600 years after closure rather than about 500 years after...
The change is very modest, because the effect of the chloride on the average corrosion rate across all the Magnox packages is small, and considerably less than the maximum factor of 100. This change would propagate through to the calculated risks in the medium post-closure period (as shown in Table 7.9).

Figure 7.9  Calculated generation rates for carbon-14 containing gases from reactive metals from Legacy UILW / ULLW during GDF operations and early post-closure for Chloride Migration Variant Case (chloride reaches packages containing Magnox between 100 and 3000 years after GDF closure)
7.3.3 Aerobic Uranium Corrosion during Operations

The third variant concerns the time that the uranium wastes become anaerobic. Although there is a body of evidence that uranium corrosion will tend to go anaerobic very quickly unless there is a ready supply of oxygen to replenish that consumed in this variant it is assumed that the uranium is corroding aerobically until shortly after the GDF is closed. The uranium corrosion rate is lower under aerobic conditions, and consequently, more uranium metal would remain at the time of closure.

Figure 7.11 shows the generation rates of carbon-14 from legacy UILW/ULLW during the operational and early post-closure periods; Figure 7.12 shows the same generation rates during the late post-closure period. The results for Magnox, uranium and all other wastes are shown separately, along with the overall total. The results are for the total amount of carbon-14 released; no account is taken at this stage for the proportion released as methane.

Uranium still gives the highest generation rate for much (but not all) of the operational period, although lower than previously, and then it dominates around closure.
Figure 7.11 Calculated generation rates for carbon-14 containing gases from reactive metals from Legacy UILW / ULLW during GDF operations and early post-closure for aerobic uranium corrosion during operations variant
Calculated generation rates for carbon-14 containing gases from reactive metals from Legacy UILW / ULLW in the long term for aerobic uranium corrosion during operations variant

The results for Magnox are unchanged from the reference case, and so the discussion is focused on uranium. The maximum generation rates in the various periods are shown in Table 7.10. This table can be compared with the reference case shown in Table 7.6. The generation rates are high during the backfilling period because a significant amount of uncorroded uranium metal remains at the time of backfilling.

Table 7.10 Maximum generation rates of carbon-14 (TBq yr\(^{-1}\)) from irradiated uranium for the different phases of the GDF, before and after closure, in the variant with aerobic conditions until shortly after the GDF is closed

<table>
<thead>
<tr>
<th>Uranium</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>Generation rate</td>
<td>1.75 (10^1)</td>
<td>1.24 (10^0)</td>
<td>1.24 (10^0)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The methodology for assessing operational discharges (Section 6.2) is applied to the pre-backfilling period (the emplacement period). For releases following backfilling, there is some uncertainty as to whether they will be discharged through the ventilation system or whether they will be retained within the engineered system until after closure (when the post-closure methodology would be...
applicable). Given the uncertainties in this stage, it is considered appropriate to apply both the OESA and post-closure methodologies (see Section 6.3) during the backfilling period.

The revised results for the operational phase are shown in Table 7.11.

Table 7.11 Calculated effective doses (Sv yr\(^{-1}\)) corresponding to generation rates during the temperature peak for uranium wastes, assuming 100% generation of each of carbon monoxide and methane, in the variant with aerobic conditions until shortly after the GDF is closed

<table>
<thead>
<tr>
<th>Age Group</th>
<th>Carbon monoxide</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infant</td>
<td>1.5 (10^8)</td>
<td>1.9 (10^8)</td>
</tr>
<tr>
<td>Child</td>
<td>8.8 (10^6)</td>
<td>1.1 (10^8)</td>
</tr>
<tr>
<td>Adult</td>
<td>8.9 (10^5)</td>
<td>1.1 (10^8)</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 1.5 \(10^8\) mSv yr\(^{-1}\). The doses are now the same as the maximum effective dose rate constraint to members of the public from a new facility of 0.15 mSv yr\(^{-1}\) adopted by RWM. The value for methane is well below the design target. However, at most a modest proportion is expected to be carbon monoxide, and so expected effective doses are expected to be below the design target.

These are the largest effective doses calculated for the cases considered in this report. It underlines the importance of understanding:

- The extent of uranium corrosion in these wastes on emplacement;
- The inventory of carbon-14 associated with uranium metal on emplacement;
- The amount of uranium metal remaining once the wastes are backfilled; and
- The fate of gases generated shortly after backfilling, and in particular whether they are released through the ventilation system or whether they are retained within the system, and possibly released later (this may depend on the geological environment).

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. There is only a little uranium remaining at this time and 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.

7.4 Total System Model

To complement the SMOGG modelling already described, a total system model has been developed for the gas pathway. This model is in the early stage of development, and at this time it is a ‘demonstration of capability’. In SMOGG, parameter uncertainty can be taken into account by running a number of variant calculations. However, there are many uncertain parameters, and the alternative approach is to capture the uncertainty values in the form of probability distribution functions (PDFs) in order to represent the uncertainty explicitly. Many realisations are then run with the parameter values sampled from these PDFs. At this stage the total system model is restricted to the source term for reactive metals. In time other parts of the system (e.g. other wastes and the geosphere) would also be represented in the model.

This provides a structured approach to the treatment of uncertainty. It is the approach used for the groundwater pathway [60]. Such a structured modelling approach for the consideration of uncertainty addresses one of the requirements from the environment agencies [Error! Bookmark not defined.].
The models used in such a probabilistic approach are often complemented by more detailed models. The understanding developed from the more detailed models is captured in an appropriate manner in the simplified approach used in probabilistic models.

The development of a total system model has been undertaken with the GoldSim computer program [61, 62]. This program is used in assessments of the groundwater pathway [60]. In this section, the details of the model are summarised (Section 7.4.1) and some example results are presented (Section 7.4.2). The results are compared with the SMOGG results in Section 7.4.3. Further details can be found in the companion modelling report [16].

7.4.1 Details of the modelling undertaken

The focus on this initial development of a total system model for gaseous carbon-14 is the post-closure release from reactive metals (Magnox and uranium) in UILW vaults within a GDF; release from other wastes is included as a 'result' from SMOGG, but with an estimate of uncertainty included. It is intended to be representative of a cementitious ILW concept in a higher-strength rock appropriate for a generic context (i.e., in the absence of site-specific information). The model and findings represent the first stage in a much longer cycle of development.

The development of the total system model has been undertaken in parallel with the development of the SMOGG model. Thus the more detailed understanding in the SMOGG models that has been reported in the rest of this section is not included in the total system model; this particularly includes:

- The understanding of when chloride reaches the waste; and
- The time at which the uranium wastes become anaerobic.

In the total system model there is uncertainty in when chloride reaches the Magnox waste, but in a particular realisation when chloride reaches the waste, it reaches all the Magnox wastes. The treatment of uranium is analogous to the treatment in Section 7.3.3.

So there are important aspects that differ between the two models. The emphasis for the total system model has been 'demonstration of capability', rather than the detailed application.

PDFs have been developed for a number of parameters; these include:

- Inventory (activity – TBq);
- Corrosion rates for Magnox and uranium, including the impact of chloride on the Magnox corrosion rate;
- Geometric descriptions of the wastes;
- The fraction of the carbon-14 that is released as methane;
- The time for chloride to reach the Magnox waste;
- The temperature in the vault before closure, the increase in temperature arising from heat of hydration on backfilling, and temperature in the vault after closure;
- The quantity of water that is initially available for corrosion; and
- The time to resaturate the vaults.

Individual realisations are developed by sampling parameters from the PDFs. The results from many realisations can be processed to calculate, for example, estimates of 'mean' outcomes.

7.4.2 Example results

The results can be examined in a number of ways. The examination of individual realisations is a good way to ensure that the model, and the results it produces, are understood; however, individual realisations looked at in isolation do not provide a good indication of the uncertainty associated with the model.
To do this using the Monte Carlo method, the results from each of these realisations need to be brought together. In combining these realisations, each produced from a different range of values, the overall result itself will also be a range. From this, understanding can be gained relevant to the risk and uncertainty associated with the model. The intention is to create a better view of the potential system outcomes. One measure of this is the expectation value (similar to a numerical average).

Figure 7.13 shows the expectation value of the near-field flux of carbon-14 to the geosphere for 10,000 realisations. It can be seen that the largest contributions to the total expectation value (from the sum of all the source term components) up until 200 years from the start of the calculation are due to contributions from uranium and other sources (the results for other sources are taken from SMOGG – see above). Beyond 200 years the largest contribution to the total expectation value for the near-field carbon-14 flux is associated with Magnox. Furthermore, it can be seen that the near-field flux associated with gas from other source terms tends to coincide with the early peak contributions from uranium, giving rise to the peak expectation value on this graph.

The cumulative probability for the time until complete reactive metal degradation is shown in Figure 7.14. As this model is restricted to the post-closure period, uranium corrodes considerably later than in the SMOGG model; it is fully corroded in all realisations between 1000 and 2000 years after first emplacement. In a small number of realisations some Magnox remains at the time the calculations end (6,000 years in this case). These times are rather longer than in the SMOGG runs presented earlier, and this reflects the slower corrosion rates associated with certain parameter combinations.

![Figure 7.13 Expectation value of flux of carbon-14 bearing methane from the GDF near field to the geosphere for 10,000 realisations](image-url)
Comparison with the SMOGG results

The results can be compared with the SMOGG case shown in Figure 7.11 and Figure 7.12 (the variant where uranium is corroding aerobically before emplacement); they are broadly consistent. The uranium peak from SMOGG is just over 1 TBq yr\(^{-1}\), which is factor of around 25 higher than that from the total system model, and the Magnox peak from SMOGG is just over 0.1 TBq yr\(^{-1}\), which a factor of 3 higher than that from the total system model. There are three main factors that account for these differences:

- The approach used in the total system model to take account of the uncertainties in the timing of chloride enhancement of Magnox corrosion; this leads to the releases being spread in time.
- The approach to modelling uranium corrosion, which is later in the total system model as it only accounts for the post-closure period.
- In the SMOGG case, the total amount of carbon-14 released is shown (before a fraction released as methane is applied); in the total system model, the fraction released is an uncertain quantity – this difference is considered to correspond to a factor of around 2.5.

There are significant differences in the way the Magnox release is modelled. In the SMOGG calculations it is spread as a result of the spread in times that chloride reaches the waste (variability), this leads to an average corrosion rate that is only slightly above the corrosion rate in the absence of chloride. In the total system model the spread arises from parameter uncertainty and, in particular, the time for chloride to reach the Magnox. In a particular realisation, once the chloride reaches the Magnox, all the Magnox in the GDF corrodes over a comparatively short period of time.

In assessments, variability and uncertainty are regarded as different, and are treated in distinct ways.
7.4.4 Summary and future work

The largest contributions to the total expectation value up until 200 years from the start of the calculation (the start of emplacement) are due to contributions from uranium and other sources. Beyond 200 years the largest contribution to the total expectation value for the near-field carbon-14 flux is associated with Magnox.

The model has demonstrated the capability to undertake probabilistic assessments of the gas pathways, but could be extended, for example, by:

- Including wastes other than reactive metals;
- Including the understanding of chloride migration developed as part of the vault-scale and package-scale modelling;
- Treating the pre-closure period as well as the post-closure period [63];
- Including migration through the geosphere, taking into account the approach developed in Section 6.3.
8 Alternative Management Approaches

Much of the waste containing reactive metals originates from Sellafield. As shown in Table 2.1, many of the streams have either already been packaged or are currently being packaged in a cementitious wasteform in 500 litre drums. These waste streams account for 98 of the 115 TBq of carbon-14 in the reactive metal wastes. The waste streams arise from high hazard facilities at Sellafield [64]. All of the reactive metals containing a significant inventory of carbon-14 are classified as UILW.

As part of Phase 1 [1], 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 to be confident that this can be demonstrated in modelling over the long timescales involved\(^\text{18}\).

- **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 inventory for disposal. 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. There is uncertainty as to whether gas generated during backfilling will migrate into the unbackfilled areas and then be released through the ventilation system and stack.

- **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.

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\(^{18}\) The possibility of inverting packages to provide an isolating ullage space could be considered, but this would have to take into account the possibility of contaminated water being flushed from the package.
As plans are developed for the packaging of reactive metal wastes, alternative options, such as pre-treatment, may be worthy of consideration. These options studies should consider the inventory of the waste streams, along with the characteristics of the wastes under consideration and, in particular, whether the characteristics are similar to wastes already packaged or are significantly different.
9 Summary and Conclusions

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 as part of the Phase 2 work, 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). The corrosion rates also depend on temperature: the higher the temperature, the higher the corrosion rate. 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 modelling also concludes that the chloride does not reach the waste until after the period of elevated temperature arising from the hydration of the cement backfill has passed.

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 have corroded unless there is very limited water availability, and there are no calculated risks.

There remain some uncertainties, which could make a difference to the calculated consequences 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 [33], or if the wasteform is highly cracked, may be somewhat higher. There are also uncertainties in the timescale over which the GDF will resaturate; this may affect water availability once the water initially available in the packages has been utilised. 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 be considered as part of option studies for wastes having a significant carbon-14 inventory, which 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 from active waste packages, but these data will take several years to obtain. Such data would be valuable for comparison with the assessed releases. Consideration could also be given to further developments of the total system model.

A summary of the current position is provided in Table 9.1. The status is described in the context of the ‘AND’ questions identified in Section 1.3.
Table 9.1 Summary of the current position on irradiated reactive metals

The grey boxes indicate the issue for these wastes is closed by an earlier question.

<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 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>
<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 when they corrode anaerobically. Corrosion is not expected to be limited by water availability.</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 very site specific. Risks are expected to be tolerable provided releases are not focused area and a significant proportion of the carbon-14 is not released as $^{14}$CH$_4$ or $^{14}$CO, 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>
10 References


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Appendix 1
Evolution of Chloride Concentration

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A1 Evolution of Chloride Concentration

A1.1 Introduction

The presence of chloride will accelerate the rate of corrosion of Magnox alloy, possibly by as much as two orders of magnitude [1], and therefore this groundwater solute is significant for assessments of carbon-14 release from a Geological Disposal Facility (GDF).

There is some uncertainty about the threshold concentration above which the chloride will enhance the rate of Magnox corrosion (by causing breakdown of the passive film) but, based on reviews of Magnox corrosion data (see Subsection 3.6.2 in Reference [1], as well as parallel work by the NNL [2]), a value of about 100 ppm seems reasonable.

To put this number into context, the concentration of chloride is:

- About $2 \times 10^4$ ppm in seawater [3];
- About $2 \times 10^4$ ppm in the groundwater of some higher-strength rocks at coastal locations [4];
- About $1 \times 10^4$ ppm in the groundwater of Opalinus clay (as measured at the Mont Terri Underground Research Laboratory; [5]); and
- About $2 \times 10^3$ ppm in the groundwater of both Boom clay (although only 26 ppm is present in the reference Boom clay porewater at the Mol site, up to $3.1 \times 10^3$ ppm has been measured at Essen; [6]) and Oxford clay (as measured at the Bure Underground Research Laboratory; e.g. [7, 8]).

Clearly the groundwater composition will be site-dependent, but it is likely that at many sites the concentration of chloride in the groundwater will be above the threshold at which the rate of Magnox corrosion would increase.

Therefore, it is appropriate to ask how chloride (in solution) might migrate into a vault, and then into a waste package, before contacting the Magnox wastes. It is also appropriate to consider the timescales on which the migration of chloride could occur.

A1.2 Overview of Chloride Migration

The first process by which chloride will migrate into a vault is advection by the flow of groundwater into the vault during re-saturation (shown schematically in Figure A1.1).

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 some of the vault relatively quickly.

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19 Although this is the first appendix, because that is where it belongs logically, the work it describes was performed after the package-scale numerical modelling that is reported in Appendices 2 – 4.
Figure A1.1 Schematic showing chloride transport during re-saturation

After the vault has re-saturated, a regional groundwater flow could continue to transport chloride through the backfill surrounding the waste packages (shown schematically in Figure A1.2).

Figure A1.2 Schematic showing chloride transport due to a regional groundwater flow
Prior to numerical modelling at the package-scale (see Appendix 3 and Appendix 4), the authors expected that advection of chloride into the waste packages would be unimportant, at least at early times (i.e. up to about a thousand years) post-closure. The reasons for this expectation included:

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

If indeed advection into the waste packages were negligible, then chloride would have to diffuse from the backfill through grout before it could come into contact with the Magnox wastes. However, the results obtained from package-scale models by both Quintessa (see Appendix 3) and AMEC (see Appendix 4) suggest that the corrosion of Magnox alloy, which will consume water and produce hydrogen\(^{20}\), will set up a system of flows both around and into the waste packages (see Figure A1.3, and also Appendix 4).

Figure A1.3 Gas pressure and gas saturation around and inside a waste package. The right-hand plot is an expansion of the top of the package on the left-hand plot; it includes the direction (but not magnitude) of the liquid velocity vectors.

\(^{20}\) In more detail, the consumption of water and production of hydrogen due to the corrosion of Magnox alloy will lead to a two-phase flow system in the wasteform. As the porewater in the grout is consumed, both the gas saturation and the capillary pressure in the immediate vicinity of the corroding wastes will increase. At early times (i.e. before the pressure of the gas phase has built up), the pressure of the water in the grout will decrease because it is equal to the pressure of the gas phase minus the capillary pressure. As a result, water will flow into the waste packages. At later times, the pressure of the gas phase might build up to the point where there no longer is an inflow of water.
This flow of porewater will transport chloride downwards into the wasteform inside a waste package (shown schematically in Figure A1.4).

Figure A1.4 Schematic showing chloride transport down through the wasteform

All of the above mechanisms by which chloride could migrate from the groundwater around a GDF into the waste packages (i.e. advection through the backfill, both during re-saturation and thereafter, and advection into the waste packages) will be influenced by the presence of cracks in the backfill and / or the grout.

Following this overview, the next subsections consider in turn:

- The processes by which chloride could migrate through a vault backfill and into packages containing grouted Magnox wastes (see Subsection A1.3);
- Chloride migration in the backfill (see Subsection A1.4);
- Chloride migration in the wasteform (see Subsection A1.5); and
- Chloride migration in the ullage\(^{21}\) at the top of the waste packages (see Subsection A1.6).

### A1.3 Processes

There is a well-established understanding of solute transport in porous media (e.g. [9, 10]).

As regards chloride migration in a GDF, advection could be an important transport process; chloride will move with a groundwater velocity determined by Darcy’s law, corrected for flow through the pores. Therefore, Subsection A1.3.1 computes typical values of the groundwater velocity in a vault.

There could be cracks in the backfill and / or the grout, in which case advection of chloride through the cracks would be coupled to diffusion into the surrounding cement matrix (this is the process of “rock-matrix diffusion”). In order to account for this process, Subsection A1.3.2 introduces a conceptual and mathematical model for transport of chloride through a network of cracks, and Subsection A1.3.3 reviews the literature on chloride diffusion through concrete.

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\(^{21}\) The ullage is a void space at the top of a waste package, which is not filled by the grout.
A1.3.1 Groundwater Flow and Advection

A1.3.1.1 Model

The simplest model of advection is the plug-flow model, which neglects longitudinal and transverse mixing. Using this model, a solute (e.g. chloride) will move with a transport velocity defined by the flow, $Q$, divided by the area of the pores normal to the flow.

After the GDF has re-saturated (which could be relatively rapid in a higher-strength rock; see Appendix 2 in Reference [11]), the flow of groundwater through a vault will be given by:

$$Q = AKiY$$  \hspace{1cm} (A1.1)

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 ($m$ s$^{-1}$);
- $i$ is the hydraulic head gradient ($\cdot$); and
- $Y$ is a flow-focusing factor, which accounts for the possible focusing of flow into the vault ($\cdot$).

A1.3.1.2 Hydraulic Conductivity and Specific Discharge in a Higher-strength Rock

The flow of groundwater through the 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. Examples of these host rocks include higher-strength rocks, lower-strength sedimentary rocks, and evaporites.

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

- The hydraulic conductivity, $K$, of a higher-strength host rock$^{22}$ is likely to be in the range $10^{-12} - 10^{-9}$ m s$^{-1}$ (over length scales of tens of metres) [12]. (For comparison, the hydraulic conductivities of mudrocks are typically less than $10^{-12}$ m s$^{-1}$, and of evaporite-dominated sequences are even lower.)
- The head gradient, $i$, might be in the range from zero to a few percent [12], determined, to some degree, by the topography of the surface.

The specific discharge of the groundwater in the host rock is obtained by multiplying the hydraulic conductivity, $K$, and the head gradient, $i$. Assuming values of the hydraulic conductivity ($10^{-9}$ 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 $2 \times 10^{-11}$ m s$^{-1}$ (or $6 \times 10^{-4}$ m yr$^{-1}$; the 2010 generic Disposal System Safety Case (DSSC) [13] assumes that this is the central value for the specific discharge in a higher-strength host rock, with an order of magnitude uncertainty).

A1.3.1.3 Geometry of the GDF

The flow of groundwater through a vault will also depend on the geometry of the GDF.

Figure A1.5 shows an illustrative layout for a GDF in a higher-strength rock (although this is the design developed for the 2010 DSSC [14], the results presented below are generally relevant).

---

$^{22}$ This is the hydraulic conductivity at a generic GDF depth of several hundred metres. The hydraulic conductivity of a higher-strength rock is always (slightly) higher at depths down to about 200m than at deeper levels.
The GDF consists of a number of parallel disposal tunnels and vaults, arranged in a horizontal plane. In this design, the vaults for ILW and LLW will have an approximately square cross-section, with sides of size about 16m, and will be about 300m long. For reasons of geotechnical stability, the vaults will be separated by rock pillars of about 50m size.

A1.3.1.4 Flow Enhancement

The vaults, in general, could have a markedly higher effective hydraulic conductivity than the surrounding rock. (This could be because the backfill has a relatively high hydraulic conductivity\(^{23}\), or possibly because the vault has a “crown space” above the waste stack that is left open.)

The presence of an inclusion of enhanced hydraulic conductivity within a background material of lower hydraulic conductivity leads to a focusing of the flow into the inclusion. Thus the specific discharge within the inclusion will be higher than it would have been in the undisturbed rock if there were no inclusion. The degree of flow enhancement will depend on both the geometry of the inclusion and the hydraulic conductivity contrast.

In particular, the effect of a vault on the specific discharge can be estimated from analytical results [15] 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-focusing factors”, \(Y\). The flow-focusing factors are computed to be (see Appendix 2 in Reference [11]):

- About 85 for horizontal flow parallel to the axes of the vaults; and
- Approximately 2 for flows in the orthogonal directions.

A1.3.1.5 Application to a GDF in a Higher-strength Rock

Using Equation (A1.1), and assuming that:

- The vault has an approximately square cross-section, with sides of size about 16m, and is about 300m long;
- The hydraulic conductivity, \(K\), of the higher-strength rock is \(10^{-9}\) m s\(^{-1}\);

23 The backfill will be designed to provide chemical conditioning rather than to have a low hydraulic conductivity, and, in addition, might develop a connected network of cracks due to processes such as plastic settlement and early-age thermal contraction (see Subsection A1.4.3).
- The head gradient, \( i \), is 0.02;
- The flow-focusing factor, \( Y \), is about two orders of magnitude for horizontal flow parallel to the axes of the vaults, and about 2 for flows in the orthogonal directions;

it is possible to compute that the groundwater flow through a vault could be as much as about 16 m\(^3\)yr\(^{-1}\) for flow parallel to the axes of the vaults, and 6 m\(^3\)yr\(^{-1}\) for the orthogonal directions.

Note that these flows are for a relatively permeable GDF host rock, and are directly proportional to the hydraulic conductivity of the rock.

### A1.3.2 Advection through Cracks Coupled to Diffusion into Cement Matrix

#### A1.3.2.1 Model

Next, we consider the possibility that there could be cracks in the backfill and/or the grout.

A simple model for chloride transport through a network of cracks approximates the cracks by a set of parallel, equally-spaced fissures, each having the same aperture and flow of porewater (see Figure A1.6).

![Figure A1.6 Conceptual model of flow and transport through a network of cracks in the cement backfill](image)

Advection of a solute through the cracks will be coupled to diffusion into the surrounding matrix. This model of solute transport has been studied widely (e.g. [16]), and analytical solutions have been developed for it (e.g. [17]).

Equations for the chloride concentration per unit volume of water in the crack, \( c \), and the concentration in the matrix, \( c' \), are, respectively:

\[
\]
\[
R \frac{\partial c}{\partial t} + v \frac{\partial c}{\partial z} = D^* \frac{\partial^2 c}{\partial z^2} + \frac{D'_{\text{eff}}}{b} \frac{\partial c'}{\partial x} \bigg|_{x=b} \tag{A1.2}
\]

and:
\[
\varphi' R' \frac{\partial c'}{\partial t} = D'_{\text{eff}} \frac{\partial^2 c'}{\partial x^2} \tag{A1.3}
\]

where:
- \( R \) is the crack retardation factor, given by \( 1 + \frac{K}{b} \);
- \( K \) is the chloride distribution coefficient per unit area of crack surface, which we shall set to zero (i.e. no sorption to crack surfaces – neglecting this sorption process will produce cautious estimates of transport times);
- \( b \) is half of the crack aperture (m);
- \( t \) is time (s);
- \( v \) is the transport velocity in the crack (m s\(^{-1}\));
- \( z \) is distance along the crack (m);
- \( D^* \) is the longitudinal dispersion coefficient (m\(^2\) s\(^{-1}\); this dispersion coefficient can be expressed as \( D^* = D + a_L v \) where \( D \) is the chloride diffusion coefficient in water and \( a_L \) is the dispersivity in the direction of the flow [18]);
- \( D'_{\text{eff}} \) is the matrix effective diffusion coefficient (m\(^2\) s\(^{-1}\); see Subsection A1.3.3 below);
- \( x \) is distance perpendicular to the crack (m);
- \( \varphi' \) is the matrix porosity; and
- \( R' \) is the matrix retardation factor, given by \( 1 + \frac{(1-\varphi')\varrho \cdot K_d}{\varphi'} \) (see Subsection A1.3.3).

To complete the specification of the model, initial and boundary conditions are required. Initially, the concentrations in the crack and matrix will be zero. At the crack surface, the concentration will be continuous:
\[
c(z, t) = c'(x = b, z, t) \tag{A1.4}
\]

and midway between neighbouring cracks, there will be no flux of chloride:
\[
\frac{\partial c'}{\partial x} \bigg|_{x=b} = 0 \tag{A1.5}
\]

**A1.3.2.2 Analytic Solutions**

Although these equations do not have analytic solutions for general values of the parameters, there are some simple solutions for certain values of the parameters [16, 17].

At very early times, the effects of diffusion into the matrix will be insignificant. Then, the solution for a step function boundary condition at the inlet, i.e.:
\[
c = \begin{cases} 
0 & t < 0 \\
\varepsilon & t > 0
\end{cases} \tag{A1.6}
\]

is [9, 10]:

\[
\begin{align*}
R \frac{\partial c}{\partial t} + v \frac{\partial c}{\partial z} &= D^* \frac{\partial^2 c}{\partial z^2} + \frac{D'_{\text{eff}}}{b} \frac{\partial c'}{\partial x} \\
\varphi' R' \frac{\partial c'}{\partial t} &= D'_{\text{eff}} \frac{\partial^2 c'}{\partial x^2}
\end{align*}
\]
Later, diffusion into the matrix between cracks will become an important process retarding the solute. Initially, the solute will diffuse into the matrix as though it were infinite. For the case \( D^* = 0 \) and \( B = \infty \) (i.e. negligible hydrodynamic dispersion in the cracks, and effectively an infinite matrix perpendicular to the crack), the solution for the step function boundary condition is [17]:

\[
\begin{align*}
  c &= \frac{c_s}{2} \left\{ \text{erfc} \left( \frac{z - vt}{R D^* t} \right) + \exp \left( \frac{v z}{D^*} \right) \text{erfc} \left( \frac{z + vt}{R D^* t} \right) \right\} \quad (A1.7)
\end{align*}
\]

where:

- \( T \) is the variable \( t - \frac{R z}{v} \) (s); and
- \( A \) is the parameter \( \frac{b R}{\varphi' \sqrt{D_{app}^*}} \) (s\(^{1/2}\)).

Eventually the influence of the neighbouring cracks will become important. Lever and Bradbury [16] state that this will occur around the position:

\[
  z_T \approx \frac{v b B}{D_{eff}^*} \quad (A1.9)
\]

Much further, a region of quasi-equilibrium will be reached where the solute concentration in the cracks and matrix are approximately in equilibrium. In this region, solute transport can be modelled as transport in an equivalent porous medium, and the concentration again satisfies approximately an advection-dispersion equation:

\[
  R_E \frac{\partial c}{\partial t} + v \frac{\partial c}{\partial z} = D_E \frac{\partial^2 c}{\partial z^2} \quad (A1.10)
\]

with enhanced values of the retardation factor and dispersion coefficient:

\[
  R_E = R + \frac{\varphi' R' B}{b} \quad (A1.11)
\]

\[
  D_E = D^* + \frac{\varphi' R' B^3 v^2}{3 b D_{app}^* R_E^2} \]

In other words, the equivalent porous medium behaves as though solute is being transported through all of its matrix porosity. The solution given previously for the case of pure hydrodynamic dispersion (i.e. Equation (A1.7)) is again appropriate, but with \( R \) replaced by \( R_E \) and \( D^* \) replaced by \( D_E \).

Note that the transition from the “thick matrix” solution (i.e. Equation (A1.8)) to the quasi-equilibrium solution will take place over a large distance (i.e. several times the distance \( z_T \) [16]).
A1.3.3 Diffusion

The previous subsection has described the process of rock-matrix diffusion (i.e. advection of chloride though cracks, for example in the backfill, coupled to diffusion into the surrounding cement matrix). It follows that diffusion of chloride will be another important transport process in a GDF, and that is the subject matter of this subsection.

There is a large literature on chloride diffusion through concrete, because this process is critical for assessing the lifetimes of bridges subjected to de-icing salts, structures in marine environments, etc. Estimating the diffusion coefficient of chloride is a key feature of computer programs to assess lifetimes of reinforced concrete structures (a recent program is described in [19]).

The diffusion equation for chloride in concrete (or grout) is written as:

\[ \phi \frac{\partial c}{\partial t} + (1 - \phi) \rho_s \frac{\partial F}{\partial t} = D_{\text{eff}} \frac{\partial^2 c}{\partial x^2} \]  

(A1.12)

where:
- \( \phi \) is the porosity;
- \( c \) is the chloride concentration in the porewater;
- \( \rho_s \) is the density of the solids (a little less than 3,000 kg m\(^{-3} \) for concrete);

and there are two other quantities:
- The mass of chlorides adsorbed per unit mass of solid, \( F \) (see Subsection A1.3.3.1); and
- The effective chloride diffusion coefficient, \( D_{\text{eff}} \) (see Subsection A1.3.3.2).

A1.3.3.1 Adsorption

Considering adsorption first, it is believed that when chloride enters concrete, it exists in essentially three forms:
- As free chloride ions in the pore fluid;
- Adsorbed to the CSH gel; and
- Chemically bound (as Friedel's salt) to calcium aluminate hydrates.

There are many reviews concerned with the binding of chlorides in concrete (a recent review by cement chemists is given in [20]). The literature has used various models to describe binding of chlorides (a brief review of the literature is given in the PhD thesis [21]).

Although many experiments have shown that the relationship between bound and free chlorides is non-linear, often it is assumed to be linear for modelling purposes. For a linear sorption isotherm \( F = K_d c \), where \( K_d \) is the distribution coefficient, and then the diffusion equation simplifies to:

\[ \phi \left( 1 + \frac{(1 - \phi) \rho_s K_d}{\phi} \right) \frac{\partial c}{\partial t} = D_{\text{eff}} \frac{\partial^2 c}{\partial x^2} \]  

(A1.13)

Saetta et al. [22] assumed a linear binding relationship when analysing chloride penetration profiles in Ordinary Portland Cement (OPC) concretes, with water to cement materials ratio (w/cm) ranging from 0.4 to 0.75, exposed to different environmental conditions. Their data were consistent with:

\[ (1 - \phi) \rho_s K_d = 0.7 \]  

(A1.14)

This implies that \( K_d \) is approximately \( 3 \times 10^{-4} \) m\(^3\) kg\(^{-1} \), or 0.3 ml g\(^{-1} \). The latter value is in fair agreement with values that have been measured under the Nirex research programme [23].
although it is a factor of 3 larger than the central value of the chloride distribution coefficient that was assumed in the generic Disposal System Safety Case [13].

Other authors have used a Langmuir sorption isotherm:

$$F = \frac{K_1 c}{1 + K_2 c}$$  \hspace{1cm} (A1.15)

where the constants $K_1$ and $K_2$ vary with the concrete composition. Sergi et al. [24] computed the values of $K_1$ and $K_2$ as 1.67 ml per g of cement and 4.08 l per mol, respectively, from a linear regression analysis of data for OPC paste samples with $w/cm = 0.5$ ($c$ and $F$ were expressed as mol per l and mmol per g of cement, respectively). Although the authors recognised the nonlinear nature of the relationship, they concluded that a linear approximation (i.e. $K_2 = 0$) also gave a good description of the behaviour. Tang and Nilsson [25] have stated that the relationship between bound and free chlorides is best described by the Langmuir isotherm when the concentration of chlorides in the pore solution is less than 1.773 kg m$^{-3}$ (i.e. 0.05M, or about 1,773 ppm).

The slope of the Langmuir sorption isotherm approaches zero as the concentration of free chlorides increases, suggesting that there is an upper limit to the amount of chlorides that can be bound. Because this was contrary to their observations, Tang and Nilsson [25] proposed the use of the Freundlich isotherm:

$$F = K_3 c^\alpha$$  \hspace{1cm} (A1.16)

for free chloride concentrations larger than 0.355 kg m$^{-3}$ (i.e. 0.01M, or about 355 ppm) of pore solution.

### A1.3.3.2 Effective Diffusion Coefficient

Effective diffusion coefficients$^{24}$ for both the grout in a waste package and a potential backfill have been measured (see Table 9 in [26]).

**Table A1.1** Best Estimates of Effective Diffusion Coefficients (m$^2$s$^{-1}$; from Harris and Nickerson [26])

<table>
<thead>
<tr>
<th>Material</th>
<th>Ionic Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFS / OPC grout</td>
<td>$-1\dagger$</td>
</tr>
<tr>
<td></td>
<td>$(3 \pm 2) \times 10^{-13}$</td>
</tr>
<tr>
<td>Nirex Reference Vault Backfill</td>
<td>$0\dagger$</td>
</tr>
<tr>
<td></td>
<td>$(340 \pm 70) \times 10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>$(690 \pm 40) \times 10^{-13}$</td>
</tr>
</tbody>
</table>

$\dagger$ Diffusion coefficients were measured using iodide ions

$\dagger$ Diffusion coefficients were measured using tritiated water

A model for the effective diffusion coefficient (which assumes that the porous medium is saturated with water) can be written as:

$$D_{ef} = \gamma \varphi \tau D$$  \hspace{1cm} (A1.17)

where:

$\gamma$ is an "anion exclusion" factor$^{25}$;

---

$^{24}$ These were called intrinsic diffusion coefficients in the Nirex research programme. Here, we have chosen to use the terminology from cement science.
φ is the porosity;
τ is the tortuosity\textsuperscript{26} of the pore structure (describing whether the pathways through the porous medium are tortuous); and

$D$ is the diffusion coefficient in free water, approximately $2 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ at $25^\circ\text{C}$ for both chloride and iodide [3].

In the case of the grout in a waste package, the effective diffusion coefficient for a neutral species has been measured as $8 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ and the porosity will be about 0.2 [27]. Therefore the tortuosity will be about 0.002. Experimental measurements (see Table A1.1) suggest that the effective diffusion coefficient for an anion (such as chloride) will be smaller by an anion exclusion factor of about 0.4.

In the case of the backfill, the effective diffusion coefficient for a neutral species has been measured as $6.9 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ and the porosity will be about 0.5 [28]. Therefore the tortuosity will be about 0.069. The effective diffusion coefficient for an anion will be smaller by an anion exclusion factor of about 0.5.

A1.3.3.3 Apparent Diffusion Coefficient

Assuming a linear sorption isotherm, the above diffusion equation (see Equation (A1.13)) can be rewritten as\textsuperscript{27}:

$$\frac{\partial c}{\partial t} = D_{\text{app}} \frac{\partial^2 c}{\partial x^2}$$  \hspace{1cm} (A1.18)

where $D_{\text{app}}$ is the apparent diffusion coefficient:

$$D_{\text{app}} = \frac{D_{\text{eff}}}{\phi \left(1 + \frac{(1-\phi)\rho_s K_d}{\phi}\right)}$$  \hspace{1cm} (A1.19)

Substituting the various parameter values given above, we find that $D_{\text{app}}$ for chloride is approximately:

- $3.3 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ in the grout inside a waste package; and
- $3.6 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ in the backfill.

Note that the apparent diffusion coefficient is approximately two orders of magnitude larger for the backfill than the grout. Therefore, chloride will diffuse an order of magnitude further into backfill compared with grout during a given period of time.

A1.3.3.4 Other Sources of Data

The apparent diffusion coefficient we have derived for grout is similar to values that have been reported elsewhere in the literature (e.g. see [29] for a tabulation of values up until the mid-1990s).

\textsuperscript{25} This factor accounts for the fact that negatively-charged species, i.e. anions, may be prevented from entering certain pore spaces in the backfill due to electrostatic repulsion, a process that is known as “anion exclusion”.

\textsuperscript{26} Note that alternative definitions of the “tortuosity” are used in the literature.

\textsuperscript{27} Fick’s first law relates a diffusive flux to the gradient of concentration. This law also applies to a saturated porous medium, but a smaller diffusion coefficient than in free water must be used, because of the obstruction to transport caused by the solid phase. This is the “effective diffusion coefficient” (see Equation (A1.17) in the main text).

Fick’s second law predicts how diffusion causes the concentration to change with time. In the case of a saturated porous medium, the time-dependent diffusion equation is written in terms of the “apparent diffusion coefficient” (see Equations (A1.13) and (A1.18) in the main text).
A compilation of apparent diffusion coefficients [30], which is broadly consistent with our value for grout, is shown in the figure below.

**Figure A1.7** This figure shows a compilation of apparent diffusion coefficients for chloride in grout [30] (from [19]). Also shown is the effect of age on the diffusion coefficient.

Figure A1.7 also shows that the apparent diffusion coefficient of chloride in concrete seems to decrease with time. Computer models for assessing the lifetimes of reinforced concrete structures [19, 31] typically account for this decrease.

### A1.4 Chloride Migration in the Backfill

Having introduced the various processes which could transport chloride through a vault backfill and into packages containing grouted Magnox wastes, this subsection goes on to consider chloride migration in the backfill.

#### A1.4.1 Re-saturation

Post closure of a vault, most of its gas-occupied porosity will fill with groundwater. Groundwater will flow into the vault, and although it might move far into the backfill in some locations (e.g. where
there is a crack), on average it will occupy a band around the outer edge of the vault; the porewater that is present initially inside the vault will flow towards the centre. These flows will continue until almost all of the gas-occupied porosity has been filled.

For the case of a vault in a higher-strength rock, it is possible to use the information in the generic disposal facility designs report (see Figure A1.8; [14]) to estimate that the waste might be emplaced so that there is about 40 m$^3$ of conditioned waste and about 200 m$^3$ of local and peripheral backfill per metre length of vault.

![Figure A1.8](image)

**Figure A1.8** Schematic cross-section through an UILW / ULLW vault: higher-strength rock [14]

Many of the wastes of greatest interest to the Carbon-14 Project will be encapsulated in grout. For such wastes, the conditioned waste will comprise a significant volume of grout, with a porosity of about 0.2 [26]. The liquid saturation of the grout at the time of backfilling will depend on both the duration of waste storage and the relative humidity in the store. Here we assume an average liquid saturation of 0.5 [26], in which case the conditioned waste will have a gas-occupied volume of about 0.5 \times 0.2 \times 40 = 4 \text{ m}^3 \text{ per metre length of vault]}^{28}.

---

28 This calculation neglects the volume occupied by the waste itself, and also the ullage space present at the top of many waste packages. These contributions will change the result, but only by a small amount.
In a higher-strength rock, a cement backfill will be placed around the conditioned wastes. After curing, the porosity of the design backfill (i.e. Nirex Reference Vault Backfill, NRVB) will be slightly less than 0.5, and the liquid saturation will be about 0.95 [28]. Thereafter the liquid saturation might continue to change as a result of ventilation of the vault. Here it is assumed that the ventilation system will be switched off and the vault closed soon after backfilling. Therefore a gas-occupied volume of about $0.05 \times 0.5 \times 200 = 5$ m$^3$ per metre length of vault will be associated with the backfill at closure$^{29}$.

These gas-occupied volumes can be compared with the total pore volume of about $0.2 \times 40 + 0.5 \times 200 = 108$ m$^3$ per metre length of vault.

The comparison suggests that on average the chloride front (the water used in the cement backfill mix is assumed to have low chloride content) will move only a small distance into the vault during re-saturation. Assuming that the vault has a square cross-section (see Figure A1.8), the distance would be less than 0.3m, which is much smaller than the dimensions of the vault (i.e. about 16m).

This conceptual picture is somewhat simplified, because:

- The flow of groundwater into the vault will be heterogeneous (e.g. it could occur at discrete points associated with fractures);
- The flow of porewater inside the vault will be heterogeneous (e.g. it could occur through cracks in the backfill$^{30}$); and
- Two-phase flow effects mean that more water will flow in at the bottom of the vault than at the top.

Notwithstanding these simplifications, the overall conclusion is that only a small volume of groundwater will flow into the backfill during re-saturation. Therefore, although a very small fraction of the wastes might be contacted by groundwater containing chloride, almost all of the waste will not be contacted by such water.

A similar argument can be made for the case of a vault in a lower-strength sedimentary rock. The illustrative design for this host rock assumes that a cement backfill will be placed around the conditioned wastes, and the vaults will be smaller (see Figure A1.9; [14]). The porosity of the backfill might be less than that of NRVB, but this uncertainty has been neglected below.

---

$^{29}$ The illustrative design for intermediate- and some low-level wastes in a higher-strength rock assumes that the crown space above the waste stack will be backfilled.

$^{30}$ It is considered improbable that these cracks would form a network connecting the host rock to the vicinity of a majority of the waste package vents, which potentially could enable the groundwater to bypass much of the cement backfill.
Each vault will contain only a fraction (about 0.3) of the conditioned waste and backfill per metre length as compared to a vault in a higher-strength rock. Using similar reasoning to the case of a higher-strength rock, the gas-occupied volume will be about 3 m$^3$ and the total volume will be about 30 m$^3$ per metre of vault.

As before, this suggests that on average the chloride front will move only a small distance into the vault during re-saturation. Assuming that the vault has an elliptical cross-section (see Figure A1.9), the distance would be less than 0.2m.

We observe that a lower-strength sedimentary rock will have very small pores. From the Young-Laplace equation [32], it follows that a large capillary pressure$^{31}$ will be needed before the free gas phase can migrate away from the vault into the surrounding host rock$^{32}$. Therefore, in this geological environment, re-saturation will be influenced by ongoing gas generation and pressurisation of the gas phase. Pressurisation is likely to oppose the flow of groundwater into the vault before it has re-saturated fully.

---

$^{31}$ 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.)

$^{32}$ This is different from the behaviour in a higher strength rock, where the apertures of fractures in the rock will be relatively large, and the capillary pressure when the gas phase can migrate into the host rock will be small.
Lastly, for the case of an evaporite there will be very little flow of groundwater (i.e. brine) into the vault (see Subsection 2.5 in [33]).

A1.4.1 Summary

In summary, it is considered unlikely that re-saturation of a vault will be associated with the ingress of chloride to a significant number of waste packages.

A1.4.2 Advection of Chloride through Intact Backfill

Advection by groundwater could transport chloride into the vault after re-saturation, but this process will be significant only for the case of a higher-strength host rock. (It is likely that the hydraulic conductivity, and therefore the groundwater flow, would be much smaller in other potential host rocks.)

In order to understand the process of advection through the backfill, it might be helpful to consider some scenarios.

In the first scenario, we assume that the host rock has a high hydraulic conductivity (e.g. $10^{-9}$ m s$^{-1}$). If we neglect the presence of cracks within the backfill (cracks are considered in Subsection A1.4.3 below), then the hydraulic conductivity of the vault will be comparable to that of intact backfill, which is about $10^{-9}$ m s$^{-1}$ [34]. It follows that there will be minimal flow focusing. Therefore the specific discharge inside the vault will be similar to the specific discharge in the host rock, which, as discussed in Subsection A1.3.1.2 above, might be about $2 \times 10^{-11}$ m s$^{-1}$. The transport velocity through the backfill can be calculated from this specific discharge. In particular, allowing for the porosity of the backfill (about 0.5) and the fact that the waste packages will block a fraction (assumed to be 0.5) of the flow path, the transport velocity of the groundwater inside the vault will be about $8 \times 10^{-11}$ m s$^{-1}$. If this were the transport velocity, then it would take a solute in the groundwater (such as chloride, neglecting its sorption for the present) about 400 yr to flow across a distance of 1m. Depending on whether the flow is normal to the axis of the vault (dimension 16m) or along the axis (dimension 300m), it will take between 6,000 yr and 120,000 yr for the chloride to contact all of the waste packages.

In a second scenario, if the host rock has a low hydraulic conductivity (e.g. $10^{-11}$ m s$^{-1}$) then the specific discharge in the host rock might be about $2 \times 10^{-13}$ m s$^{-1}$, and there will be a large contrast between the hydraulic conductivity of the vault and the host rock. In general, the specific discharge in the host rock will not be aligned either parallel or perpendicular to the axes of the vaults. (However, in a vault, the largest component of the specific discharge will be in the direction along its axis, because the flow-focusing factor will be significant only in this direction.) If the flow were along the axis of the vault, then flow focusing (by a factor of about 85) would mean that the value of the specific discharge inside the vault would be similar to the specific discharge in our first scenario. Therefore the transport velocity would also be similar (i.e. about $8 \times 10^{-11}$ m s$^{-1}$). If the flow were normal to the axis of the vault, then the specific discharge inside the vault would be about double the value in the host rock, i.e. $4 \times 10^{-13}$ m s$^{-1}$. Converting this to a transport velocity using the same algorithm as previously, the transport velocity of the groundwater inside the vault would be about $1.6 \times 10^{-12}$ m s$^{-1}$. If this were the transport velocity, then it would take a non-sorbing solute about 20,000 yr to flow across a distance of 1m. If follows that, whether one considers flow to be in the direction along the axis of the vault (dimension 300m) or normal to this (dimension 16m), it will take several tens of thousand years for the chloride (which is assumed to be non-sorbing here) to contact a significant fraction (i.e. of the order of a half) of the waste packages.

In point of fact, these travel times are underestimates, because the chloride will sorb to the backfill. The effect of the sorption will be to increase the travel times for the chloride by a retardation factor $R$ [9]:

$$R = 1 + \frac{(1 - \varphi) \rho_s K_d}{\varphi}$$  \hspace{1cm} (A1.20)

where:
\( \varphi \) is the porosity; 
\( \rho_s \) is the density of the backfill solids (a little less than 3,000 kg m\(^{-3}\) for concrete); and 
\( K_d \) is the distribution coefficient for the backfill.

Experiments [22], which have been discussed in Subsection A1.3.3.1 above, have established that:

\[
(1 - \varphi) \rho_s K_d \approx 0.7 \quad \text{(A1.21)}
\]

and it is known that the porosity of cured backfill [28] will be:

\[
\varphi \approx 0.5 \quad \text{(A1.22)}
\]

Therefore, the travel times that were computed above should be increased by a factor of about 2.4 for chloride.

A1.4.2.1 Summary

The results of the above calculations can be summarised (see Table A2.2), showing how long it will take chloride to contact all of the waste packages in a vault for the different scenarios.

**Table A2.2 Time for Chloride to Contact All the Magnox Waste Packages in a Vault**

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Hydraulic Conductivity of Host Rock (m s(^{-1}))</th>
<th>Hydraulic Conductivity of Backfill (m s(^{-1}))</th>
<th>Time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relatively high hydraulic conductivity of host rock; intact backfill; advection along axis of vault</td>
<td>10(^{-9})</td>
<td>10(^{-9})</td>
<td>285,000</td>
</tr>
<tr>
<td>Relatively high hydraulic conductivity of host rock; intact backfill; advection normal to axis of vault</td>
<td>10(^{-9})</td>
<td>10(^{-9})</td>
<td>15,200</td>
</tr>
<tr>
<td>Lower hydraulic conductivity of host rock; intact backfill; advection along axis of vault</td>
<td>10(^{-11})</td>
<td>10(^{-9})</td>
<td>336,000</td>
</tr>
<tr>
<td>Lower hydraulic conductivity of host rock; intact backfill; advection normal to axis of vault</td>
<td>10(^{-11})</td>
<td>10(^{-9})</td>
<td>761,000</td>
</tr>
</tbody>
</table>

These results suggest that it will take many thousands of years for chloride in the groundwater to contact a significant fraction of the waste packages for scenarios in which the chloride has to migrate through a substantial amount of intact backfill.

Note that the discussion in this subsection has been based around estimates of (i) the specific discharge in the host rock, and (ii) the effects of flow focusing. However, in the case of a higher-strength rock, the groundwater will flow into the vault at a number of discrete points associated with fractures. The transport velocity through the backfill could be larger than has been assumed here in the vicinity of a fracture with a particularly big flow, but will fall off towards our estimate with increasing distance from the fracture. Thus, there will be some variability in the transport velocity within a vault, which will depend on site-specific details about the geometry of the fractures in the host rock. The results that are presented here are for the “average” transport velocity within the vault.
A1.4.3 Transport of Chloride through Cracks in the Backfill

An earlier study considered it likely that the backfill will contain cracks [35]. A comprehensive range of processes and scenarios were assessed, and the processes identified as potentially causing cracking were as follows:

- During placement of the backfill, plastic settlement under solid waste package surfaces could result in horizontal gaps of up to 2 mm under each package. These would extend only as far as the edge of the packages, and therefore would not form a connected network by themselves. (Gaps are less likely to occur under stillages, which would have holes in their base plates that would allow flows of backfill and bleed water [33].)

- Within days of backfilling, early-age thermal contraction of the backfill could result in vertical cracks of up to 0.2 mm. These would extend between waste packages at locations where the backfill is at its thinnest. Some of these cracks might connect with the gaps formed previously under the packages.

- Later, degradation of the waste could be associated with volume changes that cause expansion of the waste packages (and possibly associated gas generation), which could result in more cracking if the crown space were not filled [34]. We shall assume that this will happen at some time after chloride has migrated into the waste packages.

The cracks will have various effects, including increasing the effective hydraulic conductivity (and potentially the flow-focusing factor) of the vault, and providing preferential pathways for the flow of groundwater and the transport of solutes.

We shall assume that:

- The specific discharge in the host rock has a high value of $2 \times 10^{-11} \text{ m s}^{-1}$; and

- Based on the work reported in Reference [35], a network of cracks forms inside the cement backfill, and the cracks [35] have aperture 0.2 mm and a large spacing (i.e. 1m).

The specific discharge associated with the cracks will be equal to the specific discharge in the host rock multiplied by a flow-focusing factor [36]. If the flow is along the axis of the vault, then flow focusing (by a factor of about 85; see Subsection A1.3.1) means that the specific discharge inside the vault will be about $1.7 \times 10^{-9} \text{ m s}^{-1}$. If the flow is normal to the axis of the vault, then the specific discharge inside the vault will be about double its value in the host rock, i.e. $4 \times 10^{-11} \text{ m s}^{-1}$.

The specific discharge is converted into a transport velocity through the cracks by dividing by the porosity of the cracks. The effective porosity of the cracks will be equal to the crack

\[
K \approx \frac{\rho g}{\mu} \frac{b^3}{3B}
\]

where $\rho$ is the groundwater density; $g$ is the gravitational acceleration; $\mu$ is the groundwater viscosity; $b$ is half of the crack aperture; and $B$ is half of the crack spacing.

This hydraulic conductivity becomes comparable to the hydraulic conductivity of the intact backfill (i.e. about $10^{-9} \text{ m s}^{-1}$) when the crack aperture is about 0.01 mm. Thus, if the apertures of the cracks were much smaller than has been assumed here, then the flow through the cracks would be negligible.

For the given assumptions, the network of cracks will have a much larger effective hydraulic conductivity than the host rock, and therefore the flow-focusing factors that have been derived earlier can be applied.
aperture (0.2mm) divided by the crack spacing (1m), and therefore for our particular assumptions will be about $2 \times 10^{-4}$. It follows that the transport velocity through the cracks\(^{37}\) will be about:

- $8.5 \times 10^{-6}$ m s\(^{-1}\) for flow along the axis of the vault; or
- $2 \times 10^{-7}$ m s\(^{-1}\) for flow normal to the axis of the vault.

The point beyond which the concentrations of chloride in the cracks and the cement matrix will be approximately in equilibrium is given by a multiple of $z_T$ (see the earlier discussion in Subsection A1.3.2), where, for the parameter values given above:

- $z_T \approx 12.5$ m for flow along the axis of the vault; or
- $z_T \approx 0.29$ m for flow normal to the axis of the vault.

Thus, beyond about a tenth of either the vault length or breadth\(^{38}\), chloride transport can be modelled by an equivalent porous medium, and the concentration will satisfy an advection-dispersion equation with enhanced values of the retardation factor, $R_E$, and dispersion coefficient, $D_E$. Using the formulae given above (see Equation (A1.11)), and doing the arithmetic:

- $R_E \approx 6,000$;

and:

- $D_E \approx 2.8 \times 10^{-5}$ m\(^2\) s\(^{-1}\) for flow along the axis of the vault; or
- $D_E \approx 1.5 \times 10^{-8}$ m\(^2\) s\(^{-1}\) for flow normal to the axis of the vault.

After the chloride has been transported away from the edge of the vault, the solution of the advection-dispersion (see Equation (A1.7)) simplifies, and therefore the concentration of chloride will be given by:

$$
c \approx \frac{c_s}{2} \text{erfc} \left( \frac{z - \frac{vt}{R_E}}{2 \sqrt{\frac{D_E t}{R_E}}} \right)
$$

(A1.23)

Assuming that the concentration of chloride in the groundwater is similar to the concentration in seawater (i.e. about 20,000 ppm), we can use this equation to compute when the concentration in the backfill will increase to the threshold for accelerated Magnox corrosion (i.e. about 100 ppm). We find that:

$$
\frac{z - \frac{vt}{R_E}}{2 \sqrt{\frac{D_E t}{R_E}}} \approx \text{erfc}^{-1} \left( \frac{1}{2} \times \frac{2 \times 100}{20,000} \right) \approx 1.821
$$

(A1.24)

and therefore:

$$
t \approx \frac{R_E}{v} \left( \sqrt{1.821^2 \frac{D_E}{v} + z} - \sqrt{1.821^2 \frac{D_E}{v}} \right)^2
$$

(A1.25)

---

\(^{37}\) The values quoted are comparable to the transport velocities shown in Reference [35], which were calculated using a fracture network approach.

\(^{38}\) The illustrative design for intermediate- and some low-level wastes in a higher-strength rock [14] assumes that the vaults will be about 300m long, with sides having dimensions of about 16m.
This expression can be used to work out how long it will take for the chloride to be transported through the backfill. If the groundwater flow is along the axis of the vault, then it will take the chloride about 200 yr to migrate a tenth of the vault length (i.e. $z = 30$ m) and about 4,600 yr to migrate throughout the vault (i.e. $z = 300$ m). If the flow is normal to the axis of the vault, then it will take the chloride about 700 yr to migrate a tenth of the vault breadth (i.e. $z = 1.6$ m) and about 11,900 yr to migrate throughout the vault (i.e. $z = 16$ m).

**A1.4.3.1 Summary**

The results of the above calculations can be summarised (see Table A2.3), showing how long it will take chloride to contact all of the waste packages in a vault for the different scenarios.

**Table A2.3 Time for Chloride to Contact All the Magnox Waste Packages in a Vault**

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Hydraulic Conductivity of Host Rock (m s$^{-1}$)</th>
<th>Hydraulic Conductivity of Backfill (m s$^{-1}$)</th>
<th>Time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relatively high hydraulic conductivity of host rock; cracked backfill; advection along axis of vault</td>
<td>$10^{-9}$</td>
<td>$&gt;&gt; 10^{-9}$</td>
<td>4,600</td>
</tr>
<tr>
<td>Relatively high hydraulic conductivity of host rock; cracked backfill; advection normal to axis of vault</td>
<td>$10^{-9}$</td>
<td>$&gt;&gt; 10^{-9}$</td>
<td>11,900</td>
</tr>
</tbody>
</table>

These results suggest that, even though the transport velocity in a crack might be large, the process of “rock-matrix diffusion” into the surrounding intact backfill will ensure that the timescale to transport chloride through a vault will be long (i.e. many thousands of years).

**A1.5 Chloride Migration in the Wasteform**

Having dealt with migration of chloride in the backfill, this subsection goes on to consider transport in the wasteform.

Our understanding of the various processes that will occur inside a package containing Magnox wastes is based on the results obtained from package-scale numerical models (see Appendix 3 and Appendix 4).

**A1.5.1 Advection of Chloride through Intact Grout**

The Magnox alloy inside a waste package will corrode, consuming water and producing hydrogen.

The consumption of water will cause the waste package to dry out (to some extent), and therefore the pressure associated with the liquid phase inside the package will fall$^{39}$. Simultaneously, hydrogen will flow out through the package’s vent and into the surroundings. After the vault has been backfilled, this flow of gas will cause the gas saturation of the backfill to increase, particularly in the region close to the vent. Correspondingly, the liquid saturation, and consequently the relative permeability of the backfill to the liquid phase, will decrease.

---

$^{39}$ In more detail, the consumption of water and production of hydrogen due to the corrosion of Magnox alloy will lead to a two-phase flow system in the wasteform. As the porewater in the grout is consumed, both the gas saturation and the capillary pressure in the immediate vicinity of the corroding wastes will increase. At early times (i.e. before the pressure of the gas phase has built up), the pressure of the water in the grout will decrease because it is equal to the pressure of the gas phase minus the capillary pressure. As a result, water will flow into the waste packages. At later times, the pressure of the gas phase might build up to the point where there no longer is an inflow of water.
In broad terms, therefore, we would expect porewater from the backfill to flow into the package at a rate that depends on:

- The rate of gas generation inside the waste package; and
- The hydraulic conductivity and two-phase flow properties of the backfill and the grout.

A complicating factor is the behaviour of the ullage at the top of the waste package (see Subsection A1.6 below). Assuming that the ullage will allow porewater to flow into the waste package, the package-scale numerical models show that the surrounding backfill can supply water at approximately the rate it is being consumed by corroding Magnox alloy inside the package\(^{40}\) (see Appendix 4). This observation makes it possible to develop a simple understanding for the transport of chloride inside the package.

In particular, making the following assumptions:

- The waste package is an “average” package of encapsulated Magnox cladding from waste stream 2D38/C, and therefore contains about 150 kg of Magnox alloy, which is present in the form of plates with a thickness of about 2 mm [36]; and
- The vault has reached a medium-term post-closure temperature of about 30 °C;

then the rate of Magnox corrosion is 0.428 $\mu$m yr\(^{-1}\) [1], and it is possible to calculate that before any chloride has entered the package, water will be consumed (i.e. $\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2$) at the rate of $3.02 \times 10^{-12}$ m\(^3\) s\(^{-1}\).

The transport velocity of water within the wasteform will be given by the rate of water flow (m$^3$s\(^{-1}\)) divided by the wasteform’s horizontal area (0.471 m\(^2\) in the AMEC model; see Appendix 4) and its porosity (0.165 in the AMEC model; this includes an allowance for the volume occupied by the Magnox waste). Thus, at steady-state before any chloride has entered the package, the transport velocity in the wasteform, $u_0$, will be of the form:

$$ u_0(z) = U \frac{z}{h} $$

(A1.26)

where:

- $U$ is a derived velocity parameter, $3.89 \times 10^{-11}$ m s\(^{-1}\) (or, about 0.001 m yr\(^{-1}\)) for the values listed above;
- $z$ is position (m) measured upwards from the bottom of the wasteform; and
- $h$ is the height of the wasteform (1.04 m in the AMEC model).

Once chloride has migrated 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 chloride will be transported with an increased velocity down through the wasteform.

At the chloride-enhanced rate of corrosion (assumed to be $0.428 \times 100 = 42.8 \mu$m yr\(^{-1}\)) it will take only about 20 years to corrode all of the Magnox at an individual location within the wasteform. The AMEC reference case simulation (see Appendix 4) shows that all of the Magnox at the very top of the wasteform will have corroded by the time that the chloride front has advanced a distance of about 0.1 m.

Thereafter, the chloride will move downwards through the wasteform, with a transport velocity of about $4 \times 10^{-10}$ m s\(^{-1}\) (or, about 0.01 m yr\(^{-1}\)); this velocity is an order of magnitude larger than the

---

\(^{40}\) The package-scale numerical models assumed that water would be plentiful at their outer boundary (this is likely to be the condition in a higher-strength rock, but may not be true in other host rocks), and then showed that the backfill would not limit the flow of porewater into a waste package.
velocity before any chloride has entered the package) and behind the chloride front a narrow band (several centimetres high) of Magnox will be corroding at the enhanced rate (see Figure A1.10).

![Figure A1.10 AMEC result showing: (left) Magnox density (kg m$^{-3}$ of wasteform); (middle) liquid saturation; and (right) chloride concentration (ppm)](image)

At this transport velocity, it would take only about a hundred years for the chloride to be transported down the height of the wasteform. Actually, experiments show that chloride is weakly sorbing to concrete [20, 22], and therefore this time should be multiplied by a retardation factor of about 4.5 (see Subsection A1.3.3.1).

The package-scale numerical models also found that the key controls on the transport of chloride within the waste package include:

- The amount of dispersion (or spreading) around the chloride front; and
- The behaviour of the ullage (i.e. does it allow inflow of water).

The particular simulation used to compute Figure A1.10 assumes that:

- The porewater diffusion coefficient of chloride in the grout has a realistic value, based on a review of the extensive experimental data (see Appendix A1.3.3);
- There is no mechanical dispersion; and
- The liquid phase is fully mobile in the ullage at all saturations.
Some variant simulations assumed a large amount of dispersion (see Appendix 3 and Appendix 4), and these predicted that chloride would migrate faster down through the wasteform (and a thicker band of Magnox would be corroding at the enhanced rate).

Other variant simulations considered the effect of the ullage (see Subsection A1.6).

### A1.5.1.1 Summary

The key conclusions from the AMEC modelling (see Appendix 4) are that:

- Chloride will be transported slowly down an uncracked wasteform over a period of about 100 yr.
  - In fact, experiments show that chloride is weakly sorbing to concrete [20], and therefore this time should be multiplied by a retardation factor of about 4.5.
- No more than a small fraction of the Magnox alloy inside a waste package will be corroding at the chloride-enhanced rate at any one time.

These conclusions could be altered by the presence of cracks in the grout, which might accelerate the transport of chloride inside the waste package (see the discussion in Subsection A1.5.3 below).

### A1.5.2 Example Calculation – Diffusion of Chloride through Intact Grout

The previous subsection has considered advection of chloride through intact grout. This subsection confirms that porewater diffusion will transport chloride much more slowly than advection.

Because the apparent diffusion coefficient of chloride will be much smaller in the grout than in either the backfill or, particularly, the ullage at the top of a waste package, we would expect the concentration of chloride in the ullage to attain a constant value $c_s$ before chloride can diffuse far into the grout.

Hence, ignoring advection and assuming one-dimensional diffusion of chloride from the ullage into the grout, the concentration of chloride in the grout porewater at depth $z$ after time $t$ will be given by:

$$
\frac{c}{c_s} = \text{erfc}\left(\frac{z}{2 \sqrt{D_{app} t}}\right) \quad (A1.30)
$$

(This equation has been used widely to interpret the results of chloride diffusion experiments, e.g. [37, 38].)

Assuming that the concentration of chloride in the ullage is similar to the concentration in seawater (i.e. about 20,000 ppm; this is considered to be a reasonable, large value for the concentration of chloride in the porewater), we can use this equation to calculate when the concentration in the concrete will increase to the threshold for accelerated Magnox corrosion (i.e. about 100 ppm). We find that:

$$
\frac{z}{2 \sqrt{D_{app} t}} = \text{erfc}^{-1}\left(\frac{100}{20,000}\right) \approx 1.985 \quad (A1.31)
$$

and therefore:

$$
t \approx 7.14 \times 10^{10} z^2 \quad (A1.32)
$$

where $t$ is in seconds (measured from the time when the concentration of chloride in the ullage attains the value $c_s$) and $z$ is in metres. Converting the units of time to years, gives:
\[ t \approx 2.260 z^2 \]  

(A1.33)

where \( t \) is now in years.

Thus, the time for chloride to diffuse down the wasteform (i.e. about 2,000 years; the height of the wasteform is about 1m) would be much longer than the corresponding times calculated by the package-scale numerical models (see Appendix 3 and Appendix 4). This result shows that advection of chloride will be the dominant transport process inside a package containing Magnox wastes.

### A1.5.3 Transport of Chloride through Cracks in the Grout

The encapsulation grout could be cracked, and therefore it is relevant to ask how the presence of cracks in the grout would affect the ingress of chloride to a waste package.

The Magnox waste inside a package will corrode, consuming water and producing hydrogen (as well as carbon-14 bearing gases). After re-saturation, water will flow into the package to replace the water consumed by Magnox corrosion. And later still, after chloride first comes into contact with the Magnox waste, water will flow towards the region of enhanced corrosion from both outside and inside the package.

These flows can be understood only by performing detailed numerical modelling of a package containing Magnox waste. Our package-scale models (see the earlier discussion) suggest that in the absence of cracks, the timescale for chloride to be transported down the wasteform will be less than a few hundred years.

The presence of cracks in the grout could shorten this timescale. However, referring back to the analyses in Subsection A1.4, it is clear that it is the backfill, rather than the encapsulation grout, which will contribute most to the delay in chloride coming into contact with the Magnox alloy.

Therefore, our conceptual picture is that chloride will be transported slowly through the backfill. Close behind the chloride front, parts of waste packages containing Magnox alloy will be undergoing corrosion at an accelerated rate due to the presence of the chloride. Since the time to corrode all of the Magnox waste in a package will be short compared with the time for chloride to migrate between nearby packages, the affected packages will be present only in a narrow zone.

### A1.6 Chloride Migration in the Ullage

This subsection considers the behaviour of the ullage\(^{41}\) at the top of the waste package. The ullage will fill with pressurised gas, and that could stop the inflow of liquid water and the ingress of chloride to the package.

As mentioned already, the Magnox alloy will generate hydrogen, which will migrate upwards through the encapsulating grout. This gas will accumulate in the ullage until its pressure there exceeds the sum of the liquid pressure and “gas entry pressure” in the overlying backfill, because it will be unable to move into the backfill until this has happened. Within the ullage, which is a large unfilled space with a negligible capillary pressure, the pressure of the gas phase will be approximately equal to the pressure that would be associated with a liquid phase (i.e. referring to Figure A1.11 below, \( P_g \) (ullage) \( \approx P_l \) (ullage)), but within the backfill, the pressure of the gas phase will be larger than the pressure of the liquid phase (i.e. \( P_g \) (backfill) \( > P_l \) (backfill)) \([9]\). Therefore, for the whole period while gas is migrating away from the waste package (which means that \( P_g \) (ullage) \( > P_g \) (backfill)), the pressure of an incipient liquid phase in the ullage would exceed the pressure of the liquid phase in the backfill (i.e. \( P_l \) (ullage) \( > P_l \) (backfill)). This circumstance will oppose the flow of liquid water into the waste package, and could stop the ingress of chloride.

---

\(^{41}\) The ullage is a void space at the top of a waste package, which is not filled by the grout.
Figure A1.11 Schematic defining the gas pressure, $P_g$, and the liquid pressure, $P_l$, in the various materials (i.e. the cement backfill, ullage, and wasteform)

The package-scale numerical models (see Appendix 3 and Appendix 4) considered the effect of the ullage. Variant simulations showed a range of behaviours, including:

- The ullage pressurised with gas before chloride could get into the waste package (see Figure A1.12). In this variant, pressurisation of the ullage stopped the inflow of water after about ten years, and the rate of Magnox corrosion was never enhanced by the presence of chloride. The grout in the package dried out after almost 700 years, and then corrosion effectively stopped (i.e. diffusion of water vapour was too slow to maintain the corrosion).

- Chloride entered into the waste package, and then the ullage pressurised with gas. In this variant, the ullage restricted (but did not stop) the supply of water to the Magnox wastes, and so the package dried out quickly. Thereafter, corrosion continued 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, but it is difficult to know with certainty how the ullage will behave in a real GDF. Therefore, although the presence of the ullage is recognised as being potentially beneficial, we shall not take credit for it when assessing the release of carbon-14 from packages of Magnox wastes.

### A1.7 Summary and Conclusions

Various processes (e.g. advection and diffusion) will contribute to the transport of chloride into a vault, and then into a waste package.

Various scenarios have been modelled, and it has been shown that most of the travel time is associated with transport of chloride through the cement backfill. Travel times of more than a thousand years are indicated if the chloride has to be transported through a small length (i.e. 1m) of intact backfill (see Table A2.4). Even if the backfill is cracked, travel times probably will be hundreds of years for transport across a tenth of the vault dimension and thousands of years for transport throughout the vault (see Table A2.4).
Table A2.4  Time for Chloride to Contact All the Magnox Waste Packages in a Vault

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Hydraulic Conductivity of Host Rock (m s$^{-1}$)</th>
<th>Hydraulic Conductivity of Backfill (m s$^{-1}$)</th>
<th>Time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relatively high hydraulic conductivity of host rock; intact backfill;</td>
<td>$10^{-9}$</td>
<td>$10^{-9}$</td>
<td>285,000</td>
</tr>
<tr>
<td>advection along axis of vault</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relatively high hydraulic conductivity of host rock; intact backfill;</td>
<td>$10^{-9}$</td>
<td>$10^{-9}$</td>
<td>15,200</td>
</tr>
<tr>
<td>advection normal to axis of vault</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower hydraulic conductivity of host rock; intact backfill;</td>
<td>$10^{-11}$</td>
<td>$10^{-9}$</td>
<td>336,000</td>
</tr>
<tr>
<td>advection along axis of vault</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower hydraulic conductivity of host rock; intact backfill;</td>
<td>$10^{-11}$</td>
<td>$10^{-9}$</td>
<td>761,000</td>
</tr>
<tr>
<td>advection normal to axis of vault</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relatively high hydraulic conductivity of host rock; cracked backfill;</td>
<td>$10^{-9}$</td>
<td>$&gt;&gt; 10^{-9}$</td>
<td>4,600</td>
</tr>
<tr>
<td>advection along axis of vault</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relatively high hydraulic conductivity of host rock; cracked backfill;</td>
<td>$10^{-9}$</td>
<td>$&gt;&gt; 10^{-9}$</td>
<td>11,900</td>
</tr>
<tr>
<td>advection normal to axis of vault</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In contrast, package-scale numerical models (see Appendix 3 and Appendix 4) have shown that chloride, following its ingress to a waste package, will be transported down the height of the wasteform over a period of only 100 yr. This timescale is determined by the flow of porewater into the package that is needed to supply the Magnox corrosion reaction, and could be longer if sorption were taken into account or shorter if, for example, there were a large amount of dispersion or cracks in the grout$^{42}$.

Lastly, the ullage at the top of a waste package has been identified as an important feature, which could affect how the Magnox alloy in a waste package might corrode. The ullage will fill with pressurised gas, and that could stop the inflow of liquid water and the ingress of chloride to the package. Because it is difficult to know how the ullage will behave in a real GDF, we shall not take credit for it when assessing the release of carbon-14 from packages of Magnox wastes.

On the basis of these considerations, it seems justifiable (and probably is very cautious) to assume that chloride will access Magnox inside waste packages over a timescale of between 100 years and 1,000 years post-closure. This timescale is most likely to be realised in a higher-strength host rock, with a longer timescale being appropriate for a lower-strength sedimentary host rock.

A1.8 References


$^{42}$ However, if the timescale is shorter, this is not significant, as the timescale is determined by vault-scale processes.


21 B. Martín-Pérez, Service Life Modelling of R.C. Highway Structures Exposed to Chlorides, PhD Thesis submitted to the Graduate Department of Civil Engineering, University of Toronto, 1999.


Appendix 2
Data for the Package-scale Models

Contents

Introduction
Events and Timescales
Geometry
Thermal Data
Hydraulic Data
Mechanical Data
Chemical Data
Additional Parameterisation for Quintessa Modelling
Additional Parameterisation for AMEC Modelling
References
A2 Data for the Package-scale Models

A2.1 Introduction

Reactive metal wastes will corrode, which will consume water and produce gases (e.g. hydrogen), and this will set up a system of flows both around and into the waste packages. In order to understand these flows, both Quintessa (see Appendix 3) and AMEC (see Appendix 4) have performed numerical modelling at the package scale.

The waste package that was considered is an “average” package of encapsulated Magnox cladding from waste stream 2D38/C, and therefore contains about 150 kg of Magnox alloy, which was represented in the models as being in the form of plates with a thickness of about 2 mm, inside a 500l drum [1].

A specification of the data that should be used in the package-scale models was produced at the beginning of the work. This appendix tabulates these agreed data. Some additional data that were required for variant cases are also shown, highlighted in green.

Note that the package-scale models were developed towards the beginning of the Carbon-14 Project, and therefore the specified data are not always consistent with the data used by models which were developed later in the project. However, any discrepancies are not significant, and will not have affected the general conclusions of the work.

This appendix is structured as follows:

- Subsection A2.2 identifies events (and timescales) in the lifetime of the waste package;
- Subsection A2.3 defines the geometry of the waste package;
- Subsections A2.4 – A2.7 list various thermal, hydraulic, mechanical and chemical data respectively;
- Subsection A2.8 gives additional data used by Quintessa when simulating a number of variant cases; and Subsection A2.9 gives additional data used by AMEC when simulating a more extensive set of multi-component, two-phase flow and transport processes.

A2.2 Events and Timescales

This subsection lists the assumptions made about the events and timescales in the lifetime of a waste package.

At first, the waste package will be in a surface store. The time that will be spent in the surface store can be estimated by observing that the Magnox Encapsulation Plant was commissioned in 1990 [2], and processing of the Magnox waste is scheduled to complete in 2021 [3].

- Assuming a waste package produced in 2005, and moved to a GDF sometime between 2040 and 2090 (see Table 4-1 in Reference [3]), the time in surface storage is taken to be 2065 – 2005 = 60 yr.

Next, the waste package will be moved to a Geological Disposal Facility (GDF). The time spent in an operational vault (i.e. prior to backfilling) can be estimated by assuming that backfilling will occur from 2140 to 2150, with closure at 2150 (see Table 4-1 in Reference [3]).

- The time underground before backfilling is taken to be 2145 – 2065 = 80 yr.

Then, the waste package is assumed to be surrounded by backfill, and the vault sealed.

A2.3 Geometry

A2.3.1 Vault

The reference case simulations will consider a waste package inside a UILW / ULLW vault situated in a higher-strength host rock (Figure A2.1).

More specifically, the Quintessa model assumed a 500l drum in a stillage at the top of the middle waste stack. (In this model the roof of the vault is 16.0 – 8.715 – 0.25 – 0.50 = 6.535m above the top of the drum.) The AMEC model assumed a 500l drum at an indeterminate location in the waste stacks.

![Figure A2.1 UILW / ULLW vault in a higher-strength host rock (e.g. [4])]()
to give the correct internal volume. In the AMEC model, the heights of the capping grout and ullage were increased instead, to 100 mm and 50 mm respectively.

![Figure A2.2](image_url) A waste package, consisting of a 500 litre drum filled with Magnox alloy, encapsulant and capping grout [5]

**Table A2.1 Waste Package Geometry Data**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>External Height</td>
<td>1200 (mm)</td>
<td>[6]; §4.5</td>
</tr>
<tr>
<td>Drum External Diameter</td>
<td>800 (mm)</td>
<td>[6]; §4.5 – (maximum value)</td>
</tr>
<tr>
<td>Drum Internal Diameter</td>
<td>794 (mm)</td>
<td>800 (mm) – 2 × wall thickness (maximum value)</td>
</tr>
<tr>
<td>Wall Thickness</td>
<td>3 (mm)</td>
<td>[7]; Table 7.21</td>
</tr>
<tr>
<td>Height Encapsulated Waste</td>
<td>1099 (mm)</td>
<td>see Figure A2.2</td>
</tr>
<tr>
<td>Height Capping Grout</td>
<td>70 (mm)</td>
<td>[7]; Table 3.4 gives a volume of 35l, which equates to a thickness of ~70 mm</td>
</tr>
<tr>
<td>Height Ullage</td>
<td>25 (mm)</td>
<td>[8]; 500l drums are typically filled to 2.5 to 5 cm from the top, yielding ullage volumes of 12.5 to 25l per package. 25 mm is consistent with [9].</td>
</tr>
<tr>
<td>Diameter Vent / Filter</td>
<td>150 (mm)</td>
<td>assume same as PCM drum [10], and consistent with Drawing M095847 Fairey-Microfiltrex</td>
</tr>
<tr>
<td>Height Filter</td>
<td>8.25 (mm)</td>
<td>Drawing M095847 Fairey-Microfiltrex</td>
</tr>
<tr>
<td>Lid Thickness</td>
<td>3 (mm)</td>
<td>assume same as wall thickness</td>
</tr>
<tr>
<td>Payload</td>
<td>0.466 (m$^3$)</td>
<td>[7]; Table 7.2</td>
</tr>
<tr>
<td>Displacement Volume</td>
<td>0.571 (m$^3$)</td>
<td>[7]; Table 7.2</td>
</tr>
</tbody>
</table>
### A2.3.3 Waste

The package-scale models will consider gas generation due to corrosion of the wastes only. Gas will be generated due to corrosion of the 500l drum as well. However, the wastes will corrode much more rapidly than the drum, and therefore will be the dominant source of gas over the period of interest. Gas generation due to corrosion of the 500l drum will not be included in the models.

Table A2.2 describes the geometry of the waste materials. The waste inventory and corrosion rates are given in Subsection A2.7.

#### Table A2.2 Waste Materials Geometry Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Material</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry</td>
<td>Magnox</td>
<td>plates</td>
<td>[7]; Table E9 for stream 2D38/C</td>
</tr>
<tr>
<td></td>
<td>Uranium</td>
<td>plates</td>
<td>[1]</td>
</tr>
<tr>
<td>Characteristic Dimension</td>
<td>Magnox</td>
<td>plate thickness 0.002 (m)</td>
<td>[7]; Table E9 for stream 2D38/C</td>
</tr>
<tr>
<td></td>
<td>Uranium</td>
<td>plate thickness 0.001 (m)</td>
<td>[1]</td>
</tr>
</tbody>
</table>

### A2.4 Thermal Data

The following temperatures will be assumed for the different stages of the package life:

- Following encapsulation: there may be a temperature spike in the 500l drum associated with curing of the cement encapsulant and exothermic corrosion reactions. (This will not be included in the reference case simulations, but could be considered in variant cases.)
- In a surface store: 15 °C. (It is assumed that the store is not actively heated. 15 °C is a typical temperature for such stores, e.g. [11–14].)
- In an operational vault: 25 °C. (This is consistent with the expected geothermal temperature at 650m depth [see also Appendix 1 in Reference [15].])
- In a GDF following backfilling: the crown space will be backfilled, and the following additional assumptions will be made.
  - At the time of backfilling, the waste package will have been in the vault for 80 yr (see Subsection A2.2).
  - Both the temperature excursions associated with curing of the backfill and radiogenic heating will be accounted for in the models. Table A2.3 gives a typical temperature-time relationship for the package-scale models. This temperature-time relationship is based on Figure 20 of Reference [Error! Bookmark not defined.] at early times and on the analysis in Appendix 1 of Reference [15] at longer times.
Note that corrosion of Magnox is exothermic, and the corrosion rate increases with temperature. However, it is expected that the coupling between exothermic corrosion, the temperature and the corrosion rate will be relatively unimportant [16]. In the first instance, the package-scale models will neglect the coupling, and assume a uniform temperature throughout the waste package and its surrounding backfill; variant cases could investigate the effects of the coupling.

### A2.5 Hydraulic Data

#### A2.5.1 Two-phase Flow

The reference case simulations will assume that the material properties are constant. (Note that backfilling of the vaults will be represented as a change in the material type. Variant cases could consider changes in the material properties, for example gradual cracking of the encapsulant due to expansive corrosion, which would result in an increased permeability; see Subsection A2.8.2.4.)

Intrinsic permeability and porosity values for the various materials are given in Table A2.4.

### Table A2.4 Intrinsic Permeability and Porosity

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Material</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic Permeability</td>
<td>Backfill</td>
<td>$1 \times 10^{-16}$ (m$^2$)</td>
<td>[17]; for intact NRVB</td>
</tr>
<tr>
<td></td>
<td>Encapsulant</td>
<td>$1 \times 10^{-18}$ (m$^2$)</td>
<td>typical value (assumed)</td>
</tr>
<tr>
<td></td>
<td>Capping Grout</td>
<td>$1 \times 10^{-18}$ (m$^2$)</td>
<td>typical value (assumed)</td>
</tr>
<tr>
<td></td>
<td>Filter</td>
<td>$5.3 \times 10^{-11}$ (m$^2$)</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>Ullage</td>
<td>$1 \times 10^{-10}$ (m$^2$)</td>
<td>arbitrary high value</td>
</tr>
<tr>
<td>Porosity</td>
<td>Backfill</td>
<td>0.55 (–)</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>Encapsulant</td>
<td>0.2 (–)</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Capping Grout</td>
<td>0.2 (–)</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Filter</td>
<td>0.87 (–)</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>Ullage</td>
<td>~1.0 (–)</td>
<td></td>
</tr>
</tbody>
</table>

van Genuchten forms [20] of the saturation functions, which are required to model two-phase flow, will be used. Information on the saturation functions is listed in Table A2.5.
Table A2.5  Saturation Functions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Material</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>van Genuchten $P_r$</td>
<td>Backfill</td>
<td>$3.20 \times 10^5$ (Pa)</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>Encapsulant</td>
<td>$1.62 \times 10^6$ (Pa)</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Capping Grout</td>
<td>$1.62 \times 10^6$ (Pa)</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Filter</td>
<td>not specified</td>
<td>model as void – or use the Kelvin equation</td>
</tr>
<tr>
<td></td>
<td>Ullage</td>
<td>not specified</td>
<td>model as void – or use the Kelvin equation</td>
</tr>
<tr>
<td>van Genuchten $m$</td>
<td>Backfill</td>
<td>0.5 (–)</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Encapsulant</td>
<td>0.5 (–)</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Capping Grout</td>
<td>0.5 (–)</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Filter</td>
<td>not specified</td>
<td>model as void</td>
</tr>
<tr>
<td></td>
<td>Ullage</td>
<td>not specified</td>
<td>model as void</td>
</tr>
<tr>
<td>Irreducible Water Saturation $S_{irr}$</td>
<td>Backfill</td>
<td>0.25 (–)</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Encapsulant</td>
<td>0.25 (–)</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Capping Grout</td>
<td>0.25 (–)</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Filter</td>
<td>~0 (–)</td>
<td>model as void</td>
</tr>
<tr>
<td></td>
<td>Ullage</td>
<td>~0 (–)</td>
<td>model as void</td>
</tr>
<tr>
<td>Residual Gas Saturation $S_{gr}$</td>
<td>Backfill</td>
<td>0 (–)</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Encapsulant</td>
<td>0 (–)</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Capping Grout</td>
<td>0 (–)</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td>Filter</td>
<td>0 (–)</td>
<td>assumed</td>
</tr>
<tr>
<td></td>
<td>Ullage</td>
<td>0 (–)</td>
<td>assumed</td>
</tr>
</tbody>
</table>

A2.5.2 Diffusion

A2.5.2.1 Diffusion of Dissolved Gases and Solutes in Water

The effective diffusivity for the diffusion of all dissolved gases and solutes in the pores of the different materials is equal to:

$$D_e = S_w D \phi \tau$$  \hspace{1cm} (A2.1)

where:

- $D_e$ is the effective diffusivity (m²s⁻¹);
- $S_w$ is the saturation of water (–);
- $D$ is the free water diffusivity (m²s⁻¹);
- $\phi$ is the porosity (–); and
- $\tau$ is the tortuosity (–).

The free water diffusivity depends on temperature according to:
\[ D = \frac{AT}{\mu} \]  
(A2.2)

where:

- \( A \) is a constant \( (N \text{ K}^{-1}) \);
- \( T \) is the temperature (K); and
- \( \mu \) is the viscosity of water (\( \text{Pa s} \)), which also varies with temperature.

The constant \( A \) is equal to:

- \( 1.57 \times 10^{-14} \) (N K\(^{-1}\)) for \( \text{H}_2 \)
- \( 5.97 \times 10^{-15} \) (N K\(^{-1}\)) for \( \text{O}_2 \)
- \( 5.61 \times 10^{-15} \) (N K\(^{-1}\)) for \( \text{N}_2 \)

For Cl\(^-\), the free water diffusivity is equal to \( 2.09 \times 10^{-9} \text{ m}^2\text{s}^{-1} \) at 25 °C [22].

The diffusivity also depends on the tortuosity of the various materials (see Equation A2.1); tortuosity values are listed in Table A2.6.

### Table A2.6 Tortuosity

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Material</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tortuosity</td>
<td>Backfill</td>
<td>0.15 (–)</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>Encapsulant</td>
<td>0.013 (–)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Capping Grout</td>
<td>0.013 (–)</td>
<td>this tortuosity gives the ( D_e ) for structural concrete in Reference [24], assuming a porosity of 0.2</td>
</tr>
<tr>
<td></td>
<td>Filter</td>
<td>1 (–)</td>
<td>assumed</td>
</tr>
<tr>
<td></td>
<td>Ullage</td>
<td>1 (–)</td>
<td>assumed</td>
</tr>
</tbody>
</table>

#### A2.5.2.2 Diffusion of Gases in Gas Phase

The effective diffusivity for the diffusion of gaseous components in unsaturated pores of the different materials is equal to:

\[ D_e = D \left( \frac{P_0}{P} \right) \left( \frac{T}{T_0} \right)^\zeta \phi \tau \]  
(A2.3)

where:

- \( D_e \) is the effective diffusivity of a gas component (m\(^2\text{s}^{-1}\));
- \( D \) is the diffusivity of the component in the gas phase (m\(^2\text{s}^{-1}\); e.g. for water vapour in H\(_2\), \( D = 9.5 \times 10^{-5} \text{ m}^2\text{s}^{-1} \) [25]);
- \( P \) is the pressure (Pa);
- \( P_0 \) is the reference pressure (Pa; e.g. \( P_0 = 1 \times 10^5 \) Pa);
- \( T \) is the temperature (K);
- \( T_0 \) is the reference temperature (K; e.g. \( T_0 = 293 \)K);
- \( \phi \) is the porosity (–); and
- \( \tau \) is the tortuosity (–).
Note that the exponent on the ratio of temperatures, i.e. 1.75, is a generic value.

The reference case simulations will consider only H₂. Air that is present in the waste package at the time of backfilling will be replaced with H₂. Variant calculations could consider the gas phase to be a mixture of components: H₂, O₂ and N₂. This would be particularly important when considering uranium metal wastes, because the rate of uranium corrosion will depend on the presence of O₂. If $P_0 = 1 \times 10^5$ Pa and $T_0 = 293$K, then the diffusivities of the various components in the gas phase will be:

- $7.82 \times 10^{-5}$ (m²s⁻¹) for H₂
- $2.02 \times 10^{-5}$ (m²s⁻¹) for O₂
- $2.02 \times 10^{-5}$ (m²s⁻¹) for N₂
- $2.36 \times 10^{-5}$ (m²s⁻¹) for water vapour in air

### A2.5.3 Solubility of Gases

The gaseous components will dissolve in the porewater according to Henry’s law. Henry’s law constants are given in Table A2.7.

#### Table A2.7  Henry’s Law Constants

<table>
<thead>
<tr>
<th>Gaseous Component</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (at 20 °C)</td>
<td>$1.455 \times 10^{-5}$ mol fraction atm⁻¹ = $8.08 \times 10^{-6}$ mol m⁻³ Pa⁻¹</td>
<td>[26]</td>
</tr>
<tr>
<td>H₂ (at 35 °C)</td>
<td>$1.350 \times 10^{-5}$ mol fraction atm⁻¹ = $7.49 \times 10^{-6}$ mol m⁻³ Pa⁻¹</td>
<td>[26]</td>
</tr>
<tr>
<td>O₂ (at 20 °C)</td>
<td>$2.501 \times 10^{-5}$ mol fraction atm⁻¹ = $1.39 \times 10^{-6}$ mol m⁻³ Pa⁻¹</td>
<td>[26]</td>
</tr>
<tr>
<td>O₂ (at 35 °C)</td>
<td>$1.982 \times 10^{-5}$ mol fraction atm⁻¹ = $1.10 \times 10^{-6}$ mol m⁻³ Pa⁻¹</td>
<td>[26]</td>
</tr>
<tr>
<td>N₂ (at 20 °C)</td>
<td>$1.274 \times 10^{-5}$ mol fraction atm⁻¹ = $6.97 \times 10^{-6}$ mol m⁻³ Pa⁻¹</td>
<td>[26]</td>
</tr>
<tr>
<td>N₂ (at 35 °C)</td>
<td>$1.047 \times 10^{-5}$ mol fraction atm⁻¹ = $5.70 \times 10^{-6}$ mol m⁻³ Pa⁻¹</td>
<td>[26]</td>
</tr>
</tbody>
</table>

### A2.5.4 Initial and Boundary Conditions

Both the grout inside the waste package and the cement backfill will be water saturated when they are poured, but will dry as the cement cures due to uptake of water by mineral formation. This chemical process will not be included in the reference case simulations, but will be taken into account when specifying the initial water saturations of these materials. Variant cases could consider curing of the cement materials, which would result in changes to the permeability, porosity, and water content (see Subsection A2.9.3).

Table A2.8 lists the initial water saturations.
During storage, the relative humidity (RH) in the store will be the boundary condition for the package-scale models. (From the Kelvin equation, this is equivalent to specifying the capillary pressure at the boundary of the model.) RH values in a surface store and then an operational vault are given in Table A2.9.

**Table A2.9 Relative Humidity Boundary Condition**

<table>
<thead>
<tr>
<th>Location</th>
<th>RH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Store</td>
<td>70%</td>
<td>based on typical values:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>▪ for stores that are passively or naturally ventilated [11]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>▪ inside concrete storage tubes at B55, Winfrith [12]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>▪ for the atmosphere inside experimental 4m box [13]</td>
</tr>
<tr>
<td>Operational Vault in GDF</td>
<td>70%</td>
<td>assumed (required to prevent corrosion of steel containers)</td>
</tr>
</tbody>
</table>

It is assumed that the RH close to a waste package will be controlled by the ventilation until the level of the backfill reaches the top of the waste package. After the backfill reaches the top of the waste stacks, the ventilation will be turned off to allow the crown space to be backfilled, and the RH will increase to 100%. Backfilling the crown space may take 1 month, but, for modelling purposes, it will be assumed to be instantaneous.

Post-closure, the porewater pressure in the backfill will increase with time as water flows from the host rock into the vault. It is assumed that the pressure in the backfill will return to the in situ hydrostatic pressure over a period of 5 years. In the package-scale models this will be specified as a boundary condition at the top of the vault, i.e. the pressure should increase from one atmosphere, when the ventilation is turned off, to $6.5 \times 10^5$ Pa (corresponding to a GDF at an assumed depth of approximately 650m overlain by non-saline water) by 5 yr later.

**A2.6 Mechanical Data**

It will be assumed that the porous materials are incompressible.

**A2.7 Chemical Data**

**A2.7.1 Waste Inventory**

The 2007 Derived Inventory [7] gives the packaged volume of waste stream 2D38/C as $12,142.3$ m$^3$ (see Table 5.6 in Reference [7]), which contains 3,580.16 tonnes of Magnox alloy (see Table E9 in Reference [7]).
The underlying waste stream datasheet states that currently there are 14,338 packages, which have a packaged volume of 8,187.1 m$^3$. Including future arisings, the total conditioned waste volume is 12,142.3 m$^3$ (in agreement with Reference [7]) and the associated packaged volume is 14,207.5 m$^3$. Extrapolating from the current number of packages, this implies that there will be 24,881 packages. The average inventory of Magnox alloy per package is 143.9 kg. This inventory will be rounded to 150 kg in the package-scale models. The waste stream datasheet also states that approximately 1.4 %wt of the package contents will be uranium. These inventory data are summarised in Table A2.10.

### Table A2.10 Inventory of Reactive Metals in a 500L Drum

<table>
<thead>
<tr>
<th>Material</th>
<th>Density</th>
<th>500l Drum Inventory</th>
<th>500l Drum Inventory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnox Alloy</td>
<td>1738 (kg m$^{-3}$)</td>
<td>~150 (kg)</td>
<td>6170 (mol)</td>
</tr>
<tr>
<td>Uranium Metal</td>
<td>18950 (kg m$^{-3}$)</td>
<td>~12.6 (kg)</td>
<td>53 (mol)</td>
</tr>
</tbody>
</table>

### A2.7.2 Corrosion

The Magnox alloy and uranium metal will corrode. The relevant corrosion reactions are shown in Table A2.11.

### Table A2.11 Corrosion Reactions

<table>
<thead>
<tr>
<th>Material</th>
<th>Conditions</th>
<th>Corrosion Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnox Alloy</td>
<td>Oxic</td>
<td>As anoxic</td>
<td>[27]</td>
</tr>
<tr>
<td>Uranium Metal</td>
<td>Oxic</td>
<td>$U + \frac{1}{2} (2+x) O_2 \Rightarrow UO_{2+x}$</td>
<td>[27]</td>
</tr>
<tr>
<td>Magnox Alloy</td>
<td>Anoxic</td>
<td>$Mg + 2H_2O \Rightarrow Mg(OH)_2 + H_2$</td>
<td>[27]</td>
</tr>
<tr>
<td>Uranium Metal</td>
<td>Anoxic</td>
<td>$U + (2+x) H_2O \Rightarrow UO_{2+x} + (2+x) H_2$</td>
<td>[27]</td>
</tr>
</tbody>
</table>

A period of acute corrosion may follow encapsulation of the wastes, or a disturbance of the waste package (e.g. during transport). However, this is unlikely to dominate the total amount of corrosion (or the volume of gas produced). Therefore, acute corrosion will not be included in the simulations.

The package-scale models will use the relationship between Magnox corrosion rate and temperature derived for the SMOGG gas generation model [27]. The corrosion rate also will depend on the concentration of chloride.

### Table A2.12 Chronic Corrosion Rates

<table>
<thead>
<tr>
<th>Material</th>
<th>Value at high pH, 35 °C</th>
<th>Value at high pH, 50 °C</th>
<th>Value at high pH, 80 °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnox Alloy (low Cl)</td>
<td>$7.8 \times 10^{-7}$ (m yr$^{-1}$)</td>
<td>$4.3 \times 10^{-6}$ (m yr$^{-1}$)</td>
<td>$8.4 \times 10^{-5}$ (m yr$^{-1}$)</td>
<td>[27]</td>
</tr>
<tr>
<td>Magnox Alloy (high Cl)</td>
<td>$7.8 \times 10^{-5}$ (m yr$^{-1}$)</td>
<td>$4.3 \times 10^{-4}$ (m yr$^{-1}$)</td>
<td>$8.4 \times 10^{-3}$ (m yr$^{-1}$)</td>
<td>[27]</td>
</tr>
<tr>
<td>Uranium Metal (oxic)</td>
<td>$7.3 \times 10^{-6}$ (m yr$^{-1}$)</td>
<td>$3.0 \times 10^{-5}$ (m yr$^{-1}$)</td>
<td>$3.4 \times 10^{-4}$ (m yr$^{-1}$)</td>
<td>[27]</td>
</tr>
<tr>
<td>Uranium Metal (anoxic)</td>
<td>$2.6 \times 10^{-4}$ (m yr$^{-1}$)</td>
<td>$8.6 \times 10^{-4}$ (m yr$^{-1}$)</td>
<td>$7.0 \times 10^{-3}$ (m yr$^{-1}$)</td>
<td>[27]</td>
</tr>
</tbody>
</table>
A metal will corrode under anaerobic conditions only when free water is available to support the reaction. For metals that are encapsulated in grout, it is presumed that corrosion will proceed while there is free liquid water present, in other words, while the water saturation is greater than the irreducible saturation. Therefore, the package-scale models should couple corrosion to the water saturation. If the water saturation falls to the irreducible saturation, then both the flow of liquid water and corrosion should stop.

### A2.7.3 Chloride

The rate of Magnox corrosion is very sensitive to the presence of chloride. Once the vault has been backfilled, chloride that is dissolved in the groundwater may be transported into the 500l drums, thereby increasing the corrosion rate.

In those calculations that include chloride, the concentration of chloride will be taken to be 20,000 ppm, which is a typical concentration for seawater and also for the groundwater in some higher-strength rocks at coastal locations (see Appendix 1.1).

### A2.8 Additional Parameterisation for Quintessa Modelling

This subsection gives some additional information relevant to Quintessa’s package-scale models.

#### A2.8.1 Representation of the Ullage

Quintessa found that their simulated drying of the encapsulant / capping grout during storage was influenced significantly by the treatment of vapour transport through the ullage / filter, and hence the relative humidity in the ullage. Two different treatments were investigated (see Appendix 3):

- Assume that the atmosphere in the ullage and the atmosphere in the surface store / GDF operational vault are well mixed, and therefore have the same relative humidity. This gave a conservative prediction of the extent of drying of the encapsulant / capping grout.

- Assume that the relative humidity in the ullage / filter is higher than in the atmosphere outside the drum. This was simulated by specifying an appropriate effective capillary curve for the ullage space / filter: van Genuchten \( P_r = 10^3 \) Pa; van Genuchten \( m = 0.7 \); irreducible water saturation \( S_{irr} = 0.001 \).

#### A2.8.2 Parameterisation of the Variant Cases

A number of variant cases were investigated, and these are listed in Table A2.13 below.
Table A2.13  Key to the Variant Cases Considered by Quintessa

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 0</td>
<td>As described in this appendix, but with zero suction in the ullage / filter</td>
</tr>
<tr>
<td>Case 1a</td>
<td>As described in this appendix, but with the RH in the ullage fixed pre-backfilling</td>
</tr>
<tr>
<td>Case 1b</td>
<td>As described in this appendix, but the RH in the ullage was calculated pre-backfilling</td>
</tr>
<tr>
<td>Case 1c</td>
<td>As described in this appendix, and the relative permeability of the ullage / filter was set to unity for water and gas (rather than varying linearly with the water saturation)</td>
</tr>
<tr>
<td>Case 2a</td>
<td>As described in this appendix, but the Magnox corrosion rate increased linearly during the first 5 years post-backfilling, until it was 15× higher than in Case 1a</td>
</tr>
<tr>
<td>Case 2b</td>
<td>As described in this appendix, but the Magnox corrosion rate increased linearly during the first 5 years post-backfilling, until it was 100× higher than in Case 1a</td>
</tr>
<tr>
<td>Case 3</td>
<td>As in Case 1a, but with the addition of chloride transport</td>
</tr>
<tr>
<td>Case 4</td>
<td>As in Case 3, but with an alternative vault backfill material</td>
</tr>
<tr>
<td>Case 5</td>
<td>As in Case 3, but with a crack around the capping grout</td>
</tr>
<tr>
<td>Case 6</td>
<td>As in Case 3, but with evolving encapsulant / capping grout properties (representing cracking of the encapsulant / grout as corrosion proceeds)</td>
</tr>
<tr>
<td>Case 7a</td>
<td>As in Case 3, but the peak temperature associated with curing of the backfill is 5 °C hotter</td>
</tr>
<tr>
<td>Case 7b</td>
<td>As in Case 3, but the peak temperature associated with curing of the backfill is 10 °C hotter</td>
</tr>
<tr>
<td>Case 7c</td>
<td>As in Case 3, but the peak temperature associated with curing of the backfill is 15 °C hotter</td>
</tr>
<tr>
<td>Case 7d</td>
<td>As in Case 3, but the peak temperature associated with curing of the backfill is 20 °C hotter</td>
</tr>
<tr>
<td>Case 7e</td>
<td>As in Case 3, but the peak temperature associated with curing of the backfill is 20 °C hotter, and it remains hot thereafter</td>
</tr>
</tbody>
</table>

A2.8.2.1 Chloride Transport

Some variant cases included chloride. The parameters that characterised chloride transport in the Quintessa package-scale models are given in Table A2.14.

Table A2.14  Parameters for Chloride Transport

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Water Diffusivity</td>
<td>2.09 $10^{-9}$ (m$^2$s$^{-1}$)</td>
<td>[22]; value at 25 °C</td>
</tr>
<tr>
<td>Longitudinal Dispersivity</td>
<td>0.6535 (m)</td>
<td>assumed</td>
</tr>
<tr>
<td>Transverse Dispersivity</td>
<td>0.06535 (m)</td>
<td>assumed</td>
</tr>
</tbody>
</table>

A2.8.2.2 Case 4 – Alternative Vault Backfill

The backfill properties in the reference case simulations are based on Nirex Reference Vault Backfill; a variant case considered the use of Nagra mortar type M1 instead (see Table A2.15).
### Table A2.15  Parameters for Alternative Vault Backfill

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic Permeability</td>
<td>$4 \times 10^{-12}$ (m$^2$)</td>
<td>[28]</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.25 (--)</td>
<td>see Table A.5 in Reference [29]</td>
</tr>
<tr>
<td>van Genuchten $P_r$</td>
<td>$4 \times 10^3$ (Pa)</td>
<td>see Table 3-5 in Reference [30]</td>
</tr>
<tr>
<td>van Genuchten $m$</td>
<td>0.5 (--)</td>
<td>see Table A.5 in Reference [30]</td>
</tr>
<tr>
<td>Irreducible Water Saturation $S_{irr}$</td>
<td>0.3 (--)</td>
<td>see Table A.5 in Reference [30]</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>0.15 (--)</td>
<td>unchanged from NRVB</td>
</tr>
</tbody>
</table>

#### A2.8.2.3 Case 5 – Cracked Capping Grout

In this variant case, there is assumed to be a small shrinkage crack between the capping grout and container, which allows water to flow more easily into the encapsulant. Rather than modelling the crack explicitly, the sensitivity to greater availability of water is explored by increasing the permeability of the capping grout. The shrinkage crack (see Figure A2.3) is assumed to have an aperture (a) of 0.1 mm. This aperture was selected on the basis that a larger crack aperture would give an effective permeability that implies the capping grout provides essentially no resistance to flow, which would not be consistent with the conceptual model to be explored in this variant case.

![Figure A2.3 Illustration of Shrinkage Crack](image)

The permeability of the capping grout plus the shrinkage crack is equal to:

$$k = \frac{k_cA_c + T_f}{A} \tag{A2.4}$$

where:

- $k$ is the effective permeability of the capping grout plus crack (m$^2$);
\( k_c \) is the permeability of the capping grout \((\text{m}^2)\);  
\( A_c \) is the cross-sectional area of the capping grout \((\text{m}^2)\);  
\( T_f \) is the transmissivity of the shrinkage crack \((\text{m}^3)\); and  
\( A \) is the cross-sectional area of the 500l drum \((\text{m}^2)\); this is almost identical to the cross-sectional area of the capping grout).

The transmissivity of the shrinkage crack per metre crack width, \( T \,(\text{m}^3) \), is equal to [30]:

\[
T = \frac{a^3}{12} \tag{A2.5}
\]

where:  
\( a \) is the crack aperture \((\text{m})\).

Then:

\[
T_f = T \cdot w \tag{A2.6}
\]

where:  
\( w \) is the crack width \((\text{m})\).

The permeability of the capping grout is \(1 \times 10^{-18} \text{ m}^2\) (see Table A2.4) and the internal radius of the drum is 0.3675m (see Table A2.1). Therefore, the effective permeability of the capping grout plus a 0.1 mm aperture crack will be \(4.54 \times 10^{-13} \text{ m}^2\).

It will be much easier for gas to migrate through the crack than the capping grout. Therefore, the gas entry pressure \((\text{van Genuchten } P_r)\) of the capping grout will also be reduced. The average permeability of the capping grout plus crack is calculated to be comparable to that of Nagra mortar type M1 (see Table A2.15), so the same gas entry pressure is assumed here, i.e. \(4 \times 10^3\) Pa.

### A2.8.2.4 Case 6 – Evolving Encapsulant / Capping Grout

Magnox corrosion is an expansive reaction (i.e. the Magnox corrosion product occupies a larger volume than the original metal alloy). As corrosion proceeds the encapsulant / capping grout may crack, increasing the permeability and decreasing the gas entry pressure. In this variant case, the properties of the encapsulant / capping grout are assumed to evolve from initial to degraded values as a function of the amount of Magnox alloy that has corroded.

The properties of the encapsulant are calculated for each numerical model compartment, based on the fraction of Magnox alloy in that compartment that has corroded. Although there is no Magnox alloy in the capping grout, it still may be cracked by expansion of the underlying encapsulant. Degradation of the capping grout is assumed to be proportional to the fraction of total Magnox in the drum that has corroded. (This is less arbitrary than linking degradation of the capping grout to an assumed expansion of the immediately underlying encapsulant compartments.)

Table A2.16 gives the properties of intact and cracked encapsulant / capping grout that are assumed for this variant case. The properties of the cracked encapsulant / cracking grout are based on Nagra mortar type M1, which has hydraulic properties akin to a degraded structural concrete, and a much higher permeability and lower gas entry pressure than intact encapsulant / capping grout.

Although the encapsulant / capping grout are assumed to be damaged by cracking, there is assumed to be no significant change in the porosity. (This would imply a change in pore geometry, which is considered unlikely given that there is only physical degradation and little chemical degradation, i.e. limited leaching, carbonation.) Likewise, there is assumed to be no change in the residual water and gas saturations.
Table A2.16  Properties of the Intact and Cracked Encapsulant / Capping Grout

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Intact Value (see earlier)</th>
<th>Cracked Value</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic Permeability</td>
<td>$1 \times 10^{-18} , (m^2)$</td>
<td>$4 \times 10^{-12} , (m^2)$</td>
<td>increase linearly with cracking</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.2 (–)</td>
<td>0.2 (–)</td>
<td>assume no significant increase (that would imply a change in pore geometry)</td>
</tr>
<tr>
<td>van Genuchten $P_r$</td>
<td>$1.62 \times 10^6 , (Pa)$</td>
<td>$4 \times 10^3 , (Pa)$</td>
<td>Reduction consistent with cracking</td>
</tr>
<tr>
<td>van Genuchten $m$</td>
<td>0.5 (–)</td>
<td>0.5 (–)</td>
<td>assume no change</td>
</tr>
<tr>
<td>Irreducible Water Saturation $S_{irr}$</td>
<td>0.25 (–)</td>
<td>0.25 (–)</td>
<td>assume no change</td>
</tr>
</tbody>
</table>

It is necessary to describe how the permeability and gas entry pressure evolve as the encapsulant / capping grout are degraded by the expansive corrosion of Magnox alloy. It is assumed that:

- The crack permeability is much greater than the matrix permeability, so that all of the permeability is provided by the cracks.
- The expansive corrosion of Magnox alloy results in one crack in the encapsulant for each piece of metal.
- As corrosion proceeds, the crack aperture increases, and hence so does the permeability.
- The crack aperture increases linearly with the amount of corrosion.
- The spacing between cracks is of the order 1 cm (based roughly on the number of pieces of Magnox swarf in a drum, as illustrated by Figure A2.2; note that that figure shows a pre-production drum, in which there was much more settling than would be the case for a production drum).

The permeability of the cracks is equal to:

$$k = \frac{a^3}{125}$$  \hspace{1cm} (A2.7)

where:
- $k$ is the effective permeability of the cracks ($m^2$);
- $a$ is the crack aperture ($m$); and
- $S$ is the crack spacing ($m$).

Table A2.17 shows how the crack aperture and the permeability of the cracks are calculated to evolve with time. The crack apertures have been chosen to give permeabilities of $1 \times 10^{-18} \, m^2$ and $4 \times 10^{-12} \, m^2$, for 0% and 100% Magnox corroded respectively (see Table A2.16). Then, the crack aperture has been interpolated linearly between these two values in proportion to the fraction of Magnox alloy corroded. The permeability increases rapidly as the cracks begin to form, but then increases more slowly as the cracks open. The crack permeability rapidly becomes much greater than the matrix permeability.

It is assumed that the gas entry pressure will evolve oppositely to the permeability, so that it decreases rapidly as the cracks form, and then decreases more slowly as the fractures open.
### Table A2.17 Evolution of Permeability and Gas Entry Pressure with Fraction of Magnox Corroded

<table>
<thead>
<tr>
<th>Fraction of Magnox Corroded (–)</th>
<th>Crack Aperture (m)</th>
<th>Permeability (m²)</th>
<th>van Genuchten $P_r$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$4.94 \times 10^7$</td>
<td>$1.00 \times 10^{-18}$</td>
<td>$1.62 \times 10^6$</td>
</tr>
<tr>
<td>0.1</td>
<td>$8.27 \times 10^6$</td>
<td>$4.72 \times 10^{-15}$</td>
<td>$7.21 \times 10^5$</td>
</tr>
<tr>
<td>0.2</td>
<td>$1.61 \times 10^5$</td>
<td>$3.45 \times 10^{-14}$</td>
<td>$5.09 \times 10^5$</td>
</tr>
<tr>
<td>0.3</td>
<td>$2.38 \times 10^5$</td>
<td>$1.13 \times 10^{-13}$</td>
<td>$3.83 \times 10^5$</td>
</tr>
<tr>
<td>0.4</td>
<td>$3.16 \times 10^5$</td>
<td>$2.63 \times 10^{-13}$</td>
<td>$2.93 \times 10^5$</td>
</tr>
<tr>
<td>0.5</td>
<td>$3.94 \times 10^5$</td>
<td>$5.10 \times 10^{-13}$</td>
<td>$2.23 \times 10^5$</td>
</tr>
<tr>
<td>0.6</td>
<td>$4.72 \times 10^5$</td>
<td>$8.75 \times 10^{-13}$</td>
<td>$1.66 \times 10^5$</td>
</tr>
<tr>
<td>0.7</td>
<td>$5.50 \times 10^5$</td>
<td>$1.38 \times 10^{-12}$</td>
<td>$1.17 \times 10^5$</td>
</tr>
<tr>
<td>0.8</td>
<td>$6.27 \times 10^5$</td>
<td>$2.06 \times 10^{-12}$</td>
<td>$7.47 \times 10^4$</td>
</tr>
<tr>
<td>0.9</td>
<td>$7.05 \times 10^5$</td>
<td>$2.92 \times 10^{-12}$</td>
<td>$3.47 \times 10^4$</td>
</tr>
<tr>
<td>1</td>
<td>$7.83 \times 10^5$</td>
<td>$4.00 \times 10^{-12}$</td>
<td>$4.00 \times 10^3$</td>
</tr>
</tbody>
</table>

### A2.9 Additional Parameterisation for AMEC Modelling

This subsection lists some additional data that were used in AMEC’s package-scale models.

#### A2.9.1 Multi-component Gas Mixture

AMEC used the computer program TOUGH2v2 [31-33] to simulate the flows of porewater and gases around the 500l drum assuming a two-dimensional, axi-symmetric geometry. In TOUGH2v2, the flow of each phase is modelled using mass conservation and a modified form of Darcy’s Law (with the two-phase nature of the flow taken into account through a relative permeability function).

In the past, AMEC has adapted the “EOS7R” fluid property module [34] of TOUGH2v2, so that the computer program can model the bulk gases hydrogen ($H_2$), oxygen ($O_2$) and nitrogen ($N_2$), in addition to water.

Using this modified fluid property module, AMEC’s package-scale model was able to consider the gas phase to be a mixture of components ($H_2$, $O_2$ and $N_2$)\(^{44}\).

\(^{44}\) Quintessa’s simulations considered only a single component ($H_2$; the air that was present in the waste package at the time of backfilling was replaced with $H_2$). Although QPAC, the computer program used by Quintessa, is able to model multi-component gas mixtures, it was decided that the additional complexity was not justified for cases with no uranium metal.
The more extensive set of multi-component, two-phase flow and transport processes is needed particularly when taking account of uranium metal that could be present in the waste, because the rate of uranium corrosion will depend on the availability of \( \text{O}_2 \).

### A2.9.2 Representation of the Ullage

Figure A2.4 shows the numerical grid that was used to discretise the ullage in the AMEC package-scale model.

![Figure A2.4](image)

**Figure A2.4** Plot showing a close-up view of the numerical grid in the region around the package vent (the ullage is 50 mm high, and the capping grout is 100 mm high)

Three alternative representations of the ullage were investigated. In all of the cases, the intrinsic permeability and porosity of the filter / ullage were as specified in Table A2.4.

- First, in the reference case simulation, the ullage was modelled as a void that allowed fluids (i.e. both water and gas) to migrate freely through it. This was achieved by:
  - Using a van Genuchten model for the capillary pressure function in the ullage (with van Genuchten \( P_r = 10^2 \) Pa; van Genuchten \( m = 0.333 \); irreducible water saturation \( S_{irr} = 0 \); and residual gas saturation \( S_{gr} = 0 \)); and by
  - Setting both the relative permeability functions (i.e. for the liquid and the gas) to unity.
- Secondly, in a variant case, the ullage was modelled as a void that could pressurise with gas, and thereby prevent further ingress of porewater. This was achieved by:
Modifying the capillary pressure function in the ullage (a linear extrapolation was used for liquid saturations below 0.2, in order to prevent the capillary pressure from decreasing towards negative infinity as the liquid saturation in the ullage approached zero); and by

- Using a linear relative permeability function for the liquid phase in the ullage, so that water would stop flowing through the ullage as the void filled with gas (the relative permeability function for the gas phase was still set to unity).

Thirdly, in another variant case, it was assumed that the ullage was filled with capping grout (i.e. there was no void at the top of the waste package).

It may be worth adding that during storage, the RH in the store was implemented as a boundary condition outside the waste package, and the RH in the ullage was computed to be very similar to the RH in the store. This behaviour is as expected, but is different to that found in some of the Quintessa package-scale models (see Appendix 3), where there were numerical difficulties with transferring the value of the RH from the store into the ullage.

### A2.9.3 Curing of the Backfill

The permeability, the porosity and the degree of saturation of a cement backfill will evolve as the backfill sets and hardens. Previously, a numerical model has been developed for the curing of a candidate cement backfill (i.e. Nirex Reference Vault Backfill; [35]), which accounts for the evolution of these material properties [17].

This numerical model was incorporated into AMEC’s package-scale model, in order to investigate the interactions between a waste package and its surrounding backfill during the process of curing.

### A2.9.4 Chloride Transport

The AMEC package-scale model was able to make use of information from the review of literature about chloride transport through cement materials presented in Appendix 1.3.3. The Quintessa numerical modelling was performed before the review, and therefore used the data presented earlier in this appendix. Both modelling teams made simple and conservative assumptions about the timescale on which chloride would reach the boundary of the model domain.

In the AMEC model, chloride transport was modelled as an advection-diffusion process, and:

- The effective diffusion coefficient of chloride in the saturated grout was $3 \times 10^{-13}$ m$^2$s$^{-1}$, and there was also a retardation factor of 4.5 due to sorption.
- The effective diffusion coefficient of chloride in the cement backfill was $3.4 \times 10^{-11}$ m$^2$s$^{-1}$, and there was a retardation factor of about 2.5 due to sorption.

In the Quintessa model, on the other hand, chloride transport was modelled as an advection-dispersion process, and:

- The effective diffusion coefficient of chloride in the saturated grout was $5.4 \times 10^{-12}$ m$^2$s$^{-1}$. Mechanical dispersion was modelled as well, with a longitudinal dispersivity of 0.6535m, but sorption was not included.

---

In the Quintessa model, the boundary conditions were:

- A fixed concentration of chloride (i.e. 20,000 ppm) on the top boundary for a period of five years post closure, while the vault re-saturated though only the top boundary (the package is assumed to be at the top of a waste stack); followed by
- A change to upwards flow through the vault, with the fixed concentration of chloride being applied on the bottom boundary of the model as well.

In the AMEC model, there was no imposed groundwater flow through the vault following re-saturation, and the concentration of chloride (i.e. 20,000 ppm) was fixed on the top boundary of the model from six years after closure. As shown by the later work reported in Appendix 1, these are considered to be cautious model setups (i.e. in reality, it will take much longer for chloride to migrate into the vicinity of a waste package).
Note that in the Quintessa model, the transport velocity behind the chloride front would have increased to about $3.9 \times 10^9$ m s$^{-1}$ following the ingress of chloride to the waste package (see the discussion in Appendix 1.5.1). Therefore, the longitudinal dispersion coefficient in the grout would be about $2.5 \times 10^9$ m$^2$s$^{-1}$, which is much larger than the effective diffusion coefficient used by AMEC in their model.

- The effective diffusion coefficient of chloride in the cement backfill was $1.7 \times 10^{-10}$ m$^2$s$^{-1}$.

- Mechanical dispersion, but not sorption, was also modelled.

In the Quintessa model, the transport velocity in the backfill between the packages would be about $2.25 \times 10^{-10}$ m s$^{-1}$ (see Appendix 3.3.6; and note that most of the pressure drop is over the height of the waste package, because that is the locale of most of the flow resistance). Therefore, the longitudinal dispersion coefficient in the backfill would be about $3.2 \times 10^{-10}$ m$^2$s$^{-1}$, which is larger than the effective diffusion coefficient used in the AMEC model.

Comparing the AMEC and Quintessa models, the differences between the effective diffusion coefficients can be largely explained as being due to AMEC taking proper account of the processes of anion exclusion and sorption (see Appendix 1.3.3). However, a noteworthy discrepancy between the two models is that Quintessa also chose to include a large amount of mechanical dispersion in their model, and as a result chloride spreads more quickly throughout the waste package in their simulations (see Appendix 3).

### A2.10 References


# Appendix 3
Quintessa Package-scale Modelling

## Contents

- Introduction
- Conceptual Model
- Numerical Model
- Application of the Model
- Variant Cases
- Summary and Conclusions
- References
A3 Quintessa Package-scale Modelling

A3.1 Introduction

The generation of carbon-14 bearing gases within a geological disposal facility (GDF) is a potential issue for the safety case of the facility. Whilst hydrogen is likely to be the predominant gas generated within the facility, smaller amounts of carbon-14 gases such as methane and carbon dioxide may also be generated, and will be transported with the bulk gas.

One potential source of hydrogen is the corrosion of reactive metals (e.g. Magnox) disposed of in a GDF. The work reported herein is a numerical modelling study that investigates the rate at which hydrogen could be generated by corrosion of Magnox metal in a waste package, and the flux of this gas out of the waste package.

A3.1.1 Scope and Objectives

This study aims to improve understanding of the controls on the rate of hydrogen generation, and the flux of bulk gas out of a single waste package containing Magnox metal. It is intended to provide input to assessments of the risk resulting from the release of carbon-14 gas from waste packages containing reactive metals. The models presented are intended to scope out the range of likely behaviours, for example determining whether water availability could limit the rate of gas generation, and, if so, under what conditions. As such, the models are designed to be as simple as is commensurate with providing useful information, and were developed progressively during the study to investigate a wide range of Features, Events and Processes (FEPs) of interest.

Given the importance of this issue to the safety case, two different numerical implementations of the conceptual model were developed to build confidence in the results. Quintessa were tasked with implementing the model in QPAC, whilst AMEC were to implement the model in TOUGH2. This appendix details the conceptual model agreed by both teams, and then goes on to discuss the numerical modelling done by Quintessa. Note that this work was carried out before the analysis of vault-scale flows reported in Appendix 1, and also the AMEC modelling reported in Appendix 4.

The objectives of this work are:

- To build a numerical model of gas generation and migration in a waste package containing Magnox swarf throughout its entire life (in a surface store, and then in a GDF during the operational period, backfilling and post-closure).
- To use the model to explore which processes and parameters have a significant influence on the rate at which gas is generated in and released from the waste package.

Different waste packages within a vault in the GDF will experience different conditions at different times; this will not be considered in the numerical model, which represents a single waste package. Only the bulk gas flux is considered in the Quintessa model, but carbon-14 gas release could be estimated from this flux and the carbon-14 inventory in the waste package.

A3.1.2 Structure of this Appendix

This appendix is structured as follows:

- The conceptual model is introduced in Subsection A3.2;
- The basic numerical model is described in Subsection A3.3, including the mathematical model for gas generation;
- Results for the initial numerical models are presented in Subsection A3.4, followed by a description of the development of the model to include the transport of chloride;
- A series of variant cases are discussed in Subsection A3.5; and
Lastly, Subsection A3.6 summarises the work and draws some conclusions.

### A3.2 Conceptual Model

#### A3.2.1 Timescales

The lifetime of one waste package is considered, starting immediately after the waste has been encapsulated at the Magnox Encapsulation Plant (MEP) at Sellafield. The MEP was commissioned in 1990 [1] and processing of Magnox is scheduled to be completed in 2021, so 2005 represents the mid-point of the processing at MEP and is assumed to be the start date of the model.

Assuming emplacement of the package within the GDF occurs between 2040 and 2090, and backfilling occurs between 2140 and 2150 (see Table 4-1 in Reference [2]), the different conditions the package experiences are:

- **0 – 60 years**: The waste is in an above ground store that is passively or naturally ventilated [3] at a temperature of 15 °C and a relative humidity of 70% (see Appendix 2 in Reference [3], and [4-6]).

- **60 – 140 years**: The waste is stored in the GDF in an open vault which is assumed to be ventilated at 70% relative humidity to prevent steel corrosion. The temperature is 25 °C, consistent with the expected geothermal temperature at 650m depth [see Appendix 1 of 7].

- **140 years**: The vault is backfilled with a cement material.

- **140 – 146 years**: The vault re-saturates and re-pressurises over a period of 5 years, which is assumed to be representative of the time for re-saturation in a vault constructed in higher strength rock [8]; the temperature spike associated with backfill curing lasts 6 years [Error! Bookmark not defined.].

- **146 years onwards**: The temperature of the vault moves to its long term average of about 30 °C (this is slightly less, i.e. 5 °C cooler, than has been used elsewhere in the Integrated Project on carbon-14; but see Appendix 1 in Reference [7]) and the groundwater flow through the vault returns to the background flow field.

#### A3.2.2 Magnox Inventory and Corrosion

The Magnox inventory is derived from the 2D38/C waste stream, which comprises drums of encapsulated Magnox swarf produced at the MEP. The conditioned volume of waste stream 2D38/C is 12,142.3 m³ (Table 5.6 in Reference [9]), and this contains 3,580.16 tonnes of Magnox metal (Table E9 in Reference [9]). The waste stream datasheet states that the total packaged volume of waste, including future arisings, will be 14207.5 m³ [10]. The waste stream data sheet states that 14338 packages with a packaged volume of 8187.1 m³ existed on 1st April 2007. Assuming the same volume per package over the entire inventory gives 24,881 packages to dispose of 3,580.16 tonnes of Magnox metal, or 143.9 kg of Magnox per waste package.

Magnox corrosion requires water. The reaction rate is influenced by temperature and the presence of chloride ions. Chloride ions may be introduced into the waste package if groundwater enters the package. Corrosion is an exothermic reaction, and so a positive feedback could exist such that increasing corrosion rate increases temperature which in turn increases the corrosion rate.

#### A3.2.3 Waste Package

The waste package comprises a 500l drum with a lid and a filter fitted in the middle of the lid. The drum is made of thin stainless steel which, during the time period considered here, will provide a barrier to fluid flows into or out of the package but not to heat flows. The stainless steel will corrode and produce gas, but this is likely to be a small volume compared with the gas produced by Magnox corrosion so has been ignored in this study. The filter in the lid is designed to allow gas to escape from the package but also to prevent particles exiting and consists of a mesh of metal...
wires. All fluids entering and leaving the waste package will do so through the filter, whilst the steel drum is intact.

The drum is filled with Magnox swarf mixed into a cement encapsulant, with a capping grout on top of the encapsulant (Figure A3.1) and an ullage space between the capping grout and the lid of the drum. The corrosion of Magnox is associated with an increase in volume, so over time, both the encapsulant and capping grout are likely to become stressed and may crack due to the volume change. This will change the effective hydraulic properties of these materials.

![Figure A3.1](image_url) A waste package consisting of a 500l drum that is filled with encapsulant and capping grout [11]

### A3.2.4 Vault

The waste package is emplaced in a UILW / ULLW vault within a GDF in higher strength rock (Figure A3.2). The package that was modelled by Quintessa was assumed to be at the centre of the vault and at the top of the stack of waste packages. The vault above the waste package is backfilled with NRVB and the roof of the vault is 6.535m above the top of the waste package.
As the vault is in higher strength rock, water is expected to flow through the vault. The water flow through the vault could have any direction, but in the Quintessa model, water was assumed to flow upwards through the vault following re-saturation.

### A3.2.5 System Evolution

At the start of the surface storage period, the encapsulant and capping grout within the package will be nearly saturated. During storage of the waste package in a surface store and underground in a disposal vault, the contents of the package will dry as water vapour moves out of the package through the filter. Experiments on 4m boxes indicate that the relative humidity in the ullage is likely to be similar to the relative humidity in the store or vault [6]. During the storage period, gas will be generated within the package and flow out of the package via the ullage and filter.

Once the vault is backfilled, it will be less easy for gas to escape from the waste package through the filter, so the gas pressure in the ullage will increase. The supply of water into the package to support continuing gas generation will depend on the water flow through the filter and ullage. One possibility is that the gas-saturated ullage, with a high gas pressure and zero capillary suction, would prevent liquid water from entering the package, although water vapour could still enter the package. However, a more realistic scenario is that some liquid water will get into the package, whether through droplet formation in the filter, running down the inside of the drum wall or through mechanical failure of either the container wall or the backfill, allowing gas to escape from the package. The most appropriate conceptual model to use for water flow through the gas-saturated ullage represents a significant uncertainty, which has been explored in the numerical modelling (see Subsection A3.4.1).

The temperature within the waste package is likely to increase during backfill curing and, to a lesser extent, when corrosion rates are high, but a positive feedback between high corrosion rate and temperature will only occur if there is sufficient water to sustain the high corrosion rate.
The GDF is assumed to be in a higher strength rock at a depth of 650m so re-saturation of the disposal vault is assumed to occur relatively quickly over a few years. Water moving from the host rock into the vault will contain chloride and the Magnox corrosion rate is very sensitive to very small amounts of chloride, so if the groundwater enters the package, it will result in an increase in Magnox corrosion rate. Magnox corrosion will continue until either the Magnox is all corroded or until there is insufficient water available to support further corrosion.

### A3.3 Numerical Model

The numerical model has been implemented in Quintessa’s in house modelling software QPAC [13]. A single waste package is explicitly represented in the model along with surrounding vault backfill. The following subsections describe the equations that are solved, the grid that is used to represent the waste package and the parameterisation of the model.

#### A3.3.1 Two-phase Flow and Transport

The numerical model solves equations for two-phase flow of hydrogen gas and water through porous media, coupled to equations for gas generation during the corrosion of Magnox. It also represents the transport of chloride through the system. The model doesn’t calculate temperatures, which are specified as an input time series. However, there is the possibility to couple heat transport into future versions of this model.

The two-phase flow model uses a standard saturation dependent version of Darcy’s law to explicitly model the flow of gas and water [14]. Saturation dependent parameters are specified using van Genuchten curves unless stated otherwise. The equations for relative permeability of water are of the form:

\[
K_{rw} = S_{ew}^{0.5} \left( 1 - \left( 1 - S_{ew}^{1/m} \right)^m \right)^2
\]

\[
S_{ew} = \begin{cases} 
S_c & S_{res} \leq S_c \\
S_{res} & S_c < S_{res} < 1 - S_c \\
1 - S_c & S_{res} \geq 1 - S_c 
\end{cases}
\]

\[
S_{res} = \frac{S_w - S_{irr}}{1 - S_{irr}}
\]

where:

- \( K_{rw} \) is the water relative permeability (-);
- \( m \) is the van Genuchten shape parameter (-);
- \( S_w \) is water saturation (-);
- \( S_{irr} \) is the irreducible water saturation (-);
- \( S_c \) is a saturation cut-off, which is set to \( 10^{-6} \) (-).

The capillary pressure is given by the equation:

\[
P_{cap} = P_r \left( \left( \frac{1}{S_{ew}} \right)^{1/m} - 1 \right)^{1-m}
\]

where:

- \( P_{cap} \) is the capillary pressure (MPa);
- \( P_r \) is the capillary entry pressure (MPa).

Both transport of hydrogen dissolved in water and transport of water vapour in gas are represented in the model. In some of the model runs, the transport of chloride ions dissolved in water is represented. The representation includes advection, dispersion and diffusion of the chloride ions.
The effective diffusivity \((D_e)\) of all dissolved gases and solutes in the pores of different materials is equal to:

\[
D_e = S_w D \phi \tau
\]  
(A3.5)

where:
- \(D\) is the free water diffusivity (\(m^2 s^{-1}\));
- \(\phi\) is the porosity (-);
- \(\tau\) is the tortuosity (-).

### A3.3.2 Gas Generation

The model only considers gas generation due to corrosion of Magnox swarf within the package; the production of gas from Magnox corrosion will dominate over steel corrosion for the time period of interest. The model could easily be extended to include corrosion of additional reactive metals.

The Magnox swarf is assumed to be uniformly distributed throughout the encapsulant and gas generation is calculated per unit volume of encapsulant.

Magnox corrosion requires water; one mole of Magnox reacts with two moles of water to produce one mole of hydrogen gas.

\[
Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2
\]

The Magnox metal is assumed to be of plate geometry, with a plate thickness of \(2 \times 10^{-3} \text{ m}\) ([9], Table E9 waste stream 2D38/C). The gas generation rate assuming excess water is equal to:

\[
R_G = C.A.s. \rho_M / M_W
\]  
(A3.6)

where:
- \(R_G\) is the gas generation rate (mol y\(^{-1}\));
- \(C\) is the corrosion rate (m y\(^{-1}\));
- \(A\) is the surface area of the metal (m\(^2\));
- \(s\) is the reaction stoichiometry, and is equal to unity (i.e. one mole of Magnox reacts to generate one mole of hydrogen gas);
- \(\rho_M\) is the density of Magnox metal (1738 kg m\(^{-3}\));
- \(M_W\) is the molecular weight of Magnox, 24.31 \(10^{-3}\) kg mol\(^{-1}\) (for Mg).

The surface area of the metal is equal to:

\[
A = a.M/(x.\rho_M)
\]  
(A3.7)

where:
- \(a\) is a geometry factor, and is equal to 2 for a plate, i.e. corrosion from both sides of the plate (-);
- \(M\) is the initial mass of metal (kg);
- \(x\) is the initial thickness of the plate (m).

The corrosion rate depends both on temperature and on the concentration of chloride ions in the water. At 20 °C the chronic corrosion rate in the absence of chloride is \(1.2 \times 10^{-7}\) m y\(^{-1}\) and the factor by which the corrosion rate increases with temperature is shown in Figure A3.3. The corrosion reaction is exothermic, but the heat energy associated with corrosion is not explicitly accounted for in the model.
Chloride ions are assumed to only affect the corrosion rate if the concentration exceeds 100 mg l⁻¹, but once this concentration is exceeded, the corrosion rate increases by a factor of 100 in a single step.

Each drum contains around 150 kg of Magnox metal, which requires around 0.25 m³ of water to corrode fully. The volume of the encapsulant is 0.466 m³, and the porosity is 0.2. Therefore 2.65 encapsulant pore volumes of water are required to react with all the Magnox.

### A3.3.3 Coupling Magnox Corrosion to Water Availability

Corrosion of metals can only proceed when there is free water available to support the reaction. For metals in air, water will become available at the point of deliquescence. For encapsulated metals, it is assumed that there is no deliquescence of water vapour in unsaturated pores. Corrosion is only able to proceed while there is free liquid water available. Therefore, in the model, corrosion is coupled to the water saturation and not the relative humidity.

In the model of Magnox corrosion, we must specify a point at which corrosion becomes limited by the availability of water. A first assumption may be that corrosion proceeds at the full rate until the water saturation is close to the irreducible saturation, at which point water is no longer able to move through the pore space. In reality, the corrosion rate may become water-limited before the irreducible saturation is reached if the flow of water through the encapsulant is slower than the consumption of water by the Magnox corrosion reaction. To determine whether this is a significant effect, the following calculations were carried out.

The corrosion rate depends on temperature, chloride concentration and the availability of water. For the calculations here, we initially assume a temperature of 20 °C and no chloride is present. This would result in a corrosion rate $R = 1.2 \times 10^{-7}$ m y⁻¹.

The rate of water supply required to maintain the corrosion rate per unit area of corrosion can be calculated by:

$$q = \frac{R \cdot \rho \cdot M \cdot \alpha \cdot m_w}{\rho_w}$$  \hspace{1cm} (A3.8)

where:
- $q$ is the flow of water to the corroding Magnox per unit area (m y⁻¹);
- $R$ is the rate of Magnox corrosion (m y⁻¹);
\( \rho_{mM} \) is the molar density of Magnox, 71493 mol m\(^{-3}\);
\( m_w \) is the molar mass of water, 18 g mol\(^{-1}\);
\( \rho_w \) is the density of water, 1000 kg m\(^{-3}\).

Based on these values, the rate of water flow to the Magnox must be 3.09 \( \times \) \( 10^{-7} \) m y\(^{-1}\) to maintain the full rate of corrosion.

The rate of water flow to the Magnox depends on the pressure gradient between the Magnox and the source of water and the permeability of the encapsulant (assuming unit area). The permeability of the encapsulant will decrease as the saturation of water decreases, as given by Equation (A3.1). The head gradient that is required to maintain water flow at a rate required to sustain corrosion can be calculated by dividing the water flow rate by the hydraulic conductivity (Figure A3.4).

![Figure A3.4](image.png)

**Figure A3.4** The head gradient that is required to maintain water flow at 3.09 \( \times \) \( 10^{-7} \) m y\(^{-1}\) for different saturations

The irreducible saturation of water in the encapsulant is 0.25 (see Appendix 2). A reasonable estimate of the head gradient in the encapsulant can be made by assuming that the saturation next to the Magnox just before corrosion becomes water-limited would be around 0.251 because as soon as saturation reaches 0.25, the permeability drops to 0 and no more water can flow to the Magnox. This means that the suction next to the Magnox would be 1215 MPa (Equation (A3.4)). If we then consider the saturation at 1 cm from the piece of Magnox (i.e. directly in between two pieces of Magnox, assuming a spacing of 2 cm), we can determine what the saturation there would need to be in order for the flow of water to the Magnox to be maintained (Table A3.1).
Table A3.1  Calculated Head Gradient Required for Flow, and the Head Gradient that May Occur Between Pieces of Magnox

<table>
<thead>
<tr>
<th>Head Gradient Required for Flow (Figure A3.4)</th>
<th>Saturation at 1 cm</th>
<th>Suction at 1 cm (MPa)</th>
<th>Estimate of Head Gradient over 1 cm</th>
<th>Flow?</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.12 (10^6)</td>
<td>0.26</td>
<td>121.49</td>
<td>1.09 (10^7)</td>
<td>Yes</td>
</tr>
<tr>
<td>4.96 (10^6)</td>
<td>0.27</td>
<td>60.73</td>
<td>1.15 (10^7)</td>
<td>Yes</td>
</tr>
<tr>
<td>8.00 (10^5)</td>
<td>0.28</td>
<td>40.47</td>
<td>1.17 (10^7)</td>
<td>Yes</td>
</tr>
<tr>
<td>2.19 (10^3)</td>
<td>0.29</td>
<td>30.33</td>
<td>1.18 (10^7)</td>
<td>Yes</td>
</tr>
<tr>
<td>8.02 (10^2)</td>
<td>0.30</td>
<td>24.25</td>
<td>1.19 (10^7)</td>
<td>Yes</td>
</tr>
<tr>
<td>3.53 (10^2)</td>
<td>0.31</td>
<td>20.19</td>
<td>1.19 (10^7)</td>
<td>Yes</td>
</tr>
<tr>
<td>1.76 (10^2)</td>
<td>0.32</td>
<td>17.28</td>
<td>1.20 (10^7)</td>
<td>Yes</td>
</tr>
<tr>
<td>9.64 (10^1)</td>
<td>0.33</td>
<td>15.10</td>
<td>1.20 (10^7)</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Based on these results, we could expect Magnox corrosion in a compartment to occur even when saturation between Magnox pieces reaches 0.26. If the peak saturation is 0.26 and the saturation at the Magnox is 0.251, then the average saturation will be somewhere between these values. However, these results depend on several assumptions. If the distance between pieces of Magnox were smaller, the gradients would be higher and flow would occur at lower saturations. Similarly, as saturation next to the Magnox drops from 0.251 to 0.2505, the suction doubles and flow would occur at lower saturations.

If the corrosion rate of Magnox were 100 times higher, the required water flow to the Magnox would also be 100 times higher and the required head gradient would be two orders of magnitude greater. This means that water flows at a saturation of 0.26 would not be high enough to sustain corrosion but flow at a saturation of 0.27 would.

Given that these calculations are intended only to give a rough estimate of the cut-off saturation and that the calculated values are not much higher than the irreducible saturation, the irreducible saturation has been used in the model as the cut-off point above which corrosion proceeds at the full rate and below which corrosion ceases.

**A3.3.4 Model Geometry**

Half of a 500l drum at the top of the waste stack in the middle of the vault is represented, using a cylindrical grid. The backfill surrounding the drum and extending up to the top of the vault is explicitly represented along with the filter, ullage, capping grout and encapsulant (Figure A3.5), but the steel drum is not. The drum is represented by not allowing any fluxes between the backfill compartments and the compartments on the inside of the drum.

The drum is approximated as a cylinder with dimensions that conserve the volume of the waste package; the ribs on the drum and the tapering at the top are not explicitly represented. This simplification is not expected to affect the results. The geometry of the model is given in Appendix 2.

The grid used in the modelling is shown in Figure A3.6. (Some convergence tests were performed on this grid.)
Figure A3.5  Model geometry (dark blue = encapsulant, light blue = capping grout, green = ullage, yellow = vent / filter, red = outside package)
A3.3.5 Material Properties and Parameterisation of the Ullage and Filter

For the initial cases, it is assumed that the material properties of the backfill, capping grout and encapsulant are constant through time. The backfill is assumed to be Nirex Reference Vault Backfill (NRVB) and the encapsulant and capping grout are cementitious materials. The hydraulic properties of these materials are given in Appendix 2. The three cementitious materials are assumed to be incompressible.

The ullage and filter are not porous media, and so there is some question about how to best represent the hydraulic properties of these features using equations for two-phase flow. This uncertainty led to a number of parameterisations of the hydraulic properties of the ullage and filter being tested before one was chosen to be used in further modelling. There are two factors to be considered: first, how to parameterise the suction pressure within these very open features; and secondly, how well mixed the air in the ullage space is with the air in the surrounding store or open vault.
From a purely mathematical perspective, it might be expected that the ullage would have zero capillary suction because it is a large open void. On the other hand, it is likely that some amount of water will enter the ullage whether due to capillary effects along the walls of the steel drum or droplet formation in the filter. Therefore, there is also an argument for giving the filter and ullage properties with a small amount of capillary suction. Two models have been implemented to test this:

**Table A3.2 Two Models of the Ullage with Different Values of the van Genuchten Parameter $P_r$**

<table>
<thead>
<tr>
<th>Model</th>
<th>van Genuchten $P_r$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 0</td>
<td>0</td>
</tr>
<tr>
<td>Case 1a</td>
<td>1000</td>
</tr>
</tbody>
</table>

The degree of mixing between the air in the ullage space and the air in the store / vault is investigated in two models, the first of which assumes the relative humidity in the ullage is constant at 70% and the second of which calculates vapour transport between the capping grout, ullage and the air in the store / vault.

### A3.3.6 Initial and Boundary Conditions

The backfill, encapsulant and capping grout will be water-saturated when first poured, but as the cement sets and cures, water will be taken into the minerals. The manufacture of the waste package is not included in the calculations, but the initial saturation of 95% for these materials at the start of the storage period takes into account the loss of water to the mineral phase. The initial conditions in the ullage and filter reflect the humidity of the store at 70% through the specification of very low liquid water saturation.

Prior to backfilling, the model compartments that represent the backfill have a fixed relative humidity of 70% and fluid flows are not calculated. At backfilling, the water saturation of the backfill is set to 95% and the fluid flow calculations are turned on.

The radial boundary of the model is a no-flow boundary representing symmetry between adjacent waste packages in the stack. The top boundary of the model represents the top of the vault. Prior to the backfilling, the relative humidity in the vault is fixed and the top boundary condition is no flow. Once the vault has been backfilled, the top boundary has a constant water pressure equal to hydrostatic pressure at a depth of 650m.

The bottom boundary of the model is at the base of the waste package, which is within the vault. Along the base of the waste package, the boundary is set to no flow, as there will be no flow through the base steel of the package. The boundary next to the waste package within the backfill is set to no flow until 145 years as it is assumed that the vault will take five years to re-saturate and water will only start to flow across this boundary once re-saturation has occurred. An upwards pressure gradient is assumed to exists across the vault, with an excess pressure of 1190 Pa at the base of the waste package driving the upwards flow (the model has a vertical size of 7.732m). This is equivalent to an excess pressure of $10^5$ Pa at 650m depth compared with equilibrium pressure at the ground surface, which is reasonable for this sort of environment.

The temperature of the model through time accounts for the difference in temperature between the store and vault, and also has a temperature peak associated with backfill curing (Figure A3.7). The long-term temperature in the GDF does not take into account any heat generated by radioactive...

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This is a modelling assumption adopted here (and elsewhere). Resaturation times in different geological environments are discussed in 3.2.
decay from the waste in the GDF. Given this temperature time series, the resulting corrosion rate under fully-saturated conditions without chloride is shown in Figure A3.8.

![Temperature time series imposed on the model](image)

**Figure A3.7** Temperature time series imposed on the model

![Gas generation rate under fully saturated conditions for a half-package containing 75 kg Magnox metal, assuming there is no chloride present](image)

**Figure A3.8** Gas generation rate under fully saturated conditions for a half-package containing 75 kg Magnox metal, assuming there is no chloride present
A3.4 Reference Case

The first step in applying the numerical model was to generate a reference case. A number of key uncertainties were identified whilst parameterising the conceptual model, and so it was considered useful to perform some initial model runs to understand (i) the general behaviour of the system and (ii) the sensitivity of the model to certain parameters, before settling on a reference case and defining variant cases. The two main questions were:

- What is the most realistic parameterisation for the ullage and filter?
- Should chloride transport be modelled in the reference case, or should the presence of chloride in the model simply be imposed in a similar way to the temperature?

These questions were investigated in a series of model runs described below, and then the results were used to define the reference case.

A3.4.1 Parameterisation of the Ullage and Filter

The parameterisation of the ullage and filter was discussed in Subsection A3.3.5. To assess the implications of different numerical representations of the ullage and filter, four models were run (Table A3.3). The first model (Case 0) assumes no suction in the ullage and filter and that the gas in the ullage is well mixed with the store and vault prior to backfilling. Cases 1a and 1b explore models in which the filter and ullage have a small suction; the relative humidity in the ullage and filter prior to backfilling is set equal to that in the store and vault for Case 1a, but is calculated in Case 1b. The results for these three models are described in detail, both to demonstrate the implications of the ullage and filter parameterisation but also to familiarise the reader with the key features of the system behaviour. A fourth case (Case 1c) is based on Case 0, but the relative permeability of water in the ullage and filter is set to 1. The results for Case 1c are very similar to Case 0 and are not discussed further.

Table A3.3 Description of model runs to assess the parameterisation of the ullage and filter.

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 0</td>
<td>The relative humidity outside the package, in the ullage space and filter are fixed during storage and the GDF operational phase. There is assumed to be no suction in the ullage space and filter post-backfilling.</td>
</tr>
<tr>
<td>Case 1a</td>
<td>As Case 0, but there is assumed to be a small suction in the ullage space and filter post-backfilling. The Van Genuchten parameters for the ullage and filter were: $P_r = 0.001$ MPa, $m = 0.7$, $S_{ev}$ minimum = $10^{-6}$.</td>
</tr>
<tr>
<td>Case 1b</td>
<td>The relative humidity outside the package is fixed during storage and the GDF operational phase. The relative humidity in the ullage space and filter are calculated. The ullage space and filter are given a weak capillary curve, $P_r = 0.001$ MPa, $m = 0.7$, $S_{ev}$ minimum = $10^{-6}$.</td>
</tr>
<tr>
<td>Case 1c</td>
<td>As Case 0, but the relative permeability of the ullage and filter was set to unity for water and gas, rather than varying linearly with $S_{ev}$.</td>
</tr>
</tbody>
</table>

A3.4.1.1 Gas Generation

In Case 1a and Case 1b, gas generation occurs at the peak rate for a given temperature (compare Figure A3.9 with Figure A3.8) until all the Magnox is corroded, between 1500 and 2000 years (Figure A3.10). In Case 0, corrosion ceases by 750 years, when around one third of the Magnox inventory has been corroded.
The flux of gas that leaves the package (Figure A3.11) has a similar shape to the gas generation curve (Figure A3.9), but the peak gas flux is around one third of the peak gas generation in Case 1b and only around one fifth of the peak gas generation in Case 0 and Case 1b. The gas that does not leave the package is stored in the ullage and pore space within the package and causes a significant increase in gas pressure (Figure A3.12).

The maximum gas pressure in the ullage is 6.68 MPa for all three cases. This is about 0.08 MPa above the hydrostatic pressure, so the gas pressure in the package is not sufficient to crack the backfill [16] and release the gas from the package.

Figure A3.9 Gas generation rate versus time for Case 0, and Variant Cases 1a and 1b
Figure A3.10 Cumulative gas generation versus time for Case 0, and Variant Cases 1a and 1b

Figure A3.11 Flux of free gas out of package post-backfilling for Case 0, and Variant Cases 1a and 1b
A3.4.1.2 Storage Period

When the package is first encapsulated (t = 0 years), the encapsulant and capping grout are 95% water saturated and the backfill compartments, representing the store, are dry (Figure A3.13).

Figure A3.13 Water saturation at time t = 0y for Case 0. Variant Cases 1a and 1b are identical to Case 0.

At the end of the storage period (t = 60 years), the water saturation in Case 1b is significantly higher than in Cases 0 and 1a (Figure A3.14) because the relative humidity in the ullage and filter in Case 1b is higher than in the store, whereas in Cases 0 and 1a, the relative humidity in the ullage and filter is fixed equal to the value in the store (Figure A3.15). Case 1b therefore has a lower relative humidity gradient between the capping grout and the ullage, so the diffusion of water vapour is slower and the package remains wetter. A second factor is that the suction on the top
surface of the capping grout, which is calculated using the Kelvin equation, decreases with increasing relative humidity. Therefore less water is "drawn" to the top surface of the encapsulant, where it can be lost through evaporation, in Case 1b compared with Cases 0 and 1a.

In all three cases, Magnox corrosion is not limited by water, so the fractional corrosion rate (the actual corrosion rate / corrosion rate with no water limitation) equals 1 (Figure A3.16).

![Figure A3.14 Water saturation at time t = 60y for Case 0, and Variant Cases 1a and 1b (left to right)](image)

![Figure A3.15 Relative humidity at time t = 60y for Case 0, and Variant Cases 1a and 1b (left to right)](image)
Figure A3.16 Fraction of potential corrosion rate at time $t = 60y$ for Case 0. Variant Cases 1a and 1b are identical to Case 0. (Note that results are only relevant for the encapsulant, which is where the corroding wastes are located – indicated by orange bounding box.)

A3.4.1.3 GDF Operational Period

During the GDF operational period, the waste package continues to dry, but again, Case 1b remains wetter than Cases 0 and 1a because the relative humidity in the ullage is higher when it is modelled explicitly (Figure A3.17 and Figure A3.18). Corrosion is not water limited in any of the cases (Figure A3.19).

Figure A3.17 Water saturation at time $t = 139y$ for Case 0, and Variant Cases 1a and 1b (left to right)
A3.4.1.4 Post-backfilling

When the backfill is emplaced in the vault, the saturation of the backfill is 95% while the ullage space remains full of gas (Figure A3.20). After half a year, the water saturation in the package in Case 0 has changed very little, whereas saturation has increased very slightly at the top of the waste package in Cases 1a and 1b (Figure A3.21). This is because Case 0 has zero suction in the ullage, whereas the other two cases have a saturation dependent suction and hence pull more water into the package. The capping grout and encapsulant in Case 1b are much wetter than Case 0 and Case 1a, so there is a smaller pore volume for gas storage, which explains the higher gas flux during the temperature peak (Figure A3.11). After 2.5 years, all three cases have similar saturations, but Cases 0 and 1a are slightly drier at the base of the package, reflecting the drier conditions at backfilling and Case 1b still has a very dry ullage because the suction is zero (Figure A3.22). By 150 years, all three cases have similar water saturation, although Case 0 is slightly drier (Figure A3.23). After 750 years, all three packages are drying out because Magnox corrosion is consuming water faster than water flows into the package (Figure A3.24), although
water already within the package can still be transported sufficiently rapidly to support the corrosion reaction. The drying is greater in Case 0 because the properties assigned to the ullage mean that liquid water cannot enter the waste package from the backfill.

In Case 0, there is no suction in the ullage or filter, so the water pressure in the ullage / filter is equal to the gas pressure. The gas pressure in the ullage is higher than in the backfill because gas is generated within the package. The gas pressure in the ullage will build up until it exceeds the hydrostatic pressure in the backfill, at which point the water pressure gradient would drive water out of the ullage and into the backfill. The ullage will therefore dry out and water will not be able to flow into the package. In Cases 1a and 1b, there is a capillary suction in the ullage and filter so the water pressure is always less than the gas pressure and there will be a water pressure gradient that drives water flow into the package, even though this flow is small for the parameters considered.

Figure A3.20 Water saturation at time $t = 140\text{y}$ for Case 0, and Variant Cases 1a and 1b (left to right)

Figure A3.21 Water saturation at time $t = 140.5\text{y}$ for Case 0, and Variant Cases 1a and 1b (left to right)
Figure A3.22 Water saturation at time $t = 142.5\,\text{y}$ for Case 0, and Variant Cases 1a and 1b (left to right)

Figure A3.23 Water saturation at time $t = 150\,\text{y}$ for Case 0, and Variant Cases 1a and 1b (left to right)
Whilst the water saturation in the three cases is different in the 10 years after backfilling, there is sufficient water in all cases that the Magnox corrosion rate is not limited by water availability. By 750 years, the water saturation in Case 0 drops to the irreducible saturation, and there is insufficient water available to support Magnox corrosion, so the corrosion fraction drops to near zero (Figure A3.25) and there is no corrosion in the package (Figure A3.9). Whilst the saturation in Cases 1a and 1b has dropped by 750 years, there is still sufficient water to support corrosion at the full rate.

A3.4.1.5 Summary

The main difference between the four cases is whether liquid water is able to flow into the package after backfilling to maintain gas generation. The suction in the ullage is the crucial parameter for determining whether water will flow into the package. If suction is zero, when the gas pressure in the ullage rises above the hydrostatic pressure, the water pressure gradient will drive water flow out of the package and into the backfill. With non-zero suction, the water pressure will be less than
the gas pressure and water will be able to flow into the ullage from the backfill. The greater the
suction in the ullage, the greater the water flow into the package will be.

For the cases presented, the peak gas flux occurs due to a temperature pulse associated with
backfill curing at a time when there is sufficient water in the package in all models to support the
corrosion rate. However, there may be circumstances in which the corrosion rate is much higher
(e.g. higher temperatures due to exothermic corrosion or the presence of chloride ions) and water
availability is more critical.

Case 0 and Case 1c present an end-member case in which liquid water cannot enter the package
once the gas pressure increases above hydrostatic. Whilst this story is consistent with the
mathematical parameterisation, it will return results in which the package dries out very quickly and
corrosion stops early, so does not constitute a conservative case and may not be representative of
a real package that is 140 years old. It is very possible that a small amount of liquid water is able
to enter the package even when the gas pressure is high, either by forming droplets in the filter or
by running down the inside of the steel drum, the surface of which will have a small suction
pressure associated with it. Therefore it was decided to continue the modelling study with a model
that has a small suction in the ullage and filter.

The difference between Case 1a and Case 1b is very minor in terms of the gas generation story,
although some differences in saturation were observed. Case 1a has been carried forward to the
next modelling steps (i.e. to the reference case) because there is evidence that the air in the ullage
is likely to be well mixed with the air in the store in experimental work [6].

A3.4.2 Effect of Chloride

The Magnox corrosion rate increases significantly in the presence of even small concentrations of
chloride. The host rock groundwater will contain chloride, and will enter the GDF as it re-saturates
and re-pressurises. Two scoping models (Case 2a and Case 2b; see Table A3.4) that did not
explicitly model the transport of chloride were set up in which the corrosion rate increased after
backfilling to represent the arrival of chloride ions into the waste package. These cases were
designed to inform a decision as to whether a more complex model with chloride transport should
be developed.

The results of Case 2a and Case 2b showed that increasing the corrosion rate to simulate the
presence of chloride ions increased the flux of gas out of the package and in Case 2b led to gas
generation becoming limited by the availability of water. In these cases, the chloride concentration
was assumed to increase over 5 years following backfilling, such that the corrosion rate was
enhanced by both the temperature peak and high chloride at the same time. The time for chloride
to enter the package wasn’t explicitly modelled.

Given the results of Case 2a and Case 2b (not presented), it was decided to build a model that
explicitly represents the transport of chloride (Case 3; see Table A3.4) so that the timing of the
chloride ions reaching the waste package could be better accounted for. Case 3, which includes
transport of chloride, is the reference case for this study.
### Table A3.4  Description of cases for investigating the importance of chloride.

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 2a</td>
<td>As Case 1a, but the Magnox corrosion rate increases linearly during the first 5 years post-backfilling until it is 15x higher than Case 1a. This is consistent with the assumed re-pressurisation time for the vault and provides an indication of the impacts of Cl⁻ in groundwater. 15x increase is less than the expected increase due to the presence of Cl⁻.</td>
</tr>
<tr>
<td>Case 2b</td>
<td>As Case 1a, but the Magnox corrosion rate increases linearly during the first 5 years post-backfilling until it is 100x higher than Case 1a. This is consistent with the assumed re-pressurisation time for the vault and provides an indication of the impacts of Cl⁻ in groundwater. The hundredfold increase in the corrosion rate is taken from Reference [15].</td>
</tr>
<tr>
<td>Case 3</td>
<td>As Case 1a, but with the transport of Cl⁻ in groundwater explicitly represented in the model and with the corrosion rate coupled to chloride concentration as described in Subsection A3.3.2.</td>
</tr>
</tbody>
</table>

#### A3.4.2.1 Chloride Transport

The advection, diffusion and dispersion of chloride are included in the model using the Tracer Transport module in QPAC [17]. The parameters that describe chloride transport are given in Appendix 2.8.2.

Initially, the concentration of chloride in the model is assumed to be zero as the engineering materials will be made with water having an as yet unspecified content of chloride. Chloride will enter the vault with the groundwater, so chloride enters the model through the boundary conditions set on the top and bottom boundaries. Both boundaries have a fixed concentration of chloride of 20,000 mg l⁻¹ from the time at which water is assumed to flow across the boundary. For the top boundary, this is at 140 years, when the vault is backfilled and for the bottom boundary this is at 145 years, when the vault is assumed to have re-pressurised. Given the location of the package at the top of a waste stack, the bottom boundary condition is considered to be very cautious, but still allows an exploration of the relevant issues without having to make further arbitrary assumptions (this work was completed before the analysis described in Appendix A1 had been carried out).

#### A3.4.2.2 Results

This case (i.e. Case 3) was selected as the reference case for the study. The model results still show the corrosion peak at 145 years associated with backfill curing, but there is a much larger peak at around 190 years which is associated with chloride ions entering the waste package (Figure A3.26). The higher rate of corrosion means that it takes less time for all the Magnox to corrode (Figure A3.27); in Case 3, the Magnox has all corroded by 1000 years whilst it takes until 2000 years in Case 1a.

The peak flux of gas out of the package was around one fifth of the peak generation rate for Case 1a, and in Case 3, this is true for the initial peak at 140 years, but for the chloride-related peak in gas generation, around 90% of the generated gas leaves the package very quickly (Figure A3.28). The gas pressure rises at 140 years in both cases, but in Case 3, there is a further small rise in gas pressure associated with the high gas generation rate at 190 years (Figure A3.29).
Figure A3.26 Gas generation rate versus time for Case 1a (no chloride) and Case 3 (with chloride)

Figure A3.27 Cumulative gas generation versus time for Case 1a (no chloride) and Case 3 (with chloride)
Figure A3.28 Flux of free gas out of the package for Case 1a (no chloride) and Case 3 (with chloride)

The high gas generation rate at 190 years can be understood in terms of the chloride transport into the waste package (Figure A3.30). Chloride first enters the model from the top boundary,
corresponding to the top of the vault, at 140 years and subsequently migrates down through the vault due to advection and density driven flow. At 145 years, re-saturation / re-pressurisation is complete and an upwards flow regime is established so that chloride can enter the model from the base, corresponding to the bottom of the highest package in the waste stack. Chloride is advected up the backfill from the base of the model because of the slight over pressure condition on the bottom boundary. Chloride enters the waste package at around 155 years, but it takes until 166 years for the concentration to be high enough to affect the corrosion rate. There is a gradient of chloride concentration through the waste package and it takes until 200 years for the chloride to reach the base of the package at a high enough concentration for corrosion there to be enhanced (Figure A3.31). The corrosion process consumes water, which results in chloride concentrations exceeding the groundwater concentration where there is a high corrosion rate. In the long term, the concentration is constant throughout the model at 20,000 mg l\(^{-1}\).

In this model, the chloride takes 15 years to reach the package after backfilling, so the temperature peak from backfill curing is over by the time the chloride enters the package. This means that the corrosion rate is increased by temperature first and then by the presence of chloride, but the two peaks do not overlap. This finding is very sensitive to the assumed water flow through the vault and the suction in the ullage, which both determine how fast groundwater can get into the package.

![Figure A3.30 Chloride concentration at given times in the whole model domain for Case3](image-url)
Figure A3.31 Chloride concentration in the encapsulant for grid compartments located at three heights on the axis of the waste package shown alongside the temperature of the container

The higher corrosion rate in the package compared with the no-chloride case means that water is consumed faster than it can flow into the package. At 190 years, the saturation has dropped sufficiently that the corrosion rate is limited by water availability (Figure A3.32 and Figure A3.33). As the chloride concentration varies through the package, so does the corrosion rate and the water consumption, such that the top of the package runs out of water before the bottom of the package. At 200 years there is little corrosion in the package because there is insufficient water, but as water enters the top of the package, corrosion occurs at a front above which there is no Magnox remaining in the package.

In this case, the peak corrosion rate is limited by the availability of water, so if for some reason the thermal peak were to coincide with the chloride peak, then it is unlikely that gas generation could occur at a significantly higher rate before the availability of water becomes the limiting factor.
Figure A3.32 Water saturation in the package and surrounding backfill from 150 years to 1000 years

Figure A3.33 Fraction of potential corrosion rate. (Note that results are only relevant for the encapsulant, which is where the corroding wastes are located – indicated by orange bounding box.)
A3.4.2.3 Summary

This subsection has explained why it was decided that the reference case should include calculations of the transport of chloride. It has presented the results obtained for such a case, which also builds on the understanding developed through an exploration of the parameterisation of the ullage. This case (i.e. Case 3) is the reference case for the rest of the study.

The corrosion rate is increased by temperature first and then by the presence of chloride, but the two do not overlap. The presence of chloride ions during Magnox corrosion increases the corrosion rate by a factor of 100. In the calculation presented, we show that whilst it may take several years for the chloride ions to enter the package, the corrosion peak due to chloride is an order of magnitude higher than the corrosion peak due to the temperature increase associated with backfill curing. A large proportion of the gas that is generated during the temperature peak at 140 years is stored within the waste package, contributing to an increase in pressure in the ullage, but the gas pressure is already high when the gas generation rate increases again at around 190 years, so the gas generated in association with high chloride concentrations is mostly released from the waste package.

Although the peak gas generation from the thermal pulse and the chloride pulse do not overlap in this model, it is expected that, if they were to overlap, gas generation would quickly become limited by the availability of water (see the discussion of Case 2b at the beginning of Subsection A3.4.2), so the exact timing of the chloride peak in relation to any thermal effects is not an important consideration. Thus the precise timing of the arrival of chloride in the package is not an issue if the output of interest is the bounding gas generation rate from a single package.

Given that the presence of chloride increases the peak gas generation by a factor of 4.5 and that the gas generated in the peak leaves the package, it was decided to include chloride in all remaining models.

A3.5 Variant Cases

This section considers the performance of a number of variants of the reference case (i.e. Case 3 described above). These variant cases (Table A3.5) were set up to look at different material properties (Case 4 and Case 5), material properties that change as the corrosion reaction occurs (Case 6) and the impact of higher temperatures in the vault (Cases 7a - 7e).

Table A3.5 Description of Variant Cases

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 4</td>
<td>Vault backfill has a higher permeability and lower capillary suction</td>
</tr>
<tr>
<td>Case 5</td>
<td>Assumes a shrinkage crack between the capping grout and the drum wall</td>
</tr>
<tr>
<td>Case 6</td>
<td>Evolving encapsulant and capping grout properties representing cracking of the encapsulant and grout as corrosion proceeds</td>
</tr>
<tr>
<td>Case 7a</td>
<td>Thermal peak 5 °C hotter</td>
</tr>
<tr>
<td>Case 7b</td>
<td>Thermal peak 10 °C hotter</td>
</tr>
<tr>
<td>Case 7c</td>
<td>Thermal peak 15 °C hotter</td>
</tr>
<tr>
<td>Case 7d</td>
<td>Thermal peak 20 °C hotter</td>
</tr>
<tr>
<td>Case 7e</td>
<td>Thermal peak 20 °C hotter and the peak temperature is maintained</td>
</tr>
</tbody>
</table>
A3.5.1 Material Properties

Case 4 considers a higher permeability backfill with a lower gas entry pressure to investigate whether a backfill that lets gas pass through more easily will also result in more water entering the package and a higher corrosion rate. Case 5 also considers a scenario in which water supply to the Magnox might be enhanced, by assuming a crack between the capping grout and the drum wall providing a pathway for water flow to the encapsulant. The parameterisation of these cases is given in Appendix 2.8.2.

In Case 4 (high permeability backfill), peak gas generation is 3 times higher than in Case 3 (reference case) and the peak is 40 years earlier (Figure A3.34). Over 95% of the gas generated at the peak leaves the package very quickly (Figure A3.35). The reason for the earlier corrosion peak can be found by looking at the chloride concentration in the package (Figure A3.36), which shows that chloride enters the package much earlier in Case 4 than in Case 3. This is caused by density driven flow as the saline groundwater is denser than the fresh water in the backfill and so the saline water sinks down through the vault. This effect is significantly greater in Case 4 compared with Case 3 because the permeability is higher in Case 4. The effect of the faster chloride transfer into the package dominates this model, and the effect of the lower gas entry pressure enabling gas to escape the ullage is not significant.

The peak corrosion rate is over three times higher in Case 4 (high permeability backfill) than Case 3 (reference case) because the chloride enters the package much earlier, at a time when the initial water in the encapsulant has not been consumed by corrosion. In Case 3, corrosion at the top of the package becomes water limited before chloride reaches the base of the package, but in Case 4 the chloride reaches the base of the package at around the same time as the corrosion becomes water limited. This means that in Case 4, the chloride-related high corrosion rate is present in almost the whole package before it becomes water-limited.

![Figure A3.34 Gas generation rate versus time for Case 3 (low permeability backfill) and Case 4 (high permeability backfill)](image-url)
Figure A3.35 Gas flux out the package versus time for Case 3 (low permeability backfill) and Case 4 (high permeability backfill)

Figure A3.36 Chloride concentration at the top of the encapsulant through time for Case 3 (low permeability backfill) and Case 4 (high permeability backfill)
Case 5 considers how the presence of a shrinkage crack between the capping grout and the drum wall could affect the water supply to the encapsulant. The hydraulic properties of the capping grout were calculated by averaging properties for the capping grout with the flow properties of a 0.1 mm crack between the grout and the wall of the drum. The result is that the capping grout has a higher permeability and a lower gas entry pressure (see Appendix 2.8.2). The consequences of this parameterisation are that the waste package dries out very quickly as there is insufficient suction in the capping grout to pull water into the package. Water flow into the package stops as in Case 0. This would not happen in reality and demonstrates the need for cracks in the capping grout to be represented explicitly, so that the intact capping grout maintains its suction, whilst the cracks can act as a water flow path.

**A3.5.2 Evolving Properties**

Magnox corrosion is an expansive reaction. As corrosion proceeds the encapsulant and capping grout may crack, increasing the permeability and decreasing gas entry pressure. In Case 6, the properties of the encapsulant and capping grout are assumed to evolve from initial to degraded values, in direct proportion (i.e. linearly) to the amount of Magnox metal that has corroded (see Appendix 2.8.2).

The properties of the encapsulant are calculated for each model compartment, based on the fraction of Magnox metal in that compartment that has corroded. Although there is no Magnox metal in the capping grout, it is assumed that it may still be cracked by expansive stresses in the underlying encapsulant. Degradation of the capping grout is assumed to be directly proportional to the fraction of total Magnox in the drum that has corroded.

Initially, gas generation in Case 6 (evolving encapsulant and capping grout properties) is the same as in Case 3 (reference case), but at around 170 years the gas generation increases much more rapidly in Case 6 than in Case 3 (Figure A3.38). The peak gas generation in Case 6 is three times that of Case 3 and the flux of gas out of the package increases in proportion to the gas generation.
rate (Figure A3.39). The reason for the increased gas generation rate is that the permeability of the capping grout and encapsulant are two orders of magnitude greater at backfilling in Case 6 compared to Case 3 (Figure A3.41), so water flows into the package more easily and chloride enters the package earlier in Case 6 (Figure A3.40). In Case 6, a greater volume of the package is subjected to chloride enhanced corrosion before water availability starts to limit corrosion. (Note that the Case 6 run was stopped after 250y once corrosion was complete.)

Figure A3.38 Gas generation rate versus time for Case 3 (constant properties) and Case 6 (evolving encapsulant and capping grout properties)
Figure A3.39 Gas flux versus time for Case 3 (constant properties) and Case 6 (evolving encapsulant and capping grout properties)

Figure A3.40 Chloride concentration versus time for Case 3 (constant properties) and Case 6 (evolving encapsulant and capping grout properties)
A3.5.3 Additional Heat from Corrosion

Magnox corrosion is an exothermic reaction, so we could expect temperatures to increase as the Magnox corrosion proceeds. To examine the sensitivity of results to the effects of higher temperatures, a number of cases were run with increasing peak temperatures and the final case maintained the peak temperature for the remainder of the model run (Figure A3.42). These temperature profiles are not based on any modelling of the effects of exothermic corrosion on the temperature, but were chosen to illustrate the possible range of behaviours.

The peak gas generation rate associated with backfill curing at 140 years increases as the temperature associated with the curing increases. When the peak temperature is 55 °C, the gas generation peak due to the temperature pulse exceeds that due to the later chloride pulse (Figure A3.43). In Case 7d and Case 7e, the gas generation reaches a peak value of just over 3 m³ yr⁻¹, but almost immediately decreases again, despite the temperature remaining high (Figure A3.44). The gas generation peak decays much faster than the temperature peak and this is caused by limited water availability. This result supports earlier findings that even if the chloride and temperature peaks were to overlap, the peak gas generation rate would be limited by the availability of water.
Figure A3.42 Temperature time series for Cases 7a to 7e in comparison with Case 3

Figure A3.43 Gas generation in the package through time
This appendix describes the development of a QPAC model to calculate the gas flux from a waste package containing encapsulated Magnox waste in a GDF. The model is designed to improve understanding of the controls on gas generation and migration, rather than to provide a robust prediction of gas generation rates. The peak gas flux out of the waste package is very closely linked to the peak gas generation rate because there is limited gas storage within the package.

A large part of the work considers the parameterisation of the ullage and filter as these materials are not typical porous media and yet are treated as such in the numerical model. The work has demonstrated that re-saturation of the waste package and therefore water availability for corrosion, is sensitive to the parameterisation of the ullage and filter, and this therefore represents a significant uncertainty in the model results.

Despite the uncertainty in the representation of the ullage and filter, it seems likely that the gas generation rate, and hence gas flux out of the package, will be limited by water availability during the post-closure period; water availability does not appear to be a limiting factor during storage and GDF operations. Water limitation was observed in cases where no suction was assumed in the ullage and filter, and also in cases where there was suction and groundwater carrying chloride ions entered the package.

The transport properties (e.g. the permeability, the presence of cracks) of the backfill, capping grout and encapsulant all influence how quickly chloride ions can enter the package, and more permeable systems have higher concentrations of chloride at earlier times which results in higher corrosion rates.

The temperature reached during backfill curing affects how large the gas generation peak is, but when corrosion rates are higher, corrosion becomes water-limited at an earlier time. Corrosion under high temperatures or in the presence of chloride becomes water-limited, so if chloride were to be present at the same time as high temperatures occur, the gas generation would still be water limited. However, the extreme conservatism of the chloride boundary conditions should be noted, and the analysis presented in Appendix 1 indicates that it is unlikely chloride will enter a package before the heat from backfill curing has dispersed.
A3.7 References

Appendix 4
AMEC Package-scale Modelling

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A4 AMEC Package-scale Modelling

A4.1 Introduction

Reactive metal wastes will corrode, which will consume water and produce gases (e.g. hydrogen), and this will set up a system of flows both around and into the waste packages. In order to understand these flows, both Quintessa (see Appendix 3) and AMEC have performed numerical modelling at the package-scale.

The waste package that was considered is an “average” package of encapsulated Magnox cladding from waste stream 2D38/C [1], and therefore contains about 150 kg of Magnox alloy, which was represented in the model as being in the form of plates with a thickness of about 2 mm, inside a 500l drum [2].

A4.1.1 Scope and Objectives

This appendix describes AMEC’s work to model gas generation in a waste package containing Magnox alloy, and the consequent flows of gases out of the package’s vent into the surrounding backfill. The work is intended to illustrate the range of behaviours for the release of carbon-14 bearing gases from the waste package, for example, determining:

- Whether gas generation might be limited by the supply of water from the surroundings; and
- How the ingress of chloride to the waste package will affect gas generation.

The objectives of this work are:

- To build a numerical model of gas generation and migration in a waste package containing Magnox swarf throughout its entire life (in a surface store, and then in a GDF during the operational period, backfilling and post-closure).
- To use the model to explore which processes and parameters have a significant influence on the rate at which gas is generated in and released from the waste package.

A4.1.1 Structure of this Appendix

This appendix is structured as follows:

- The numerical model is described in Subsection A4.2;
- Results for the reference case simulation are presented in Subsection A4.3;
- There are some differences between the Quintessa results (see Appendix 3) and the AMEC results, and the reasons for these differences are identified in Subsection A4.4;
- A set of variant cases is discussed in Subsection A4.5; and
- Lastly, Subsection A4.6 summarises the work and draws some conclusions.

A4.2 Model

Appendix 2 provides a detailed specification of the data that should be used in the package-scale models. This subsection goes on to describe AMEC’s implementation of the model; the description focuses on the differences between the Quintessa model (see Appendix 3) and the AMEC model rather than the similarities.
A4.2.1 Timescales

The lifetime of one waste package is considered, starting from when the waste is encapsulated at the Magnox Encapsulation Plant, Sellafield. The different conditions that the package experiences (see Appendix 2) were modelled by AMEC as follows:

- **0 – 60 years**: The waste is in an above ground store, which is passively or naturally ventilated, at a relative humidity (RH) of 70% and a temperature of 15 °C.
- **60 – 140 years**: The waste is stored in the GDF, in an open vault which is assumed to be ventilated, at a RH of 70% to prevent steel corrosion. The temperature is 25 °C, which is consistent with the expected geothermal temperature at 650m depth.
- **140 years**: The vault is backfilled with a cement material.
- **140 – 141 years**: The backfill cures, and the temperature in the vault is approximated as being at a constant value of 45 °C.
- **141 years**: The pressure of the porewater at the boundary of the package-scale model increases to the in situ hydrostatic pressure, assumed to be 6.5 \(10^6\) Pa.
- **141 – 146 years**: The backfill re-saturates and re-pressurises; the temperature in the vault is approximated as being at a constant value of 35 °C.
- **146 years onwards**: The temperature in the vault falls to its long-term value of about 30 °C (this is slightly cooler, i.e. 5 °C less, than has been used elsewhere in the Integrated Project on carbon-14; see Appendix 1 in Reference [6]), and chloride reaches the boundary of the model.

Note that because the package-scale model considers only a single package, it is not possible to simulate either the re-saturation of the vault or the evolution of temperature explicitly. Rather, these changes have to be imposed on the model.

AMEC used the computer program TOUGH2v2 [3-5] to simulate the flows of porewater and gases around the waste package. In this computer program, it is most convenient to assume that the boundary conditions and the temperature field vary in a stepwise way. Therefore, we have assumed that:

- There is a step change in the pressure of the porewater at the boundary of the model one year post-closure. This is not unreasonable, because:
  - We would expect a vault in a higher-strength rock with a relatively high permeability of \(10^{-16}\) m\(^2\) to re-saturate on a timescale of about a year (see Appendix A2.3 in Reference [6]).
  - The pressure in the vault will increase more or less hyperbolically from atmospheric pressure to the in situ hydrostatic pressure as the vault re-saturates. (This is a consequence of the (i) ideal gas law, and (ii) the fact that groundwater will flow into the vault at a roughly constant rate until the vault is almost re-saturated, and therefore the gas-occupied volume will reduce linearly with time.)
- The temperature field varies in a number of steps. Although this is an approximation (see Table A2.3), the period when the temperature field will be changing rapidly is short, and therefore there will be an insignificant effect on overall Magnox consumption. During the short period when the temperature field is changing rapidly, the predicted rates of gas generation will be in error by a small factor (i.e. up to a factor of 3).

A4.2.2 Two-phase Flow and Transport

TOUGH2v2 [3-5] was used to simulate the flows of porewater and gases around the 500l drum assuming a two-dimensional, axi-symmetric geometry. In TOUGH2v2, the flow of each phase is modelled using mass conservation and a modified form of Darcy's Law (with the two-phase nature of the flow taken into account through a relative permeability function).
In the past, AMEC has adapted the “EOS7R” fluid property module [7] of TOUGH2v2, so that the computer program can model the bulk gases hydrogen (H₂), oxygen (O₂) and nitrogen (N₂), in addition to water. Particular features of the modified fluid property module are:

- The density of the gas phase is computed by assuming that the gas phase is an ideal gas, and the partial pressures of its pure components add;
- The viscosity of the gas phase is obtained from the pure component viscosities using Wilke's method [8];
- The solubility of a pure component is determined using Henry's law (i.e. the solubility is proportional to the partial pressure of the gas); and
- The physical properties of the aqueous phase are assumed to be independent of the dissolved gas concentrations.

Thus, AMEC’s package-scale model considered the gas phase to be a mixture of components (H₂, O₂ and N₂), in contrast with Quintessa’s simulations, which considered only a single component (H₂; the air that was present in the waste package at the time of backfilling was replaced with H₂).

The more extensive set of multi-component, two-phase flow and transport processes was needed mainly when taking account of uranium metal that could be present in the waste, because the rate of uranium corrosion will depend on the availability of O₂.

### A4.2.3 Coupling Corrosion to Water Availability

The reactive metals (i.e. Magnox alloy and uranium) within a waste package will corrode. Appendix 2 gives information on the reactive metal inventory, the geometry, the corrosion reactions, and the corrosion rates for waste stream 2D38/C. The representation of corrosion in AMEC’s package-scale model is the same as in Quintessa’s model (see Appendix 3.3.2).

Anoxic corrosion of metals will proceed only when there is water available to support the reaction. In the package-scale models, therefore, we must specify how corrosion becomes limited by the availability of water. The nature of the coupling between corrosion in a grout matrix and the availability of water has not been established experimentally, and therefore is an area of uncertainty in the package-scale models. Notwithstanding, it is possible to suggest a “reasonable” hypothesis for the coupling.

As the grout in the package dries out (i.e. the liquid saturation falls towards the irreducible liquid saturation), AMEC’s package-scale model assumes that:

- First, the liquid phase becomes immobile (or discontinuous). This is taken to happen when the capillary pressure\(^{47}\) (or suction) in the grout increases to 3 \(10^7\) Pa.
- Corrosion may continue to consume water in the grout, in which case the capillary pressure will increase further. Corrosion is taken to occur at its unlimited rate until the capillary pressure in the grout increases to 5 \(10^7\) Pa, when the corrosion stops.

Note that the values of the capillary pressure at which first flow and then corrosion stops are arbitrary modelling choices. However, the values chosen are sufficiently large that they correspond to the liquid saturation in the grout being approximately equal to the irreducible water saturation \(S_{irr}\).

This coupling is broadly the same as the coupling used by Quintessa in their package-scale model (see Appendix 3.3.3). Although there are some differences in detail (e.g. the precise value of the liquid saturation at which anoxic corrosion stops), these are expected to have only a minor effect on the results obtained with the two numerical models.

\(^{47}\) 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.
A4.2.4 Model Geometry

The geometry of the waste package is described in Appendix 2.

AMEC simulated the flows of porewater and gases around the 500l drum using a two-dimensional, axi-symmetric numerical grid. The 500l drum is approximated as a cylinder, with dimensions that preserve the volume of the waste package. (The ribs on the drum and the taper at its top are not represented explicitly. This simplification will not affect the results.)

The backfill surrounding the 500I drum is represented explicitly (see Figure A4.1), together with the filter, ullage, capping grout and encapsulant, but the stainless steel container is not.

![Diagram of a waste package](image)

**Figure A4.1** Model representation of a waste package, consisting of a 500 litre drum filled with Magnox alloy, encapsulant and capping grout

Figure A4.2 shows part of the numerical grid used in the modelling.
A4.2.5 Material Properties and Parameterisation of the Filter / Ullage

The encapsulant and capping grout are cement materials, and the backfill is assumed to be Nirex Reference Vault Backfill [9]. The properties of these materials are given in Appendix 2.

The filter / ullage are not porous media, and so there is a question about how best to represent the hydraulic properties of these features using the equations for two-phase flow.

Three alternative representations of the ullage were investigated. In all of the cases, the intrinsic permeability and porosity of the filter / ullage were as specified in Table A2.4.

- First, in the reference case simulation (see Subsection A4.3), the ullage was modelled as a void that allowed fluids (i.e. both water and gas) to migrate freely through it. This was achieved by:
  - Using a van Genuchten model for the capillary pressure function in the ullage (with van Genuchten $P_r = 10^2$ Pa; van Genuchten $m = 0.333$; irreducible water saturation $S_{irr} = 0$; and residual gas saturation $S_{gr} = 0$); and by
  - Setting both the relative permeability functions (i.e. for the liquid and the gas) to unity.
Secondly, in a variant case (see Subsection A4.5.3.1), the ullage was modelled as a void that could pressurise with gas, and thereby prevent further ingress of porewater. This was achieved by:

- Modifying the capillary pressure function in the ullage (a linear extrapolation was used for liquid saturations below 0.2, in order to prevent the capillary pressure from decreasing towards negative infinity as the liquid saturation in the ullage approached zero); and by
- Using a linear relative permeability function for the liquid phase in the ullage, so that water would stop flowing through the ullage as the void filled with gas (the relative permeability function for the gas phase was still set to unity).

Thirdly, in another variant case (see Subsection A4.5.3.2), it was assumed that the ullage was filled with capping grout (i.e. there was no void at the top of the waste package).

A4.2.6 Initial and Boundary Conditions

The numerical model requires that initial and boundary conditions should be specified for a set of variables, namely: pressure, liquid saturation (or capillary pressure), concentrations of gaseous components, concentration of chloride; and temperature.

A4.2.6.1 Storage (0 – 140 years)

First, we summarise the choice of initial and boundary conditions for the storage period.

Initial conditions:

- Although the encapsulant and capping grout will be saturated with water when they are poured, some of this water will be incorporated into cement minerals as the materials set and harden. The manufacture of the waste package is not modelled in our simulations. However, the initial liquid saturation of 0.95 specified for the encapsulant and capping grout at the start of the storage period (see Appendix 2) takes into account the loss of water during cement hydration.
- The gas phase will have a pressure of approximately 1 atm, and the composition of air.
- Chloride will not be present.
- The temperature of the waste package will increase from 15 °C in a surface store to 25 °C in an operational vault in a GDF.

Boundary conditions:

- During storage, the grid cells that represent the backfill act as boundary cells (i.e. fluid flows are not calculated there), with a fixed capillary pressure\(^{48}\) corresponding to a relative humidity of 70%.
- The other boundaries of the model are no-flow boundaries.

A4.2.6.2 Post-backfilling (140 – 141 years)

Next, the waste package is surrounded by a cement backfill. This is associated with the following changes in initial and boundary conditions.

Initial conditions:

- Many of the variables inside the waste package will not change at the moment of backfilling. Only the temperature of the waste package and its surroundings is assumed to change, increasing discontinuously in the model from 25 °C to 45 °C (before falling back to 30 °C; see Subsection A4.2.1).

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\(^{48}\) It may be worth adding that during storage, the relative humidity (RH) in the store was implemented as a boundary condition outside the waste package, and the RH in the ullage was computed to be very similar to the RH in the store.
The package-scale model represents changes in the properties of the cement backfill as it cures. Initially, the backfill has a permeability of $10^{-15}$ m$^2$, a porosity of 0.615, and a liquid saturation of 1. These properties fall as the backfill cures. Eventually, the permeability of the backfill is $5 \times 10^{-17}$ m$^2$, the porosity is 0.452, and, if there were no other exchanges of water, the liquid saturation would be 0.942.

**Boundary conditions:**
- At the top boundary of the model, the gas phase will still have a pressure of approximately 1 atm and the composition of air. The RH, however, will increase to 100%, because the ventilation is assumed to have been turned off.

**A4.2.6.3 Early Post-closure (141 – 146 years)**

Then, the GDF will re-saturate. In the model, this is assumed to happen at one year after closure (see Appendix A2.3 of Reference [6]).

**Initial conditions:**
- The temperature of the waste package is assumed to fall from 45 °C to 35 °C.

**Boundary conditions:**
- The only change to the model associated with re-saturation is that the pressure at the top boundary of the model will increase from 1 atm to the *in situ* hydrostatic pressure, assumed to be $6.5 \times 10^6$ Pa.

**A4.2.6.4 Late Post-closure (146 years onwards)**

Later still, chloride will migrate into the vicinity of the waste package. In the package-scale models, this is assumed to happen at six years after backfilling. (Note that the analyses in Appendix 1 suggest that chloride actually will migrate more slowly through the backfill than is implied by this assumption.)

**Initial conditions:**
- The temperature of the waste package is assumed to fall from 35 °C to 30 °C.

**Boundary conditions:**
- The only change to the model associated with the migration of chloride, is that the chloride concentration at the top boundary of the model will increase from 0 ppm to its concentration in the groundwater, assumed to be 20,000 ppm (see Appendix 2).

**A4.3 Results for the Reference Case**

This subsection presents results for the AMEC reference case. Some key features of this particular simulation are that:
- The waste comprises only Magnox alloy;
- Neither the wasteform nor the backfill have cracks; and
- The ullage allows fluids (i.e. both water and gas) to migrate freely through it.

Variant cases (see Subsection A4.5) will explore the consequences of changing these assumptions.

**A4.3.1 Storage (0 – 140 years)**

During storage, the waste package dries because the relative humidity (RH) in the store is less than 100%. Although corrosion of the Magnox alloy does consume some water, drying is the dominant process by which water is lost from the capping grout and encapsulant.

Figure A4.3 shows how the liquid saturation in the waste package evolves during storage. It may be compared with Figure A3.14, from which it appears that the AMEC model is in good agreement with Quintessa Case 0 (and Variant Case 1a).
Figure A4.3 Liquid saturation in the waste package: (left) immediately following encapsulation of the waste; and (right) after 60 yr storage in a surface facility where the RH is 70% and the temperature is 15 °C.

Even though the package does dry during storage, the package-scale models found that the water content of the package would not fall sufficiently to limit corrosion, apart from in a variant case (see Subsection A4.5.2.1) where it was assumed that the wasteform was extensively degraded.

After a short transient (lasting for only a few months), hydrogen flows out of the vent at a constant rate of:

- $9.05 \times 10^{-3} \text{ m}^3 \text{ STP yr}^{-1}$ in the surface store; and
- $3.38 \times 10^{-2} \text{ m}^3 \text{ STP yr}^{-1}$ in the operational vault.

These are the same flows that the SMOGG gas generation model [11, 12] would have computed.

A4.3.2 Post-backfilling (140 – 141 years)

Next, the waste package is surrounded by backfill. The backfill sets and hardens, rapidly at first and then more slowly.
During the first few days following backfilling, the water content of the backfill evolves in a complicated manner, due mostly to the hardening of the cement material, but also to the formation of a gas pathway from the package vent to the model boundary.

Interestingly, for this particular simulation, in which water is able to flow easily through the ullage, the wasteform starts to re-saturate, and correspondingly the liquid saturation in the backfill close to the vent falls (see Figure A4.4).

The explanation of this behaviour is that the wasteform, following its storage in an atmosphere at a RH of 70%, is in a state of suction. It therefore has a tendency to pull water from out of its surroundings. In this case, water flows from the boundary of the backfill (where the pressure is at 1 atm, and water is assumed to be plentiful) to the vent, and then into the waste package.

The rate at which hydrogen flows out of the waste package increases gradually, and by 1 yr after backfilling the rate is:

- \( 3.20 \times 10^{-1} \text{ m}^3 \text{ STP yr}^{-1} \) in the backfilled vault.

This is equal to 92% of the flow that the SMOGG gas generation model would have predicted.

### A4.3.3 Early Post-closure (141 – 146 years)

Then, the GDF will re-saturate. In the model, this is taken to happen at 1 yr post-backfilling, and is associated with an increase in the pressure at the top boundary of the model, from 1 atm to the \textit{in situ} hydrostatic pressure (assumed to be \( 6.5 \times 10^6 \) Pa).

As a result of the pressure increase, water starts to flow from the backfill into the waste package (see Figure A4.5). Initially, the water collects in the ullage, where it compresses the gas phase.
Once the ullage has re-saturated, the water flows down into the remainder of the wasteform. The waste package is predicted to re-saturate fully on a timescale of about 100 days.

![Figure A4.5 Liquid saturation in the waste package: (left) 7 days from start of early post-closure period; (middle) 70 days from start of early post-closure period; and (right) 140 days from start of early post-closure period](image)

Even while the waste package is re-saturating, corrosion of the Magnox alloy continues to generate gases. The gases that are generated migrate upwards through the wasteform (see Figure A4.6). Capillary forces prevent the gas phase migrating onwards into the backfill, and therefore the gases accumulate in the ullage. For this particular simulation, in which water is able to flow easily through the ullage, the gas phase gradually flushes water (as well as dissolved gases) out of the ullage and into the backfill.
Figure A4.6 Liquid saturation in the waste package: (left) 1 yr from start of early post-closure period; (middle) 2 yr from start of early post-closure period; and (right) 5 yr from start of early post-closure period

The AMEC package-scale model predicts that the gas phase will not flow out of the waste package throughout this period, and indeed will remain unable to do so until after the ullage has filled with gas at a pressure that is equal to the in situ hydrostatic pressure plus the gas entry pressure of the backfill.

This is different to the behaviour that might have been inferred from the SMOGG gas generation model.

**A4.3.4 Late Post-closure (146 years onwards)**

The package-scale models assume that chloride will migrate into the vicinity of the waste package at about six years after backfilling. In the AMEC model, unlike the Quintessa model, there was no imposed groundwater flow through the backfill following re-saturation, and the concentration of chloride (i.e. 20,000 ppm) was fixed on the top boundary of the model from six years after closure.

Before any chloride has entered the package, the rate of Magnox corrosion is 0.428 μm yr⁻¹ at the prevailing temperature of 30 °C [13], and it is possible to calculate that water will be consumed (i.e. \( \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \)) at the rate \( 3.018 \times 10^{-12} \text{ m}^3 \text{ s}^{-1} \) (or \( 9.523 \times 10^{-5} \text{ m}^3 \text{ yr}^{-1} \)).

The transport velocity of water within the wasteform is given by the rate of water flow (\( \text{m}^3 \text{ s}^{-1} \)) divided by the wasteform’s horizontal area (0.471 m² in the model) and its porosity (0.165 in the model; this includes an allowance for the volume occupied by the Magnox waste). Thus, at steady-state before any chloride has entered the package, the transport velocity in the wasteform, \( u_0 \), is of the form:

\[
\dot{u}_0(z) = \frac{U}{h} \frac{z}{h} \quad (A4.1)
\]
where:

\[ U \] is a derived velocity parameter, \(3.893 \times 10^{-11}\) m s\(^{-1}\) (or, about 0.001 m yr\(^{-1}\)) for the values listed above;
\[ z \] is position (m), measured upwards from the bottom of the wasteform; and
\[ h \] is the height of the wasteform (1.036 m in the AMEC model).

Once chloride has migrated into the waste package, the rate of Magnox corrosion (and therefore the rate of water consumption) increases locally by a factor of about a hundred. As a consequence, the flow of water into the package grows, and chloride is transported with an increased velocity down through the wasteform.

At the chloride-enhanced rate of corrosion (i.e. 42.8 \(\mu\)m yr\(^{-1}\)) it takes only about 20 years to corrode all of the Magnox at an individual location within the wasteform. The AMEC reference case simulation shows that all of the Magnox at the very top of the wasteform will have corroded by the time that the chloride front has advanced a distance of about 0.1 m.

Thereafter, the chloride moves downwards through the wasteform, with a transport velocity of about \(4 \times 10^{-10}\) m s\(^{-1}\) (or, about 0.01 m yr\(^{-1}\); this velocity is an order of magnitude larger than the velocity before any chloride has entered the package), and behind the chloride front a narrow band (several centimetres high) of Magnox corrodes at the enhanced rate (see Figure A4.7).

![Figure A4.7](image_url)

**Figure A4.7** Variables in the waste package after the ingress of chloride, showing: (left) Magnox density (kg m\(^{-3}\) of wasteform); (middle) liquid saturation; and (right) chloride concentration (ppm)
At this transport velocity, it would take only about a hundred years for the chloride to be transported down the height of the wasteform. Actually, experiments show that chloride is weakly sorbing to concrete (see Appendix A1.3.3.1), and therefore this time should be multiplied by a retardation factor (of about 4.5; see Appendix A1.3.3.1).

The rates at which gases flow out of the waste package are shown in Figure A4.8 and Figure A4.9.

Figure A4.8  Calculated flows of gases out of the waste package early post-closure for the reference case. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.

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49 The AMEC model also accounted for the congruent release of carbon-14 (with an initial inventory computed to be $5.22 \times 10^5$ TBq per waste package at 1st April 2014 [1]) as the Magnox metal corroded. The results shown confirm that the release rate of carbon-14 is proportional to the release rate of bulk gas, as expected.
Figure A4.9  Calculated flows of gases out of the waste package in the medium term for the reference case. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.

The following sequence of events explains how the gas flows vary with time:

- The ullage continues to pressurise (see Subsection A4.3.3), and eventually, almost 20 yr after backfilling, a gas phase starts to flow out of the waste package and into the surrounding backfill.

- The rate at which hydrogen flows out of the package is initially about $6 \times 10^{-2}$ m$^3$ at STP yr$^{-1}$. This matches the flow that the SMOGG gas generation model would have predicted.

- Chloride starts to enter the package at about 200 yr after backfilling, and as a result the rate at which hydrogen flows out of the package increases to about $1 \times 10^{0}$ m$^3$ at STP yr$^{-1}$. This is about 17% of the flow that the SMOGG gas generation model would have predicted, because only a fraction of the Magnox alloy is corroding at the chloride-enhanced rate.

- By about 350 yr after backfilling, the Magnox alloy has corroded completely away, and the flow of hydrogen out of the package drops to about $4 \times 10^{-4}$ m$^3$ at STP yr$^{-1}$. The source of
this hydrogen is vestigial gas that is left in the ullage and, to a lesser extent, the 
wasteform, which migrates out through the vent and into the surrounding backfill as the 
package re-saturates gradually for a second time. However, there is no longer a gas 
pathway to the boundary of the model, because gas generation has stopped, and so the 
gases dissolve into the pore waster and then diffuse away from the package.

- The rate at which carbon-14 bearing gas flows out of the package is essentially a scaling 
of the rate at which hydrogen flows out of the package.

It is instructive to compare the above flows with those that would have been obtained if there had 
been no chloride in the groundwater (see Figure A4.10 and Figure A4.11).

Figure A4.10 Calculated flows of gases out of the waste package early post-closure for a 
case with no chloride. The carbon-14 bearing gas (which assumes that the 
carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ 
during corrosion) is plotted against the left-hand axis, and the bulk gas 
(hydrogen) is plotted against the right-hand axis.
Figure A4.11 Calculated flows of gases out of the waste package in the medium term for a case with no chloride. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.

Apart from the increase in the flows of gases that is associated with the ingress of chloride to the waste package, the sequence of events is very similar to that predicted for the reference case.

A4.3.5 Discussion

Generally, the conceptual picture that emerges from the reference case simulation is reasonable. In particular:

- The encapsulant will dry while the waste package is stored in an atmosphere at an RH of 70%. However, both Quintessa and AMEC found that drying would not be pervasive enough that water availability would limit corrosion.
  - At this time, after a short transient (lasting for only a few months), gases will flow out of the vent at a constant rate equal to the flows that the SMOGG gas generation model would have predicted.
Emplacing cement backfill around the waste package will be associated with a complicated pattern of flows, as the backfill hardens and a gas pathway forms from the package’s vent through the backfill\textsuperscript{50}. The waste package might be in a state of suction following storage, in which case there could be some re-saturation of the package.

Later, re-saturation of the vault will result in re-saturation of the waste package. The gas phase inside the package will be compressed into a small pocket of gas at the top of the ullage; the encapsulant will be re-saturated.

- Note that gases will be generated inside the waste package, and will be released from the package at approximately the rate that they are generated.

Later still, chloride will migrate into the waste package.

- As a result, there will be increases in the consumption of porewater inside the package due to Magnox corrosion, and correspondingly the flow of water into the package. The transport velocity inside the package will build up to a value (in the AMEC reference case simulation, about $4 \times 10^{-10}$ m s$^{-1}$ or $0.01$ m yr$^{-1}$) that is intermediate between the value before the ingress of chloride (i.e. $4 \times 10^{-11}$ m s$^{-1}$, or $0.001$ m yr$^{-1}$) and a hundred times the latter value (i.e. $4 \times 10^{-9}$ m s$^{-1}$, or $0.1$ m yr$^{-1}$).

- In the AMEC reference case, the porewater diffusion coefficient of chloride in the grout has a realistic value, based on a review of the extensive experimental data (see Appendix A1.3.3), and there is no mechanical dispersion. For this case, the Péclet number,

$$ Pe = \frac{vL}{D_{app}} $$

where $v$ is the transport velocity (m s$^{-1}$), $L$ is a characteristic length (m), and $D_{app}$ is the apparent diffusion coefficient (m$^2$s$^{-1}$), is much greater than one. This means that advection by the flow of water will be more significant than porewater diffusion for transporting chloride downwards through the wasteform. Because the transport velocity is computed to be $v \approx 0.01$ m yr$^{-1}$ inside the waste package, it will take about 100 yr for chloride to migrate from the top to the bottom of the waste package.

- At the chloride-enhanced rate of corrosion, it will take only about 20 yr to corrode all of the Magnox at a point. The AMEC reference case simulation shows that all of the Magnox at the very top of the wasteform will have corroded by the time that the chloride front (defined as being the locus where the chloride concentration is equal to 100 ppm) has advanced a distance of about 0.1m. Thereafter, a narrow band (several centimetres high) of Magnox will be corroding at the enhanced rate behind the chloride front, as it migrates downwards through the wasteform.

- Because only a fraction of the Magnox in the waste package will be corroding at the chloride-enhanced rate, the rate at which gases flow out of the package will increase to about 10% – 20% of the flows that the SMOGG gas generation model would have predicted.

Lastly, once the Magnox alloy has corroded away, the waste package will re-saturate. Gases from the ullage will dissolve into the backfill porewater and diffuse away from the package, while water from the backfill will drain into the package.

Although most aspects of the AMEC reference case results are reasonable, the approximation of the ullage as a porous medium does affect the computed flows. For example, the gas phase is predicted to flush water out of the ullage and into the backfill following re-saturation, but that may not happen. This behaviour is a consequence of the pressurisation of the ullage, which is modelled.

\textsuperscript{50} Current research, which has not yet been reported, suggests that there is the potential for the gas to form a “wormhole” through wet grout, which will be preserved as the grout hardens.
as a porous medium with a very high permeability. It seems more likely that a gas pocket will form at the top of the ullage, and gas will migrate from there into the surrounding backfill. Some water will remain at the bottom of the ullage, and will be driven downwards into the encapsulant to replace water that has been consumed by corrosion of the Magnox alloy. While the representation of the ullage in the numerical model may not capture the complexity of the flows in the real system, it is considered that this will affect the results that are obtained only slightly.

A4.4 Explanation of the Differences from the Quintessa Model

The conceptual picture presented in Subsection A4.3.5 above, is different in some respects to the conceptual picture presented by Quintessa in Appendix 3.

Specifically, Quintessa have argued from their reference case (i.e. Case 3; see Appendix A3.4.2) that post closure:

- Chloride will spread throughout the waste package quickly (i.e. in $200 \text{ yr} - 166 \text{ yr} = 34 \text{ yr}$; see Figure A3.31). This is faster than in the AMEC reference case (i.e. 100 yr).
- Next, the porewater inside the package will be consumed due to corrosion of the Magnox faster than it can be replaced by the flow of water into the package. Thus, the package will dry out, limiting the fraction of the Magnox alloy that can corrode at the chloride-enhanced rate (see Figure A3.32). This is different to the AMEC reference case, where the package did not dry out.
- Then, corrosion of the Magnox, and associated gas generation, will occur at a rate that is controlled by the flow of water into the waste package (see Figure A3.26).

This subsection clarifies the causes of the differences. It turns out that there are two main causes:

- First, the AMEC model uses a chloride diffusion coefficient that is based on literature data (see Appendix A1.3.3, which was written after the Quintessa modelling had been performed), while the Quintessa model includes a considerable amount of hydrodynamic dispersion (see Appendix A2.3.4).
  - This explains why chloride spreads throughout the waste package more quickly in the Quintessa reference case (34 yr) than in the AMEC reference case (100 yr). We note that the difference in the timescales is small, and argue that the actual value is likely to lie somewhere in the range between the Quintessa result and the AMEC result (depending, for example, on the extent of cracking of the grout inside the waste package).

This point is discussed further in Subsection A4.4.1 below.

- Secondly, the two models use alternative representations of the transport processes in the ullage. In the Quintessa reference case, the ullage restricts the movement of water into the waste package, but in the AMEC reference case, water can flow easily across the ullage.
  - This explains why, after the encapsulant has dried out due to the consumption of water by Magnox corrosion, corrosion occurs at a lower rate in the Quintessa reference case than in the AMEC model. We note that it is difficult to know how the ullage will behave in a real GDF over the very long timescales that have to be considered (see Subsection A4.5.3), and argue that both the Quintessa result and the AMEC result are plausible variants.

This point is discussed further in Subsection A4.4.2 below.

A4.4.1 Effect of Dispersion

The first point to note is that Quintessa’s package-scale model includes a considerable amount of hydrodynamic dispersion (see Appendix A2.9.4).
The longitudinal dispersivity is set to 0.6535m, which is large when compared with the size of a waste package. With this value of the longitudinal dispersivity, hydrodynamic dispersion is an important process, as well as advection, for spreading chloride through the wasteform. The greater spreading of the chloride around the front compared with the AMEC model also has a secondary effect. It means that at any one time more of the Magnox alloy will be corroding at the chloride-enhanced rate; as a consequence, there will be a greater flow of porewater into the waste package, and so the chloride will be transported down the wasteform more quickly.

In order to test the hypothesis that the differences between the two models are due to hydrodynamic dispersion, AMEC ran a variant of their model in which the diffusion coefficient of the chloride was set to a large value. (Note that the “EOS7R” fluid property module [5] of TOUGHv2 cannot model hydrodynamic dispersion, and so increasing the diffusion coefficient was a workaround that should give a similar behaviour to the Quintessa model.)

This variant shows chloride migrating down through the wasteform more quickly than in the reference case; it takes the chloride about 10 yr to migrate from the top to the bottom of the encapsulant. This is less than the 20 yr it would take for all of the Magnox at a point to corrode at the chloride-enhanced rate, and therefore there is the potential for all of the Magnox inside the package to be corroding at this rate.

It also shows the encapsulant drying out (see Figure A4.12). The backfill, capping grout and encapsulant provide a resistance to flow, which restricts the flow of water into the waste package to about two-thirds of the maximum rate of water consumption due to all of the Magnox corroding at the chloride-enhanced rate. Therefore, the liquid saturation falls to the irreducible water saturation $S_{irr}$ in the bottom one-third of the waste package, and then corrosion stops there.

Figure A4.12 Variables in the waste package after the ingress of chloride, showing: (left) Magnox density (kg m$^{-3}$ of wasteform); (middle) liquid saturation; and (right) chloride concentration (ppm)
The rates at which gases flow out of the waste package are shown in Figure A4.13 – Figure A4.15.

Figure A4.13 Calculated flows (on a linear scale) of gases out of the waste package early post-closure for a case with increased diffusion of chloride. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.
Figure A4.14 Calculated flows of gases out of the waste package early post-closure for a case with increased diffusion of chloride. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.
Figure A4.15 Calculated flows of gases out of the waste package in the medium term for a case with increased diffusion of chloride. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.

The following sequence of events explains how the gas flows vary with time (refer to Figure A4.13, in particular):

- Chloride (at a concentration of 100 ppm) enters the encapsulant at about 20 yr after backfilling, and migrates to the bottom of the wasteform within a further 10 yr. As a result, the rate of hydrogen generation increases to about $6\times10^8$ m$^3$ at STP yr$^{-1}$. This matches the flow that the SMOGG gas generation model would have predicted.

- The bottom part of the waste package dries out by about 10 yr later, and therefore the rate of hydrogen generation falls to less than $5\times10^7$ m$^3$ at STP yr$^{-1}$.

- The Magnox in the top part of the package has corroded completely away by about 55 yr after backfilling, and so the rate of hydrogen generation drops to less than $2\times10^9$ m$^3$ at STP yr$^{-1}$, arising from corrosion of the Magnox in the bottom part of the package.

- The Magnox in the remainder of the package has corroded completely away by about 75 yr after backfilling, and then hydrogen generation stops.
It appears that treating hydrodynamic dispersion in the same way is sufficient to reconcile some of the main differences between the AMEC package-scale model results and the Quintessa results. For example, both models show:

- Chloride migrating quickly through the wasteform; and
- The encapsulant drying out due to consumption of water by Magnox corrosion.

Nonetheless, there still are some differences, notably the fact that Magnox corrosion continues at a very low rate for a long time (i.e. hundreds of years) in Quintessa Case 3 (see Figure A3.26), but is over by about 75 yr after backfilling in the AMEC variant (see Figure A4.13).

### A4.4.2 Effect of Alternative Behaviour of the Ullage

The explanation of the outstanding differences between the AMEC variant and Quintessa Case 3 involves the representation of the ullage in the two models.

In the AMEC variant, it has been assumed that fluids (i.e. water and gases) can move easily across the ullage. In Quintessa Case 3, however, the permeability of the ullage to the liquid phase is essentially a linear function of the reduced saturation, $S_{ew}$:

$$
S_{ew} = \frac{S_w - S_{irr}}{1 - S_{irr}}
$$

where $S_w$ is the liquid saturation (–), and $S_{irr}$ is the irreducible water saturation (–). Thus, there is the potential for the ullage to provide a significant resistance to flow in the Quintessa simulation, but not in the AMEC model. This could account for the very slow re-saturation found in Quintessa Case 3 (see Figure A3.32, reproduced as Figure A4.16 below for convenience).

In order to test this hypothesis, Quintessa ran a variant of their Case 3, in which the main change was to increase the gas entry pressure (van Genuchten $P_r$) for the ullage / filter from $10^3$ Pa to $10^4$ Pa. The implication of this particular change is that for a given set of pressures inside the waste package, the liquid saturation in the ullage, and therefore the permeability to the liquid phase, will be larger in the variant simulation than in Case 3 (e.g. see Equation (A3.4)).

The results from the variant simulation (which was called “Case_1b_Cl”) are shown in Figure A4.17 and Figure A4.18. It is apparent from these results that this variant of Quintessa Case 3 is behaving more similarly to the AMEC variant (see Figure A4.12 and Figure A4.13).

Any remaining discrepancies between the two models may be explained as being due to different assumptions about the geometries (e.g. the ullage is smaller in the Quintessa model), the transport processes (e.g. advection-dispersion in the Quintessa model, but advection-diffusion in the AMEC model) and properties (e.g. the parameterisation of the saturation functions for the ullage / filter).
Figure A4.16 Quintessa model results for Case 3 (see Appendix 3): (top) a close-up view showing liquid saturation in a waste package as a function of time; (bottom) chloride concentration in the package (which is towards the bottom of the model region) and in the overlying cement backfill as a function of time.
Figure A4.17 Quintessa model results for a variant of Case 3 (see Figure A4.16), in which the gas entry pressure (van Genuchten $P_r$) for the ullage / filter has been increased from $10^3$ Pa to $10^4$ Pa: (top) a close-up view showing liquid saturation in a waste package as a function of time; (bottom) chloride concentration in the package (which is towards the bottom of the model region) and in the overlying cement backfill as a function of time.
Figure A4.18 Quintessa model predictions of gas generation rate (from half a package) versus time for:

**Case_1b**  this is a case with no chloride. It corresponds to Case 1a in Appendix 3, but the gas entry pressure (van Genuchten $P_r$) for the ullage / filter has been increased from $10^3$ Pa to $10^4$ Pa.

**Case_1f**  this is a case with chloride. The corrosion rate increases linearly during re-saturation until it is $100\times$ higher than in Case_1b; it is similar to Case 2b mentioned in Appendix A3.4.2.

**Case_1b_Cl**  this is a case with chloride. It corresponds to Case 3 in Appendix 3, except that the gas entry pressure for the ullage / filter has been increased from $10^3$ Pa to $10^4$ Pa.

In conclusion, as discussed in Appendix A1.6, the ullage could pressurise with gas, and thus stop the inflow of liquid water and the ingress of chloride to the waste package.

In the AMEC package-scale model results that have been shown here, it has been assumed that fluids (i.e. water and gases) can move easily across the ullage. In the Quintessa model results, the ullage limits the inflow of liquid water either partly (see Figure A4.17 and Figure A4.18) or almost completely (see Case 3 in Appendix 3).

Regarding Quintessa Case 3, some chloride does get into the waste package before the ullage can pressurise, but then the ullage pressurises and the supply of water to the package drops. As a consequence, the wasteform dries out, and thereafter the Magnox alloy corrodes at a rate that is determined by a very restricted flow of water across the ullage and into the wasteform.

**A4.4.3 Discussion**

The package-scale numerical models have shown that the key controls on the transport of chloride within the waste package include:

- The amount of dispersion (or spreading) around the chloride front; and
- The behaviour of the ullage (i.e. does it allow inflow of water after pressurising with gas).
Some variant simulations have assumed a large amount of dispersion (see Subsection A4.4.1, and also Appendix 3), and these predict that chloride will migrate a little faster down through the wasteform (and a thicker band of Magnox will be corroding at the enhanced rate).

Other variant simulations have considered the effect of the ullage (see Subsection A4.4.2, and also Subsection A4.5.3 below). Clearly the ullage is an important feature, affecting how the Magnox alloy in a waste package might corrode. There is some evidence that the ullage could be a barrier to water flow [14], but it is difficult to know with certainty how the ullage will behave in a real GDF over the very long timescales that have to be considered. Therefore, although the presence of the ullage can be recognised as being potentially beneficial, we have not taken credit for it when assessing the release of carbon-14 from packages containing Magnox wastes.

It follows that, of the various results which have been presented up until now, arguably the AMEC reference case, which did not restrict the movement of water into the waste package, should be used to inform the assessment models of the release of carbon-14 from Magnox wastes. This particular simulation assumed that:

- The porewater diffusion coefficient of chloride in the grout has a realistic value, based on a review of the extensive experimental data (see Appendix A1.3.3);
- There is no hydrodynamic dispersion; and
- The liquid phase is fully mobile in the ullage at all saturations.

The key conclusions from the AMEC modelling are that:

- Chloride will be transported slowly down an uncracked wasteform over a period of about 100 yr. In fact, experiments show that chloride is weakly sorbing to concrete [20], and therefore this time should be multiplied by a retardation factor (of about 4.5).
- No more than a small fraction of the Magnox alloy inside a waste package will be corroding at the chloride-enhanced rate at any one time.

**A4.5 Variant Cases**

A set of variant cases were run to investigate particular questions about the rates at which gases will be generated in, and released from, a waste package. The questions were as follows:

- Assuming that the waste includes trace quantities of uranium metal as well as Magnox alloy, how will the concentration of oxygen (which will be consumed during oxic corrosion of the uranium) vary with position through the encapsulant? (see Subsection A4.5.1)
- How will the presence of cracks in the wasteform, or in the backfill, affect the rates at which gases are released from the waste package? (see Subsection A4.5.2)
- What is the range of behaviours that could be manifested by the ullage, which is an important feature that will affect how gases might be released from the waste package? (see Subsection A4.5.3)

**A4.5.1 Uranium**

An “average” package of encapsulated Magnox cladding from waste stream 2D38/C [1] will also contain some uranium metal. The rate of uranium corrosion will depend on the redox potential (Eh), and is known to be much faster under anoxic conditions than in an oxic environment (see Appendix A2.7.2 and [13]).

This variant case adds some uranium metal into the wasteform, and couples its corrosion to the presence of oxygen. The purpose of the variant is to investigate whether:

- Oxygen will be consumed fast enough by uranium corrosion that conditions are anoxic; or
- Oxygen will migrate sufficiently quickly through the wasteform that conditions are oxic.
This is a question mostly for the storage period of the waste package, because after backfilling the package could be cut off from its supply of oxygen, and in that case all of the oxygen inside the package would be consumed in less than a year (at a temperature of 45 °C).

The variant case assumes that initially the encapsulant and capping grout inside the package are saturated with water. Then, as the package dries out in a surface store (at a relative humidity of 70%), oxygen starts to migrate into the gas-occupied porosity inside the wasteform.

Figure A4.19 and Figure A4.20 show results from our model for the variables inside the waste package after 0.1 yr and 1 yr in the surface store respectively.

Figure A4.19 Variables in the waste package after 0.1 yr in a surface store, showing: (left) uranium density (kg m\textsuperscript{-3} of wasteform); (middle) gas saturation; and (right) oxygen concentration (volume fraction)
Figure A4.20 Variables in the waste package after 1 yr in a surface store, showing:
(left) uranium density (kg m$^{-3}$ of wasteform); (middle) gas saturation; and
(right) oxygen concentration (volume fraction)

The rates at which gases flow out of the waste package are shown in Figure A4.21.
Figure A4.21 Calculated flows of gases out of the waste package during storage for a case with uranium metal in the inventory. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.

Initially, conditions inside the waste package are anoxic, and the uranium metal corrodes relatively rapidly, releasing both hydrogen and carbon-14 gas. However, conditions throughout the package become oxic within a year, and thereafter the uranium metal corrodes more slowly, releasing only carbon-14 gas. Apart from the initial transient, these are the same flows that the SMOGG gas generation model would have computed (assuming oxic conditions).

It is instructive to compare the above flows with those that were obtained from the AMEC reference case (see Figure A4.22).
Figure A4.22 Calculated flows of gases out of the waste package during storage for the reference case. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.

Note that the flows of bulk hydrogen, which originates only from Magnox corrosion, are the same in Figure A4.21 and Figure A4.22. However, the flows of carbon-14 gas are different, because corrosion of the uranium metal contributes an additional source of carbon-14 gas.

Although this variant case suggests that the conditions inside the wasteform should be oxic, it turns out that this is only a part of the story.

The encapsulant that is being used to condition the Magnox cladding from waste stream 2D38/C incorporates Blast Furnace Slag (BFS). BFS is known to lower the redox potential; for example, Glasser [15] has observed that:

"Cement pore fluids also have an Eh or redox potential. 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 electro-active substances affect the Eh. Blast
furnace slag, which typically contains ~1% sulfide, markedly lowers the Eh to -300 mV and provides a poising reserve.”

Thus, the eventual conclusion of this variant case is that although it is possible oxygen will be amply present throughout the wasteform, the cement encapsulant itself could establish a low Eh, which would increase the rate of uranium corrosion.

**A4.5.2 Effect of Cracks in the Wasteform or Backfill**

**A4.5.2.1 Cracks in the Wasteform**

This subsection is concerned with the possible presence of cracks in the wasteform. This scenario was modelled simply by increasing the permeability of the encapsulant and capping grout.

The main consequence of the presence of the cracks, as seen in the AMEC package-scale model, was more extensive drying of the wasteform during storage (see Figure A4.23) as compared to the reference case (see Figure A4.3).

![Figure A4.23 Liquid saturation in a waste package with cracked encapsulation grout: (left) soon after encapsulation of the waste; (right) after 60y storage in a surface facility where the RH is 70% and the temperature is 15 °C](image-url)
The rates at which gases flow out of the waste package are shown in Figure A4.24.

Figure A4.24 Calculated flows of gases out of the waste package during storage (at a RH of 70% and a temperature of 15 °C) for a case with cracked encapsulation grout. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}\text{CH}_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.

Interestingly, gas generation does not stop in the waste package, even though the liquid saturation has fallen to approximately the irreducible water saturation $S_{irr}$. That is a result of AMEC’s assumption (see Subsection A4.2.3) that:

- First, the liquid phase becomes immobile (or discontinuous); but
- Corrosion continues to consume water in the grout, until the liquid saturation has decreased by an additional small amount.

Next, considering the post-closure period, the reason why there is little change in the predicted behaviour of the waste package is that migration of chloride through the wasteform is an advective process, and the transport velocity in the numerical models is determined by the fraction of the
Magnox alloy that is corroding at the chloride-enhanced rate. It is acknowledged that the presence of cracks in the grout might change the nature of the advective flow, and that could shorten the timescale for chloride to be transported down the wasteform. However, this is not an important consideration, because, referring back to the analyses in Appendix 1, it is clear that it is the backfill, rather than the encapsulation grout, which will contribute most to the delay in chloride coming into contact with the Magnox alloy inside a vault.

Lastly, the results obtained here are similar to those for Quintessa Case 6 (in which the grout has an increasing permeability; see Figure A3.38 and Figure A3.39), and are different to those for the Quintessa reference case (i.e. Case 3). With the benefit of the insights from Subsection A4.4.2 on the flow of water through the ullage, it may be worth adding that Quintessa Case 6 is unlike Quintessa Case 3 because:

- As modelled, gas will be able to migrate at higher liquid saturations in a package with a cracked wasteform; but
- In the Quintessa package-scale model, a higher liquid saturation in the ullage would mean that water is able to flow more easily there.

Thus, it is only to be expected that Quintessa Case 6 should be more like Quintessa Case_1b_Cl (see Subsection A4.4.2), and also this AMEC variant case.

A4.5.2.2 Cracks in the Backfill

This subsection is concerned with the possible presence of cracks in the backfill. This scenario was modelled simply by increasing the permeability of the backfill, and reducing the gas entry pressure (van Genuchten $P_r$) correspondingly.

The consequence of this change is that fluids (i.e. both water and gas) can migrate more freely through the backfill than in the AMEC reference case. Therefore, the waste package re-saturates a little more quickly, and the gas phase migrates away from the package at a lower pressure.

The rates at which gases flow out of the waste package are shown in Figure A4.25 and Figure A4.26.
Figure A4.25 Calculated flows of gases out of the waste package early post-closure for a case with cracked backfill. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}\text{CH}_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.
Calculated flows of gases out of the waste package in the medium term for a case with cracked backfill. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis. These rates are similar to those for the AMEC reference case (see Figure A4.8 and Figure A4.9).

Lastly, the results that were obtained for the corresponding Quintessa variant (i.e. Case 4, in which the vault backfill has a higher permeability; see Figure A3.34 and Figure A3.35) can be reconciled with the results shown here, although they are dissimilar to the Quintessa reference case (i.e. Case 3$^{51}$).

**A4.5.3 Effect of Alternative Behaviour of the Ullage**

It has been argued already in Subsection A4.2.2 that the ullage is an important feature, affecting how the Magnox alloy in a waste package might corrode and release gases.

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$^{51}$ Quintessa Case 4 behaves differently to Quintessa Case 3, because the pressures calculated in the ullage are lower for the former variant than for the latter, and as explained previously (see Subsection A4.5.2.1), that means water can flow through the ullage into the waste package more easily for Quintessa Case 4.
In Quintessa Case 3 (see Appendix 3), for example, chloride got into the waste package, and then the ullage pressurised with gas. In this variant, the ullage restricted the supply of water to the Magnox wastes, and so the package dried out. Thereafter, corrosion continued at a lower rate determined by the transport of water through the ullage into the waste package.

It is difficult to know with certainty how the ullage will behave in a real GDF, and therefore this subsection investigates the range of behaviours that could be manifested by the ullage. In particular, results are presented for two variant cases:

- In the first variant, the ullage pressurises with gas, and that prevents the flow of liquid water (and chloride) into the waste package (see Subsection A4.5.3.1).
- In the second variant, the ullage is filled with capping grout, so that there is no void space at the top of the waste package (see Subsection A4.5.3.2).

### A4.5.3.1 Ullage Pressurises with Gas which Prevents the Flow of Liquid Water

In this variant case, the saturation functions for the ullage / filter were modified so that the liquid saturation would go to zero as gas accumulated in the ullage / filter. As a result:

- The ullage / filter becomes impermeable to the liquid phase; and
- Solutes are unable to diffuse through the liquid phase across the ullage / filter.

It takes about 20 yr for the ullage to pressurise with gas. Thereafter, the interior of the waste package is cut off from the external liquid phase. No more liquid water or chloride can migrate into the waste package. The Magnox alloy corrodes, gradually consuming the available water inside the waste package. Because the ullage pressurises with gas before any chloride has migrated into the waste package (see Figure A4.27), the rate of Magnox corrosion is not enhanced. Eventually, at about 675 yr after backfilling, all of the available water is consumed (see Figure A4.27) and the corrosion stops. Some (approximately two-thirds; see Figure A4.27) of the Magnox alloy is left behind when the corrosion stops.
Figure A4.27 Variables at 1,000 yr after packaging in a waste package with an ullage that can prevent the flow of liquid water, showing: (left) Magnox density (kg m$^{-3}$ of wasteform); (middle) liquid saturation; and (right) chloride concentration (ppm).

The rates at which gases flow out of the waste package are shown in Figure A4.28.
Figure A4.28 Calculated flows of gases out of the waste package in the medium term for a case where the ullage pressurises with gas, which prevents the flow of liquid water. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.

Following on from the discussion in Appendix A1.6, arguably this variant case may be the most accurate simulation of the actual behaviour of a package of encapsulated Magnox waste in a geological disposal facility. That being said, it is possible that a small amount of liquid water could enter the package even after the ullage is pressurised (as happens in the Quintessa reference case), either flowing as a film on the steel surface of the 500l drum or forming droplets. Therefore, even though the presence of the ullage is recognised as being potentially beneficial, no credit will be taken for it when assessing the release of carbon-14 from packages containing Magnox wastes until we have a better understanding of its performance.

A4.5.3.2 Ullage is Filled with Capping Grout

The ullage is a void space at the top of the waste package, which will function as both a gas reservoir and a fast pathway for transport of solutes. This variant case assumes that the ullage has been filled with capping grout, so that there is no void space.
Because there is no gas reservoir at the top of the waste package:

- It will take less time for the package to re-saturate; and
- Gases will flow out of the package at essentially their rate of generation.

A slightly less obvious consequence of the ullage being filled is that it changes the way in which chloride migrates into the wasteform. In the AMEC reference case, chloride spreads throughout the ullage, and then is transported downwards into the wasteform; this is a one-dimensional linear advection-diffusion process. In this variant case, however, transport of chloride from the package vent is initially radial (see Figure A4.29), and only later does it become mainly vertical (see Figure A4.30).

**Figure A4.29** Variables at 350 yr after packaging in a waste package with an ullage that has been filled with capping grout, showing: (left) Magnox density (kg m$^{-3}$ of wasteform); (middle) liquid saturation; and (right) chloride concentration (ppm)
Variables at 420 yr after packaging in a waste package with an ullage that has been filled with capping grout, showing: (left) Magnox density (kg m\(^{-3}\) of wasteform); (middle) liquid saturation; and (right) chloride concentration (ppm)

The rates at which gases flow out of the waste package are shown in Figure A4.31 and Figure A4.32.
Figure A4.31 Calculated flows of gases out of the waste package early post-closure for a case where the ullage is filled with capping grout. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}\text{CH}_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.
Figure A4.32 Calculated flows of gases out of the waste package in the medium term for a case where the ullage is filled with capping grout. The carbon-14 bearing gas (which assumes that the carbon-14 inventory of the Magnox alloy is released congruently as $^{14}$CH$_4$ during corrosion) is plotted against the left-hand axis, and the bulk gas (hydrogen) is plotted against the right-hand axis.

These flows differ somewhat from those for the AMEC reference case (see Figure A4.8 and Figure A4.9). Specifically, the flows of gases out of the waste package start to increase sooner, but rise more slowly, in this variant case than in the AMEC reference case. The explanation of this behaviour is the different geometry (i.e. 3D radial versus 1D linear) for the initial transport of chloride into the wasteform.

A4.6 Summary and Conclusions

A package-scale model has been developed, and used to calculate the flows of gases out of a waste package containing encapsulated Magnox cladding from waste stream 2D38/C.

Because the presence of chloride will accelerate the rate of corrosion of Magnox alloy, possibly by as much as two orders of magnitude, this groundwater solute is significant for assessments of carbon-14 release from a geological disposal facility. Therefore, it is appropriate to ask how chloride (in solution) might migrate into the waste package, before contacting the Magnox wastes.
The numerical model shows that advection of chloride downwards through the wasteform will be an important transport process. The timescale for chloride to be transported throughout the wasteform is predicted to be about 100 yr (which is short when compared with the timescale for chloride to migrate through the backfill; see Appendix 1).

The apparent diffusion coefficient of chloride through the grout determines how much the chloride will spread around the advection front. For the parameter values in the AMEC reference case simulation, there is very little spreading (i.e. the Péclet number is much larger than one), and therefore the chloride will migrate as a sharp front.

Because corrosion of Magnox at the chloride-enhanced rate is very fast, it will take only about 20 yr for all of the Magnox at a point to corrode. The AMEC reference case simulation shows that all of the Magnox at the very top of the wasteform will have corroded by the time that the chloride front (defined as being the locus where the chloride concentration is equal to 100 ppm) has advanced a distance of about 0.1m. Thereafter, a narrow band (several centimetres high) of Magnox will be corroding at the enhanced rate behind the chloride front, as it migrates downwards through the wasteform.

Because only a fraction of the Magnox in the waste package will be corroding at the chloride-enhanced rate, the flows of gases out of the package will increase to about 10% – 20% of the flows that the SMOGG gas generation model would have predicted for a single package.

The ullage has been identified as an important feature, influencing how the Magnox alloy in a waste package might corrode and release gases. It has the potential to limit the ingress of both water and chloride to the package. If the supply of water to the wastes were limited, then the Magnox could consume all of the available water inside the package. Thereafter, corrosion would stop, possibly while there is still some Magnox remaining inside the package; corrosion would resume only after the 500l drum had failed. If the ingress of chloride were prevented, then the rate of Magnox corrosion might never be enhanced.

That being said, it is possible that a small amount of liquid water could enter the package even after the ullage is pressurised, either flowing as a film on the steel surface of the 500l drum or forming droplets. Therefore, even though 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.

### A4.7 References

2. A.C. Adeogun and M. Plews, *Carbon-14 Project Phase 2 – Inventory*, AMEC Report to RWM, AMEC/200047/003 Issue 1, 2016.


