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Preface

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Summary

The current UK baseline assumption for the disposal of irradiated graphite wastes, particularly large volumes of reactor core graphite, is disposal in a Geological Disposal Facility (GDF). No firm decisions have yet been made concerning the conditioning and packaging of the graphite wastes, and these wastes potentially pose significant challenges because of their relatively large volume and the radionuclide inventory associated with them.

NDA RWMD is currently considering how a range of multi-barrier disposal concepts might be optimised for graphite wastes. The objective of this project is to better understand the behaviour of irradiated graphite wastes in the GDF, how GDF performance is influenced by different disposal options, and the potential impact of our current uncertainties in process understanding and parameterisation. The results of this study will therefore inform RWMD’s selection of an optimal graphite disposal strategy and the development of the future Research Programme. The outputs from this project will also support RWMD’s contributions to the CARBOWASTE project.

The project is being undertaken in two phases over an eighteen-month period. The focus of the project is on the post-closure performance of the GDF. This document reports the findings of the first phase.

The key radionuclides in irradiated graphite are C-14 and Cl-36 both of which can be leached from graphite. C-14 will exhibit complex behaviour in the GDF. It will be partitioned between water, gas and solid phases. The abundances in the different phases will be controlled by carbonate chemistry, reaction with cement minerals, and by microbial and gas generating processes. C-14 can be released from the GDF to the geosphere in water and in gas. Cl-36 will behave more simply, only being released in water, and does not interact significantly with any of the materials expected to be present in the GDF.

The inventories of both key radionuclides are uncertain. The inventory of Cl-36 is particularly uncertain due to the potential for volatile release during storage (including reactor ‘SafeStore’) and core dismantling. Release during core dismantling will be sensitive to the method used, i.e. removal of whole blocks or ‘nibble and vacuum’.

Features, Events and Processes (FEPs) analysis was used to develop a conceptual model of the physico-chemical evolution of the GDF, and the behaviour of the key radionuclides in graphite during the post-closure period. The analysis focussed on RWMD’s illustrative example disposal concept for ILW/LLW in higher strength host
rock. Interactions between graphite and other Intermediate Level Waste (ILW) and Low Level Waste (LLW), and the effects of lower strength sedimentary and evaporite host rocks have also been considered. This analysis has been used to identify desirable safety features and alternative Engineered Barrier System (EBS) options. Clay backfill (assumed to be a sand-bentonite formulation) was carried forward for more detailed assessment.

It is anticipated that following closure of the GDF, the entire inventory of Cl-36 will rapidly be leached from graphite. Leaching of C-14 will be slower, although still fast on post-closure timescales. A potentially significant proportion of the C-14 inventory may be incorporated in the graphite lattice, and may only be released very slowly, or not at all. However, this proportion is unknown, so in this work the base assumption is that C-14 is leached at the rates measured in short-term experiments until the entire inventory has been released. This provides a simple common basis to compare different systems and GDF conditions in the context of optimisation. Variant calculations have been presented herein to show the effects of using potentially more realistic long-term release rates. The development of a safety case for a particular disposal concept might make different assumptions and explore alternative conceptual models for radionuclide release from graphite.

Mathematical models have been used to examine the physio-chemical evolution of the GDF, and partitioning and release of C-14 from the GDF, for higher strength and lower strength sedimentary host rocks. The calculations have focussed on C-14 due to its complex behaviour and the resulting uncertainties. Modelling results from previous studies are used to understand the behaviour of Cl-36. Model results confirm that as anticipated the very low permeability lower strength sedimentary host rock provides a significantly more effective barrier to the migration of water and gas, and hence to the transport of C-14, than the fractured higher strength host rock.

The model results show that segregation of waste packages containing graphite waste from other ILW/LLW waste packages is desirable in order to minimise releases of C-14, including:

- segregation from organic wastes to minimise the potential for development of methanogenic conditions and incorporation of C-14 in methane; and

- segregation from reactive metals in lower strength sedimentary host rock to prevent relatively rapidly rising vault pressures (compared with pressure recovery in the EDZ and immediately adjacent host rock), and high peak gas pressures, pushing radionuclides in water out of the GDF. Although the host rock provides a significant barrier to radionuclide transport, this minimises the potential for transport in the EDZ, and bypass of vault seals.
Further work is required to understand the potential ‘knock-on’ effects of segregation: e.g. concentration of reactive metals in a smaller number of vaults may result in higher peak GDF gas pressures in lower strength sedimentary host rock; and any potential implications for the consequences of human intrusion.

The major volume of graphite waste is reactor core graphite, and this contains the majority of the radionuclide inventory. Due to the SafeStore strategy, reactor core graphite will arrive later than the majority of other ILW/LLW and therefore could potentially be relatively easily segregated. However, reactor core graphite is classified as Shielded ILW (SILW), and there are much smaller quantities of organics and reactive metals in SILW compared with Unshielded ILW (UILW). Therefore segregation of SILW graphite may not offer significant benefits compared with the effort required to implement it. Segregation of UILW graphite is however desirable on grounds of minimising fluxes of C-14 from the GDF, but may not be worthwhile in practice given that UILW graphite is a minor component of the overall graphite inventory.

These conclusions are based on the model assumption of homogeneous conditions in the vault. Conditions may be heterogeneous, with methanogenic conditions most likely to develop in packages containing organic wastes. This implies that C-14 would need to be transported from packages of graphite wastes into packages of organic wastes in order to be incorporated into methane. This is unlikely to occur. Improved understanding of package scale heterogeneity in the vaults might significantly reduce the driver to segregate packages of graphite waste.

Combining segregation of graphite with the use of a sand-bentonite backfill offers further potential safety benefits: reducing the fluxes of C-14 in gas, and Cl-36 in water in higher strength host rock compared with the reference case. This option may have the best overall performance for graphite, although the work undertaken within this study has not progressed to the stage of demonstrating this. The practicalities of emplacing a sand-bentonite backfill need to be considered further. In lower strength sedimentary host rock, sand-bentonite backfill may not be so beneficial since it adds little to the low permeability barrier provided by the host rock.

Irradiated graphite should not be placed in the same container as organic waste to minimise the potential for generation of C-14 labelled methane. Similarly, graphite should not be placed in the same container as reactive metals. As a result there should be very little gas generation from containers of graphite waste, e.g. only H₂ from corrosion of the inner surface of the container. Therefore, the size of the container vent hole could potentially be reduced to a minimum.

The impact on performance would be particularly significant for C-14 in higher strength host rock, where the barrier provided by the container may be significant.
compared with the half-life of C-14 and the geosphere travel time. Reducing the vent size also has the potential to reduce interactions between graphite and other wastes while the containers are intact. This minimises the potential for incorporation of C-14 in methane.

Overall, the complex mathematical models developed in this study have been used to test and build confidence in our understanding of vault evolution, and in particular the complex behaviour of C-14. The models have revealed behaviours that otherwise might not have been anticipated, e.g. gas pressure pushing water and associated radionuclides out of the vault in lower strength sedimentary host rock.
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1 Introduction

The current UK baseline assumption for the disposal of irradiated graphite wastes, particularly large volumes of reactor core graphite, is disposal in a Geological Disposal Facility (GDF). No firm decisions have yet been made concerning the conditioning and packaging of the graphite wastes, and these wastes potentially pose significant challenges because of their relatively large volume and the radionuclide inventory associated with them. In particular, C-14 may be released in radiolabelled gases during both the operational and post-closure phases. Radionuclides may also be released to water during the post-closure phase, with the most significant being C-14 and Cl-36.

NDA RWMD is currently considering how a range of multi-barrier disposal concepts might be optimised for graphite wastes. The objective of this project is to better understand the behaviour of irradiated graphite wastes in the GDF, how GDF performance is influenced by different disposal options, and the potential impact of our current uncertainties in process understanding and parameterisation. The results of this study will therefore inform RWMD’s selection of an optimal graphite disposal strategy and the development of the future Research Programme.

The European Commission (EC) CARBOWASTE project, in which NDA RWMD is participating, is currently exploring options for the management and disposal of irradiated graphite (Banford et al., 2008; EC, 2008). The outputs from this project will also support RWMD’s contributions to the CARBOWASTE project.

The project is being undertaken in two phases over an eighteen-month period. The focus of the project is on the post-closure performance of the GDF. This document reports the findings of the first phase.

1.1 Report Structure

Section 2 further describes the scope of the first phase of the project and the methodology that has been used to analyse the behaviour of graphite wastes in the GDF. Section 3 provides relevant background information, including a summary description of the disposal systems under consideration, the volumes of different graphite wastes, and the inventories and form of key radionuclides associated with those wastes. Section 4 describes the analysis of the behaviour of graphite in the GDF and the resultant conceptual model that forms the basis for mathematical models. Section 5 describes the mathematical models. These models are used to help analyse the performance of different options. The model results are presented in Section 6 and
the implications are discussed in Section 7. Conclusions for optimisation of GDF performance are drawn in Section 8.

2 Scope and Methodology

2.1 Scope

A number of options exist for the management of graphite wastes, including treatment and recycling possibilities, and options for deep and near-surface geological disposal. The baseline UK strategy is for deep geological disposal of packaged untreated wastes. This scope of this project is limited to the optimisation of deep disposal, and this first phase focuses on wastes that are not treated with the aim of reducing their volume, radiouclide inventory, etc.

The project is considering the behaviour of graphite wastes for the three generic geological environments and associated disposal system designs considered in RWMD’s generic Disposal System Safety Case (DSSC) (RWMD, 2010a). Opportunities for optimisation include:

- packaging and GDF Engineered Barrier System (EBS) design.

- GDF disposal strategy:
  
  o should graphite wastes be disposed of all together in one discrete area of the GDF?

  o alternatively is it acceptable (or preferable) to dispose of packages of graphite wastes with packages of different ILW wastes, such as organic wastes?

  o or, are there specific ILW wastes where there may be benefits to not disposing packages of these wastes in the same vault as packages of graphite waste?

- GDF disposal schedule:

  o The present UK reactor SafeStore strategy will result in the generation of the majority of graphite wastes (core graphite, Section 3.2.1) over a relatively short time period towards the end of GDF ILW disposal operations (e.g. Magnox South, 2009), providing the opportunity to easily segregate graphite wastes.
Other graphite wastes need to be packaged for safe storage until the GDF is available. Does the proposed packaging strategy constrain options?

For this first phase of the project, optimisation of the GDF disposal strategy and schedule are analysed together with the option of using a clay-based backfill, instead of the cement-based backfill considered in the DSSC illustrative example disposal concepts in higher strength and lower strength sedimentary host rocks.

### 2.2 Methodology

The approach used follows the ISAM methodology (IAEA, 2004), which is reflected in the structure of this report. The three generic geological environments and associated disposal system designs that form ‘boundary conditions’ for this project are described in Section 3.1, and the graphite wastes and the associated radionuclide inventory are described in Section 3.2.

Features Events and Processes (FEPs) analysis is used in Section 4 to underpin the development of conceptual models that describe GDF evolution, release of radionuclides from graphite wastes and their subsequent transport, for each of the three generic geological environments and associated disposal system designs. Based on these conceptual models, six calculation cases (and associated variant cases) are identified for quantitative analysis of the generic designs and their associated uncertainties, and the implications of alternative disposal strategies, packaging and EBS.

Quantitative analysis is undertaken using mathematical models (Section 5). Detailed models are used to analyse specific aspects of the system evolution (Section 5.1), while more abstracted assessment models describe the behaviour of the whole system, and the transport of radionuclides (Section 5.2). The detailed models inform the configuration and parameterisation of the assessment models. The model results (Section 6) inform the discussion of opportunities for optimisation of disposal of graphite to a GDF (Section 7). Conclusions are presented in Section 8.
3 Background

NDA RWMD’s generic Disposal System Safety Case (DSSC; RWMD, 2010a) provides a basis for discussion, analysis and research relating to the issues surrounding deep geological disposal for the UK’s radioactive waste inventory. The generic DSSC considers three different potential host rocks, whose properties impose conditions that bound the range of potential disposal concepts, engineering and operational issues, and long-term evolution and safety performance. These host rocks comprise:

▲ higher strength host rock;

▲ lower strength sedimentary host rock; and

▲ evaporite host rock.

Higher Strength Host Rock

Such a host rock would typically comprise a crystalline igneous or metamorphic rock, where any fluid movement is predominantly through discontinuities (mostly fractures). “Higher strength” refers to rocks in which it is possible to excavate stable tunnels and disposal vaults requiring only limited rock support (rock bolting and shotcrete). Spans of the order of 20 m are possible at disposal depths up to approximately 500 m, decreasing to spans of 16 m at a depth of approximately 1000 m. The degree and orientation of the fracturing is important in determining geotechnical and hydrogeological characteristics. The higher strength host rock may extend all the way to the ground surface or it may be overlain by a sedimentary sequence.

Lower Strength Sedimentary Host Rock

In the UK, lower strength sedimentary host rocks tend to be geologically younger than the higher strength host rocks described above, and they tend to be clay-rich. In the generic DSSC the rock is assumed to be a low-permeability indurated clay formation, which has similar characteristics to the host rocks being evaluated by Andra (the Callovo-Oxfordian Clay) and by Nagra (the Opalinus Clay). In this host rock, any fluid movement is predominantly through the rock matrix. “Lower strength” refers to rocks in which it is possible to excavate tunnels of 10 to 15 m in diameter at disposal depths up to 800 m, although these excavations are likely to require considerable excavation support, possibly including full linings. Fractures in the Engineering Damaged Zone (EDZ) around the excavations tend to heal with time as a result of creep and other processes (Andra, 2005).
Evaporite Host Rock

Evaporites are formed by the evaporation of water from water bodies containing dissolved salts, the most common types being anhydrite (anhydrous calcium sulphate) and halite (rock salt). The strength of evaporites varies markedly with composition and the presence or otherwise of impurities. However, a key characteristic of evaporites from the point of view of a GDF is their ability to creep and seal voids. This property also varies widely with factors such as composition, purity, and temperature.

3.1 Generic Disposal System Design

The GDF will be designed to accommodate all the UK’s higher activity wastes. Different disposal concepts and associated designs will be required for the different waste types. There will be a distinct concept and associated area of the GDF for ILW/LLW, and a different concept and associated area of the GDF for HLW plus any Spent Fuel (SF) that is declared as waste. The UK’s stocks of uranium and plutonium could also potentially be declared as waste. In this instance, the large volume of Depleted Natural and Low Enriched Uranium (DNLEU) could be classified as ILW.

ILW/LLW is sub-divided into two types: Shielded ILW (SILW) packages that can be contact handled, and Unshielded ILW (UILW) packages that needs to be remote handled. SILW and UILW may be further sub-divided into specific types of waste, e.g. graphite. Potentially these specific types of waste could have different EBS designs, each optimised for that waste type. DNLEU would be classified as UILW. This may be disposed in the same vaults as other UILW, or separated and disposed in a separate set of vaults. In the context of this study, the treatment of DNLEU affects the average inventory of gas generating materials in an average UILW vault. For the purposes of this study, DNLEU is assumed to be segregated.

The GDF designs are described in NDA RWMD’s design report (RWMD, 2010b). A summary is provided in the following sub-sections. The illustrative geological disposal concepts assumed in the DSSC are described in Table 3-1. The HLW/SF areas and associated EBS are not described since they are not relevant to this study.

Table 3-1. DSSC illustrative geological disposal concepts for ILW/LLW

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<td>Higher strength host rock</td>
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<tr>
<td>Lower strength sedimentary host rock</td>
<td>Opalinus Clay Concept (Nagra, Switzerland)</td>
</tr>
<tr>
<td>Evaporite host rock</td>
<td>WIPP Bedded Salt Concept (US-DOE, USA)</td>
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3.1.1 Higher Strength Host Rock

The generic GDF layout for higher strength host rock is illustrated in Figure 3-1. The ILW/LLW area is to the left of the access drift, and the (larger) HLW/SF area to the right. It is notionally assumed that the GDF will be constructed at a depth of 650 m, and the ILW/LLW and HLW/SF areas are separated by a distance of 500 m. There are 6 SILW vaults, 13 UILW vaults excluding DNLEU, and 19 UILW vaults including DNLEU.

It should be noted that this layout will need to be tailored for site specific conditions, for example to provide sufficient ‘respect’ distances from the more significant fracture zones, or due to the site specific volume of suitable rock.

![GDF layout in higher strength host rock](image)

Figure 3-1. GDF layout in higher strength host rock (RWMD, 2010b)

Figure 3-2 shows a schematic cross-section along the length of a UILW vault. For the UILW vaults, the access tunnel provides construction and operational access. However wastes will not be brought into the vault via the access tunnel, but rather via a separate (perpendicular) transfer tunnel. The transfer tunnel will be constructed in a ‘rock bench’, which is not illustrated in Figure 3-2. Waste packages will be lifted out of the transfer tunnel and placed in the vault using a crane. Fresh air enters the vault via the access tunnel, and potentially contaminated air leaves via the ventilation tunnel at the far end of the vault. SILW/LLW will be moved and emplaced using a stacker truck as it does not require remote handling.

The excavation is unlined, although rock bolting and shotcrete may be used where necessary. In a higher strength host rock it is anticipated that it will be possible to hold the vault open for 100 years or more. Therefore, the vaults will be developed as required, but none of the vaults will be backfilled until immediately prior to closure. At closure, it is assumed that the access and ventilation tunnels will be sealed by means of
concrete seals. The disposal vaults will be backfilled using a cementitious grout (Nirex Reference Vault Backfill (NRVB)).

Peripheral NRVB backfill will be emplaced in the vault before the wastes are disposed. At closure, NRVB will be injected into the vaults to fill the remaining void space. Injection will be via boreholes drilled from backfilling tunnels. It is intended that the backfill will ensure that the pH within the vault remains high for an extended period of time. This is estimated to be more than a million years based on the groundwater flow rates and geochemical conditions assumed in the design, and assuming 100% accessibility of the backfill cement mineral inventory.

Low permeability bentonite seals, retained by a concrete structure, will also be used to isolate the vault modules, different areas of the GDF, ventilation shafts and the access drift. Crushed rock will be used as bulk infill between the low permeability seals, to backfill remaining void spaces in the access, transfer and ventilation tunnels.

The approximate event timing for the construction and operation of a GDF in higher strength rock is described in Table 3-2.

![Figure 3-2. Cross-section along the length of an UILW vault in higher strength host rock (RWMD, 2010b)](image-url)
Table 3-2. Approximate event timing for GDF in higher strength host rock

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<td>Initial ILW/LLW vaults and associated waste handling and other tunnels have been constructed and disposal of ILW/LLW begins.</td>
</tr>
<tr>
<td>35</td>
<td>Initial HLW/SF tunnels and associated waste handling and other tunnels have been constructed and disposal of HLW/SF begins.</td>
</tr>
<tr>
<td>85</td>
<td>ILW/LLW disposal largely complete, although small numbers of packages will continue to arrive until closure.</td>
</tr>
<tr>
<td>100</td>
<td>HLW/SF disposal complete.</td>
</tr>
<tr>
<td>100 - 110</td>
<td>Sealing, backfilling and closure.</td>
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3.1.2 Lower Strength Sedimentary Host Rock

It is notionally assumed that the GDF will be constructed at a depth of 500 m, and the ILW/LLW and HLW/SF areas are separated by a distance of 500 m. It should be noted that the layout will need to be tailored to site specific conditions, for example to due to the site specific volume of suitable rock.

The design for the ILW/LLW area is similar to that for higher strength host rock. However, the vaults are shorter and of smaller dimensions, reflecting the lower strength of the host rock. It would not be possible to maintain open excavations for timescales of the order of 100 years; therefore individual vaults would be excavated, filled with waste, backfilled and sealed in succession. Transfer and access (service) tunnels would have to be maintained open for the lifetime of individual modules. There are 77 SILW vaults, 116 UILW vaults excluding DNLEU, and 169 UILW vaults including DNLEU.

The ILW/LLW vaults would be backfilled with cementitious mortar. For the purposes of this study it was agreed with RWMD to assume this has the properties of Nagra structural mortar (Nagra, 2008). This is a cementitious backfill that has different properties to NRVB. Peripheral backfill will be emplaced prior to disposal. Final backfill will be emplaced using ducting attached to the roofs of the vaults. Individual vaults would be sealed using concrete plugs and each ILW/LLW module would be sealed using bentonite retained by a concrete structure.

Access (service) tunnels throughout the GDF would be backfilled with sand-bentonite (70:30). Additional 40 m long bentonite seals, retained by concrete structures, would be placed in the access tunnels at the bases of the ventilation shafts and drift.
The approximate event timing for a GDF in lower strength host rock is the same as for a GDF in higher strength host rock, except that ILW/LLW vaults will be constructed, filled with wastes, backfilled and sealed in succession.

3.1.3 Evaporite Host Rock

It is notionally assumed that the GDF will be constructed at a depth of 650 m, and the ILW/LLW and HLW/SF areas are separated by a distance of 500 m. The GDF design for evaporites is based on the WIPP concept for the ILW/LLW component, adapted to suit UK wastes and geological conditions. There are 38 SILW vaults, 115 UILW vaults excluding DNLEU, and 167 UILW vaults including DNLEU.

Due to the propensity of the evaporate host rock to creep, the LLW/ILW vaults would be excavated, filled with waste, and sealed in succession. The ILW/LLW vaults would not be backfilled, since creep of the host rock will fill any voids. In thin evaporite deposits, crushed evaporite backfill would be used to minimise perturbation of the host rock deposit due to creep. Sacks of magnesium oxide (MgO) would be placed on top of the waste stacks. The MgO absorbs CO₂ gas and water vapour, and potentially provides a chemical (elevated pH) barrier for some radionuclides, e.g. uranium.

Low permeability ‘salt’ concrete seals would be used to isolate vault modules, deposition areas and shafts. Crushed evaporite backfill would be placed between the low permeability seals.

The event timing for a GDF in evaporite is the same as for a GDF in higher strength host rock, except that ILW/LLW vaults will be constructed, filled with wastes, backfilled and sealed in succession.

3.2 Graphite

3.2.1 Waste Types

The irradiated graphite wastes comprise six main types (Adeogun et al., 2010): Magnox and AGR reactor core graphite; graphite sleeves (Hunterston A and AGR reactors); graphite struts (Berkeley); core graphite from research reactors and the Windscale Piles. The Magnox and AGR core graphite is the major volume. There are two major differences between the Magnox and AGR graphite.

The Magnox graphite is much purer than the AGR graphite and therefore contains much lower concentrations of activation products. For example, while irradiated
Magnox graphite samples can be handed without shielding in the laboratory, AGR samples have to be shielded (in particular due to Co-60).

The second major difference is that AGR graphite has significantly greater radiolytic oxidation than Magnox graphite. This is due to the much higher CO₂ coolant gas pressures and, whilst mitigated by the addition of gaseous inhibitors, has resulted in much greater average mass loss from the AGR graphite. Therefore, radionuclide leaching rates could potentially be higher from AGR graphite than Magnox graphite due to the more open pore structure.

The 2010 NDA RWMD derived inventory (Adeogun et al. 2010) is based on the 2007 National Inventory. It gives the following information regarding the amounts of graphite wastes and their associated radionuclide inventories. It should be noted that this information contains inherent assumptions, for example with regards to the remaining operational lifetime of reactors, time of decommissioning and assumptions inherent in the methods that have been used to calculate the radionuclide inventories. Such assumptions and uncertainties are discussed in the next sub-section.

Adeogun et al. (2010) describes the main contributions to the graphite waste inventory by mass to be¹: Magnox reactor graphite 64.6%, AGR reactor graphite 28.2% and AGR fuel element graphite 7.2%. However, note that AGR graphite has significantly greater mass loss than Magnox graphite and therefore the volumes are more similar. Table 7.15 of Adeogun et al. (2010) states that, for the reference case volume there is 9,524.2 tonnes of UILW graphite, 69,561.7 tonnes of SILW graphite and 15,901.9 tonnes of LLW graphite.

Appendix F of Adeogun et al. (2010) details that UILW graphite comprises AGR graphite fuel assembly components, miscellaneous activated and contaminated components, fuel stringer debris and FED (Fuel Element Debris) graphite. SILW comprises reactor core graphite, including graphite from the Windscale Piles. Reactor core graphite will be SILW because the reactor cores will be left in-situ for an extended period to allow short-lived radionuclides to substantially decay prior to final dismantling and disposal (the SafeStore strategy).

3.2.2 Key Radionuclides

From a post-closure perspective, there are two key radionuclides associated with graphite: C-14 and Cl-36, which have half lives of 5730 y and 301,000 y respectively.

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¹ Excludes Windscale Pile Graphite (4%) when included.
Smaller quantities of other long-lived activation products are also present in the graphite wastes, including Ni-59. The shorter-lived radionuclides H-3 and Co-60 are important in terms of decommissioning, storage, transport, and GDF operations.

Current knowledge regarding the form, location and release of C-14 and Cl-36 is summarised below. Table 6.16 of Adeogun et al. (2010) gives the C-14 activity in graphite at 2090 as 6.04E+03 TBq in SILW and 6.88E+01 TBq in UILW. Adeogun et al. (2010) does not give an inventory for Cl-36 in graphite. Limer et al. (2010) gives the inventories of C-14 and Cl-36 as 5960.63 and 24.79 TBq respectively, in 76,820.73 tonnes of graphite. Comparing against the data in Adeogun et al. (2010), the C-14 inventory has increased by the same factor (1.0295) as the mass of graphite. Applying this factor to the Cl-36 inventory of Limer et al. (2010) gives a Cl-36 inventory of 25.52 TBq.

Form and Location in Graphite

C-14

The important routes for the formation of C-14 are:

- from elemental $^{13}\text{C}$ (present at 1.1% in the graphite and therefore a high source term, albeit with a low cross-section) via $^{13}\text{C}(n,\gamma)^{14}\text{C}$; and

- from $^{14}\text{N}$ (99.6% of natural nitrogen and its compounds) via $^{14}\text{N}(n,p)^{14}\text{C}$ (low source term from quinoline compounds in the graphite precursors and other impurities, but high cross section).

A third route from $^{17}\text{O}$, via $^{17}\text{O}(n,\alpha)^{14}\text{C}$, is significant in CO$_2$ and air-cooled reactors, particularly at high coolant pressure, but the efficiency with which this coolant-borne C-14 can be incorporated into the graphite is thought to be very low. Therefore, there will only be limited retention in the graphite, e.g. in the form of carbonaceous deposits present on the graphite at the end of its life, particularly associated with the lower blocks of Magnox reactor cores.

A great deal of published ‘data’ on isotopics in graphite waste is derived from calculation, using codes which may not take all source terms into consideration and may also contain assumptions about the contributions from differing routes, which themselves may not always be appropriate. Significant issues have been identified with regards to code data libraries and selected capture cross-sections in work undertaken for EPRI (Wickham, 2010). Similar issues likely exist for other radionuclides.

A summary of the principal issues which affect the correct identification of C-14 content in graphite wastes are as follows:
Nitrogen content at the time of irradiation. The cross-section for formation from $^{14}$N is very large, and so only small amounts of nitrogen are needed to make this a dominant source. However, there is much disagreement on the assumed nitrogen content. Most estimates simply assume a number of order 30 – 70 wppm, based in some cases upon impurity assays at the time of graphite manufacture. One source of nitrogen that can be confirmed is from quinolines in the pitch binder, and this nitrogen can be incorporated directly into the graphite matrix (hexagons) in a stable form. There may also be some small amounts of nitrogen in mineralised impurities introduced with the coke.

At the time of manufacture of UK moderator graphites, assay techniques for nitrogen were extremely basic, and nitrogen is an element which is often assayed only 'by difference'. There have been some measurements, sometimes contradictory for the same material. Modern measurements utilise secondary-ion mass spectrometry, which looks only at the near surface (up to ~ 200 nm); other techniques tried include dissolution in molten metal and subsequent gas analysis. A major problem with all measurements is that handling and preparation of samples has not been identified, and that contamination from atmospheric air ahead of the measurements is almost certain. Also, there are few credible measurements on irradiated material. A programme of work is being initiated by Idaho State University in combination with a number of bodies (INL, The University of Manchester, Boise State University) to undertake more reliable measurements over the next few years. The NDA are currently funding a study on the characterisation of the radionuclide content of some irradiated graphite from UK reactors (e.g. Lansdell and Newland 2010; Parry and Cox, 2010).

Use of an appropriate capture cross-section. Appropriate input data need to be used within code calculations, including selection of values appropriate to the irradiation temperature. There are examples of industry papers where inappropriate values are assumed. Mills and Riaz (2010) provide examples of where inappropriate cross-section $\nu$ energy has been used due to inappropriate interpolation of input data by the code.

Understanding the role of the coolant. It is a common misconception that the major source of C-14 in graphite is nitrogen impurity in the coolant. This source is at very low concentrations in the coolant; typically between 50 and 250 wppm in the carbon dioxide coolants of Magnox reactors, and somewhat less in AGRs. Nitrogen impurity in the coolant has been considered to be the major source because it was regarded as a constantly replenished source. However, this consideration did not recognise that the efficiency of transfer from the gas to the solid matrix is low, since nitrogen is essentially unreactive.

The open porosity of the graphite is subject to small amounts of carbon deposition. This carbon is derived from CO, which is the graphite oxidation product formed by reaction of oxygen free radicals (generated from irradiation of the CO$_2$ coolant) with
graphite. Any C-14 generated from nitrogen impurity in the coolant would be initially deposited in the open porosity. This deposition is balanced by radiolytic oxidation and removal to the gas phase of surface material, such that the net deposition of C-14 from nitrogen impurity in the coolant will be small. Only the open porosity on the surface of the graphite is relevant because solid-state diffusion of carbon atoms is insignificant at reactor temperatures.

C-14 may also be transferred from the gas phase into the solid matrix by recoil during formation. However, this is considered to be a minor process.

The current view is that nitrogen impurity in the coolant contributes very little to C-14 in UK graphite.

Understanding the role of recoil energy. Calculations have recently undertaken independently by Nuclear Technology Consultancy, IPNS at Université Lyon 1, and Forschungszentrum Jülich (Wickham, 2010), which all agree on the following approximate values of recoil energy: for the $^{14}\text{N}(n,p)^{14}\text{C}$ reaction, 42 keV; and for the $^{13}\text{C}(n,\gamma)^{14}\text{C}$ reaction, a range up to 470 eV dependent upon emitted photon energy and direction. These values should be compared with the energy required to remove a carbon atom from the lattice (around 25 eV)$^2$.

The implication of these numbers is that all C-14 atoms formed from $^{14}\text{N}$ and the majority of those formed from $^{13}\text{C}$ will be displaced from any lattice position immediately upon formation. They thus fall into the same situation as general carbon atoms displaced from the lattice by interaction with fast neutrons (the ‘normal’ graphite damage process). They can be referred to collectively as ‘displaced atoms’, for example the average carbon atom in an AGR core at end of life will have been displaced more than 12 times. Atoms displaced through fast-neutron processes can occupy a variety of interstitial positions: as discreet atoms; lines and small new ‘rings’; and bridging position between the individual layer places in the graphite crystallites. The majority of C-14 atoms (when formed) will be in this category.

Upon further irradiation, all displaced atoms have the opportunity to re-occupy lattice site positions through irradiation (and thermal) annealing processes, and so the ‘older’ C-14 atoms might reasonably be expected to slowly become re-integrated into the lattice.

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$^2$ Note that this is larger than the chemical bond energy of around 4.78 eV for the conjugated bonding in the carbon hexagons, but this is a credible experimental value based upon ion-irradiation experiments.
Leaching Data for C-14 add little to the understanding of the bonding and nature of C-14 in graphite. This is because measured leach rates vary by orders of magnitude, including between measurements using sub-samples of the same material by different laboratories. However, a significant feature overall, is that the C-14 leach rate is rather slow in comparison with other isotopes. (The same is true for H-3 for reasons that are not understood). Leach rates are further discussed in the next sub-section.

Chemical Form. On the basis that C-14 atoms are distributed around the graphite lattice in a similar manner to atoms displaced by collision with fast neutrons, they are anticipated to be in a similar chemical form. Essentially, they remain as carbon atoms, bonded to other carbon atoms, and only when present at edge sites are there ‘unsatisfied’ bonds which are normally terminated with hydrogen atoms at edge sites. No permanent compounds adherent or incorporated into the graphite are formed as a result of the interaction with the air or carbon dioxide coolants: all carbon atoms reacting with the coolant are removed to gaseous products and lost during reactor operation.

Experimental Radioactivity Measurement Programmes. EdF CIDEN has commissioned a comprehensive measurement programme upon samples of graphite recovered from their cores. Although the number of samples from each UNGG (Uranium Natural Graphite Gaz) reactor has been limited to about 20, they do form a fairly consistent set into which data from Latina and the extremely limited UK data appear to fit. On this basis, for a ‘full-term’ Magnox-type reactor, we might expect that the peak C-14 activity would be around $10^5$ Bq g$^{-1}$ in the flattened and hence concentrated region of neutron flux, with minimum values in the active core around $10^4$ Bq g$^{-1}$.

In summary, the majority of C-14 is formed by activation of $^{13}$C in the graphite, and $^{14}$N impurities in the graphite originating from manufacture. C-14 is displaced from the graphite lattice upon formation, but is progressively re-integrated into the lattice. C-14 that has been reintegrated into the lattice may be less mobile than displaced C-14.

Cl-36

The principal source of Cl-36 in graphite is considered to be from the elemental chlorine or Freon compounds used in the purification stage of manufacture. These gases become entrained in the closed porosity and remain there unless that closed porosity is breached by oxidation during irradiation. Chlorine-containing compounds are no longer used in modern graphite production.

In all other contexts, strenuous efforts have been made to avoid contamination of reactor circuits by chlorine and its compounds because of the risk they present to metals through initiation of stress-corrosion cracking. However, air-cooled reactors in coastal locations (e.g. Windscale) are subject to the entrainment of wind-borne sea salt.
Chlorine is a modest catalyst for thermal oxidation of graphite. However in CO$_2$-cooled reactor systems this can take place only during fault conditions with air ingress into the coolant.

There is no form of chemical bonding which can allow chlorine to be incorporated directly into a graphite lattice. The only exceptions are when some degradation of that structure has occurred, perhaps through a combination of fast-neutron damage and oxidation, to generate organic structures in which the functional groups could include the C-Cl covalent bond. However, further research would be required to better understand this.

Cl$_{36}$ has not yet been studied to the same extent as C-14, although a study is about to be undertaken (Wickham, 2010). NIREX (1997) contains some reasonably comprehensive data on Cl$_{36}$ contents of various unirradiated UK graphite sources, and discusses its potential mobility within the reactor, where deposits of almost pure ammonium chloride have been discovered in cool parts of the circuits. There is no discussion of chemical form within the graphite, and no further comment about potential losses from the graphite in handling or reactor operation.

Awareness of the potential mobility of the weak beta emitters in irradiated graphite led EdF, CIDEN and CEA to conduct some specific studies (Rahmani, 2005). The first observation was that the unirradiated graphite in storage, especially in powder form, accumulated chlorine, and the chlorine content increased upon reactor irradiation in the French UNGG plant, the inference being that the graphite was somehow contributing to a ‘clean-up’ of chlorine-containing impurities in the coolant gas. This was based upon a CEA observation in the 1990s (Rahmani, 2005) that the Cl$_{36}$ content of the material was greater than the presumed chlorine impurity content that the material would allow.

Conversely, the opposite effect is reported in NIREX (1997) for UK irradiation, with some 30% of the expected Cl$_{36}$ being unaccounted for. It was postulated that there was a quick release of chlorine in reactor from open pores in the graphite, followed by a slower release when the closed pores are opened up by radiolytic oxidation.

ENRESA noted that graphite dust collected from ventilation ducts had on average 44% less Cl$_{36}$ specific activity than samples drilled from the moderator blocks. This alerted EdF to investigate the potential for Cl$_{36}$ release more comprehensively. Samples kept in PVC bags for 20 years were found to have increased their (chemical) chlorine content by factors of 3 - 4 but, after maintaining some of the powdered material at 400°C for two weeks, 90% of the chlorine escaped. It can be reasonably assumed that similar release would occur in a reactor. This corroborated a 1985 observation by
COGEMA Marcoule on heating fuel sleeves to 580°C for 65 hours, which eliminated 72% of the chlorine.

Irradiated Bugey 1 fuel-sleeve graphite powder was analysed twice for Cl-36 at an interval of 12 years. The material was stored in a Pyrex flask in the interim. Only 3 – 5% of the original Cl-36 activity was found at the second measurement.

Rahmani (2005) considers four models to explain the losses: (i) instability of closed porosity; (ii) oxidation; (iii) ‘decay’ by ‘random’ failure of chemical bonds; and (iv) diffusion. Conclusions were not drawn. However, consideration of the effects of particle size was offered; grinding opens closed porosity and, the finer the particles, the greater penetration of such pores is achieved in addition to markedly increasing the available surface area per unit mass, allowing a greater release rate. The more detailed modelling did not really distinguish between the movement of chemical chlorine and of Cl-36, but some chemical bonding between graphite and chlorine within the porosity was proposed.

The consequences of the apparent mobility of Cl-36 are:

- A major fraction of the anticipated inventory of Cl-36 could actually be lost during storage, prior to closure of the GDF, including during ‘SafeStore’.

- The Cl-36 inventory may be significantly influenced by the method used to disassemble reactor cores. Far more Cl-36 may be lost if nibble and vacuum is used rather than removal of intact blocks.

Therefore the Cl-36 inventory may actually be far smaller than anticipated and listed in the current UK inventory. This needs to be taken into account when analysing the potential advantages and disadvantages of different options for management of graphite, i.e. it could drive optimisation of barrier performance towards consideration of C-14 over Cl-36.

**Radionuclide Release from Graphite**

Radionuclide release rates from graphite have been measured using leaching experiments. Wickham and Bradbury (2008) report all leach-rate data currently available. The Wickham and Bradbury (2008) report was not available to this study, however the following summary of the principal conclusions has been provided by Wickham (2010).

1. The database is unsatisfactory because very small numbers of samples have been studied, and the studies have been undertaken use non-standard methodologies (static, semi-dynamic, and variations, and non-standard sample configurations). (A standard
IAEA methodology exists although it was never formally endorsed (Hespe, 1971)). The conditions in terms of pH and composition, duration of test, frequency of sampling, extent of shrouding or immersion etc., are also very variable. Different graphite sources appear to behave differently, and different laboratories fail to reach the same leach rates on equivalent samples where comparisons have been undertaken, for example a difference of four orders of magnitude exists in C-14 data. In addition, uncertainties in the experiments and analytical and counting procedures are not reported.

2. Leaching data have been acquired over periods of between 90 and several hundred days. These timescales have been driven by the duration of core dismantling under water, should such an approach be required by EdF CIDEN. Longer-term data relevant to storage and post-closure are not available.

- Release rates of H-3 and C-14 are slow: that of H-3 is perhaps particularly surprising given that it is likely to be bound chemically to surface groupings which are rather susceptible to exchange with hydrogen atoms in the water. This perhaps implies that the easily released material had already exchanged with atmospheric water vapour and that the leaching is driven by diffusion through the graphite matrix which is known to be very slow.

- Alkaline waters appear to inhibit the release rates of Co-60 and Cs-137, perhaps through limiting their solubility, whilst acidic conditions favour the release of the majority of isotopes studied.

- Temperature has a significant effect on release rate in most cases.

- A steady-state leach rate appears to have been achieved for most isotopes after about 150 days have elapsed, but mainly at low overall release fractions. Chemical equilibrium between graphite and leachant is unlikely to have been achieved for almost all isotopes within the timescale of these experiments.

- Some results are usually given for aerobic (even deliberately aerated) environments but, in other tests, an inert gas atmosphere has been employed. The GDF will initially be aerobic at closure, but conditions will very rapidly become anaerobic. Leaching rates under anaerobic conditions, and potentially influenced by microbial processes, may be significantly different to the measured rates.

- Little data are available for grouted and impregnated graphite, and there is significant experimental variability. However, such data are more relevant to the base assumption of cement encapsulated wastes.
3. Tests conducted to date do not collect (and identify) all chemical forms of the leached material, especially in regard to whether gaseous materials are released as well as dissolved materials, and whether these materials are organic or inorganic in nature.

C-14

Initial work was undertaken by Baston et al. (2004) and Handy (2006) to identify all the chemical forms of C-14 leached from graphite, and the relative proportions thereof. However, are number of limitations were identified:

- the timescale of the experiments was short;
- the activities measured were low compared with background; and
- there was inconsistency of separation of carbonate and organic product.

Similar issues have challenged more recent work, and the relative importance of inorganic and organic products is still unknown. Recent work reported to CARBOWASTE has identified release of gaseous C-14 as CO. However the chemical mechanism leading to release in CO is unknown and this result is therefore uncertain. Partitioning of C-14 between solid, aqueous and gaseous phases; organic and inorganic forms, will be even more complicated in the GDF.

The current understanding of the radionuclide release mechanism from graphite is as follows. The mechanism is not well understood, but the bulk of the (limited) evidence suggests that the mechanism of release from solid graphite (i.e. C-14 in the matrix material) is through oxidation, not by the water but from oxygen dissolved in it. This was the deduction reached by workers at Hanford (Gray, 1982). This implies that the rate of release will decrease as anoxic conditions are established in the GDF. This is anticipated to occur on a timescale of a few years, to a few decades for vaults with a low chemical oxygen demand.

However, the results of more recent leaching tests suggest rates which are much higher than the Hanford result (albeit still rather slow in comparison with other isotopes), and which fall exponentially with time. This indicates that there is a labile source of C-14 which can be removed more easily than C-14 in the graphite matrix, and this source is depleted faster than it can be replenished by some diffusion process. This more labile source seems to be C-14 atoms that have been displaced from the lattice, either due to recoil during formation, or interaction with fast-neutrons. After a few hundred days this more labile source of C-14 has been exhausted and the residual rate of release has become slow.
Depending upon the graphite component irradiation history and source, there may be other carbonaceous compounds containing C-14 present within the porosity and on geometrical surface: the leaching behaviour for these will be dependent upon the chemical form in which the C-14 is held. However, little data are available.

**Other Radionuclides**

The specific activity of weak long-lived beta emitters is unlikely to be significantly different in different graphites because the source terms are similar. It will however be related to the total fluence to which the graphite has been exposed and which will therefore increase in the order Research reactor/Windscale: Magnox: AGR. Sleeve graphite waste stocks should have received a lower fluence than the flattened-zone regions of the core at end of life, but are more susceptible to matter transfer to and from the flowing coolant gas.

**Release Rates**

Leach rates have been measured experimentally using samples of irradiated graphite from the following reactors:

- **Harwell BEPO, UK** (McDermott et al., 2010);
- **Marcoule NPP, France** (Costes et al., 1990; Gray and Morgan, 1989);
- **Tokai-mura NPP, Japan** (Takahashi et al., 1999);
- **Trawsfynydd Power Station, UK** (White et al., 1984);
- **WAGR³, UK** (Handy, 2006).

The experiments show a consistent pattern of a high initial release rate, falling to a lower long-term rate once the most readily available radionuclides have been leached. Based on the results of these experiments, the leach rates given in Table 3-3 are selected for modelling purposes.

The Cl-36 release rate during the very early period is sufficiently high that more than 90% of the initial inventory is released during the first 30 days. Therefore instantaneous release can be assumed. There is little difference in the leaching rates of C-14 between the very early period and at later times, so for simplicity a constant release rate of 2.0E-2 y⁻¹ is assumed. However, it is noted that the long-term rate may be too high on

³ There is some uncertainty over the provenance of the graphite.
post-closure timescales. A later period (long-term) C-14 leach rate of 1.83E-5 y\(^{-1}\) (Takahashi et al., 1999) is proposed for sensitivity analysis.

### Table 3-3: Graphite leaching rates

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Fractional Leaching Rate (y(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Very Early Period (≤ 30 days)</td>
</tr>
<tr>
<td>C-14</td>
<td>2.0E-02</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl-36</td>
<td>1.1E+01</td>
</tr>
</tbody>
</table>

* Alternative value for sensitivity analysis

For all radionuclides, the entire waste inventory is assumed to be available to be leached. This may be too conservative, for example, for C-14 a proportion of the inventory is incorporated into the graphite matrix and therefore may never be released. However, because the release mechanisms are not fully known and there are no long term experimental leaching data, uncertainty remains.

### 3.2.3 Bulk Material

Graphite is extremely stable chemically, and requires reagents such as hot nitric/sulphuric acids before it will react. It survives as native graphite in the natural environment over geological timescales (Natural flake graphite has a different structure from nuclear-grade synthetic graphite, which might be considered as an array of fine (natural) crystallites, many crystallographically imperfect, suspended in a disordered way and interspersed with porosity. The resulting material has different properties to natural graphite, e.g. it is much harder). Graphite does oxidise in water, albeit extremely slowly. Oxidation in air at measurable rates commences at temperatures of around 350°C; in carbon dioxide the onset is at a higher temperature, in excess of 450°C.

In storage and in the GDF, graphite may be considered to be essentially unreactive, although if it comes into contact with water, absorbed material and/or impurities originally present may be leached out. Mechanical and physical properties are altered by the irradiation process, with displacements of atoms and the creation of vacancies within the crystallite structure. However, these changes cease when irradiation ceases, and the graphite may be expected to retain the strength, density, thermal conductivity and so forth with which it entered the storage regime.

Some of the wastes contain ‘stored’ Wigner energy. This is particularly important for graphite from sources such as the Windscale Piles, where there remain regions of the cores in which the potential rate of release of stored energy as a function of increasing
temperature exceeds the specific heat capacity of the graphite. In such a circumstance, spontaneous heating is possible under adiabatic conditions if the graphite is first allowed to exceed its original irradiation temperature by a significant margin, typically (but not universally) 50 K. For Magnox and AGR material (including WAGR), no such concerns exist. The accumulated stored energy is much lower and is confined to the lower brick layers, and irradiation temperatures were much higher such that there is little likelihood of self heating under any conceivable circumstance.

Nirex had concerns that the thermal pulse associated with curing of cementitious backfill could initiate Wigner energy release from the Windscale Pile graphite. They were also concerned that very slow releases could occur over long timescales which would have the effect of slowly heating the packaging and perhaps become self-sustaining. The GDF specification (RWMD, 2010d) specifies the maximum permitted temperature during backfilling, which is significantly less than the original irradiation temperature. Mathematical modelling undertaken by Minshall and Wickham (2008) indicates that slow long-term release of Wigner energy will not result in significant package heating. The very low rates of long-term Wigner energy release that can be expected, and hence insignificant package heating, are supported by measurements on Windscale pile graphite (Marsden et al. 1998) which show no loss of stored energy over a period of 54 y.

Whilst the different graphite types vary structurally, they are similar chemically, with one important difference. Most sleeve material will have been pond stored at some point, and maybe resided in wet or damp vaults subsequently. All AGR fuel sleeves have been exposed to pond water.

Pond storage means that the most readily leached radionuclides will have already been lost from the graphite. If the radionuclide inventories have been estimated by calculation (Section 3.2.2) then radionuclides lost in pond water are unlikely to be accounted for. In particular, the Cl-36 inventory may be overestimated. Given the leach rates in Table 3-3, it is possible that almost the entire Cl-36 inventory may have already been lost. Uncertainties in the national inventory data have not been investigated.
4 Conceptual Models

4.1 Approach

The physico-chemical evolution of the GDF will affect release of radionuclides from graphite wastes, and transport of radionuclides from the GDF to the host rock. Conceptual models of the physico-chemical evolution of the GDF have already been developed, e.g. Section 3 of Towler and Bond (2011), RWMD (2010c). These conceptual models form the framework within which to analyse release and transport of radionuclides from graphite wastes.

Development of conceptual models was undertaken by analysing the Features, Events and Processes (FEPs) relevant to graphite with cementitious backfill, in higher strength host rock. This analysis was undertaken using the interaction matrix approach (Figure 4-1).

In the interaction matrix approach, features of the waste and barrier system are identified and represented on the leading diagonal elements of a matrix. Phenomena that could potentially influence interactions between these features are then entered into off-diagonal elements.

In practice, FEPs were identified using the following approach:

- A draft interaction matrix was developed for graphite wastes with cementitious backfill in higher strength host rock. Phenomena were identified by expert judgment, supported by relevant information from previous research reported by the NDA, Nirex and radioactive waste management organisations in other countries.

- The draft matrix was analysed during a FEPs workshop. The participants comprised the authors of this report and Simon Norris (RWMD).

- At the workshop, FEPs were prioritised and follow-up actions instigated to provide relevant information and supporting references. FEP priorities were indicated in the interaction matrix using a simple colour coding system.

- The implications of lower strength sedimentary or evaporite host rock for the relevant FEPs, and FEP priorities, were analysed.

- Interactions between graphite and other wastes were then considered, and the key safety features / functions were analysed.
Design optimisation and the implication for the relevant FEPs, and FEP priorities, were considered.

<table>
<thead>
<tr>
<th>Waste</th>
<th>Influence of the waste on the container 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Influence of the waste on the container 2</td>
</tr>
<tr>
<td></td>
<td>Influence of the container on the waste 1</td>
</tr>
<tr>
<td></td>
<td>Container</td>
</tr>
</tbody>
</table>

**Key:**

- **Red:** Key FEP that needs to be taken into account in performance assessment. *(Priority = high).*
- **Amber:** FEP that may or may not be important – further work is required to determine the status of this FEP. *(Priority = medium).*
- **Green:** FEP that is not important, and would not be taken into account in performance assessment. *(Priority = low).*

**Figure 4-1. Example of a FEP interaction matrix considering the waste and container features**

**4.2 Generic Disposal System**

**4.2.1 Physico-chemical Evolution of the GDF for the Generic Design**

The base assumption is that ILW will not be segregated and sorted (except into wastes that can and can not be contact handled: SILW and UILW respectively, Section 3.2.1). Different types of ILW wastes will be disposed together. Therefore, wastes including metals and organics could be disposed of in the same vaults as graphite wastes. However, these other waste materials are unlikely to be in the same containers as the graphite. In practice, a degree of clustering may occur in the GDF due to national waste management strategies, e.g. scheduling of waste transfers from ILW stores at different sites to the GDF, but this has not been considered herein.

The current strategy for management of reactor core graphite is to leave the reactor cores in-situ to allow short lived radionuclides to decay significantly, prior to dismantling and disposal of the core to the GDF (the SafeStore strategy). This
SafesStore strategy means that the majority of reactor core graphite will arrive at the GDF after the majority of other ILW has been emplaced. Therefore reactor core graphite may be preferentially clustered in certain vaults.

The base assumption is that graphite wastes will be put into stainless steel containers with a cementitious encapsulant. At closure, the containers will be surrounded by cementitious backfill. The encapsulant and backfill will contain free water, but will not be fully saturated. The same assumptions apply to other wastes, and many ILW wastes have already been packaged and encapsulated. The free water content of the wastes and backfill is important because the water will support metal corrosion and organic degradation processes that generate gas. The encapsulant may contain less free water than the backfill due to drying whilst in low humidity stores, and consumption of water through corrosion / degradation reactions during storage.

Once the GDF is closed, gases generated from corrosion and degradation reactions will build up in the GDF. Water will seep from the host rock into the GDF, and the GDF will begin to resaturate. Resaturation is expected to be significantly faster in higher strength host rock than lower strength sedimentary host rock and evaporite host rock. Gas will freely migrate via fractures in higher strength host rock, and the GDF will resaturate quickly (on post-closure timescales).

In lower strength sedimentary host rock, the rate of water inflow to the GDF will be much lower, and gas may not be able to escape easily. The gas pressure will increase and this will further decrease the water inflow rate. Eventually the GDF may completely dry out and corrosion and degradation reactions will progress only very slowly, as the water inflow rate balances the gas loss through dissolution and diffusion. The GDF may be largely dry for very long timescales. Eventually gas generating reactions will cease and the GDF will finally resaturate.

In evaporite host rock, the availability of water may be so low that gas generation can only be supported by the amount of water present in the waste and encapsulant when it is disposed. There may be no significant inflow of water from the host rock. Sacks of MgO buffer will adsorb water vapour and therefore there may no water available to support corrosion and degradation processes. There may be very little gas generation. As the void spaces are closed by creep of the host rock the gas headspace will decrease and the pressure will increase. Creep will cease when lithostatic forces are balanced by the gas pressure plus mechanical resistance of the wastes.

Resaturation behaviour for all three host rock is further described by Towler and Bond (2011).
A GDF in higher strength host rock will be backfilled at closure, taking approximately 10 years, while the vaults in a GDF in lower strength sedimentary or evaporite host rock will be progressively backfilled. Gas generated in vaults that have been closed could enter operational tunnels if the vault seals are not sufficiently good. As cementitious backfill cures it will create a thermal pulse. This heat pulse will significantly increase the already high corrosion rate for Magnox metal waste. The resultant pulse of $\text{H}_2$ gas could potentially act as a carrier gas, transporting C-14 labelled gases from the closed vaults into the operational tunnels.

Initially conditions in the GDF will be oxic. However, conditions will rapidly become anoxic as oxygen is consumed by corrosion of metals and microbial degradation of organic wastes. Microbial consumption of oxidants (nitrate, iron, manganese and sulphate) could exceed supply such that methanogenic conditions may be established: particularly in waste packages or vaults with higher organic material content.

The pH will be high due to the cementitious backfill and encapsulant, or elevated by MgO buffer, as applicable.

### 4.2.2 FEPs Analysis for the Generic Design in Higher Strength Host Rock

The FEPs analysis considers the graphite wastes in isolation. Interactions with other wastes were considered subsequently, and are discussed in Section 4.2.4. The interaction matrix output from the FEPs workshop is presented in Table 4-1. Selected key FEPs relating to the release of radionuclides from graphite and their subsequent transport are analysed in Table 4-2.
<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Radiogenic heating Radiation damage</th>
<th>Radiogenic heating Radiation damage</th>
<th>Radiogenic heating Radiation damage</th>
<th>Radiogenic heating Water chemistry &amp; radiolysis Contaminant dissolution</th>
<th>Radiogenic heating Contaminant labelled gases (e.g. $^{14}$CH$_4$)</th>
<th>Radiogenic heating</th>
<th>Inhibit microbes</th>
<th>No significant interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retention of contaminants</td>
<td>Waste</td>
<td>Physio-chemical degradation Wigner energy</td>
<td>Galvanic corrosion Wigner energy</td>
<td>Water chemistry Colloids Wigner energy</td>
<td>Gas generation Wigner energy</td>
<td>Wigner energy</td>
<td>Microbial substrate</td>
<td>No direct interaction</td>
</tr>
<tr>
<td>Retention of contaminants</td>
<td>Hydraulic Barrier</td>
<td>Cementitious Encapsulant</td>
<td>Passivation Structural support</td>
<td>Water flow + chemistry Gas flow + chemistry</td>
<td>Gas generation + release</td>
<td>Structural support</td>
<td>Microbial substrate</td>
<td>Excludes microbes?</td>
</tr>
<tr>
<td>Restricts water</td>
<td>Restricts water</td>
<td>Restricts water</td>
<td>Container</td>
<td>Water flow + chemistry Colloids</td>
<td>Gas generation</td>
<td>Structural support</td>
<td>Microbial substrate</td>
<td>No direct interaction</td>
</tr>
<tr>
<td>Transport (advection + diffusion)</td>
<td>Leaching</td>
<td>Leaching Precipitation Cracking</td>
<td>Corrosion</td>
<td>Water</td>
<td>Dissolution / Exsolution Gas chemistry</td>
<td>Leaching Precipitation Cracking</td>
<td>Microbial substrate</td>
<td>Leaching Precipitation</td>
</tr>
<tr>
<td>Solubility limitation</td>
<td>No significant interaction</td>
<td>Carbonation</td>
<td>CO$_2$ Enhanced Corrosion</td>
<td>Dissolution / Exsolution Water chemistry</td>
<td>Gas</td>
<td>Carbonation</td>
<td>Microbial substrate</td>
<td>Hydro-fracturing</td>
</tr>
<tr>
<td>Transport (advection + diffusion)</td>
<td>Curing heat</td>
<td>Curing heat Conditions groundwater</td>
<td>Curing heat Passivation</td>
<td>Curing heat Water flow + chemistry</td>
<td>Curing heat Gas flow + chemistry</td>
<td>NRVB</td>
<td>Microbial substrate</td>
<td>Alkaline alteration Structural support</td>
</tr>
<tr>
<td>Curing heat Retention of contaminants</td>
<td>Clogging Biofilms</td>
<td>Clogging Biofilms</td>
<td>Microbially induced corrosion</td>
<td>Water chemistry</td>
<td>Gas generation, chemistry, labelled gas</td>
<td>Clogging Biofilms</td>
<td>Microbes</td>
<td>Clogging Biofilms</td>
</tr>
<tr>
<td>Complexation</td>
<td>No direct interaction</td>
<td>No direct interaction</td>
<td>No direct interaction</td>
<td>Water flow in fractures</td>
<td>Gas flow in fractures</td>
<td>Rockfall</td>
<td>Microbial substrate</td>
<td>Host Rock (incl. EDZ)</td>
</tr>
</tbody>
</table>
### Table 4-2. Analysis of Selected Key FEPs

<table>
<thead>
<tr>
<th>Interaction</th>
<th>FEP</th>
<th>Priority</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contaminants on Water</td>
<td>Contaminant dissolution</td>
<td>High</td>
<td>Contaminants in graphite will dissolve in water. Rates can be estimated from leaching experiments. Measured leaching rates are fast compared with post-closure timescales and therefore instant release could be assumed. However, even if the release period is only tens of years, this may be significant in reducing the potential C-14 fluxes in gas. The reason is that if reactive metals wastes are also present in the vault, large amounts of (H₂) carrier gas may be generated early in the post-closure phase. Assuming instant radionuclide release would overestimate the amount of C-14 in gas available to be transported by carrier gas. It is possible that some of the radionuclides, particularly C-14, will be sufficiently strongly chemically bound in the graphite matrix that they will never be released. However, this fraction is unknown.</td>
</tr>
<tr>
<td>Contaminants on Gas</td>
<td>Contaminant labelled gases</td>
<td>High</td>
<td>C-14 released from graphite will not only dissolve in water, but can also be incorporated into CO₂ and CH₄ gas. Incorporation into CO₂ gas will occur by carbonate equilibria. Incorporation into CH₄ gas will occur by microbial reduction of CO₂ to CH₄ under methanogenic conditions.</td>
</tr>
<tr>
<td>Waste on Container</td>
<td>Galvanic corrosion</td>
<td>Medium</td>
<td>Galvanic coupling between graphite wastes and stainless steel containers may result in accelerated corrosion of the containers, and consequently faster H₂ gas generation under anaerobic conditions, and more rapid failure of the containers. However, experiments undertaken by Smart et al. (2004) indicate that galvanic coupling between graphite and stainless steel did not result in corrosion cell currents significantly different from those for stainless steel alone. Therefore the inferred corrosion rates are the same. The impacts of galvanic coupling are therefore assumed to be within the bounds of general uncertainty in corrosion rates on post-closure timescales.</td>
</tr>
<tr>
<td>Cementitious Encapsulant / NRVB on Water</td>
<td>Water flow and chemistry</td>
<td>High</td>
<td>NRVB is not a hydraulic barrier. However, the cementitious encapsulant may be a more significant hydraulic barrier. The encapsulant and NRVB will chemically condition water in the vaults. The presence of cement will significantly affect the carbonate equilibria. Dissolved (inorganic) carbon will be consumed by reaction with cement minerals (Portlandite and CSH) forming calcite. Dissolved carbon will be consumed until the equilibrium concentration is reached. As dissolved carbon is consumed, gaseous CO₂ will dissolve, to be consumed itself, and the partial pressure of CO₂ (Pco₂) will decrease. The equilibrium Pco₂ in the presence of cement is lower than the background Pco₂. The presence of cement will therefore reduce the potential C-14 fluxes in gas and water, although they</td>
</tr>
<tr>
<td>Interaction</td>
<td>FEP</td>
<td>Priority</td>
<td>Description</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>----------------------------------</td>
<td>----------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>Cementitious Encapsulant / NRVB on Gas</strong></td>
<td>Gas flow and chemistry</td>
<td>High</td>
<td>As described for the above FEP, reaction of dissolved carbon with cement will result in precipitation of calcite. This consumption of carbon will reduce the partial pressure of CO₂ (P_{CO₂}) and hence the amount of C-14 in CO₂ gas. However the amount of C-14 in CO₂ will not be zero. C-14 labelled methane gas will not be consumed by reaction with cement minerals.</td>
</tr>
<tr>
<td><strong>Water on NRVB / Cementitious Encapsulant</strong></td>
<td>Leaching, precipitation, cracking</td>
<td>High</td>
<td>Dissolved carbon, sulphate and other ions in water will result in chemical alteration of the cementitious encapsulant / NRVB. This alteration can include leaching of cement minerals with consequent increases in porosity and permeability, and precipitation of new minerals with high specific volumes, resulting in cracking. Reaction with dissolved carbon can result in precipitation of calcite (carbonation), which may clog pores and ‘armour’ fracture surfaces (Swift et al. 2010). C-14 can be precipitated in calcite.</td>
</tr>
<tr>
<td><strong>Gas on NRVB / Cementitious Encapsulant</strong></td>
<td>Carbonation</td>
<td>High</td>
<td>CO₂ gas can dissolve in water (i.e. react with the water forming dissolved inorganic carbon) and react with cement minerals resulting in precipitation of calcite. Calcite can clog pores and ‘armour’ fracture surfaces (Swift et al. 2010). C-14 can be precipitated in calcite. Reactivity significantly reduced as relative humidity approaches zero.</td>
</tr>
<tr>
<td><strong>Water on Contaminants</strong></td>
<td>Transport, Solubility limitation</td>
<td>High</td>
<td>Dissolved contaminants can be transported in water by advection and diffusion. Dissolved contaminants include Cl-36 and C-14 labelled inorganic carbon. Concentrations of radionuclides may be solubility limited. Cl-36 is not anticipated to be solubility limited, while carbonate equilibria will control the solubility of C-14 associated with inorganic carbon.</td>
</tr>
<tr>
<td><strong>Gas on Contaminants</strong></td>
<td>Transport</td>
<td>High</td>
<td>Gaseous contaminants can be transported in gas by advection and diffusion. Gaseous contaminants include C-14 labelled CO₂ and CH₄.</td>
</tr>
<tr>
<td><strong>NRVB / Cementitious Encapsulant on Contaminants</strong></td>
<td>Retention of Contaminants</td>
<td>High</td>
<td>Cementitious encapsulant and NRVB will generate high pH conditions that will reduce the mobility of many radionuclides by inducing solubility limitation. Radionuclides may also sorb onto cement minerals. For the key radionuclides associated with graphite, Cl-36 will not be solubility limited and will experience little or no sorption (ONDRAF/NIRAS, 2009). The mobility of C-14 will be significantly controlled by carbonate equilibria. The presence of cement will reduce the partial pressure of CO₂ (P_{CO₂}), reducing the mobility of C-14 associated with CO₂ gas and carbonate/bicarbonate ions. C-14 will be retained in calcite precipitates formed through reaction of</td>
</tr>
<tr>
<td>Interaction</td>
<td>FEP</td>
<td>Priority</td>
<td>Description</td>
</tr>
<tr>
<td>---------------------</td>
<td>------------------------------------</td>
<td>----------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Microbes on Gas</td>
<td>Gas generation, chemistry, labelled gas</td>
<td>High</td>
<td>Microbes can degrade organics wastes resulting in the generation of anaerobic conditions in the vault. Microbes will generate CO$_2$ gas and react with dissolved nitrate, manganese, iron and sulphate. Once these terminal electron acceptors have been consumed (locally as opposed to throughout the vault), microbial degradation will proceed by methanogenesis, resulting in the formation of CO$_2$ and CH$_4$. If H$_2$ gas is present, e.g. from anaerobic corrosion of metals, microbial reduction of CO$_2$ to CH$_4$ can occur. C-14 can be incorporated in CO$_2$ and CH$_4$. The extent to which this occurs will be influenced by the fact that graphite and organic wastes will be disposed in separate containers, which have a barrier function. Microbial processes may be significantly reduced (and potentially not important) if there are no organic wastes in the vault.</td>
</tr>
<tr>
<td>Host Rock on Gas</td>
<td>Gas flow in fractures</td>
<td>High</td>
<td>Gas is readily able to migrate into fractures in the host rock, displacing water from the fractures, where the fracture aperture is sufficiently wide for the capillary suction to be small. Therefore, gas can readily migrate from the vaults into the EDZ and fractured host rock, i.e. higher strength host rock. Fractures may be concentrated into discrete zones (see next FEP), but the distribution of host rock fractures intersecting the vault is unlikely to significantly affect resaturation and gas pressures when permeable NRVB is used (see Section 9.4 of Towler and Bond, 2011).</td>
</tr>
<tr>
<td>Host Rock on Water</td>
<td>Water flow in fractures</td>
<td>High</td>
<td>Fractures are expected to be present in higher strength host rock. Fracturing may comprise small scale, high frequency fractures, and larger scale, less frequent fracture zones. The fracture characteristics will be site specific. When the fracturing is small scale and high frequency, water can flow into fractures over the entire surface area of the vault. When fracturing is concentrated into discrete zones, water will have to flow through the backfill to enter the fracture zones. The orientation of the vaults with respect to the regional hydraulic gradient and fractures will affect the flow pathlength through the backfill to the fracture zones (see Section 4.3.1 of Towler et al. 2010). The greater the flow path length through the backfill, the greater the opportunity for C-14 to react with cement minerals.</td>
</tr>
</tbody>
</table>
4.2.3 Differences in FEPs for Lower Strength Sedimentary Host Rock and Evaporite Host Rock

**Lower Strength Sedimentary Host Rock**

The GDF will resaturate far more slowly than in higher strength host rock. If the vault seals are substantially gas tight, adjacent vaults may resaturate at different rates depending on their inventory of gas generating materials (Towler and Bond, 2011). Gas may not readily escape from the GDF, and radionuclide release from the GDF will be by diffusion of anions and dissolved gases in water.

Gas and water transport through the EDZ, interfaces between seals and tunnel walls, and via the shaft / shaft EDZ may be the most significant contaminant transport routes. However, the radionuclide flux is expected to be small, except under failure scenarios, e.g. failed shaft seals. The EDZ may self-heal for argillaceous rock, further reducing the significance of this transport route. It may be desirable to engineer a gas transport system to ensure that excessive gas pressures are not achieved, e.g. Nagra (2008). However, this will result in higher radionuclide fluxes.

Geosphere transport of C-14 in gas and water, and Cl-36 in water, are not anticipated to be significant because the geosphere travel time is anticipated to be so long that there will be significant decay. Human intrusion is therefore likely to be the key exposure pathway. Hoch and Thorne (2008) concluded that potential releases of C-14 labelled methane gas, following borehole intrusion into a pressurised GDF, are significant (potentially similar to the maximum dose target of 2E-5 Sv). For NWMO’s proposed Deep Geological Repository (DGR) in Canada, Quintessa et al. (2011) calculated that for a borehole intrusion scenario, if gases from the DGR are not appropriately constrained, doses to a nearby resident could be 1E-4 Sv from inhalation of C-14 labelled gases. (The C-14 in the DGR is dominantly from ion exchange resins).

The potential consequences of an intrusion event need to be balanced against the low probability of intrusion, especially in an environment that is suitable to host a GDF which would be devoid of significant geological resources.

**Evaporite Host Rock**

Evaporite is anticipated to be the driest host rock environment, and there may be negligible water present, such that there is no significant radionuclide transport in water, even by diffusion. Therefore, there is anticipated to be negligible transport of Cl-36.
Radionuclide transport in gas can potentially occur. This could occur during the operational phase, from closed vaults into operational tunnels; and via the EDZ / shaft early post-closure as seals are attaining their long-term properties, in particular as crushed evaporite backfill is reconstituting and sealing as a result of creep of the host rock. Release of gas can also occur in response to human intrusion.

Gas generation will be limited by the amount of water present in the waste packages when they are disposed, unless, for example, water is able to drain from permeable units overlying the host rock via the shaft / shaft EDZ, before the seals attain their long-term properties. This was an important consideration for the WIPP shaft seal design (Hanson and Knowles, 1999). MgO buffer can be used to adsorb moisture from the atmosphere in the vaults, and reduce / prevent corrosion and gas generation. Significant gas generation needs to be avoided to ensure complete closure of vault void space by creep, and complete reconstitution of crushed evaporite seals (Hanson and Knowles, 1999).

There is unlikely to be any significant release of C-14 labelled CO$_2$ from closed vaults to operational tunnels so long as the water content of the packages of graphite waste is negligible and the humidity is low. Free water present in the cementitious encapsulant may permit some release and there may be small releases from graphite wastes that contain small amounts of residual water due to immersion in cooling ponds.

### 4.2.4 Potential Waste Interactions

Interactions between graphite and other wastes were discussed at the FEPs workshop. The following interactions were identified.

C-14 will be leached from graphite wastes forming aqueous carbonate and bicarbonate ions. Under methanogenic conditions, CO$_2$ may be microbially reduced by H$_2$ forming CH$_4$ gas (Geofirma and Quintessa, 2011). Radiolabelled CH$_4$ gas may be formed by this process. This process is more likely to occur when there are mixed wastes in the GDF than segregated graphite wastes alone, because the presence of organic wastes will promote the development of methanogenic conditions.

Organic wastes will also generate CO$_2$ gas. This gas will react with cementitious backfill. In particular CO$_2$ gas may react the surfaces of fractures in the backfill causing them to become armoured (e.g. Swift et al., 2010). This will reduce the effectiveness of the backfill as a chemical barrier to transport of C-14.

Graphite is a neutron moderator therefore the potential interaction of graphite with wastes containing fissile materials needs to be considered, in the context of the
potential for a post-closure criticality event. There are two competing factors to consider:

- segregation of graphite from other wastes acts to separate moderator from sources of fissile material; but

- segregation of graphite wastes maximises the concentration of moderator material (i.e. graphite) in the associated vaults. There may be concerns that if fissile radionuclides transported in water were chemically deposited in a vault containing only graphite wastes, the chances of a criticality may be higher than for a vault containing mixed ILW.

It is considered that the potential for a criticality event is not significantly increased by segregating graphite wastes and concentrating them into a single vault, and the potential for a criticality remains small, because:

- fissile material is likely to be deposited on interfaces, such as the vault wall, rather an within packages of graphite wastes;

- a precise (unlikely) combination of flow vector and changes in chemical conditions is required; and

- in any case water, which is present in all the vaults, can act as a moderator.

Therefore, from a post-closure criticality perspective, segregation of graphite which acts to separate moderator from sources of fissile material is likely to be preferable, although not specifically required.

4.2.5 Conceptual Model for the Generic Design

This section describes the conceptual model for migration of radionuclides in gas and water for the generic design in higher strength host rock and lower strength sedimentary host rock. This more detailed description underpins the development of mathematical models (Section 5), but is not required for evaporite host rock (Section 4.5).

In the high pH vault environment the stainless steel containers are anticipated to corrode uniformly (Towler et al. 2010). They may significantly influence flow of water through the vault for tens of thousands of years. Aqueous radionuclides will only be released from the containers via diffusion through the vent hole until the containers are perforated by corrosion.
Cl-36 will migrate in groundwater. C-14 can migrate in groundwater and gas. The release, partitioning and transport of C-14 will be significantly influenced by the behaviour of bulk carbon in the GDF and host rock, in particular carbonate equilibria reactions and reaction of aqueous carbon species with cement minerals.

Figure 4-2 describes the conceptual model of the behaviour of bulk carbon in the GDF. The key processes are:

- ▲ generation of \( \text{CO}_2 \) and \( \text{CH}_4 \) gas from microbial degradation of organic wastes;
- ▲ generation of \( \text{H}_2 \) gas from anaerobic corrosion of metals;
- ▲ reaction of cement minerals with \( \text{CO}_2 \) generated from degradation of organic wastes and bi/carbonate and other ions present in the host rock porewaters;
- ▲ microbial reduction of \( \text{CO}_2 \) to \( \text{CH}_4 \) with \( \text{H}_2 \) under methanogenic conditions;
- ▲ partitioning of carbon between gaseous (\( \text{CO}_2 \)), aqueous (\( \text{HCO}_3^-/\text{CO}_3^{2-} \)) and solid (\( \text{CaCO}_3 \)) species, in response to carbonate equilibria and the reactions identified above.
Evidence from leaching experiments indicates that C-14 will dominantly be leached from graphite (Section 3.2.2) as aqueous carbonate/bicarbonate ions (predominantly carbonate under high pH conditions). C-14 will therefore be incorporated into gaseous and aqueous phases by the processes described above. It can be assumed that C-14 partitions between gaseous, aqueous and solid phases in the same proportions as bulk carbon. This is termed a specific activity model.

C-14 may be preferentially associated with the aqueous / solid phases rather than gaseous phases due to isotope fraction effects, but these will be minor, and are excluded from the conceptual model. Potentially more important is the interaction of different wastes at the scale of individual containers. This is illustrated in Figure 4-3.

Available C-14 in graphite is anticipated to dissolve in water in the waste packages forming carbonate ions. There could be microbial reduction with hydrogen to form C-14 labelled CH₄ gas in the waste packages, but methanogenic conditions may not

---

4 C-14 incorporated into the graphite matrix may not be available, or only released at a much slower rate.
develop in packages of graphite waste. C-14 labelled carbonate ions are more likely to react with cementitious encapsulant, or diffuse out of the waste containers and react with cementitious backfill, forming calcite.

Reduction of CO$_2$ to CH$_4$ is more likely to occur in waste packages containing organic wastes, where methanogenic conditions are more likely to develop, and the majority of any CO$_2$ that is not reduced will react with the cementitious encapsulant and backfill.

In the backfill, reaction of CO$_2$ with cement minerals, and reduction to CH$_4$, are competing sinks for carbon, including C-14. Both processes are rapid and it is difficult to determine their relative significance within the bounds of uncertainty of the process rates. However, while rapid reaction of CO$_2$ with cement minerals can be predicted with confidence, microbial reduction of CO$_2$ is subject to greater uncertainty:

- Do methanogenic conditions occur in the backfill? Is the supply of nitrate, sulphate etc from the wastes and host rock porewater sufficient to fully suppress methanogenesis?

- How does release of aqueous organics and non-aqueous phase organic liquids from the wastes influence the above?

The relative importance of these competing sinks for CO$_2$ is significant for C-14, because while reaction with cement will ‘lock-up’ C-14 and prevent its release from the vault, reduction of CO$_2$ to CH$_4$ will maintain C-14 in a mobile form that can potentially be released from the vault.

It is not practical to conceptualise the behaviour of C-14 on a waste package by waste package basis because there are too many uncertainties associated with the potential interactions. It is therefore assumed that C-14 partitions in proportion to bulk carbon, i.e. a specific activity model.
Host rock porewater: $\text{HCO}_3^-$, $\text{SO}_4^{2-}$, etc

Backfill degradation. Leaching of cement minerals. Precipitation of calcite (carbonation) in pores and on fracture surfaces. Cracking through precipitation of high specific volume minerals.

Graphite
C-14 released as $\text{CO}_3^{2-}$, but equilibrium concentration is low in cementitious backfill

Majority of $\text{CO}_2$ reacts with cementitious backfill. However, there will still be some aqueous and gaseous $\text{CO}_2$ (equilibrium concentrations controlled by carbonate equilibria). Are conditions sufficiently reducing in the backfill for microbially mediated $\text{CO}_2$ reduction to $\text{CH}_4$ to occur?

Carbonation of backfill. Other solutes from waste may cause degradation of backfill, including $\text{Mg}^{2+}$ from Magnox metal wastes (not shown).

Organic wastes
Aqueous organic breakdown products and other solutes, plus bulk $\text{CO}_2$ and $\text{CH}_4$ gas. $\text{CO}_2$ reduction to $\text{CH}_4$ can occur in individual containers.

As $\text{CO}_2$ gas, but $P_{\text{CO}_2}$ is low in cementitious backfill

As $\text{CH}_4$ gas? Flux small if methanogenic conditions confined to organic waste containers

Whilst containers are intact, only diffusive release through vent. 10,000s+ years.

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**Figure 4-3. Conceptual model of the behaviour of C-14 in the GDF**

**Cracking of Cementitious Backfill**

The generic designs contain a sufficient inventory of cement minerals to maintain high pH conditions for more than 1 millions years in higher strength host rock, and potentially longer times in lower strength sedimentary host rock, for representative hydrogeochemical conditions. This suggests that the backfill will form a chemical barrier to release of C-14 for much longer than the time required for the C-14 inventory to decay to negligible amounts: anticipated to be ten half-lives, i.e. approximately 57,000 y. However, it is anticipated that there will be cracks in the backfill, as a consequence of the backfilling process, but also cracks that develop in response to evolution of the GDF (Swift et al. 2010).

Gas and water will preferentially migrate within the cracks compared with the matrix of the backfill, as the permeability of cracks is higher and their gas entry pressure is lower than for the matrix. Dissolved carbon in the host rock porewater, and originating from the wastes (e.g. $\text{CO}_2$ generated from organic wastes) will react with the fracture surfaces. The fracture surfaces will be become ‘armoured’ with calcite and will no
longer be a chemical barrier to the migration of C-14 (and other radionuclides). This means that the effective cement mineral inventory may be significantly less than the total cement mineral inventory.

Swift et al. (2010) have recently investigated this armouring process. They concluded that this process will occur, but there are large uncertainties as to its significance. Relevant factors are:

- site specific host rock water composition and flow rate;
- \( \text{CO}_2 \) generation from organic wastes;
- the magnesium content of the water (e.g. from Magnox waste and the host rock porewater);
- the number of fractures (as the number of fractures increases the fracture surface area increases, and hence so does the effective cement mineral inventory); and
- the fracture aperture (the larger the aperture the faster the flow rate and the less time there is for dissolved carbon to diffuse through the armoured surface to react with unaltered cement).

Swift et al. (2010) only considered the magnesium content of the host rock porewater. The potential increase in the dissolved magnesium content in the presence of Magnox wastes has not been analysed quantitatively, but this may be a consideration for segregation of high magnesium wastes from graphite (and segregation of high magnesium waste from other wastes that contain large quantities of key radionuclides that are strongly attenuated by the backfill chemical barrier in the design concept).

Swift et al. (2010) did not model the physical effects of precipitation of calcite (from reaction with dissolved carbon) or brucite (from reaction with dissolved magnesium) on the fracture surface, therefore only the chemical armouring effect was modelled. Physical armouring will significantly reduce diffusion of dissolved carbon and magnesium into the fracture wall, such that armouring will proceed more rapidly than modelled by Swift et al. (2010).

It is also possible that this process could lead to clogging of cracks, particularly those with smaller apertures. This would further confine flows of water and gas to the larger aperture fractures, thereby further reducing the effective cement inventory. If the largest cracks can be clogged, then flows will be driven through the backfill matrix, increasing the effective cement inventory.
In practical terms this introduces uncertainty into the long-term performance of cementitious backfill. It also introduces further complexity since the cracked backfill is a dual porosity system: the matrix porosity is available to be resaturated and store gas, but contaminant transport will primarily be associated with the fracture porosity.

An estimate of the effective cement mineral inventory is presented in Appendix A, for higher strength host rock, using the results of Swift et al. (2010). For the purposes of assessment calculations, the cement mineral inventory was cautiously taken to be 30% of the effective cement mineral inventory calculated using the results of Swift et al. (2010), to account for additional processes such as physical armouring.

For, lower strength sedimentary host rock, it is concluded in Appendix A that the backfill can be represented as a porous medium, with the entire cement mineral inventory being available because gas is not readily able to migrate through fractures in the backfill and into the host rock. This is because gas is likely to be trapped in the GDF.

### 4.3 Options

At the FEPs workshop, the key safety features of the generic design in relation to graphite were identified. These are described below. Desirable safety features in relation to graphite were also discussed at the workshop, and this underpinned the discussion of different options. The options for graphite wastes are described in the sub-sections below.

**Higher strength host rock**

In higher strength host rock, C-14 in gas and water, and Cl-36 in water, will be transported relatively rapidly through the geosphere compared with lower strength sedimentary host rock and evaporite host rock. Therefore, the barrier function of the EBS is particularly important in higher strength host rock.

NRVB backfill is permeable. It is not a physical barrier to the release of Cl-36, however in the high pH environment the containers are anticipated to remain intact for tens of thousands of years, forming a physical barrier to Cl-36 release. This will allow some decay to occur, but more importantly, while the containers are intact there will only be gradual diffusive release of Cl-36 via the containers vents. This will reduce the peak radionuclide flux from the near-field into the geosphere, compared with a system where the containers are not a physical barrier.
The containers may be a significant barrier to aqueous release of C-14, enabling significant decay of C-14 in the GDF. The NRVB backfill will further act as a chemical barrier to the release of aqueous C-14, but not C-14 labelled CH₄ gas.

NRVB is not a chemical barrier to Cl₃₆, and no conventional or ‘blue sky’ EBS were identified during the workshop that are significant chemical barriers to Cl₃₆.

It was concluded that for higher strength host rock, the focus for alternative EBS should be to act as a long-term physical barrier to minimise flows of water through the GDF. This would also limit the supply of water to the wastes to support corrosion reactions, including corrosion of the containers.

**Lower strength sedimentary rock**

For lower strength sedimentary rock, the permeability of the host rock is low. Radionuclide transport is anticipated to be diffusion dominated and Cl₃₆ and C-14 will likely decay to small⁵ and insignificant fluxes respectively, before reaching the biosphere. Similarly, gas migration from the GDF into the geosphere will be limited and gas migration to the biosphere is unlikely to be established.

The EDZ, tunnel and shaft / drift system may form a preferential, although still minor, route to the biosphere. Radionuclide transport via this route could occur:

- ▲ in gas while the seals are resaturating and attaining their long-term properties;
- ▲ in gas if the pressure rises above hydrostatic pressure plus the seal gas entry pressure (potentially dominated by a low seal interface gas entry pressure);
- ▲ in water, driven by the gas pressure; and
- ▲ in water if there is a significant background upward hydraulic gradient.

Options should therefore focus on minimising gas pressures and gas generation. (Such considerations also apply to ILW/LLW wastes other than graphite).

---

⁵ Since the half-life of Cl₃₆ is 301,000 y, the amount of decay will significantly depend on the thickness of low permeability rock in which transport is diffusion dominated. Depending on the thickness of rock, the diffusive travel time could be of the order of hundreds of thousands of years to millions of years. C-14 has a half-life of 5700 y and will ‘completely’ decay over such timescales.
**Evaporite host rock**

Evaporite host rock is expected to be a very good barrier to contaminant transport in water and gas. The only potentially significant route for contaminant migration is in gas, at early times while the backfill and shaft seals are evolving to their long-term properties, e.g. reconstitution of crushed evaporate backfill through creep. A key control on gas generation will be to minimise the water content of the waste packages. Options should therefore focus on minimising the water content of the waste packages.

The generic design includes sacks of MgO buffer, designed to keep the humidity too low for corrosion to occur. Options to further reduce the availability of water are non-encapsulation of graphite wastes and segregation of graphite from other wastes, e.g. encapsulated ILW.

Since the geosphere is a very good barrier to contaminant transport, the performance of the system is not reliant on the GDF engineering as a high performance barrier to radionuclide release. Other than consideration of early gas generation issues, the focus of optimisation can be on issues surrounding waste storage, transport and operations.

### 4.3.1 Disposal Strategy Options

The major volume of graphite wastes is SILW (Section 3.2.1). This is dominantly reactor core graphite, and the wastes will not arise until circa 2070 onwards (Magnox South, 2009). By this time the majority of ILW disposal will be complete, including transfer of wastes from stores at nuclear sites to the GDF. This means that it should be relatively straightforward to segregate graphite from other wastes and dispose the graphite to specific vaults.

It would also be possible to dispose of SILW graphite waste containers in redundant service tunnels while they are being backfilled. In higher strength host rock backfill such as NRVB would need to be emplaced as opposed to the usual crushed rock - bentonite backfill.

UILW graphite comprises wastes such as AGR fuel assembly components that are presently stored in vaults. These wastes are to be packaged for final disposal, and placed into ILW stores prior to availability of the GDF. It should be simple to segregate waste packages containing UILW graphite from other UILW wastes upon arrival at the GDF, if it is preferred to segregate containers of graphite waste from containers of other waste. However, it will be necessary to concurrently operate two ILW vaults in the GDF, or appropriately schedule transfers.
Alternatively, if UILW was stored for an extended period it could be reclassified as SILW and disposed in the same vaults as core graphite.

4.3.2 Engineering Design Options

At the workshop, each near-field barrier was discussed in turn. The discussions are summarised below. Potential ‘Alternative Concept’ EBS options were also considered.

Waste Characteristics

Reactor core graphite could be removed as large blocks, or as a fine powder by ‘nibble and vacuum’. Fine powder would have to be encapsulated for transport safety. Therefore the packaging fraction (i.e. volume of waste to container payload) might be lower than for blocks of graphite. If graphite blocks are encapsulated, the encapsulant would form an annulus around the wastes. Channels in the graphite blocks would be filled with other wastes (e.g. graphite or other wastes that will not interact deleteriously with graphite) or encapsulant.

Containers

Under anaerobic high pH conditions associated with cementitious backfill, an NDA 3 m$^3$ stainless steel box would have a lifetime of tens of thousands of years. Long lifetimes would also be expected with clay backfill, although corrosion rates would be higher under the lower pH conditions. A thicker box could potentially form a barrier until C-14 had decayed away to negligible concentrations. It may also permit some UILW wastes to be reclassified as SILW, making storage, transport and handling simpler.

There is not expected to be any significant gas generation from graphite. It may therefore be possible to use a container without a vent, thereby increasing the performance of the container as a barrier to radionuclide release. If the graphite is cement encapsulated, free water in the cement will support gas generation from corrosion of the inside of the metal container. There may also be a small amount of gas generation due to radiolysis of water. Therefore, the graphite would likely have to be non-encapsulated if the container is not vented. Sealed containers would be suitable for blocks of core graphite or powdered core graphite.

Encapsulants

It may be possible to have no encapsulant for graphite waste (unless powder). However, Towler et al. (2010) noted that if a large number of packages of non-
encapsulated waste are disposed to the same vault, there could be damage of the backfill once all the containers fail, because the backfill will collapse to fill the exposed void spaces. Therefore inert void filler may be required.

In France and Spain, drums of graphite wastes are being incorporated into concrete monoliths. This has the advantage that the backfilling process (of the monoliths) can be carefully controlled. A variant of this approach would be encapsulation of graphite wastes within high integrity concrete containers. The resultant additional shielding compared with a steel container may also permit some UILW wastes to be reclassified as SILW, making storage, transport and handling simpler.

Polymer encapsulants were discussed at the workshop. It was considered that whilst they would definitely perform well pre-closure, their long-term post-closure performance is more uncertain. For example, would they be microbially degraded, promoting the formation of C-14 labelled gas? Conversely they might have the advantage of sealing the open porosity in the graphite and therefore reducing leaching rates.

Polymers only have relatively modest radiation resistance (Applegate et al. 2010). Radiation damage is a major mechanism for polymer degradation, resulting in the generation of gas (usually H₂) and potentially also generating smaller organic molecules. These smaller organic molecules could potentially increase the solubility of some radionuclides (e.g. uranium associated with other ILW wastes in the same vault as graphite) or be microbially degraded, generating methane, etc.

Radiation levels in reactor core graphite will be relatively low following SafeStore, and therefore this waste will be classified as SILW. Of the various graphite wastes, following SafeStore, reactor core graphite may be most suitable for polymer encapsulation.

In Russia a molten salts process has been developed for vitrification of graphite wastes. However, it is targeted at specific graphite wastes contaminated with fission products and results in a significant volume increase. It is not considered relevant to the UK graphite wastes.

**Backfill**

A range of potential low permeability backfills that would form a physical barrier to gas and water flow were discussed at the workshop: clay, low permeability cement, polymer, clay based grout. Polymer backfill is likely to be prohibitively expensive and, as discussed above, there are greater uncertainties regarding long-term performance when compared with cement, clay and other ‘established’ backfill materials. Low
permeability cement could be viable. However the low permeability of the matrix could just act to further focus flows through cracks compared with NRVB, and promote armouring. It would be necessary to have the correct flow characteristics to ensure that no voids were left in the vaults.

Clay backfill was seen as a viable option. The backfill could comprise swelling clay, such as bentonite. Whilst this would help ensure that there are no void spaces in the vault, and seal interfaces between the backfill, wastes and vault walls, it would be necessary to ensure that the swelling pressure would not damage the containers. Alternatively a non-swelling clay could be used, or a sand-bentonite mix if low permeability to water but relatively higher permeability for gas is desired (Nagra, 2008).

Emplacement of clay backfill was seen to be the major challenge. Preformed bentonite stillages, blocks and in-situ compaction were discussed. It was clear that further work is required to develop a viable approach. However, clay backfill was considered to provide a good contrast to cementitious backfill, and be sufficiently realistic to be assessed further.

For lower strength sedimentary host rock, where the geosphere is anticipated to be a major barrier to contaminant transport, the option of having no backfill was considered. This approach is being applied by NWMO in Canada (Quintessa et al. 2011), only in unfractured higher strength sedimentary host rock.

In lower strength sedimentary host rock, inert fill would likely be required to prevent roof collapse in closed vaults while GDF operations were ongoing. Coarse aggregate would be appropriate since it would minimise the initial water content of the vaults, and minimise capillary suction, thereby minimising the rate of resaturation, and the availability of water to support gas generation and radionuclide release processes. This option could also be combined with MgO buffer to delay the onset of corrosion reactions, for example in closed vaults while operations continued, and to provide an elevated pH chemical barrier.

**Alternative Concepts**

The final stage of the workshop was to consider less conventional approaches, emerging and potential technologies. These are not considered further during the first phase of the project, but could potentially be further assessed during the second phase. This also forms a check that no significant options have been omitted.

If reactor cores are removed by nibble and vacuum, the resulting graphite dust will need to be encapsulated for safe storage and transport, unless placed in a robust non-
vented container. Encapsulation in cement has already been proven by PSI in Switzerland. An alternative approach would be to mix the graphite powder with cementitious vault / tunnel backfill. This would make very efficient use of space in the GDF.

This approach would require transport of graphite powder from reactor sites to the GDF. This would preferably be done as the powder is generated so there would be no need to store at the reactor site. If the transport issues could be overcome this would be a good option because only a single central grouting facility would be required at the GDF, rather than facilities at each reactor site. For higher strength host rock this would mean that some vaults / tunnels would have to be backfilled prior to final closure of the host rock.

Use of bitumen as an encapsulant was also discussed. There are well documented problems associated with bitumen encapsulation of wastes containing nitrate salts in France and Belgium (e.g. ONDRAF/NIRAS, 2001). However, no adverse reactions could be envisaged with graphite. Asphalt is chemically stable in the ground for geological timescales, and WIPP and NWMO (Hanson and Knowles, 1999; Quintessa et al. 2011) are proposing to use asphalt within their shaft seals due to its low permeability and chemical stability.

4.3.3 Options Selected for Assessment

For this first phase of the project it was decided to analyse options to segregate graphite wastes, and to compare a low permeability clay backfill that forms a physical barrier to flow, with the permeable cementitious backfill of the generic designs that forms a chemical barrier for some radionuclides.

For clay backfill it is assumed that graphite wastes would be non-encapsulated and segregated from other ILW wastes with cement encapsulants. This is to minimise the cement content of the vaults to prevent alkaline degradation of the clay backfill. Segregating graphite wastes from other ILW wastes would also reduce gas pressure in the vaults containing graphite wastes, and hence the potential gas fluxes from these vaults.

Potential issues associated with non-encapsulation were discussed in the previous section. Therefore, it is assumed that an inert material will be used to fill remaining voids in the containers (i.e. void filler). Low pH cement encapsulants or polymers might also be acceptable, but have not been considered further at this stage.

Given the difficulties associated with emplacing clay backfill, it is unlikely that the backfill would achieve the performance associated with pre-formed stillages / blocks.
of compacted bentonite designed for the disposal of spent fuel. The backfill could not be highly compacted uniformly throughout the vault, the backfill would have to swell to fill inaccessible voids between containers, and there would be a large number of interfaces between the backfill and the containers. Iron-bentonite reactions could occur at the interfaces. Overall it is anticipated that the resulting backfill would have performance / properties more similar to sand-bentonite backfill. The backfill was therefore assumed to have the properties of sand-bentonite backfill described by Nagra (2008).

The FEPs analysis and conceptual model for the clay backfill option are described in the next sections.

4.4 Sand-bentonite Backfill

4.4.1 Physico-chemical Evolution of the GDF with Sand-bentonite Backfill

The backfill will be partially saturated at closure. Depending on the formulation and saturation of the backfill it may exhibit sufficient capillary suction to draw water in from the host rock, but this is unlikely to occur with sand-bentonite.

The backfill is anticipated to resaturate rapidly in higher strength host rock, and over a period of hundreds of years in lower strength sedimentary host rock. Once the backfill has resaturated its permeability for water will be low. Its permeability for gas may also be low, depending on composition and the ‘quality’ of emplacement. Sand-bentonite is relatively permeable for gas compared with other clay backfill formulations, but still of low permeability for water (Nagra, 2008).

As the vault resaturates and the gas headspace decreases, and gas is generated from the wastes, the gas pressure may rise above hydrostatic pressure. Gas may migrate through bentonite backfill by piping (Wilson et al. 2011). It is possible that piping is less likely to occur with sand-bentonite due to its greater intrinsic permeability for gas, and hence large gas pressure gradients are less likely to develop. Test results presented in Section 6.2.4 of Keto et al. (2009) also suggest that 30/70 bentonite/ballast may be more resistive to piping than pure bentonite.

The pH in the vaults will be near-neutral, and with the exception of Al, metals will corrode more rapidly than at the high pHs associated with cementitious backfill. Gas generation will therefore be more rapid than with cementitious backfill, so long as water is available. There will be not be a thermal pulse and associated increase in corrosion rates with backfilling.
In higher strength host rock, with sand-bentonite backfill, gas will escape relatively rapidly. Resaturation is therefore anticipated to be relatively rapid, although slower than with cementitious backfill because the backfill is of low permeability to water.

In lower strength sedimentary host rock gas is likely to be trapped in the vaults. The gas pressure may rise above hydrostatic pressure and vaults may become dry. Eventually gas generation will cease and vaults will resaturate as the gas dissolves in the host rock porewater and diffuses away from the vault. Depending on the properties of the host rock and inventories of gas generating materials in the wastes, complete resaturation could take tens or hundreds of thousands of years.

4.4.2 FEPs Analysis for Sand-bentonite Backfill

Table 4-1 identifies the FEPs associated with NRVB in higher strength host rock. FEPs associated with component interactions with the NRVB will change with sand-bentonite backfill. In addition the cement encapsulant will be replaced by inert void filler. FEPs associated with component interactions with encapsulant will also change.

The void filler will be as chemically inert as possible and will therefore not be degraded through reaction with water and gas. The void filler will not significantly react with the waste or chemically condition the water. It will not maintain a high pH inside the containers thereby reducing the corrosion rate. CO$_2$ will not be consumed through carbonation. The void filler will not be a hydraulic barrier and may not be a significant substrate for sorption of radionuclides.

Sand-bentonite backfill will not significantly condition the groundwater or react with CO$_2$. The vault pH will be lower than with NRVB and the waste containers will corrode more rapidly, generating H$_2$ gas. The backfill will be a physical barrier to water flow, and many radionuclides will be significantly sorbed, but not C-14 or Cl-36. The backfill will not be degraded through reaction with the groundwater or CO$_2$ generated from organic wastes, but iron-bentonite reactions may occur at the interfaces with the containers. This could reduce the performance of the backfill at the interfaces. There will not be alkaline alteration of the EDZ / host rock.

For higher strength host rock, use of a sand-bentonite backfill introduces a new FEP, mass transfer resistance (Environment Agency, 2009): i.e. if fractures in the host rock are concentrated into discrete, widely spaced fracture zones, there will be a significant diffusion pathlength through the backfill to the fracture zone. This can significantly increase the performance of the backfill as a barrier to radionuclide migration, compared with host rock containing many closely spaced small fractures.
4.4.3 Conceptual Model for Sand-bentonite Backfill Design

Figure 4-4 describes the conceptual model of the behaviour of bulk carbon with sand-bentonite backfill. Key differences compared with cementitious backfill are as follows:

▲ The backfill is far more impermeable than cementitious backfill. However, the capillary properties, including the gas entry pressure, are significantly uncertain: depending on the backfill formulation and ‘quality’ of emplacement. For sand-bentonite the capillary suction and gas entry pressure are low. (Lower than NRVB but comparable to Nagra mortar – see Appendix D).

▲ The pH will be much lower than for cementitious backfill, and metal corrosion rates will be higher, assuming sufficient availability of water. The containers will fail more rapidly than with cementitious backfill.

▲ Bicarbonate will be the dominant aqueous carbon species, as opposed to carbonate under high pH conditions.

▲ CO₂ will not react with the backfill and thus C-14 will not be trapped in precipitated calcite.

▲ It is assumed that graphite wastes will be segregated from other ILW wastes. Therefore there will be no reactive metals or organics in the vault. With no organic wastes methanogenic conditions are less likely to occur, such that reduction of CO₂ to CH₄ is less likely to occur.

▲ There are no interactions at the waste package scale that might cause the behaviour of C-14 to differ from that of bulk carbon.
Figure 4-4. Conceptual model of the behaviour of bulk carbon in the GDF with Sand-bentonite Backfill

4.5 Calculation Cases

The objective of the calculation cases is to examine the sensitivity of radionuclide fluxes to different physico-chemical conditions associated with different options.

The options carried forward for detailed assessment are:

▲ The base case design comprising cement encapsulated wastes with cementitious backfill. The base case considers vaults with waste packages containing graphite wastes and waste packages containing other ILW/LLW wastes. Alternatively, graphite waste packages could be segregated from other ILW/LLW waste packages. (Applies to both UILW graphite and SILW graphite).

▲ An alternative option would comprise non-encapsulated graphite wastes (with inert void filler) and clay (sand-bentonite) backfill. The vaults would contain packages of graphite wastes only.
Higher and lower strength sedimentary host rocks are analysed quantitatively. Evaporite host rock is analysed qualitatively, informed by the results for lower strength sedimentary host rock.

4.5.1 Detailed Models

Detailed models can be used to understand the resaturation of the GDF, and the partitioning of carbon (including C-14) between aqueous and gaseous phases. Such models are complicated to develop and analyse, and often have long-run times. A number of calculation cases were identified consistent with the conceptual models and associated uncertainties described in the previous section, and the scope of this first phase of the project. These calculation cases are sufficient to support more wide ranging analyses using simpler assessment models. Additional cases can be examined in the next phase of the project if appropriate.

Two base cases are considered: graphite disposed with other waste packages containing ILW wastes with cementitious backfill in higher strength host rock, and lower strength sedimentary host rock. Although the major volume of graphite is classified as SILW, UILW vaults and associated graphite wastes are modelled for the following reasons:

- UILW waste contains a much greater proportion of reactive metals and organics than SILW (Watson et al., 2011), which have the potential to affect transport of radionuclides, in particular C-14. Calculation cases can be used to examine segregation of graphite from other UILW wastes, and the results extrapolated to SILW.

- While packaged SILW graphite will be one of the last ILW wastes to be disposed, and can easily be segregated from other ILW waste packages, packaged UILW graphite will be available for disposal concurrent with majority of other UILW wastes. Segregation should not be difficult, but it is important to understand the implications of mixing packages of UILW graphite wastes with packages of other UILW, such as reactive metals and organics.

A case is therefore considered for higher strength host rock in which the UILW graphite is assumed to be segregated. (In this case the only gas generating material in the vault is the metal containers).

The conceptual model (Section 4.2.5) identifies that methanogenic conditions may be confined to waste packages containing organic wastes, or may not occur at all. This will prevent incorporation of C-14 derived from graphite in methane gas. Net gas generation will be higher and more CO$_2$ will be generated. This maximises the
potential for CO$_2$ generation to exceed the buffering capacity of the cementitious backfill, for example due non-uniform carbonation. A variant case is therefore considered for higher strength host rock in which methanogenic conditions are assumed not to develop.

Clay has been identified as a potential alternative backfill for segregated graphite wastes. Sand-bentonite backfill is modelled for segregated graphite wastes in higher strength and lower strength sedimentary host rock.

In total, 6 detailed model calculations cases are required, as described in Table 4-3. The detailed models describe the behaviour of bulk carbon. It is assumed that once C-14 has been released (leached) from graphite, its behaviour is identical to that of bulk carbon. The detailed model results for bulk carbon are therefore fed into assessment models, which consider release of C-14 from graphite and the GDF. The assessment models are described in the next sub-section.
<table>
<thead>
<tr>
<th>Case</th>
<th>Host Rock</th>
<th>Backfill</th>
<th>Waste</th>
<th>Methanogenesis(^1)</th>
<th>Backfill cracking</th>
<th>Summary description</th>
</tr>
</thead>
</table>
| 1    | Higher strength| Cementitious | Mixed | Yes                  | Yes              | This is the base case for higher strength host rock. NRVB relative permeability and capillary suction curves are assumed for both waste and NRVB (data from Towler and Bond, 2011). The same curves are assumed for both media in order to minimise water exchange between the waste and backfill due to capillary forces. This was identified as a potentially significant FEP by Towler and Bond (2011), but the containers, which are not modelled explicitly, should limit such capillary interactions. Methanogenic conditions are assumed, with degradation of cellulose and other organics proceeding according to the reactions (Towler and Bond, 2011):
\[
\begin{align*}
C_6H_{10}O_5 + H_2O & \rightarrow 3CO_2 + 3CH_4 \\
C_8H_{m}H_2O + 6H_2O & \rightarrow 3CO_2 + 5CH_4 + mH_2O \quad (m \text{ is assumed to be zero})
\end{align*}
\]
| 2    | Higher strength| Cementitious | Segregated | No            | Yes            | No gas generation from organics or waste metals. It is assumed that methanogenic conditions are not established without organics. |
| 3    | Higher strength| Cementitious | Mixed    | No            | Yes            | If methanogenic conditions are not established then net gas generation will be greater. There will also be more CO\(_2\) gas and greater carbonation of the NRVB. Iron reducing conditions are assumed, with degradation of cellulose and other organics proceeding according to the reactions:
\[
\begin{align*}
C_6H_{10}O_5 + 24Fe(III) + 7H_2O & \rightarrow 6CO_2 + 24Fe(II) + 24H^+ \\
C_8H_{m}H_2O + 40Fe(III) + 16H_2O & \rightarrow 8CO_2 + 40Fe(II) + 40H^+ + mH_2O
\end{align*}
\]
(m is assumed to be zero, reaction between H⁺ and cement is excluded).

<table>
<thead>
<tr>
<th>Case</th>
<th>Strength</th>
<th>Material</th>
<th>Segregation</th>
<th>Methanogenic</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Higher</td>
<td>Clay</td>
<td>Segregated</td>
<td>No</td>
<td>N/A</td>
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<tr>
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<td></td>
<td></td>
<td>It is assumed that if a sand-bentonite backfill is to be adopted as an optimised EBS for graphite, then the graphite wastes will be segregated. No gas generation from organics or waste metals. It is assumed that methanogenic conditions are not established without organics. The clay is assumed to be sand-bentonite (properties data taken from Towler and Bond, 2011). The waste void filler is anticipated to have low capillary suction. Relative permeability and capillary suction curves for Nagra mortar are applied to the void filler (data from Towler and Bond, 2011). These curves are similar to the sand-bentonite backfill, and should avoid strong capillary interaction between the waste and backfill.</td>
</tr>
<tr>
<td>5</td>
<td>Lower</td>
<td>Cementitious</td>
<td>Mixed</td>
<td>Yes</td>
<td>No</td>
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<td></td>
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<td></td>
<td>This is the base case for lower strength sedimentary host rock. The backfill is Nagra mortar. Relative permeability and capillary suction curve data are taken from Towler and Bond (2011). The same curves are applied to the waste in order to avoid strong capillary interaction between the waste and backfill.</td>
</tr>
<tr>
<td>6</td>
<td>Lower</td>
<td>Clay</td>
<td>Segregated</td>
<td>No</td>
<td>N/A</td>
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<td>Comments as case 4.</td>
</tr>
</tbody>
</table>

1 Methanogenic conditions are assumed to be established immediately post-closure.

**Table 4-3. Calculation cases for detailed models**
4.5.2 Assessment Models

Towler et al. (2010) examined the impacts of non-encapsulation of graphite for higher strength host rock. The barrier function of the waste and each of the near-field engineered components was considered, as was an alternative clay backfill. Although different properties have been assumed for clay backfill in this study, and Towler et al. (2010) did not consider lower strength sedimentary host rock, the results of Towler et al. (2010) are still relevant when discussing the implications of different disposal concept options for CI-36.

Towler et al. (2010) analysed potential fluxes of C-14 in water quantitatively. Towler et al. (2010) did not have access to results from detailed models of the type presented in this report to provide information on the partitioning of C-14 between the different phases (gas, solid, liquid), and so made simple bounding assumptions. Therefore the assessment calculations in this first phase of the project focus on calculating fluxes of C-14 in water and gas based on results of the detailed modelling carried out in the current study.

A simple assessment model is used to calculate the fluxes of C-14 in water and gas from the GDF to the geosphere for each the calculation cases described in Table 4-3. The assessment model utilises the results of the detailed model and is described in Section 5.2.

The assessment model is also used to investigate sensitivity of the calculated C-14 fluxes to the assumed long-term C-14 leaching rate. The sensitivity analysis is undertaken for Case 1 (Table 4-3), with a long-term C-14 leach rate of 1.83E-5 y⁻¹ (Takahashi et al., 1999).
5 Mathematical Models

5.1 Detailed Underpinning Model

Gas generation and GDF resaturation was calculated using a coupled model of gas generation and multiphase flow. The model was based on that developed by Towler and Bond (2011) to look at resaturation of individual vaults. The reader is referred to Towler and Bond (2011) for a detailed description of the model and associated input data. The model does not represent individual waste containers, but does represent the waste stacks explicitly. A simple gas generation model is used. This model includes a number of simplifying assumptions compared to RWMD’s SMOGG model (Hoch and Swift, 2009).

The model includes the major gas generation processes for ILW including gas generation from corrosion of metals (mild and stainless steel, Magnox and Aluminium) and microbial degradation of organic wastes (cellulose and other organics under methanogenic conditions). These processes consume water, and cease if the GDF becomes dry. However, the rate of water inflow into the GDF is a function of the difference in pressure between the GDF and the surrounding host rock, and hence the amount of gas generated, i.e. these are coupled processes. The impact of the thermal pulse associated with curing of cementitious backfill on Magnox corrosion rates (Hoch et al. 2007) is considered. Radiolysis is not considered.

The model was further developed for this study, to not only describe resaturation of the vaults, but also to help understand the behaviour and partitioning of bulk carbon. The following model developments were implemented:

▲ Towler and Bond (2011) modelled a pair of adjacent half-vaults, to enable interactions between adjacent vaults to be explored. (Half-vaults were modelled because the vaults are approximately symmetrical about the mid-point along their length). Only a single half-vault was considered in this study. For the higher strength host rock design, the backfilling tunnels and backfill delivery pipes (boreholes) were omitted since the results of Towler and Bond (2011) showed that they are not a significant post-closure control on resaturation and migration of gas.

▲ The results of Towler and Bond (2011) showed that for lower strength sedimentary host rock, a major source of water supporting gas generation was inflow through the floor of the vault into the waste stacks by capillary suction. This would not occur in reality until the waste containers had failed due to
corrosion. This is now represented in the model for all host rocks: gas and water fluxes through the bases of the waste stacks are zeroed until the containers fail. The time of container failure is assumed to be 80% of the uniform corrosion time (assuming water is available) to account for heterogeneities and mechanical disruption.

The Towler and Bond (2011) model considered generation of $H_2$, $CO_2$ and $CH_4$ gases (including reduction of $CO_2$ with $H_2$ to form $CH_4$), but modelled migration of water and a single gas phase (assumed to be air). For this study the model was modified to consider migration of water, $CO_2$ and other gases (assumed to be a single gas phase with the properties of air), with $CO_2$ and other gases being treated as immiscible phases. The model was modified to consider migration of two gas phases in order to track the partitioning of carbon between gas and water. The ratio of cumulative $CH_4$ to $H_2$ generated is output from the model such that the composition of the other gases is known.

Carbonation of cementitious backfill by dissolved $CO_2$ was added to the model as a sink for $CO_2$. An effective cement mineral inventory was used to represent the estimated effects cracking and armouring (Appendix A). This attempts to provide a more realistic estimate of the effectiveness of the backfill as a chemical barrier to C-14 migration, whilst noting that there are significant uncertainties. The presence of dissolved carbon in the natural geosphere porewaters was included in the model. Dissolved $CO_2$ in the background groundwater and $CO_2$ generated from the wastes can both react with the backfill.

Carbonate equilibria were modelled in order to calculate partitioning of carbon between water and gas phases, and hence the amount of dissolved carbon available to carbonate cementitious backfill. The carbonate equilibria model is described in Appendix B.

Initially the different gases ($CO_2$ and other gases) were treated as being immiscible. However, there was some instability in the cement model results for higher strength host rock due to the high mobility of $CO_2$ and rapid reaction of $CO_2$ with cement minerals. Migration of $CO_2$ gas and reaction with cement are competing sinks. Treating the gases as miscible was found to give stable results for all cases with cementitious backfill. The immiscible model was found to give stable results for clay backfill, where gas mobility is low, and there is no reaction with cement minerals. The immiscible model is considered to be more realistic than the miscible model for clay backfill. The miscible model was used for sensitivity analysis with clay backfill.
Model input data are described by Towler and Bond (2011). Updates to the data and additional data for this study are described in Appendix D.

The model geometry for higher strength host rock is shown in Figure 5-1. The geometry for the lower strength sedimentary host rock model is similar, although the dimensions of the engineered components are different. Advective transport in water is expected in higher strength host rock, controlled by local hydraulic gradients while the GDF is resaturating and subsequently by the regional gradient. The regional gradient was represented in the detailed model by an excess head of 10m (water) on the bottom model boundary. Transport in water is anticipated to be by diffusion in lower strength sedimentary host rock, therefore a regional hydraulic gradient was not specified.

![Diagram of the detailed model in higher strength host rock](image)

**Figure 5-1. Geometry of the detailed model in higher strength host rock (EDZ and geosphere omitted)**

The model used to track carbon was developed specifically for this project, and is further described below. Whilst the new model helps understand the partitioning and behaviour of carbon, further development of the model may be required in the next stage of the project.

The carbon sources and sinks are illustrated in Figure 5-2. There is dissolved carbon present in the host rock porewater (Appendix C). This is included in the model initial
conditions, and boundary conditions. CO$_2$ is generated from microbial degradation of organics wastes. Some of the CO$_2$ will be reduced to CH$_4$. The rate of reduction is expected to be fast (Geofirma and Quintessa, 2011). However, the rate of reaction of CO$_2$ with cement minerals in the encapsulant and backfill (where relevant) is also expected to be similarly fast. Within the bounds of uncertainty CO$_2$ could partition similarly between these two competing processes, or one process could dominate.

In the model, CO$_2$ that is not reduced to CH$_4$ in the waste is available to dissolve in water in the waste and backfill, and react with cementitious backfill. CO$_2$ will be ‘consumed’ by the backfill until the entire inventory of cement minerals has reacted, or the P$_{CO_2}$ and concentration of dissolved carbon have reached equilibrium with cement.

Dissolution of CO$_2$ gas in water is calculated using a simplified carbonate equilibria model. The carbonate equilibria model is described in Appendix B, and the model calculation of partitioning and migration of carbon is illustrated in Figure 5-3. Using the carbonate equilibria model, the equilibrium concentration of dissolved carbon is calculated from the partial pressure of CO$_2$ gas. An effective Henry’s law coefficient is calculated to partition CO$_2$ between gas and water.

As the GDF resaturates the system transforms from a multi-phase flow system (water, CO$_2$ and other gases) into a single phase system (water) once gas generation has ceased and resaturation is complete. The partial pressure of CO$_2$ evolves from the partial pressure of CO$_2$ gas to the chemical partial pressure of CO$_2$ that is in equilibrium with the background dissolved carbon concentration (Appendix C).

The equilibrium concentration of dissolved carbon varies as a function of pH. These calculations are therefore undertaken for regions that are assumed to have neutral pH and regions that have high pH (i.e. backfill, waste and concrete plugs) (see Appendix B). Calcite is assumed to be in excess in all regions.

Other gases are also able to dissolve in water. Because CH$_4$ and H$_2$ only dissolve in water, and do not chemically react with the water or other minerals, a simple fixed Henry’s coefficient appropriate to the conditions is specified.

As noted above, corrosion and microbial degradation processes cease if there is insufficient water. Microbes are always assumed to be present, even if they are ‘dormant’ due to dry conditions. The model not only considers consumption of water, but also generation of water from reduction of CO$_2$ to CH$_4$ and reaction of CO$_2$ with cement minerals.

Model outputs include the amount of calcite that has precipitated from reaction of CO$_2$ with backfill, the amount of dissolved and gaseous carbon, and dissolved and aqueous carbon fluxes from the near-field to the geosphere.
Figure 5-2. Sources and sinks of carbon in the detailed model (MPF = Multi Phase Flow calculation)
### 5.2 Assessment Model

The objective of the assessment model is not to calculate C-14 fluxes in order to calculate receptor doses / risks, but to examine the sensitivity of C-14 fluxes to different physico-chemical conditions.

The detailed model describes the behaviour of bulk carbon. The conceptual model is that once C-14 is released from the waste, it will behave in the same way as bulk carbon.

The assessment model considers the behaviour of C-14 and comprises two components:

- Release of C-14 from graphite wastes.

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**Figure 5-3. Model calculation of the partitioning and migration of carbon**
Subsequent behaviour of C-14 based on the results of the detailed model.

The detailed models consider the behaviour of bulk carbon at the vault scale. The assessment models consider all the vaults in the GDF which contain graphite wastes. The number of vaults is different for the different calculation cases (Appendix D). The release rates from the detailed vault scale model are applied to all the vaults in the assessment model.

In the assessment model, release of C-14 from the wastes was modelled using a release (leaching) rate (Section 3.2.2). The entire C-14 inventory associated with graphite is considered in each case. For simplicity, the container is not accounted for. This is a conservative simplification. (It should be noted that while C-14 from graphite is the only source considered in the assessment model, it is not the only source of C-14 in the national inventory. Therefore, there would be additional sources of C-14 in an assessment model that considers all the vaults in the GDF and all the waste streams in the national inventory).

The subsequent behaviour of C-14 is described using the results of the detailed model. The following detailed model results were imported into the assessment model:

- amount of dissolved inorganic carbon;
- waste saturation;
- backfill saturation;
- rate of release of carbon in water to the geosphere;
- rate of release of carbon in gas to the geosphere; and
- rate of consumption of carbon through reaction with cement to form calcite.

The conceptual model assumes that C-14 is homogeneously mixed with stable carbon in the vault, such that the vault can be represented using a single compartment in the assessment model. Using this representation, C-14 release to the geosphere in water will be calculated to occur earlier in reality because the travel time through the vault itself is not fully accounted for. This will not be significant for C-14 in gas.

Figure 5-4 shows the structure of the GoldSim model. C-14 is released from the waste compartment to the GDF compartment at the specified release (leaching) rate (Table 3-3). This empirical leaching rate has been measured under certain geochemical conditions, which may differ from the geochemical conditions in the GDF.
It is not possible to predict how the leaching rate under GDF conditions may differ from the empirical value. The only constraint that can be calculated is the solubility limit for inorganic carbon. The dissolved C-14 concentration can not exceed the solubility limit for inorganic carbon.

The time varying solubility limit for the geochemical conditions was calculated from the detailed model results. It is equal to the total amount of dissolved inorganic carbon divided by the amount of water (accounting for the variation of saturation with time, also from the detailed model results).

The solubility limit is applied to the assessment model GDF compartment. This controls the amount of C-14 available to be released in gas / water, or to react with cement forming calcite. The amount of water in the GDF compartment takes into account that the number of vaults in which graphite will be disposed (Table D-4).

Graphite will be spread between SILW and UILW vaults, and the number of vaults will vary for the different calculation cases, e.g. there will be fewer vaults if graphite wastes are segregated. In practice this is not important because C-14 concentrations do not significantly approach the inorganic carbon solubility limits.

It is recognised that conditions in the SILW vaults may be significantly different to the UILW vaults. However, since the objective of the assessment models is to examine the sensitivity of C-14 fluxes to different physico-chemical conditions, differences in the conditions in the SILW and UILW vaults are not considered. Such differences would need to be considered when calculating C-14 fluxes in order to calculate dose / risk, although the assessment model fluxes can still be used to provide an indication of dose. The results for the calculation cases that consider segregated graphite wastes are likely to provide a good indication of conditions in SILW vaults, where the inventories of waste metals and organics are low.
While there may be some adsorption of C-14 in reality, distribution coefficients derived from batch experiments will also subsume the effect of carbonate equilibria, which is expected to be the dominant control on partitioning and mobility of inorganic carbon. These carbonate equilibria processes are modelled explicitly, such that application of distribution coefficients from batch experiments will double count carbonate equilibria processes. Therefore it is assumed that there is no sorption of C-14.

C-14 is transferred from the GDF compartment to the calcite in GDF, geosphere water and geosphere gas compartments at rates derived from the detailed model. The rates include transport of carbon (and hence C-14) in inorganic and organic forms, i.e. C-14 leached from graphite that is subsequently incorporated into methane.
6 Results

6.1 Calculation Case 1: Higher Strength Host Rock, NRVB, No Segregation

This case is the base case for RWMD’s illustrative example disposal concept in a higher strength host rock. Figure 6-1 shows the average saturation in the waste and backfill with time. At time zero the GDF has not been constructed. Dewatering of the vault begins at 1 y. The vault is dry until 99 y. At 100 y the vault is closed. Saturations attain their at closure conditions between 99 y and 100 y.

There is a general trend of rapid resaturation beyond 100 y, although the resaturation rates are influenced by gas generation and consumption of water, particularly by corrosion of reactive metals. The Magnox corrosion rate is initially very high due to the thermal pulse associated with backfilling, but decreases as the vault temperature falls to ambient.

Figure 6-1. Average saturation in the waste and backfill (Case 1)

Figure 6-2 shows the water saturation at 110 y (i.e. 10 y post-closure) on a vertical section through the middle of the vault. It shows the spatial variation in saturation that is not apparent from Figure 6-1. A ‘weak plume’ of dominantly H₂ gas from corrosion of reactive metals can be seen rising from the vault. Figure 6-1 shows that there is a
small amount of gas present in the waste throughout the simulation due to ongoing gas generation. Figure 6-3 shows that post-closure the gas pressure in the vault rapidly recovers to hydrostatic pressure. Since gas can readily migrate from the vault via fractures in the host rock, the pressure does not rise above hydrostatic. The gas is dominantly H\(_2\) and CH\(_4\), there is only trace CO\(_2\). Figure 6-4 shows the fraction that is hydrogen. The long-term increase in the methane fraction is associated with the assumption of very slow microbial degradation of more recalcitrant organics.

Gases dissolve in water in the vault, and in the geosphere. Figure 6-5 shows the concentration of other gases (i.e. H\(_2\) and CH\(_4\)) dissolved in water at 110 y. There is no dissolved H\(_2\) or CH\(_4\) in the background water. There is a plume of dissolved ‘other’ gas (Figure 6-5) which corresponds with the plume of H\(_2\) and CH\(_4\) gas (Figure 6-2). There is some lateral spreading of the dissolved gas through diffusion and dispersion.

Figure 6-2. Water saturation at 110 y (10 y post-closure, vertical section through vault, Case 1)
Figure 6-3. Gas pressure (Case 1)

Figure 6-4. Hydrogen content of gas (Case 1)
Figure 6.5 shows the concentration of dissolved CO\(_2\). Dissolved CO\(_2\) is present in the background water. CO\(_2\) reacts with the cement backfill resulting in the dissolved concentrations in the backfill being low. CO\(_2\) is actively being generated by degradation of organic wastes, however sufficient H\(_2\) is available from anaerobic corrosion of metals to reduce all the CO\(_2\) generated from organic wastes to CH\(_4\). Dissolved CO\(_2\) concentrations in the backfill are lower than in the waste because reaction with cementitious encapsulant in the waste packages is not modelled.

A geosphere plume develops in which dissolved CO\(_2\) concentrations are low. Dissolved CO\(_2\) concentrations directly above the vault are higher than elsewhere in the
plume. This is due to the presence of other gases which act to increase the gas pressure and hence CO$_2$ partial pressure.

Figure 6-6 shows dissolved CO$_2$ concentrations at a number of point locations. The behaviour described above is apparent. (“Geosphere above vault” is immediately

Figure 6-6. Concentration of dissolved CO$_2$ (oblique views, Case 1)
above the vault, where low dissolved CO$_2$ concentrations are maintained throughout the simulation). There is little change in the dissolved CO$_2$ concentrations in the geosphere at distance from the vault, because the natural background conditions are not perturbed.

![Graph of dissolved CO$_2$ concentrations](image)

**Figure 6-7. Point concentrations of dissolved CO$_2$ (Case 1)**

Figure 6-8 shows the amounts of C in different phases in the vault. Initially dissolved CO$_2$ is the dominant phase, but this is replaced by CH$_4$ gas as CO$_2$ is consumed by reaction with cement minerals and CH$_4$ is generated from degradation of organics. The timing of this transition is influenced by the bounding assumption that methanogenic conditions are established immediately post-closure. The majority of CO$_2$ in the vault is present in the wastes, since reaction with cementitious encapsulant is not considered (a simplifying assumption).

The inflection in the methane gas curve at 800 years corresponds with a reduction in the H$_2$ generation rate as Magnox corrosion is completed, and the gas saturation in the vault decreases (Figure 6-1).

Figure 6-9 shows the fluxes of carbon out of the vault in water and gas (i.e. fluxes into the vault are ignored). Figure 6-10 shows the net fluxes. During the early post-closure phase there is only flow of dissolved CO$_2$ into the vault, due to inflow of water from the host rock as the vault resaturates. Flow of dissolved CO$_2$ out of the vault occurs once the vault has resaturated.
The flux of carbon within gas out of the vault is similar to the net flux since there is no inflow of gas from the geosphere into the vault, except for some initial inflow of gas from the EDZ. (Gas is present in the EDZ as a consequence of operational dewatering of the vault).

Using the carbon fluxes out of the vault (mol/y), and the total amounts of carbon present in different phases in the vault (mol), it is possible to derive release rates (y⁻¹) (Figure 6-11). These release rates are imported into the assessment model, to calculate the fluxes of C-14 from the vault into the geosphere.

Figure 6-8. Amount of C in the vault (Case 1)
Figure 6-9. C Fluxes out of the vault (Case 1)

Figure 6-10. Net C fluxes (Case 1)
Figure 6-11. C release rates (Case 1)

Figure 6-12 shows the behaviour of C-14 in the GDF and fluxes of C-14 from the GDF into the geosphere. All the C-14 in the waste has been leached at ~700 y post-closure. In reality release may be solubility limited, but in the assessment model the empirical release rate is applied. The amount of C-14 available to be released from the GDF is then limited by the C-14 solubility limit. In this case C-14 is not solubility limited in the GDF. The peak fraction of dissolved inorganic carbon that is C-14 is 4E-5, at 170 y (70 y post-closure).

All the C-14 from graphite has been released from the GDF after ~6400 y. The flux in gas from the vault into the geosphere is much greater than the flux in water. Release in water will be calculated to occur slightly earlier in reality because the travel time through the vault itself is not accounted for, i.e. the vault is assumed to be well mixed, with C-14 always assumed to be present in proportion to total carbon.

The amount of C-14 released in gas is greater than the amount that is captured by reaction with cement. The amount captured in cement is more than an order of magnitude greater than the amount released in water.
Figure 6-12. Amounts of C-14 (solid lines, Y2 axis), and C-14 fluxes from the GDF to the geosphere (dashed lines, Y1 axis) (Case 1)

6.1.1 Calculation Case 1, C-14 Release Rate Variant

This variant case considers a lower long-term C-14 leach rate (1.83E-35 y^-3) which is consistent with the conceptual model of the form and distribution of C-14 in graphite (see Section 3.2). This may provide a more realistic indication of impacts from C-14. Note that as in the case 1 base case, this variant case assumes that conditions in the UILW vaults apply to the entire GDF. Case 2 considers conditions that may be more similar to those that would be expected in the SILW vaults, where the majority of the graphite wastes and associated C-14 inventory will be disposed.

Figure 6-13 shows the assessment model results. Fluxes of C-14 in gas and water are significantly reduced compared with the Case 1 base case. The majority of C-14 is retained in the waste. This demonstrates that performance assessment results may be very sensitive to assumptions regarding the long-term C-14 release rate from the wastes. It also indicates that the role of the containers as a barrier, which is not considered in these models, may be important.

The peak gas flux is approximately 2E9 Bq y^-1. This compares with a maximum acceptable flux to the biosphere of 1.6E8 Bq y^-1 calculated by Limer et al. (2010). Once
gas dissolution in the geosphere is taken into account, the gas peak gas flux to the biosphere is likely to be less than $1.6 \times 10^8$ Bq y$^{-1}$.

![Graph showing dissolved CO$_2$ concentrations](image)

**Figure 6-13. Amounts of C-14 (solid lines, Y2 axis), and C-14 fluxes from the GDF to the geosphere (dashed lines, Y1 axis) (Case 1 variant)**

### 6.2 Calculation Case 2: Higher Strength Host Rock, NRVB, Segregated Graphite Wastes

This case is designed to illustrate the potential impact of segregating the graphite wastes either into their own disposal vault or into a vault that contains only waste packages with a very low gas generation potential and no organic waste materials.

In case 2 it is therefore assumed that methanogenic conditions do not develop and there is no generation of C-14 labelled methane. Also there are no metal wastes, only metal containers. In addition to applying to segregated wastes, these conditions may also be more representative of SILW vaults than case 1, since SILW vaults contain relatively small amounts of reactive metals and organics compared with UILW vaults. The large volume of reactor core graphite, and associated majority of the graphite radionuclide inventory, is classified as SILW.

Figure 6-14 shows dissolved CO$_2$ concentrations at the same locations as shown in Figure 6-7. Dissolved CO$_2$ concentrations in the backfill are lower than in case 1, but
the plume of low dissolved CO$_2$ concentrations does not extend as strongly into the overlying EDZ and host rock. This reflects the lower total gas generation in the vault, and therefore lower gas pressures in the vault. CO$_2$ in the wastes is not being generated in-situ, but comes from water that has flowed from the host rock into the vault.

This behaviour is also influenced by the transition from a multi-phase system (i.e. water and gases) to a single phase system (i.e. water). In the multi-phase system the partial pressure of CO$_2$ gas is calculated explicitly. In the single phase system, the partial pressure of CO$_2$ is the specified equilibrium value based on a PHREEQC calculation (Appendix C). The gas pressure has to be high for a free gas phase to form (equal to hydrostatic pressure plus the capillary suction pressure). Therefore the partial pressure of CO$_2$ can change by orders of magnitude with the very small change in gas saturation associated with the transition from a single phase system to a multi-phase system. The low rates of gas generation and high gas mobility in this calculation case result in a system that lies in the transition zone between the two mathematical models.

This transition has a marked effect from 2,600 y when there are significant changes in the dissolved CO$_2$ concentrations in the waste and backfill. Before 2,600 y the gas saturation in the waste is just sufficient for it to be treated as a multi-phase flow system. The gas saturation in the backfill is negligible and it is treated as a single phase system. As the waste slowly resaturates and gas migrates into the backfill, beyond 2,600 y this situation reverses. The concentration of dissolved CO$_2$ in the waste falls significantly with the transition to a single phase system and the concentration of dissolved CO$_2$ in the backfill increases significantly with the transition to a multi-phase system.

Figure 6-15 shows the amount of carbon in the vault. The amount of carbon in calcite is similar to case 1. The amounts of CO$_2$ in gas and solution are higher than in case 1. This is because the majority of CO$_2$ is in the waste. CO$_2$ gas is less mobile than in case 1, such that it tends to remain within the waste, and reaction of CO$_2$ with cementitious encapsulant in the waste is not considered (a simplifying assumption). As bulk gas moves from the waste into the backfill (post 2,600 y) the amounts of CO$_2$ in gas and solution become more similar to case 1.

Although there is no gas generation from reactive metals, post-closure the gas pressure in the vault still recovers rapidly due to rapid inflow of water and reduction in the gas headspace. The gas pressure curve is therefore similar to case 1.
Figure 6-14. Point concentrations of dissolved CO$_2$ (Case 2)

Figure 6-15. Amount of C in the vault (Case 2)

Figure 6-16 shows the release rates, for use in the assessment model. The flux of dissolved CO$_2$ out of the vault is negligible because almost all the dissolved CO$_2$ reacts
with the NRVB. Although there is vertical flow of water through the vault, there is net inflow of dissolved CO$_2$ from all orientations due to advection and diffusion of dissolved CO$_2$ from the host rock into the backfill.

There is a small flux of carbon in gas, but this is much less than in case 1, because methane is not formed. Ongoing release of carbon in gas is supported by the supply of dissolved CO$_2$ from the host rock.

Figure 6-17 shows the behaviour of C-14 in the GDF and fluxes of C-14 from the GDF into the geosphere. C-14 is released more slowly than in case 1 because C-14 labelled methane does not form, and more C-14 reacts with cement forming calcite.

The results of this calculation case need to be treated with caution because the conditions are at the limit of the multi-phase flow mathematical model, and transition to the single phase mathematical model. However, this result indicates that segregation of graphite from other ILW/LLW wastes is desirable in the context of minimising releases of C-14; although not necessary significant in terms of post-closure safety.

![Figure 6-16. C release rates (Case 2)](image-url)
Figure 6-17. Amounts of C-14 (solid lines, Y2 axis), and C-14 fluxes from the GDF to the geosphere (dashed lines, Y1 axis) (Case 2)

6.3 Calculation Case 3: Higher Strength Host Rock, NRVB, No Segregation, No Methanogenesis

This case explores the extent to which incorporation of C-14 from graphite in methane influences the transport of C-14 in the system. In case 3 it is assumed that methanogenic conditions do not develop and there is no generation of C-14 labelled methane. Consequently there is an increase in the amount of CO\(_2\) gas released from organic wastes and a decrease in the amount of methane released.

Figure 6-18 shows dissolved CO\(_2\) concentrations at the same point locations as reported previously for cases 1 and 2. Figure 6-19 shows the dissolved CO\(_2\) concentrations spatially. The results are very similar to case 1 and this demonstrates that the flux of CO\(_2\) from degradation of organic wastes is buffered by reaction with the NRVB.
Figure 6-18. Point concentrations of dissolved CO\textsubscript{2} (Case 3)

Figure 6-20 shows the amounts of carbon in the vault. There is no carbon in methane. There is more carbon in water and gas, and calcite is being formed more rapidly, than in case 1. This reflects the source of CO\textsubscript{2} in the wastes.

The flux of dissolved carbon out of the vault (Figure 6-21) is smaller than in case 1, which is consistent with the majority of dissolved carbon in case 1 being dissolved methane. There is no significant flux of carbon (CO\textsubscript{2}) gas. In case 1 the flux of carbon in gas was dominated by CH\textsubscript{4}, so this result is also consistent.

Until 350 y (250 y post-closure) there is a net flux of carbon in water into the vault, associated with inflow of host rock porewater (Figure 6-22). Beyond 350 y there is a flux of carbon in water out of the vault. The release rate of carbon in water is smaller than case 1 because there is no dissolved methane (Figure 6-23).
Figure 6-19. Concentration of dissolved CO$_2$ (oblique view, 3000 y, Case 3)
Figure 6-20. Amount of C in the vault (Case 3)

Figure 6-21. C Fluxes out of the vault (Case 3)
Figure 6-22. Net C Fluxes (Case 3)

Figure 6-23. C release rates (Case 3)
Figure 6.24 shows the behaviour of C-14 in the GDF and fluxes of C-14 from the GDF into the geosphere. The flux of C-14 in gas is an order of magnitude lower than in case 1. The majority of the C-14 released from the graphite is trapped in calcite.

Figure 6-24. Amounts of C-14 (solid lines, Y2 axis), and C-14 fluxes from the GDF to the geosphere (dashed lines, Y1 axis) (Case 3)

6.4 Calculation Case 4: Higher Strength Host Rock, Sand-Bentonite Backfill, Segregated Graphite Wastes

This case is intended to test the impact of an alternative disposal concept, namely the use of a different backfill material. This case is similar to case 2, since the graphite wastes are assumed to be segregated, hence the waste does not contain any organics. It is assumed that methanogenic conditions do not develop and there is no generation of C-14 labelled methane. Also there are no metal wastes, only metal containers. However, the backfill is sand-bentonite rather than NRVB, such that there is no reaction of CO$_2$ with cement minerals. (Also there is no cementitious encapsulant, only inert void filler). The stainless steel container corrosion rate is little higher than with cementitious backfill.
At closure, the backfill and waste are 80% and 5% saturated respectively. Despite the relatively low permeability of the backfill, the vault resaturates rapidly post-closure (Figure 6-25) due to the high water pressure gradient. Subsequently, the waste and backfill slightly desaturate as H$_2$ gas is generated from corrosion of the containers. Although the gas saturation in the backfill is low between 100 and 1000 y, the gas saturation is above the level when the system starts to transition from a multi-phase system to a single phase system.

Post-closure, the gas pressure in the vault rapidly recovers to hydrostatic pressure, but does not rise above hydrostatic pressure. This is because the inventory of gas generating materials is low. (Stainless steel containers only).

Carbon is only present as CO$_2$ in gas and water, there is no methane and no precipitation of calcite through reaction with cement minerals (Figure 6-26). Dissolved CO$_2$ concentrations are low in the wastes and vault at closure, but quickly recover to be in equilibrium with background as the pressure in the vault recovers. This is reflected in the amounts of dissolved and gaseous CO$_2$.

Immediately post closure there is no outflow of carbon in water or gas from the vault (Figure 6-27, Figure 6-28 and Figure 6-29). For the first ~20 y post closure (100 y to 120 y) there is flow of carbon dissolved in water into the vault while it resaturates. Beyond ~120 y (20 y post-closure), there is a net flux of carbon in gas and water out of the vault. The flux of carbon in gas is very low.

Figure 6-30 shows the behaviour of C-14 in the GDF and fluxes of C-14 from the GDF into the geosphere. The majority of C-14 is retained in the vault. This is due to the physical barrier provided by the sand-bentonite backfill (as opposed to the chemical barrier provided by NRVB), and the consequences of segregation of the graphite wastes. The small amount of C-14 that is released is predominantly in water, the C-14 flux in gas is very small. This result indicates that segregation of graphite wastes with a sand-bentonite backfill may perform well in higher strength host rock.
Figure 6-25. Average saturation in the waste and backfill (Case 4)

Figure 6-26. Amount of C in the vault (Case 4)
Figure 6-27. C Fluxes out of the vault (Case 4)

Figure 6-28. Net C Fluxes (Case 4)
Figure 6-29. C release rates (Case 4)

Figure 6-30. Amounts of C-14 (solid lines, Y2 axis), and C-14 fluxes from the GDF to the geosphere (dashed lines, Y1 axis) (Case 4)
A variant case was undertaken in which CO\textsubscript{2} and other gases were treated as being miscible rather than immiscible. This treatment effectively increases gas mobility because gases are able to diffuse within each other. The result was greater mixing of gases in the clay backfill and increased dissolution. This increased the release rate in water by over an order of magnitude compared with the immiscible model. There was no release in gas until 15,000 y. Post-15,000 y, the release rate in gas increased to be approximately two orders of magnitude greater than the immiscible model.

Due to the low rates of gas generation, the system is within the transition zone between a single phase system and a multi-phase system. Post-60,000 y, once gas generation had ceased, the system evolved from being a multi-phase flow system to a single phase system.

Gas saturations are generally higher in the immiscible model, and the model is outside of the transition zone between the two mathematical models. There is more confidence in the immiscible model results for this reason.

6.5 Calculation Case 5: Lower Strength Sedimentary Rock, Nagra Mortar Backfill, No Segregation

Case 5 is the base case for RWMD’s illustrative example disposal concept for lower strength sedimentary host rock. Figure 6-31 shows the average saturation in the waste and backfill with time. At time zero the GDF has not been constructed. Dewatering of the vault begins at 1 y. At 3 y the vault is closed. Saturations attain their at closure conditions between 2 y and 3 y.

Post_closure, water only seeps slowly into the vault, due to the low permeability of the host rock. The saturation in the waste and backfill both initially fall because the rate of water consumption by corrosion and microbial processes exceeds the rate of water inflow into the vault. The waste dries out for 100 y. During this period there is still some flow of water from the backfill into the waste which permits ongoing gas generation, albeit at a rate limited by the supply of water. After 100 y aluminium corrosion reaches completion and the water saturation in the waste and backfill begins to increase.

Pressure recovers more slowly than in higher strength host rock, because the rate of water inflow and consequent reduction of the gas headspace is much lower. At 700 y the gas pressure (Figure 6-32) reaches hydrostatic pressure. Gas continues to be generated and the pressure rises above hydrostatic because the gas is trapped in the vault – the pressure has not risen sufficiently for it migrate into the (undamaged) host
rock, although there is some migration into the EDZ. As the gas pressure rises above hydrostatic pressure, water is pushed from the vault into the EDZ/geosphere by the gas pressure. The saturation in the waste and backfill falls, until the residual saturations (0.01 and 0.3 respectively) are reached after ~10,000 y.

Dissolved CO$_2$ concentrations are low in the backfill, due to reaction of CO$_2$ with cement minerals. Similar to higher strength host rock, a plume in which dissolved CO$_2$ concentrations are low develops in the geosphere (Figure 6-33). However, the rate of development is much slower than in the equivalent higher strength host rock case (case 1).

![Figure 6-31. Average saturation in the waste and backfill (Case 5)](image-url)
Figure 6-32. Gas pressure (Case 5)

Figure 6-33. Concentration of dissolved CO$_2$ at 5000 y (oblique view, Case 5)
Figure 6-34 shows the amounts of carbon in the vault (in water, gas and calcite precipitates). Initially carbon is dominantly dissolved in water, but with time carbon in methane and calcite precipitates become the dominant forms. After 10,000 y, when the vault is significantly dry, the amount of CO$_2$ in gas increases above the amount in water. Despite the vaults being smaller than in the higher strength rock design, the total amount of carbon in the vault rises above that in case 1. This is because methane is not readily able to migrate from the vault.

![Figure 6-34. Amount of C in the vault (Case 5)](image)

Figure 6-35 shows the fluxes out of the vault. There is initially some migration of carbon in gas (CH$_4$) and water (dissolved CO$_2$) from the vault into the EDZ. Migration of gas is consistent with the early gas pressure rise in Figure 6-32. The initial release of dissolved CO$_2$ may be an overestimate since it occurs while the chemistry is equilibrating. However, the release is of short duration and the cumulative release is small.

Between 20 y and 350 y there is no release of carbon from the vault (Figure 6-35), and inorganic carbon dissolved in the geosphere porewater enters the vault as it resaturates (Figure 6-36). Gaseous and dissolved carbon, begin to be released from the GDF after 350 y and 550 y respectively.

After 350 y the gas pressure in the vault rises above that in the EDZ, and gas begins to migrate into the EDZ. Carbon in gas is dominantly CH$_4$. The flux of carbon in water is dominantly dissolved CH$_4$. After 700 y, the gas pressure rises above hydrostatic
pressure, water (and associated dissolved CH$_4$) is pushed from the vault into the geosphere.

The release rates reflect this complex pattern of behaviour, with an initial early release and then no releases until after 350 y (Figure 6-37). The release rates are generally lower than in the equivalent higher strength host rock case (case 1: Figure 6-11).

Figure 6-35. C Fluxes out of the vault (Case 5)
Figure 6-36. Net C fluxes (Case 5)

Figure 6-37. C release rates (Case 5)
Figure 6-38 shows the behaviour of C-14 in the GDF and fluxes of C-14 from the GDF into the geosphere. Release from the GDF is slower than in the equivalent case for higher strength host rock (case 1, Figure 6-12). A little more C-14 is incorporated into calcite precipitates than in case 1. Less C-14 is released from the GDF in gas than in case 1, and the gas that is released is largely trapped in the EDZ. More C-14 is released from the GDF in water than in case 1. However, this release in water is to the EDZ and immediately adjacent host rock. Subsequently, this dissolved C-14 will only slowly migrate through the geosphere by diffusion.

Figure 6-38. Amounts of C-14 (solid lines, Y2 axis), and C-14 fluxes from the GDF to the geosphere (dashed lines, Y1 axis) (Case 5)

6.6 Calculation Case 6: Lower Strength Sedimentary Rock, Sand-Bentonite Backfill, Segregated Graphite Wastes

Case 6 explores the alternative disposal concept option in which a sand-bentonite backfill is used in a lower strength sedimentary host rock. As for case 4, this disposal concept option was only considered for segregated graphite wastes. Figure 6-39 shows the average saturation in the waste and backfill with time. At time zero the GDF has
not been constructed. Dewatering of the vault begins at 1 y. At 3 y the vault is closed. Saturations attain their at closure conditions between 2 y and 3 y.

Post-closure, water only seeps slowly into the vault, due to the low permeability of the host rock. Gas is (mostly) trapped in the vault. The saturations in the waste and backfill are generally a little higher than the previous case (case 5). This reflects the lower gas generation rate and the different backfill properties.

The initial pressure recovery (Figure 6-40) is slower than in case 5, because there are no reactive metals in the vault. However, in the long-term the gas pressure rises above hydrostatic pressure, similar to case 5. The gas pressure rises above hydrostatic pressure slightly later than in case 5: at 1200 y compared with 700 y.

Figure 6-39. Average saturation in the waste and backfill (Case 6)

Figure 6-41 shows the amounts of carbon in the vault. Carbon is only present (as CO$_2$) in gas and water, there is no methane and no precipitation of calcite through reaction with cement minerals. The amounts of CO$_2$ in water and gas are higher than in case 5 because there is no consumption of CO$_2$ by reaction with cement. At ~10,000 years the amount of CO$_2$ in gas rises above the amount of CO$_2$ in water, as the amount of water in the vault becomes small. However, the total amount of carbon in the vault is lower than in case 5.
Figure 6-40. Gas pressure (Case 6)

Figure 6-41. Amount of C in the vault (Case 6)
Figure 6-42 shows the fluxes out of the vault. Similar to case 5 there is initially some migration of gas and water from the vault into the EDZ. The flux of gas is smaller than in case 5, reflecting the lower early gas generation rate and slower early rise in gas pressure compared with case 5.

Between 15 y and 700 y there is net flux of dissolved carbon into the vault associated with inflowing host rock porewater (Figure 6-43). At ~750 y there is a small flux of dissolved carbon out of the vault, which is of similar magnitude to case 5, but there is negligible gas flux. This is because there is less gas generation in the vault than in case 5.

This behaviour is reflected in the gas release rate (Figure 6-44), which is lower than in case 5. The long-term water release rate is higher than in case 5: the fluxes in water are similar, but the total amount of carbon in the vault is lower in case 6. This is because there are no organic wastes in case 6.

![Figure 6-42. C Fluxes out of the vault (Case 6)](image)
Figure 6-43. Net C fluxes (Case 6)

Figure 6-44. C release rates (Case 6)
Figure 6-45 shows the behaviour of C-14 in the GDF and fluxes of C-14 from the GDF into the geosphere. There is a small early release of dissolved C-14, which is similar to case 5.

There is no further release of C-14, until 750 y when a small amount of dissolved C-14 is released in water and a trace amount is released in gas. The long-term release in water is higher than case 5, but release in gas is much lower. At 10,000 y almost all the C-14 remains in the GDF.

A variant case was undertaken in which CO₂ and other gases were treated as being miscible rather than immiscible. The miscible model results were very similar to the immiscible because the host rock limits the mobility of gas.
7 Discussion

Figure 7-1, Figure 7-2 and Figure 7-3 compare the assessment results for the different calculation cases. The cumulative fluxes of C-14 in water and gas from the GDF to the geosphere, and the amount of C-14 remaining in the GDF are shown. The amount of C-14 remaining in the GDF is compared with the decayed inventory.

All cases assume that short-term empirical C-14 leach rates apply to longer-term release. This assumption results in release of C-14 more rapidly than is conceptually anticipated, but provides a common and simple basis to understand system behaviour in the context of optimisation.

For higher strength host rock, segregation of graphite wastes (case 2) significantly reduces the amount of C-14 released from the GDF compared with not segregating the wastes (case 1). The key difference is that in case 2 it is assumed that there is no methanogenesis. The case 3 results (further discussed below) confirm that this is not due to other effects such as removal of ‘carrier’ gas. Release of C-14 in case 1 is dominated by release in methane gas and dissolved methane gas. There is no flux of dissolved or gaseous CO$_2$ out of the GDF in case 1 due to reaction with cement. This indicates that there may be significant performance benefits from segregating packages of graphite waste from packages of ILW/LLW containing organic wastes.

The results for case 3 further support the argument that graphite should be segregated from organic wastes to minimise the potential for development of methanogenic conditions. This would also minimise CO$_2$ generation and the potential for release of C-14 in inorganic carbon, for example there was some release of dissolved CO$_2$ (and associated C-14) in case 3, but none in case 1.

Minimising the amounts of CO$_2$ generated in the vault also minimises the potential for physico-chemical armouring of backfill fracture surfaces. However, the effective backfill cement inventory assumed for this study was not exhausted in cases 1 or 3 before the amount of C-14 released from the GDF to the geosphere had passed the peak. The cement inventory was also not exhausted anywhere in the vault for the case 1 variant, which considered slower C-14 release from the waste.

The case 3 results also highlight the importance of understanding package scale heterogeneity. There would be no benefit from segregating packages of graphite wastes if methanogenic conditions only develop in waste packages containing organic wastes and therefore incorporation of C-14 from graphite in methane is unlikely, because C-14 would have to be transported from containers of graphite waste into containers of organic waste.
In practice, since the majority of graphite is classified as SILW, and the amounts of organics and reactive metals are low in SILW compared with UILW, the benefits to be gained from segregation of SILW graphite may be limited. Similarly since only a small fraction of the graphite, and the graphite radionuclide inventory, are classified as UILW, segregation of this material will only be of limited benefit. The case 1 variant calculation indicates that the system performance would likely be acceptable even if all the graphite was placed in UILW vaults containing packages of other wastes. However, in the context of optimisation, it is concluded that in higher strength host rock it is desirable to segregate graphite from other wastes.

Slightly surprisingly, the amount of C-14 released in water from the GDF in lower strength sedimentary host rock (case 5) is greater than for higher strength host rock (case 1). This is because in lower strength sedimentary host rock the water pressure in the vaults rises above the water pressure in the EDZ and immediately adjacent host rock due to trapping of gas generated in the GDF. Water and associated dissolved C-14 is pushed out of the vaults into the rock.

The flux of C-14 from the GDF into the rock will be sensitive to the relative timing of leaching of C-14 from graphite and when the pressure in the vaults rises above that in the surrounding rock. Subsequent migration of C-14 will be by diffusion in lower strength sedimentary host rock, and so the overall system performance is expected to be better than higher strength host rock, where advective transport is assumed in the host rock/geosphere.

If the graphite wastes had been segregated from other ILW/LLW it is anticipated that, pressures in the vault would have risen more slowly during resaturation, with a smaller pressure differential to the EDZ and immediately adjacent host rock; taken longer to exceed hydrostatic pressure; and the peak pressure would have been lower. This again suggests that it is desirable to segregate graphite from other ILW/LLW in order to maximise radionuclide containment in the GDF. However, it is not expected to be beneficial in terms of overall system performance due to the effectiveness of the low permeability geosphere as a barrier.

Figure 7-3 shows that the total amount of C-14 released from the GDF in gas and water is significantly lower in case 5 (lower strength sedimentary host rock) than in case 1 (higher strength host rock). This is because for higher strength host rock, release of C-14 in methane gas is dominant. C-14 labelled methane gas is significantly trapped in the GDF in lower strength sedimentary host rock.

Case 4 shows that in higher strength host rock, segregation of graphite and use of sand-bentonite backfill offers potential performance benefits. The amount of C-14 released in gas is significantly lower than in case 1 (NRVB and mixed ILW packages).
However, there was no release of C-14 in gas in case 3 because there was no generation of C-14 labelled methane, and all C-14 labelled CO$_2$ reacted with the NRVB. This again indicates that preventing incorporation of C-14 derived from graphite in methane is important when optimising post-closure performance. More C-14 is released from the GDF in water in case 4 compared with case 1, but the total flux of C-14 out of the GDF is significantly lower than in case 1. This is because the C-14 flux in water in case 4 is small compared with the flux in gas in case 1.

The Cl-36 inventory is uncertain, potentially it could be much lower than currently assumed. Cl-36 will only be released in water. Towler et al. (2010) examined Cl-36 fluxes from a GDF in higher strength host rock for different encapsulation and backfill options. The assessment model assumed instant resaturation of the GDF, and advective transport according to the regional hydraulic gradient. The assessment results (Figure 7-4) showed that low permeability sand-bentonite backfill could offer significant performance benefits compared with permeable NRVB for Cl-36, which is not significantly chemically retarded by either backfill. This is because sand-bentonite forms a physical (low permeability) barrier to flow of water, while NRVB does not.

The performance of the sand-bentonite backfill would depend on the nature of fracturing in the host rock: the greater the concentration of fractures into discrete fracture zones, the longer the diffusive pathlength through the backfill to the fracture zones (i.e. the greater the mass transfer resistance) and the better the performance of the sand-bentonite backfill relative to NRVB. Overall, segregation of graphite wastes from other ILW/LLW and use of a sand-bentonite backfill may represent an optimised solution for graphite wastes in higher strength host rock when release of both C-14 and Cl-36 is considered.

In lower strength sedimentary rock, segregation of graphite wastes and use of a sand-bentonite backfill offers potential benefits in terms of less gas generation and a significantly reduced flux of C-14 in gas from the GDF into the geosphere. However, the flux of C-14 in water is increased compared with cementitious backfill, and the total C-14 release from the GDF is similar. Segregation of graphite prevents incorporation of C-14 in methane gas. However, C-14 is not chemically retarded by the sand-bentonite backfill, and is therefore pushed out of the GDF in water as the gas pressure rises.

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6 The clay backfill case considered by Towler et al. (2010) assumed different clay backfill properties to this study. However, the results are still appropriate to discussion of optimisation of disposal of graphite wastes.
Segregated graphite waste with cementitious backfill would probably perform better in lower strength sedimentary host rock than the two calculation cases described above. However, additional calculations were not undertaken to confirm this.

Given the anticipated very low permeability of lower strength sedimentary host rock, segregation of graphite and use of sand-bentonite backfill may not reduce C-14 fluxes to the biosphere (where receptor exposures occur) because regardless of the EBS, C-14 may decay to insignificant levels in the geosphere. Use of low permeability sand-bentonite backfill rather than permeable cementitious backfill is not anticipated to have any significant effect on the Cl-36 flux to the biosphere in water. The sand-bentonite backfill only results in a small percentage increase in the thickness of the low permeability barrier, i.e. tens or hundreds of metres of host rock plus less than one metre to metres of backfill.

Figure 7-1. Cumulative flux of C-14 from the GDF to the geosphere in water (zero flux in water for case 2)
Figure 7-2. Cumulative flux of C-14 from the GDF to the geosphere in gas (zero flux in gas for case 3)

Figure 7-3. Amount of C-14 remaining in the GDF. Dashed line shows decay of the inventory with no transport.
Figure 7-4. Comparison of Cl-36 fluxes from graphite wastes for a GDF in higher strength host rock for different encapsulation and backfill options (Towler et al. 2010).
8  Conclusions

The key radionuclides in irradiated graphite are C-14 and Cl-36 both of which can be leached from graphite. C-14 will exhibit complex behaviour in the GDF. It will be partitioned between water, gas and solid phases. The abundances in the different phases will be controlled by carbonate chemistry, reaction with cement minerals, and by microbial and gas generating processes. C-14 can be released from the GDF to the geosphere in water and in gas. Cl-36 will behave more simply, only being released in water, and does not interact significantly with any of the materials expected to be present in the GDF.

The inventories of both key radionuclides are uncertain. The inventory of Cl-36 is particularly uncertain due to the potential for volatile release during storage (including reactor ‘SafeStore’) and core dismantling. Released during core dismantling will be sensitive to the method used, i.e. removal of whole blocks or ‘nibble and vacuum’.

Features, Events and Processes (FEPs) analysis was used to develop a conceptual model of the physico-chemical evolution of the GDF, and the behaviour of the key radionuclides in graphite during the post-closure period. The analysis focussed on RWMD’s illustrative example disposal concept for ILW/LLW in higher strength host rock. Interactions between graphite and other Intermediate Level Waste (ILW) and Low Level Waste (LLW), and the effects of lower strength sedimentary and evaporite host rocks have also been considered. This analysis has been used to identify desirable safety features and alternative Engineered Barrier System (EBS) options. Clay backfill (assumed to be a sand-bentonite formulation) was carried forward for more detailed assessment.

It is anticipated that following closure of the GDF, the entire inventory of Cl-36 will rapidly be leached from graphite. Leaching of C-14 will be slower, although still fast on post-closure timescales. A potentially significant proportion of the C-14 inventory may be incorporated in the graphite lattice, and may only be released very slowly, or not at all. However, this proportion is unknown, so in this work the base assumption is that C-14 is leached at the rates measured in short-term experiments until the entire inventory has been released. This provides a simple common basis to compare different systems and GDF conditions in the context of optimisation. Variant calculations have been presented herein to the show the effects of using potentially more realistic long-term release rates. The development of a safety case for a particular disposal concept might make different assumptions and explore alternative conceptual models for radionuclide release from graphite.
Mathematical models have been used to examine the physio-chemical evolution of the GDF, and partitioning and release of C-14 from the GDF, for higher strength and lower strength sedimentary host rocks. The calculations have focussed on C-14 due to its complex behaviour and the resulting uncertainties. Modelling results from previous studies are used to understand the behaviour of Cl-36. Model results confirm that as anticipated the very low permeability lower strength sedimentary host rock provides a significantly more effective barrier to the migration of water and gas, and hence to the transport of C-14, than the fractured higher strength host rock.

The model results show that segregation of waste packages containing graphite waste from other ILW/LLW waste packages is desirable in order to minimise releases of C-14, including:

- segregation from organic wastes to minimise the potential for development of methanogenic conditions and incorporation of C-14 in methane; and

- segregation from reactive metals in lower strength sedimentary host rock to prevent relatively rapidly rising vault pressures (compared with pressure recovery in the EDZ and immediately adjacent host rock), and high peak gas pressures, pushing radionuclides in water out of the GDF. Although the host rock provides a significant barrier to radionuclide transport, this minimises the potential for transport in the EDZ, and bypass of vault seals.

Further work is required to understand the potential ‘knock-on’ effects of segregation: e.g. concentration of reactive metals in a smaller number of vaults may result in higher peak GDF gas pressures in lower strength sedimentary host rock; and any potential implications for the consequences of human intrusion.

The major volume of graphite waste is reactor core graphite, and this contains the majority of the radionuclide inventory. Due to the SafeStore strategy, reactor core graphite will arrive later than the majority of other ILW/LLW and therefore could potentially be relatively easily segregated. However, reactor core graphite is classified as Shielded ILW (SILW), and there are much smaller quantities of organics and reactive metals in SILW compared with Unshielded ILW (UILW). Therefore segregation of SILW graphite may not offer significant benefits compared with the effort required to implement it. Segregation of UILW graphite is however desirable on grounds of minimising fluxes of C-14 from the GDF, but may not be worthwhile in practice given that UILW graphite is a minor component of the overall graphite inventory.

These conclusions are based on the model assumption of homogeneous conditions in the vault. Conditions may be heterogeneous, with methanogenic conditions most likely to develop in packages containing organic wastes. This implies that C-14 would need
to be transported from packages of graphite wastes into packages of organic wastes in order to be incorporated into methane. This is unlikely to occur. Improved understanding of package scale heterogeneity in the vaults might significantly reduce the driver to segregate packages of graphite waste.

Combining segregation of graphite with the use of a sand-bentonite backfill offers further potential safety benefits: reducing the fluxes of C-14 in gas, and Cl-36 in water in higher strength host rock compared with the reference case. This option may have the best overall performance for graphite, although the work undertaken within this study has not progressed to the stage of demonstrating this. The practicalities of emplacing a sand-bentonite backfill need to be considered further. In lower strength sedimentary host rock, sand-bentonite backfill may not be so beneficial since it adds little to the low permeability barrier provided by the host rock.

Irradiated graphite should not be placed in the same container as organic waste to minimise the potential for generation of C-14 labelled methane. Similarly, graphite should not be placed in the same container as reactive metals. As a result there should be very little gas generation from containers of graphite waste, e.g. only H2 from corrosion of the inner surface of the container. Therefore, the size of the container vent hole could potentially be reduced to a minimum.

The impact on performance would be particularly significant for C-14 in higher strength host rock, where the barrier provided by the container may be significant compared with the half-life of C-14 and the geosphere travel time. Reducing the vent size also has the potential to reduce interactions between graphite and other wastes while the containers are intact. This minimises the potential for incorporation of C-14 in methane.

Overall, the complex mathematical models developed in this study have been used to test and build confidence in our understanding of vault evolution, and in particular the complex behaviour of C-14. The models have revealed behaviours that otherwise might not have been anticipated, e.g. gas pressure pushing water and associated radionuclides out of the vault in lower strength sedimentary host rock.
9 References


Handy, B. J. 2006. Experimental study of C-14 and H-3 release from irradiated graphite spigot samples in alkaline solution. AMEC NNC report 11996/TR/001.


Lansdell, T., and Newland, M. 2010. Graphite Characterisation Stage 2 – Inactive and Active Graphite Analysis and Graphite Inventory Modelling. UKAEA TSG (10) 0658.


Rahmani, L. 2005. Chlorine degassing from nuclear grade graphite; 6th International Nuclear Graphite Specialists’ Meeting, Chamonix, France, 18th – 21st September 2005; presentation archived at IAEA International Knowledge Base on Nuclear Graphite, INGSM files, accessible to participating Member States


Appendix A. Effective Cement Mineral Inventory

Figure 4.13 of Swift et al. (2010) shows that for a 2 mm crack, with a crack water flow rate of 9E-7 m s⁻¹, the crack surface has been armoured over a distance along the crack of 0.05 m after 50 y, and a distance of 0.1 m after 475 y. Figures 4.15 and 4.17 of Swift et al. confirm that the crack is fully armoured over a distance of 0.1 m after 475 y: calcite is present in the first 0.1 m of the crack, and there is no residual brucite in the first 0.1 m of the crack.

This indicates that the armoured front is developing at a rate of 0.1 m / 475 y = 2.1E-4 m y⁻¹.

The reaction stoichiometries between CO₂ and the cement minerals are:

\[ \text{Ca(OH)}_2 \text{ (Portlandite)} + \text{H}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{H}_2\text{O} \]

and for a simplified CSH composition,

\[ \text{CSH} + \text{H}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{H}_2\text{O} + \text{SiO}_2 \]

Therefore, 1 mol of CO₂ reacts with 1 mol of portlandite or CSH.

The carbon concentration assumed by Swift et al. (2010) was 1 mol m⁻³. Assuming that the alteration front is sharp, as indicated by Figures 4.14, 4.15 and 4.18 of Swift et al., the amount of carbon required to armour the fracture surface is therefore:

\[ 9E-7 \text{ m s}^{-1} \times 2E-3 \text{ m} \times 1 \text{ mol m}^{-3} \times 475 \text{ y} \times 3.16E7 \text{ s y}^{-1} = 27.0 \text{ mol per 0.1 m} \]

The length of fracture armoured during this time is 0.1 m. Therefore, the amount of carbon required to armour the fracture was 270 mol m⁻². For the simplified reaction stoichiometry given above, the effective cement inventory is 270 mol m⁻² of fracture. Note that the model only considers one side of the fracture, so the effective cement mineral inventory will actually be higher than this, as indicated by Variant Case 1 of Swift et al.

Figure 4.22 of Swift et al. (2010) shows the results for a 0.2 mm fracture. With a crack water flow rate of 3E-6 m s⁻¹, the crack surface has been armoured over a distance of 0.05 m after ~4100 y. Using the same approach as above, the amount of carbon required to armour the fracture surface was therefore:

\[ 3E-6 \text{ m s}^{-1} \times 2E-4 \text{ m} \times 1 \text{ mol m}^{-3} \times 4100 \text{ y} \times 3.16E7 \text{ s y}^{-1} = 77.74 \text{ mol per 0.1 m} \]
The length of fracture armoured during this time is 0.05 m. Therefore, the amount of carbon required to armour the fracture was 1555 mol m\(^{-2}\). For the simplified reaction stoichiometry given above, the effective cement inventory is 1555 mol m\(^{-2}\) of fracture.

Figure 4.22 of Swift et al. (2010) shows the alteration front is much less sharp in the 0.2 mm fracture than in the 2 mm fracture. This will be due to the higher water velocity in the 0.2 mm fracture. The simple calculation presented above will therefore tend to overestimate the effective cement inventory. This is offset to some extent because, again the model only considers one side of the fracture.

Swift et al. (2010) suggests that there will be four vertical 0.2 mm cracks and one horizontal 2 mm crack associated with a single stillage, or box (Figure A-1).

![Figure A-1. Fracture network model of cracks in the backfill around a single stillage developed by Swift et al. (2010)](image)

The total crack area, and hence effective cement mineral inventory is calculated in Table A-1, for higher strength host rock.
Table A-1. Estimated effective cement mineral inventory in higher strength rock (per UILW vault)

<table>
<thead>
<tr>
<th>Fracture Type</th>
<th>Number of Fractures</th>
<th>Fracture Area (m²)</th>
<th>Cement mineral inventory (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 mm vertical parallel to length of vault</td>
<td>14&lt;sup&gt;a&lt;/sup&gt;</td>
<td>14 x 16 m x 259&lt;sup&gt;b&lt;/sup&gt; m = 58,016</td>
<td>58,016 * 1555 = 9.0E7</td>
</tr>
<tr>
<td>0.2 mm vertical across width of vault</td>
<td>262&lt;sup&gt;c&lt;/sup&gt;</td>
<td>262 x 16 m x 16 m = 67,072</td>
<td>67,072 * 1555 = 1.0E8</td>
</tr>
<tr>
<td>2 mm horizontal</td>
<td>7&lt;sup&gt;d&lt;/sup&gt;</td>
<td>7 x 16 m x 259 m = 29,008</td>
<td>29,008 * 270 = 7.8E6</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td></td>
<td>1.98E8 mol</td>
</tr>
</tbody>
</table>

Notes:

<sup>a</sup> UILW packages are stacked 7 wide. Two cracks per package.

<sup>b</sup> There are 83,657 UILW packages distributed between 13 UILW vaults, stacked 7 wide and 7 high (RWMD, 2010). This gives 131 rows of waste stacks in a vault. Each package plus its associated backfill is 1.97 m long, therefore the total length of the waste stacks in a vault is 259 m.

<sup>c</sup> 131 rows of waste packages, each associated with two fractures.

<sup>d</sup> One fracture per layer in the stack.

The total cement mineral inventory in the ‘block’ of fractured backfill surrounding the waste is:

- Block volume: 259 m x 16 m x 16 m = 66,304 m³.
- Waste package volume = 1.72 m x 1.72 m x 1.225 m = 3.62 m³.
- There are 83,657 UILW packages in 13 vaults, therefore 6,435 packages per vault.
- The backfill volume is therefore 42,623 m³.
- There is 2771 mol m⁻³ of Portlandite and 758 mol m⁻³ CSH (Table 4.2 of Swift et al. (2010)). The cement mineral inventory is therefore 1.5E8 mol.
This indicates that the entire cement inventory in the block of fractured backfill surrounding the waste is effective. However, backfill in other parts of the vault, such as the transfer tunnel area may not be effective, as water flows will preferentially be through fractures and will not enter this part of the backfill.

As noted in Section 5.1, Swift et al. (2010) only modelled chemical armouring. They did not consider physical armouring of the fracture. It is beyond the scope of this first phase of the project to model physical armouring in detail, therefore it is quite cautiously assumed that the effective cement inventory is only 30% of the total in the block of fractured backfill surrounding the waste. The effective cement inventory is assumed to be zero in the backfill in the other parts of the vault.

In lower strength sedimentary host rock the groundwater flow rates through the backfill will be much lower than in higher strength host rock, such that the effective backfill inventory for dissolved carbon will be a much higher fraction than for higher strength host rock. Similar to higher strength host rock, CO$_2$ gas has the potential to migrate relatively unabated through fractures in the backfill. However, the low permeability host rock will prevent this from happening and gas will be trapped in the vaults. The entire vault cement inventory is likely available to react with dissolved carbon.

A.1 References

Appendix B. Carbonation of Cementitious Backfill and Carbonate Equilibria Model

B.1 Carbonation of Cementitious Backfill

Reaction of dissolved CO$_2$ with cement was added to the model as a sink for CO$_2$. The reaction results in the precipitation of calcite. Two different cement mineral phases are considered which have different inventories; portlandite and the CSH. The carbonation reactions are:

$$\text{Ca(OH)}_2 + \text{CO}_2 = \text{CaCO}_3 + 2\text{H}_2\text{O}$$

$$\text{CSH} + \text{H}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{H}_2\text{O} + \text{SiO}_2 \quad \text{(simplified CSH composition)}$$

Both reactions result in the generation of water and this was also included in the model. The reaction rates were set to be very fast, such that CO$_2$ will rapidly be consumed until the entire inventory of cement minerals has reacted, or until equilibrium chemical conditions are reached ($P_{CO_2}$ and carbonate ion concentration – see Section B.2).

The base model does not explicitly consider cracking of cement, and armouring of the fracture surfaces. This process is represented by using an effective cement mineral inventory (Appendix A).

B.2 Carbonate Equilibria Model

CO$_2$ gas will dissolve in water, and react to form carbonic acid (H$_2$CO$_3$). H$_2$CO$_3$ will dissociate forming H$^+$, HCO$_3^-$ and CO$_3^{2-}$. The amount of CO$_2$ that dissolves is a function of the CO$_2$ gas pressure, and increases as the pressure increases. The amount of gas that dissolves can be calculated using Henry’s law:

$$X_{CO_2} = \frac{P_{CO_2}}{H_{CO_2}}$$

Where,

$X_{CO_2}$ is the concentration of dissolved CO$_2$ (mol m$^{-3}$).

$P_{CO_2}$ is the partial pressure of CO$_2$ gas (Pa).

$H_{CO_2}$ is the Henry’s law constant (Pa m$^3$ mol$^{-1}$).
The Henry’s law constant can be derived from the equilibrium constant for the reaction:

\[ a_{H^2CO_2} = K_{CO_2} P_{CO_2} \]

Where,

- \( a_{H^2CO_2} \) is the activity of \( CO_2 \) (mol m\(^{-3}\)).
- \( K_{CO_2} \) is the equilibrium constant (mol m\(^{-3}\) Pa\(^{-1}\)).

Therefore \( H_{CO_2} = 1/K_{CO_2} \).

Many host rocks will contain calcite, or other carbonate minerals. Similarly, some calcite will likely be present in the wastes, and calcite will be generated in the GDF through reaction of \( CO_2 \) with cement minerals. The presence of calcite alters the carbonate equilibria, and hence the amount of \( CO_2 \) that will dissolve, since carbonic acid will react with calcite and other carbonate minerals.

The composition of the resulting water will be:

\[ 2m_{Ca^{2+}} + m_{H^+} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} \]  

(Drever, 1997).

Where \( m \) is the molality, i.e. moles per kg of solution, or mol l\(^{-1}\) for dilute solutions.

It can be shown that the Henry’s constant for dissolution of \( CO_2 \) is not only altered by the presence of calcite, but is no longer a constant. The Henry’s constant now varies as a function of the partial pressure of \( CO_2 \).

Natural groundwaters also contain other aqueous ions, which will alter the charge balance, and hence carbonate equilibria. In particular \( Na^+ \) and \( Cl^- \) may be particularly important. When \( Na^+ \) and \( Cl^- \) are taken into consideration, the composition of the water becomes:

\[ 2m_{Ca^{2+}} + m_{Na^+} + m_{H^+} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} + m_{Cl^-} \]

The model calculates the Henry’s constant for this system as a function of the partial pressure of \( CO_2 \).
Since NaCl is highly soluble, the Na\(^{+}\) and Cl\(^{-}\) concentrations will not be influenced by carbonate equilibria, except potentially for a NaCl saturated brine. Therefore, Na\(^{+}\) and Cl\(^{-}\) are taken as constants based on the concentrations measured in the geosphere.

At neutral pH, \(m_{H^+}\) will be equal to \(m_{OH^-}\) such that these terms cancel. The molality of \(H^+\) and \(OH^-\) will also be much lower than that of the other ions in the system, such that \(H^+\) and \(OH^-\) can be neglected from the calculation even if the pH is slightly less than, or greater than, 7. At near neutral pH \(m_{HCO_3^-}\) will be much greater than \(m_{HCO_3}\) such that \(m_{CO_3^{2-}}\) can also be neglected.

From the above charge balance equation,

\[
(2a_{Ca^{2+}}/\gamma_{Ca^{2+}}) + m_{Na^+} = (a_{HCO_3^-}/\gamma_{HCO_3^-}) + m_{Cl^-}
\]

Where,

\(\gamma\) is the ion activity coefficient (\(^{-}\)).

Equation 3-30 of Drever (1997) states that:

\[
a_{Ca^{2+}}a_{HCO_3^-} = (K_{cal}K_1K_{CO_2}P_{CO_2})/K_2
\]

Substituting this into the above charge balance equation and rearranging:

\[
(2K_{cal}K_1K_{CO_2}P_{CO_2}) + (m_{Na^+}a_{HCO_3^-}K_2\gamma_{Ca^{2+}}) - (K_2\gamma_{Ca^{2+}}a^3_{HCO_3^-})/\gamma_{HCO_3^-}) - (m_{Cl^-}K_2\gamma_{Ca^{2+}}a^2_{HCO_3^-}) = 0
\]

This equation is solved in QPAC in order to calculate \(a_{HCO_3^-}\) dependent on the partial pressure of \(CO_2\).

The Henry’s law constant is then calculated as,

\[
H_{CO_2} = P_{CO_2}/a_{HCO_3^-}
\]

This Henry’s constant for near neutral conditions is applied to the geosphere and non-cementitious components of the GDF. Values of \(m_{Na^+}\) and \(m_{Cl^-}\) are specified from groundwater data (Appendix C). Ion activity coefficients are estimated based on groundwater concentration data.

For the cementitious components of the GDF, a modified calculation is required for the high pH conditions. Under these conditions, \(m_{CO_3^{2-}}\) will be much greater than \(m_{HCO_3^-}\) such that \(m_{HCO_3^-}\) can also be neglected. \(m_{H^+}\) will be small, but \(m_{OH^-}\) may be significant.

The charge balance equation therefore becomes:
Equation 3-28 of Drever (1997) states that:

\[ a_{\text{CO}_3^{2-}} = K_{2a_{\text{HCO}_3^-}/a_{\text{H}^+}} \]

Substituting this into equation 3-30 of Drever:

\[ a_{\text{Ca}^{2+}}a_{\text{CO}_3^{2-}} = (K_{\text{cal}}K_{\text{CO}_2}P_{\text{CO}_2}K_2)/a_{\text{H}^+}^2 \]

Substituting the above into the charge balance equation and rearranging:

\[
(2K_{\text{cal}}K_{\text{CO}_2}P_{\text{CO}_2}K_2) + (m_{\text{Na}^+}\gamma_{\text{Ca}^{2+}}a_{\text{H}^+}^2a_{\text{CO}_3^{2-}}) - (2\gamma_{\text{Ca}^{2+}}a_{\text{H}^+}a_{\text{CO}_3^{2-}}/\gamma_{\text{CO}_3^{2-}}) - (m_{\text{Cl}^-}\gamma_{\text{Ca}^{2+}}a_{\text{H}^+}^2a_{\text{CO}_3^{2-}}) = 0
\]

\[ a_{\text{H}^+} \text{ and } m_{\text{OH}^-} \text{ can be estimated for the assumed pH conditions (Appendix C).} \]

The Henry’s law constant is then calculated as,

\[ H_{\text{CO}_2} = P_{\text{CO}_2}/a_{\text{CO}_3^{2-}} \]

### B.3 References

Appendix C. Groundwater Composition

Table C-1 details the groundwater composition assumed for the background groundwater. Water 1 and Water 3 bound the ranges of salinity that might be encountered at GDF depths. The dissolved inorganic carbon concentrations are similar and therefore the model results are not expected to be very sensitive to the chosen groundwater composition. Water 3 has a slightly higher dissolved inorganic carbon concentration, and is therefore likely to give slightly higher (more conservative) aqueous C-14 fluxes. Therefore, water 3 was chosen for the calculations.

Table C-2 gives the compositions for the same groundwaters, equilibrated with cement. Data are taken from Towler et al. (2010).

Using the simplified carbonate chemistry model described in Appendix B, the background $P_{CO_2}$ was calculated to be $3.17E-1$ atm and $4.5E-10$ atm for background and cement conditioned water respectively.

For this groundwater composition, the following ion activity coefficients were estimated from Figure 4.3 of Langmuir (1997):

$\gamma_{Ca^{2+}} = 0.7$

$\gamma_{HCO_3^-} = 0.9$

$\gamma_{CO_3^{2-}} = 1$

Equilibrium constant data were taken from Drever (1997) for 20 °C, which is not significantly different to the temperature of 25 °C assumed in calculating the groundwater compositions.
Table C-1: Assumed background groundwater composition from Table A-4 of Towler et al. (2010)

<table>
<thead>
<tr>
<th></th>
<th>Water 1</th>
<th>Water 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.8</td>
<td>6.8</td>
</tr>
<tr>
<td>[H2O]</td>
<td>1.000</td>
<td>0.888</td>
</tr>
<tr>
<td>[HCO3-]</td>
<td>6.30E-03</td>
<td>3.03E-03</td>
</tr>
<tr>
<td>[Fe2+]</td>
<td>1.57E-05</td>
<td>3.30E-05</td>
</tr>
<tr>
<td>T (°C)</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>pe</td>
<td>-2.54</td>
<td>-2.78</td>
</tr>
<tr>
<td>Eh (V)</td>
<td>-0.150</td>
<td>-0.165</td>
</tr>
<tr>
<td>Na</td>
<td>8.40E-04</td>
<td>3.11E+00</td>
</tr>
<tr>
<td>K</td>
<td>3.80E-05</td>
<td>8.36E-03</td>
</tr>
<tr>
<td>Mg</td>
<td>5.35E-04</td>
<td>2.86E-02</td>
</tr>
<tr>
<td>Ca</td>
<td>2.84E-03</td>
<td>7.49E-03</td>
</tr>
<tr>
<td>Si</td>
<td>1.75E-04</td>
<td>1.19E-04</td>
</tr>
<tr>
<td>Al</td>
<td>6.82E-10</td>
<td>1.34E-09</td>
</tr>
<tr>
<td>Fe</td>
<td>3.61E-05</td>
<td>1.96E-04</td>
</tr>
<tr>
<td>Cl</td>
<td>4.09E-04</td>
<td>3.08E+00</td>
</tr>
<tr>
<td>S(6)</td>
<td>4.20E-05</td>
<td>5.11E-02</td>
</tr>
<tr>
<td>S(2)</td>
<td>1.07E-10</td>
<td>1.29E-10</td>
</tr>
<tr>
<td>C</td>
<td>9.50E-03</td>
<td>1.07E-02</td>
</tr>
</tbody>
</table>

Table C-2: Cement conditioned groundwater composition from Table A-5 of Towler et al. (2010)

<table>
<thead>
<tr>
<th></th>
<th>Water 1</th>
<th>Water 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>12.38</td>
<td>12.377</td>
</tr>
<tr>
<td>[H2O]</td>
<td>0.999</td>
<td>0.887</td>
</tr>
<tr>
<td>[HCO3-]</td>
<td>4.90E-09</td>
<td>3.84E-09</td>
</tr>
<tr>
<td>[SO42-]</td>
<td>1.35E-04</td>
<td>1.13E-03</td>
</tr>
<tr>
<td>[Fe2+]</td>
<td>2.49E-28</td>
<td>3.24E-28</td>
</tr>
<tr>
<td>T (°C)</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>pe</td>
<td>-9.75</td>
<td>-9.59</td>
</tr>
<tr>
<td>Eh (V)</td>
<td>-0.576</td>
<td>-0.567</td>
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<tr>
<td>Na</td>
<td>8.40E-04</td>
<td>3.13E+00</td>
</tr>
<tr>
<td>K</td>
<td>3.80E-05</td>
<td>8.41E-03</td>
</tr>
<tr>
<td>Mg</td>
<td>1.17E-07</td>
<td>1.25E-07</td>
</tr>
<tr>
<td>Ca</td>
<td>1.64E-02</td>
<td>2.07E-02</td>
</tr>
<tr>
<td>Si</td>
<td>2.41E-06</td>
<td>6.48E-06</td>
</tr>
<tr>
<td>Al</td>
<td>2.32E-07</td>
<td>3.90E-07</td>
</tr>
<tr>
<td>Fe</td>
<td>5.01E-10</td>
<td>1.14E-09</td>
</tr>
<tr>
<td>Cl</td>
<td>1.28E-03</td>
<td>3.10E+00</td>
</tr>
<tr>
<td>S(6)</td>
<td>3.54E-04</td>
<td>1.41E-02</td>
</tr>
<tr>
<td>S(2)</td>
<td>2.59E-04</td>
<td>1.98E-04</td>
</tr>
<tr>
<td>C</td>
<td>8.61E-06</td>
<td>3.13E-05</td>
</tr>
</tbody>
</table>
C.1 References


Appendix D. Model Input Data

Hydraulic properties data were taken from Towler and Bond (2011) and are not duplicated here. However, the porosity of NRVB waste updated to 0.55, consistent with RWMD (2010a). The inventory of gas generating materials is given in Table D-1. Table D-2 and Table D-3 give the inventory of gas generating materials for segregated graphite wastes. Corrosion and organic degradation rates are as reported in Towler and Bond (2011).

The inventory of gas generating materials was taken from (Watson et al. 2011) and therefore corresponds to the 2010 Derived Inventory. The small fraction of metal waste that is present in the form of spheres was assumed to be plates.

For the simplified gas generation model used, organic materials were split into two types: cellulose, comprising amorphous and crystalline cellulose; and polymers, comprising polymers and oil.

<table>
<thead>
<tr>
<th>Table D-1. Inventory of gas generating materials in UILW wastes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>Stainless steel</td>
</tr>
<tr>
<td>Mild Steel</td>
</tr>
<tr>
<td>Aluminium</td>
</tr>
<tr>
<td>Magnox</td>
</tr>
<tr>
<td>Cellulose</td>
</tr>
<tr>
<td>Polymer</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table D-2. Inventory of gas generating materials in one vault in higher strength host rock containing segregated graphite wastes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>Stainless steel</td>
</tr>
</tbody>
</table>

$^1$ Box dimensions are 1.72 m x 1.72 m x 1.225 m (Nirex, 2005) high, wall thickness 6 mm (Anderson, 2005).

$^2$ 131 rows of 7 x 7 stacking.
Table D-3. Inventory of gas generating materials in one vault in lower strength sedimentary host rock containing segregated graphite wastes

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (kg m(^{-3}))</th>
<th>Volume of metal in a 3 m(^3) box</th>
<th>Boxes per vault</th>
<th>Mass of metal (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>8000</td>
<td>0.0861(^1)</td>
<td>361(^2)</td>
<td>248.3</td>
</tr>
</tbody>
</table>

\(^1\) Box dimensions are 1.72 m x 1.72 m x 1.225 m high, wall thickness 6 mm.

\(^2\) 48 rows of 3 x 5 stacking.

Table D-4. Distribution of Graphite Wastes in the Different Calculation Cases

<table>
<thead>
<tr>
<th>Case</th>
<th>UILW vaults</th>
<th>SILW vaults</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>4(^1)</td>
<td>Adeogun (2010) states there are 4,853 packages (4 m boxes) of core (SILW) graphite. It is assumed that UILW graphite would fit in one vault.</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>4</td>
<td>As case 2.</td>
</tr>
<tr>
<td>5</td>
<td>116</td>
<td>51</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>35(^1)</td>
<td>Adeogun (2010) states there are 4,853 packages (4 m boxes) of core (SILW) graphite. It is assumed that UILW graphite would fit in 9 vaults (equivalent to 1 vault in higher strength host rock, i.e. scaling factor 116/13).</td>
</tr>
</tbody>
</table>

\(^1\) Appendix B of RWMD (2010b) states that there are 7133 SILW + LLW packages which fit into 6 vaults in higher strength host rock, and 51 vaults in lower strength sedimentary host rock.

D.1 References

Adeogun, A.C. 2010. NDA’S Derived Inventory Based on the 2007 UK Radioactive Waste Inventory: Inventory For Non-Encapsulated Wastes. Pöyry Energy Ltd report to NDA RWMD.


