Cement materials for use as backfill, sealing and structural materials in geological disposal concepts. A review of current status
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Abstract

Cementitious materials are included in the designs for all current concepts for geological disposal of higher activity wastes worldwide. Cements are envisaged being used in a wide range of applications: as waste encapsulation grouts; waste containers and overpacks; buffers and backfills; fracture grouts; tunnel plugs; tunnel/vault linings, floors and roadways. These uses of cement materials range from those related to operational safety through to those related to post-closure safety.

This report has been commissioned by the Nuclear Decommissioning Authority to review information on the range of backfills and other cement-based materials used in designs for geological disposal facilities (GDFs). This report focuses on cements in backfilling, sealing and structural applications in a GDF; the use of cement-based grouts in waste immobilisation is excluded from this review.

The following key themes are covered:

- the emplacement of cement materials as backfill;
- the mechanical performance of cements;
- the mass transfer performance of cement backfills;
- the effect of temperature on the performance of cements;
- the effect of groundwater on the leaching and pH-buffering performance of cement backfills;
- the effects of interactions with other EBS components on cement backfills;
- the sorption properties of cementitious materials; and
- the development of novel low-pH cements for structural concretes and sealing applications.

The key considerations for the UK programme discussed in this review are placed in the UK context in summary tables at the end of the document.
Executive Summary

Cementitious materials are included in the designs for all current concepts for geological disposal of higher activity wastes worldwide. Cements are envisaged being used in a wide range of applications: as waste encapsulation grouts; waste containers and overpacks; buffers and backfills; fracture grouts; tunnel plugs; tunnel/vault linings, floors and roadways. These uses of cement materials range from those related to operational safety through to those related to post-closure safety.

This report has been commissioned by the Nuclear Decommissioning Authority, Radioactive Waste Management Directorate (NDA RWMD) to review information on the range of backfills and other cement-based materials used in designs for geological disposal facilities (GDFs). The report also examines the key considerations at the current, generic stage of the UK programme in the context of the GDF concepts for the range of geological environments currently under consideration by NDA RWMD for the disposal of high-level wastes (HLW), spent fuel (SF), intermediate-level wastes (ILW) and some low-level wastes (LLW).

This report focuses on cements in backfilling, sealing and structural applications in a GDF; the use of cement-based grouts in waste immobilisation is excluded from this review.

Technical knowledge on cement-based backfills (proposed for use in disposal concepts for ILW) is relatively well-developed from work in the UK (particularly on the Nirex research programme) and so UK-specific factors are fairly well understood. Other applications of cement-based materials have historically received limited attention under the UK research programme. For example, concerns about the deleterious effects of alkaline cement leachates on a bentonite buffer (proposed for use in some disposal concepts for HLW and SF) have lead to the development of so-called low-pH (i.e. low-alkali) cement-based grouts and concretes, and this work has been carried out predominantly overseas (e.g. in Sweden, Finland, France and Japan).

The varying applications of cements in the engineered barrier system(s) (EBS) of a GDF place a wide variety of performance requirements on the materials used to ensure safety throughout the lifetime of a GDF. As a result the cement materials under consideration differ significantly in their formulations and in their chemical and physical properties. Some of these applications are very specific and differ considerably in their requirements from the applications of conventional cements in civil engineering.

After brief overviews of the chemistry, the types and properties of cementitious materials, the following key topics are covered in this review:

- the emplacement of cement materials as backfill;
- the long-term mechanical performance of cements;
- the effect of temperature on the performance of cements;
- the mass transfer performance of cement backfills;
- the effect of groundwater on the leaching and pH-buffering performance of cement backfills;
- the effects of interactions with other EBS components on cement backfills;
- the sorption properties of cementitious materials; and
- the development of novel low-pH cements for structural concretes and sealing applications.

The review discusses in some detail aspects of the behaviour of cements and their performance in the short-, medium- and long-term in GDF applications. Much of this behaviour is complex and it is important to recognise that different aspects of performance are coupled, sometimes strongly and sometimes in a conflicting manner. Thus the specifications for cement EBS materials will inevitably represent a compromise between differing requirements. Prioritising the key aspects of
performance and the timescales over which they may be required in each application is important, therefore, for successful implementation in a GDF.

The key considerations for the UK programme identified in this review, and their relevance in the UK context, are summarised in tables at the end of this document; knowledge gaps are identified and suggestions for potential further work are outlined.

The current status of, and key considerations for, cement-based EBS materials at the current generic stage of the UK programme are summarised below.

**Cement-based backfills**

Cement-based materials are proposed as the backfill materials that will fill the void spaces around waste packages in disposal concepts for ILW materials. This provides compatibility with the predominant wasteforms for UK ILW materials, which are immobilised in cement-based grouts.

The principal requirements of a cement backfill in ILW concepts are:

- to condition the porewater around the waste container to a high pH so as to reduce steel corrosion and maintain a low solubility for many important radionuclides;
- to provide chemical and physical conditions for strong sorption and so control the rate at which radionuclides can migrate into the host rock;
- to permit the passage of gas from the waste container to prevent pressure build up.

There are a number of differing formulations for cement backfills, including the Nirex Reference Vault Backfill, NRVB, and the Swiss M1 mortar, which were designed to meet the specific requirements of ILW disposal concepts in a higher strength fractured rock and a lower strength sedimentary rock, respectively. In particular the requirements for pH-buffering capacity and compressive strength differ because of the different hydrogeological and geomechanical conditions between the rock types (higher rate of groundwater flow in mechanically strong fractured rock compared to low flows in low permeability but more plastic lower strength rock). In addition, NRVB was specified to have a low strength to enable package retrievability after backfilling. Both backfills are designed to have a high permeability to allow the passage of gas.

The performance lifetime for backfill cements is extremely long and the requirement for pH buffering has been specified for a timescale of one million years. Over these timescales, the backfill material will age and degrade due to interactions with the groundwater, the host rock, waste materials and other engineered barrier components. Thus an understanding of the long-term behaviour and evolution of cementitious backfills is essential to building confidence in their long-term performance.

The controls provided by cementitious backfills on the main aspects of near-field chemistry, in particular pH, are generally well understood. However, the impact of the groundwater on cements is strongly dependent on the groundwater composition and flow rate, and these interactions can affect the mineralogy and structural properties of cements. For this reason there is greater uncertainty concerning the type and crystallinity of pH-buffering phases at longer timescales and the ability of a backfill to maintain pH-buffering for the required period.

In general, it is expected that the backfill would become cracked shortly after emplacement as a result of plastic settlement, early-age thermal cracking and the corrosive expansion of waste packages, and that as a result the mass transfer properties of the backfill will be dominated by the pattern of cracks. It is expected that the crack pattern will evolve over time but the processes of crack enlargement and healing (e.g. due to creep under load or mineral precipitation) are not well understood. There is also uncertainty concerning the potential effects of gas release (e.g. void formation) due to the corrosion of reactive metal wastes in the UK inventory during setting and curing of the backfill.

Cement backfills provide a good barrier to radionuclide release due to their high surface area (in particular the initially amorphous calcium silicate hydrate (C-S-H) phases) and strong affinity of sorption sites to sorb many radionuclides. There is a good understanding of the strength of
sorption of many radionuclides onto freshly cured backfills from empirical batch sorption tests, including the effects of waste-derived organic complexants that may reduce sorption; detailed understanding of the mechanisms of interaction is often lacking, however. In addition, leaching and ageing of cement will lead to changes in cement mineralogy and the crystallinity of C-S-H phases that will affect their sorption capacity. Results to date on aged cements suggest that these processes may have only a limited effect but there remains limited understanding and data on the long-term effects of ageing process and interactions with groundwater and waste components (e.g. crack armouring due to reaction with carbon dioxide/carbonate in groundwater and arising from microbial degradation of organic wastes).

**Structural concretes and mortars**

A number of structural components of the engineered barrier system will be constructed from cement. These may include:

- rock bolt grouts to fill the space between the rock and tensioned steel bolts (that are inserted into the rock to strengthen the walls) to provide corrosion protection;
- vault and tunnel linings to support and seal the tunnel and vault walls and to provide structural support during the excavation and operational periods of the facility;
- bulkheads to support load bearing apertures; and
- floors and roadways, to provide level load-bearing surfaces.

The principal function of these materials is to stabilise the excavations and thus enable a safe working environment to be maintained during the construction and operational phases of the GDF. In general, the main functional requirements for these materials are high compressive strength and stiffness. In the case of a GDF located in a lower strength sedimentary rock (such as a clay-based formation) the use of concrete linings for structural support may be essential due to the effects of rock creep.

The performance lifetime of structural materials is much shorter than for cement backfills and tunnel seals (below) and in most concepts is specified only to GDF closure. The main consideration post-closure is that these materials have no long-term deleterious effects on the barrier performance of the EBS (and in particular the clay-based buffer in some disposal concepts for HLW/SF).

Cements are used routinely in structural and sealing applications in civil engineering (e.g. tunnels and mining). A GDF will need to be constructed to similar standards and codes of practice as all underground structures. Hence, transfer of current conventional cement technologies to GDFs is expected where structural (and sealing requirements), determined by the geological environment, are essentially the same as in other underground structures.

International agencies working on HLW/SF disposal concepts, have turned to low-pH cements as their preferred option for cement-based EBS materials to mitigate the deleterious effects of conventional cement leachates on bentonite. Cement paste is partially replaced by at least 20% silica fume, to produce cements with a leachate of pH ≤ 11. Low-pH shotcrete tunnel linings and rock bolt grouts have been developed and tested through the ESDRED Project.

The performance requirements of tunnel and vault linings, and other structural concretes, will be dependent on the design (e.g. vault geometry, size, etc) and geology (rock creep, etc) of a UK GDF. The pH-leaching requirements of structural concretes in different parts of a GDF containing co-located ILW and SF/HLW may be different however, and thus, differing concretes (conventional and low-pH) might be used in different locations (as in the ONKALO excavation for a SF GDF in Finland). It is envisaged that the specifications, materials and emplacement methods for low-pH structural concretes, if required, would be developed as the GDF programme progresses.
Sealing applications

Seals are required to minimise the flow of groundwater through a GDF during construction, operation, closure and post-closure phases. Two principal sealing applications can be identified in GDF concepts:

- sealing of fractures that intersect the tunnels and vaults of a GDF (in addition, cementitious tunnel and vault linings may also be specified to have a sealing function to minimise water flow into the GDF during the construction and operational phases);
- plugs for the sealing of vaults, tunnels, drifts and deposition holes once wastes have been emplaced and disposal areas backfilled.

The scale of sealing applications of cements in GDF concepts ranges from the tens of microns for fracture sealing grouts to the 1-10 metre scale for transverse tunnel and drift plugs. These differences in scale place differing requirements on the cement formulations. Fracture sealing grouts have specific requirements for penetrability into fractures and minimal bleed and are made from so-called micro-cements (with finer particle size than conventional cements); tunnel plugs are made from concrete, and due to their large mass, minimisation of temperature excursions from cement hydration becomes an important criterion.

Conventional fracture sealing technology will be transferrable to a UK GDF. However, the requirement for tunnel seals is a unique feature of a GDF. For disposal concepts that include a clay-based buffer, low-pH cements are the preferred option for waste disposal areas.

Low-pH cement fracture-sealing grouts have been developed by SKB and Posiva for fractured hard rocks where fracture apertures exceed 100 μm and have been extensively tested at ONKALO and through the ESDRED Project. These grouts, by analogy, with concretes developed in the 1950s, have good long-term durability due to their low permeability in comparison with conventional grouts.

Whether or not fracture sealing grouts will be required in a UK GDF will depend on the hydrogeological properties of the geological sequence between the surface and disposal horizon at depth at the selected site.

Low-pH concretes have also been developed for tunnel seals and plugs. These can be installed using shotcreting methods or by using ‘self-compacting’ compositions. A number of prototype designs of tunnel plugs constructed from different concrete formulations have been tested successfully in underground research laboratories on international programmes (e.g. TSX, FEBEX and ESDRED).

The number, design and specifications for tunnel plugs in a UK GDF will depend on the geological environment and the disposal concept(s) selected. Different demands may be placed on sealing plugs in different parts of a facility depending on the size and geometry of openings and local flow conditions in the host rock. Development of the design, specifications, materials and construction procedures for tunnel seals is envisaged as the GDF programme progresses.
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<th>Description</th>
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<tr>
<td>AAR</td>
<td>Alkali-aggregate reaction</td>
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<tr>
<td>AECL</td>
<td>Atomic Energy of Canada Limited</td>
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<tr>
<td>ANDRA</td>
<td>Agence Nationale pour la Gestion des Déchets Radioactifs (French nuclear waste management organisation)</td>
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<tr>
<td>BFS</td>
<td>Blast-furnace slag (referred to in general construction as ggbs, ground granulated blast-furnace slag)</td>
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<tr>
<td>CAC</td>
<td>Calcium aluminate cement (formerly high alumina cement)</td>
</tr>
<tr>
<td>CBI</td>
<td>Swedish Cement and Concrete Research Institute</td>
</tr>
<tr>
<td>CEA</td>
<td>Commissariat à l’énergie atomique et aux énergies alternatives (French Alternative Energies and Atomic Energy Commission)</td>
</tr>
<tr>
<td>CEM 1</td>
<td>Portland cement comprising up to 5% minor additional constituents (see EN-197-1 [39])</td>
</tr>
<tr>
<td>CIRIA</td>
<td>Construction Industry Research and Information Association</td>
</tr>
<tr>
<td>CRIEPI</td>
<td>Central Research Institute of Electric Power Industry (Japan)</td>
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<tr>
<td>CTE</td>
<td>Coefficient of thermal expansion</td>
</tr>
<tr>
<td>DSSC</td>
<td>Disposal System Safety Case</td>
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<td>EBS</td>
<td>Engineered barrier system</td>
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<tr>
<td>EDF</td>
<td>Électricité de France (major French-based utility)</td>
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<tr>
<td>ENRESA</td>
<td>Empresa Nacional de Residuos Radiactivos, S.A. (Spanish nuclear waste management organisation)</td>
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<tr>
<td>ESDRED</td>
<td>Engineering Studies and Demonstration of Repository Designs (project under the 6th EURATOM Framework Programme for Nuclear Research and Training, 2002-2006)</td>
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<tr>
<td>GDF</td>
<td>Geological disposal facility</td>
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<td>HFSC</td>
<td>High fly ash and silica fume cement</td>
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<tr>
<td>HLW</td>
<td>High-level waste</td>
</tr>
<tr>
<td>IETcc-CSIC</td>
<td>Instituto de Ciencias de la Construccion Eduardo Torroja (Eduardo Torroja Institute for Construction Science (IETcc), a body of the Spanish National Research Council (CSIC))</td>
</tr>
<tr>
<td>ILW</td>
<td>Intermediate-level waste</td>
</tr>
<tr>
<td>IPC</td>
<td>Inorganic phosphate cement</td>
</tr>
<tr>
<td>ISA</td>
<td>Isosaccharinic acid</td>
</tr>
<tr>
<td>JAEA</td>
<td>Japan Atomic Energy Agency</td>
</tr>
<tr>
<td>LAC</td>
<td>Low alkali cement</td>
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<tr>
<td>LHHPC</td>
<td>Low heat high performance concrete</td>
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<tr>
<td>LLW</td>
<td>Low-level waste</td>
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<tr>
<td>LPHTEK</td>
<td>Finnish project concerned with the optimising of technical properties of low-pH cement grout</td>
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<tr>
<td>LS</td>
<td>Ligno-sulphonate (superplasticiser)</td>
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MRWS  Managing Radioactive Waste Safely (government white paper, 2008)
Nagra  Nationale Genossenschaft für die Lagerung radioaktiver Abfälle (Swiss nuclear waste management organisation)
NAPL  Non-aqueous phase liquid
NDA   Nuclear Decommissioning Authority
Nirex  Predecessor organisation to NDA RWMD
NRVB  Nirex Reference Vault Backfill
NUMO  Nuclear Waste Management Organisation of Japan
(Na₂O)e Sodium oxide equivalent alkali content for cement = Na₂O + 0.658 K₂O
ONKALO Finnish underground rock characterisation facility located at Olkiluoto, which may become part of a GDF in the future
OPC   Ordinary Portland cement
ORNL  Oak Ridge National Laboratory (USA)
PCE   Polycarboxylate ether (branched co-polymer superplasticiser)
PEG   Polyethylene glycol
PFA   Pulverised Fuel Ash (also referred to as fly ash)
PMA   Polymethacrylate
Posiva Oy Organisation responsible for the final disposal of spent fuel in Finland
RH    Relative humidity
RWMD  Radioactive Waste Management Directorate (of NDA)
SCC   Self compacting concrete
SCM   Supplementary cementing material
SF    Spent Fuel
SIT   Specific interaction theory (of aqueous ion activity coefficients)
SKB   Svensk Kärnbränslehantering AB (Swedish Nuclear Fuel and Waste Management Company)
SMF   Sulphonated melamine formaldehyde (superplasticiser)
SNF   Sulphonated naphthalene formaldehyde (superplasticiser)
SRPC  Sulphate-resistant Portland cement
SSC   Super sulphate cement
TBM   Tunnel boring machine
TSX   (Canadian) Tunnel Sealing Experiment
URL   Underground Research Laboratory
VES   Vinyl ester styrene (resin)
w/c ratio Water to cement ratio (cement refers to the combination of cementing materials)
w/s ratio Water to solids ratio (solids refers to the combination of cementing materials plus any sand, aggregate or other filler)
Glossary of cement chemistry nomenclature

In cement chemistry, complex inorganic molecules are often referred to in a ‘short-hand’ notation, where chemical formulae are expressed as the sum of oxides. For example, portlandite Ca(OH)$_2$ can also be represented as CaO·H$_2$O. It is usual to abbreviate the more commonly occurring oxides to a single letter, for example C for CaO and H for H$_2$O, so that portlandite becomes CH.

The following abbreviations are commonly found in published material and can be regarded as “standard cement nomenclature”:

\[
\begin{align*}
C &= \text{CaO} \\
S &= \text{SiO}_2 \\
A &= \text{Al}_2\text{O}_3 \\
F &= \text{Fe}_2\text{O}_3 \\
M &= \text{MgO} \\
\bar{S} &= \text{SO}_3 \\
H &= \text{H}_2\text{O} \\
\bar{C} &= \text{CO}_2
\end{align*}
\]

Common cementitious phases are therefore represented in this report as:

- C$_2$ASH$_8$ Strätlingite
- C$_3$A Tricalcium aluminate
- C$_3$AH$_6$ Hydrogarnet
- C$_3$AS$_{0.8}$H$_{4.4}$ Siliceous hydrogarnet
- C$_6$AS$_3$H$_{32}$ Ettringite
- C-A-S-H Calcium aluminium silicate hydrate (no fixed stoichiometry implied)
- C-S-H Calcium silicate hydrate (no fixed stoichiometry implied)
- C$_2$S Dicalcium silicate
- C$_3$S Tricalcium silicate

Two other commonly used notations in cement chemistry are:

- AFT An abbreviation for "Alumina, Ferric oxide, tri-sulphate" or (Al$_2$O$_3$ – Fe$_2$O$_3$ – tri). It represents a group of calcium sulpho-aluminate hydrates. AFT has the general formula [Ca$_3$(Al,Fe)(OH)$_6$ 12H$_2$O]$_x$ X$_3$ nH$_2$O where X represents a doubly charged anion or, sometimes, two singly charged anions. Ettringite is the most common and important member of the AFT group (X in this case denoting sulphate).

- AFm An abbreviation for "Alumina, Ferric oxide, mono-sulphate" or (Al$_2$O$_3$ – Fe$_2$O$_3$ – mono). It represents another group of calcium aluminate hydrates with general formula [Ca$_2$(Al,Fe)(OH)$_6$] X nH$_2$O where X represents a singly charged anion or 'half' a doubly-charged anion. X may be one of many anions; the most important anions involved in Portland cement hydration are hydroxyl, carbonate and sulphate.

Full chemical notation is also used for formulae in this report where appropriate.
Introduction

As part of its Managing Radioactive Waste Safely (MRWS) programme, UK Government issued a White Paper in June 2008 setting out a framework for implementing geological disposal of the UK’s higher activity radioactive waste [1]. It is currently intended that all the UK’s higher-activity wastes will be disposed of in a single geological disposal facility (GDF), providing that this facility can be developed to provide suitable, safe containment for the waste inventory. Cementitious materials are included in the designs for all current concepts for geological disposal of higher activity wastes and have been proposed for use in a wide range of applications:

- as waste encapsulation grouts;
- waste containers and overpacks;
- buffers and backfills;
- seals and fracture grouts;
- tunnel plugs;
- tunnel/vault linings;
- supporting structures including floors, roadways, bulkheads and buttresses.

These uses of cement materials range from those related to operational safety through to those related to post-closure safety. The requirements for each application will vary with the disposal concept. At present, a number of generic disposal concepts are under consideration by the Nuclear Decommissioning Authority (NDA). Work carried out for the NDA identified a range of potential concepts for geological disposal of low-level waste (LLW) with intermediate-level waste (ILW) [2] and for high-level waste (HLW) and spent fuel (SF) [3], which drew upon previous work in the UK and the programmes of other countries. This provided a catalogue of concepts for consideration and was used to develop illustrative disposal concepts for three geological environments as shown in Table 1. Currently, these six illustrative concepts are under evaluation as part of the engineering design and safety assessments that underpin the NDA's generic Disposal System Safety Case (DSSC). The use of the illustrative concepts is aimed at enhancing understanding of how waste disposal may be carried out in different geological settings and how the safety of each can be assessed. It is not necessarily intended that one of these will be used in the relevant geological setting.

For the purposes of this review a subset of disposal concepts are focused upon to examine various aspects of cement use in GDF design, but these illustrative concepts are not necessarily the same as those used in the DSSC.

Technical knowledge of cement backfills is considered to be relatively mature from both the UK historic programme (in particular the work previously carried out by UK Nirex Ltd) and overseas programmes. The use of cement-based backfills is an important component of many ILW disposal concepts. For example, the illustrative concept for the disposal of long-lived intermediate and some low-level wastes (ILW/LLW) in higher-strength rocks uses disposal vaults backfilled with cementitious material [4, 5] and is based on a multi barrier, phased and retrievable approach. The multi barrier disposal concept is illustrated in Figure 1. To date much of the work undertaken in the UK to support these activities has been limited to a high-pH backfill composition referred to as the Nirex Reference Vault Backfill (NRVB). A cement-based backfill is also used in the illustrative disposal concept for LLW/ILW in lower-strength sedimentary rocks. The cement-based backfill fulfils many of the required generic safety functions for the DSSC by:

- conditioning the porewater around the waste container so as to reduce corrosion and maintain a low solubility for many important radionuclides;
- providing chemical and physical conditions for strong sorption and so controlling the rate at which radionuclides can migrate into the host rock;
- permitting the passage of gas from the waste container to prevent pressure build up.
### Table 1  Illustrative disposal concepts (reproduced from [6])

<table>
<thead>
<tr>
<th>Host rock</th>
<th>Illustrative Geological Disposal Concept Examples</th>
<th>ILW/LLW</th>
<th>HLW/SF</th>
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<tbody>
<tr>
<td>Higher strength rocks(^a)</td>
<td>UK ILW/LLW Concept (NDA, UK)</td>
<td></td>
<td>KBS-3V Concept (SKB, Sweden)</td>
</tr>
<tr>
<td>Lower strength sedimentary rock(^b)</td>
<td>Opalinus Clay Concept (Nagra, Switzerland)</td>
<td></td>
<td>Opalinus Clay Concept (Nagra, Switzerland)</td>
</tr>
<tr>
<td>Evaporites(^c)</td>
<td>WIPP Bedded Salt Concept (US-DOE, USA)</td>
<td></td>
<td>Gorleben Salt Dome Concept (DBE-Technology, Germany)</td>
</tr>
</tbody>
</table>

Notes:
(a) Higher strength rocks. These would typically comprise crystalline igneous, metamorphic rocks or geologically older sedimentary rocks, where any fluid movement is predominantly through divisions in the rock, often referred to as discontinuities. Granite is a good example of a rock that would fall in this category.
(b) Lower strength sedimentary rocks. These would typically comprise geologically younger sedimentary rocks where any fluid movement is predominantly through the rock mass itself. Many types of clay are good examples of this category of rocks.
(c) Evaporites. These would typically comprise anhydrite (anhydrous calcium sulphate), halite (rock salt) or other minerals that result from the evaporation of water from water bodies containing dissolved salts.

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**Figure 1** Illustrations of the UK multi barrier cement-based disposal concept for ILW/LLW [7]

### 1.1 Definitions

Cements are fine powders with particle sizes typically up to about 100 μm. Cement paste (or grout) is a mixture of cement particles in water. When sand is added (generally defined in the construction industry as particles up to about 5 mm) the grout becomes mortar. With larger aggregate particles added the mortar becomes concrete. Grout, mortar and concrete perform in
broadly the same way but with the influence of the generally inert sand and aggregate filler becoming more dominant in either enhancing or diluting the behaviour of the cement paste matrix in mortars and concrete. In normal structural concrete, the combined sand and aggregate typically comprises 70-75% of the volume.

Two parameters are often used to describe the composition of a grout, mortar or concrete mix. These are:

- the water to cement (w/c) ratio by weight in which cement refers to the combination of dry cementing materials (see section 3 for further details); and
- the water to solids (w/s) ratio by weight in which solids refers to the combination of dry cementing materials plus any sand, aggregate or other filler present in the mix.

For a cement grout with no fillers, w/c and w/s are identical; for mortars and concretes, w/c > w/s.

1.2 Objectives and scope of this report

The aim of this report is to undertake a current status review of cement. At this current, generic stage of the programme, the NDA wish to review current information on the range of cement backfills and other cement materials for use in a GDF to support the development of engineered barrier system (EBS) requirements for a range of geological environments (see Table 1). This report focuses on cements in backfilling, sealing and structural applications in a GDF; the use of cement-based grouts in waste immobilisation is excluded from this review.

The principle objectives of the document are therefore:

- to describe the current status of knowledge on the range of cement-based backfills and other cement materials that need to be considered in the UK programme for the development of a GDF;
- to review and summarise the available experimental and theoretical data;
- to place the information in a UK context;
- to identify knowledge gaps and hence, to identify requirements for further research.

In section 2, a number of specific examples are used to illustrate particular applications of cements in GDF design concepts. Relevant background material on the chemistry of cement systems and their physical properties is discussed in sections 3 and 4 respectively.

The following aspects of cement performance in geological disposal concepts are discussed in sections 5 to 13:

- the emplacement of cement materials as backfill (section 5);
- the mechanical performance of cements (section 6);
- the effects of temperature on cement materials (section 7);
- the mass transfer performance of cement backfills (section 8);
- the interactions of cements with groundwater and the host rock (section 9);
- the interactions of cements with waste, wasteform and other EBS materials, including effects of radiation (section 10);
- the pH-buffering performance of cementitious backfills (section 11);
- the sorption properties of cement backfills (section 12);
- the performance of cements in sealing applications (section 13).

Section 14 summaries the key points made in the previous chapters, focusing on those most relevant to the UK programme.
The subject of cement materials in geological disposal concepts is extremely broad. To keep this review manageable and focused, the topic of grouts used for waste encapsulation was specifically excluded from the scope. In addition, a number of topics concerned with the effects of a high-pH cementitious environment have been excluded from this review. These include the inhibition of steel corrosion; the solubility of radionuclides; and microbiological activity (which has recently been covered in another review for NDA RWMD [8]. The current understanding on these topics is outlined in the recent NDA status reports on package evolution [9], radionuclide behaviour [10] and near-field evolution [11], respectively and references therein.
2 Applications of cement-based materials in GDF Concepts

This section is designed to give an overview of the applications of cementitious materials in GDF concepts, identifying the key cement properties required for each application. The principal applications discussed are the use of cement-based materials as:

a) backfill/buffers – used to fill void spaces around waste packages before closure;

b) structural cement – for roadways, tunnel and vault linings, grouts for rock bolts;

c) sealing applications – used in construction of plugs and seals and for fracture-filling.

A key distinction examined is that between backfill materials in cement-based ILW disposal concepts where the high-pH conditions of cement porewaters contribute to the barrier performance of the near field, and structural/sealing applications in many SF/HLW disposal concepts, where high-pH conditions could have detrimental effects on the bentonite buffer. The latter concern has led to the development of so-called low-pH cement formulations.

2.1 Disposal vault backfill materials

Cementitious materials have been proposed as backfilling materials to fill the void space between waste canisters and the walls of disposal vaults or tunnels in a number of disposal concepts, primarily for intermediate level wastes. The principal functions of the cementitious backfill in these concepts are to provide a high-pH environment that will minimise the solubility of radionuclides in the near-field pore water, provide a large surface area for radionuclide sorption and to minimise the corrosion of waste packages. Additional concept specific requirements have resulted in the development of backfill materials with varying physical and mechanical characteristics.

In the following sub-sections we will illustrate some of the varying requirements of cement backfills in three disposal concepts:

- the UK illustrative concept for disposal of ILW and LLW in a higher strength rock;
- the Swiss ILW/LLW disposal concept (in Opalinus Clay); and
- the Belgian supercontainer concept for HLW (in Boom Clay).

In each case, the disposal concept will be outlined briefly and then the requirements of the backfill materials discussed.

2.1.1 UK illustrative concept for disposal of ILW and LLW

The cross-section of a disposal vault in the UK illustrative concept for disposal of ILW and LLW in a higher strength rock is shown schematically in Figure 2. Typically in this concept [11], waste is grouted into stainless steel containers and the containers placed within vaults excavated in the rock. Rock bolts and shotcrete (sprayed concrete) with metal reinforcement mesh are envisaged being used as structural support for the excavations. At some point the disposal vaults would be backfilled with a cementitious material. The local backfill surrounding the waste packages would be expected to have the same composition as the peripheral backfill between the vault wall and the waste container stacks (identified as NRVB in Figure 2). Access tunnels would also be backfilled with a cementitious material (although not necessarily with the same composition as the vault backfill) and low-permeability seals placed to restrict water flows. The cross section in Figure 2 shows a large void volume, the crown space, above the stacks of waste packages. This could either be left open or filled with backfill.

A high-pH vault backfill, the NRVB, was developed for use in this concept [12]. NRVB was designed to give alkaline conditions within the vaults and so limit the solubility of many elements in the near field and also to have a high sorption capacity. These features combine to provide a ‘chemical barrier’ to the migration of radionuclides that would be required to persist over the
timescales normally considered in performance assessments. In addition to chemical requirements a number of physical properties are specified. The compressive strength of NRVB is relatively low (compared to structural concretes) to aid retrievability, if required. NRVB is also formulated to have a higher porosity than most cements (~0.5). This gives a higher permeability, allowing uniform chemical conditions to be maintained and facilitating the release of gas generated by the waste. The higher porosity also favours a higher surface area for sorption.

Figure 2  Schematic cross section through an unshielded-ILW vault in higher-strength rock [13]

The NRVB current status report to 1994 lists the requirements that were envisaged for the backfill at the start of its development [12]. The specifications for the NRVB are reproduced in Box 1 and desirable qualities in Box 2.
Box 1. Specifications for the NRVB.

- In the long term the porewater must be maintained at pH 10.5 or greater to assist chemical retention of radionuclides in the repository near field.
- Compressive (cube) strength of not less than 1.5 MPa at 7 days and not less than 4.0 MPa at 28 days are required to provide adequate support for the placement of successive waste package and backfilling layers.
- A cube strength limit of 10 MPa at any age up to 50 years to assist grout removal should there be a future need to retrieve backfilled waste.
- The workability must be suitable for flow without vibration into a horizontal space 5m x 3m x 75mm high, which may be a typical under-package space.
- The mix must be suitable for pumping along a horizontal pipeline, at least 250m in length.
- Bleeding/settlement must not exceed 2% to reduce the possibility of under-package void formation and surfaces of weakness in the backfill.

Box 2. Desirable qualities for a backfill.

- Should act as a chemical barrier to migration of long-lived radionuclides by providing:
  - high pH to inhibit solubility;
  - good sorption capacity.
- Sufficiently permeable to promote homogeneous aqueous chemistry and to enable gas transport.
- Should inhibit corrosion of steel packages.
- Relatively low heat of hydration.
- The use of cement additives which compromise the cement performance as a chemical barrier or the engineering properties should be avoided.
- Mineral composition should be sufficiently durable to provide long-term chemical conditioning of repository porewater.
- Should possess well understood mineral characteristics which can be predicted during the repository evolution.
- Use materials which can be reasonably assured in terms of quality and quantity, during repository operational period.
- Suitable for placement by remote methods in waste vaults.
- Self levelling and compacting and able to provide a firm level base for placement of further packages.
- Suitable for easy excavation to allow retrieval of waste packages if that was required.
- Relatively inexpensive to produce.
In addition some other limitations for the mix were imposed in its development [12]:

- it would be preferable to avoid the use of organic additives (i.e. superplasticisers), which could potentially have deleterious effects on the solubilities and sorption behaviour of some radionuclides;
- to achieve an acceptable level of alkalinity, the backfill should contain a minimum of 400 kg m$^{-3}$ Ordinary Portland Cement (OPC) or equivalent alkaline material;
- a limit of 25% by weight of the total cementitious content was set for pulverised fuel ash (PFA), a supplementary cementing material, which, due to reaction with OPC, could affect the ability of the backfill to maintain high pH. No limit was set for ground granulated blast furnace slag (BFS). However, neither BFS nor PFA was included in the final composition.

The NRVB comprises OPC with a fine aggregate containing crushed limestone filler (primarily calcium carbonate) and hydrated lime (calcium hydroxide). The formulation is given in Table 2.

**Table 2 Composition of NRVB [11]**

<table>
<thead>
<tr>
<th>Components</th>
<th>Recipe (kg m$^{-3}$)</th>
<th>Weight fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordinary Portland Cement</td>
<td>450</td>
<td>0.26</td>
</tr>
<tr>
<td>Limestone Flour (principally calcite)</td>
<td>495</td>
<td>0.29</td>
</tr>
<tr>
<td>Hydrated Lime</td>
<td>170</td>
<td>0.10</td>
</tr>
<tr>
<td>Water</td>
<td>615</td>
<td>0.35</td>
</tr>
<tr>
<td>Water/cement (w/c) ratio (by weight)</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>Water/solid (w/s) ratio (by weight)</td>
<td>0.55</td>
<td></td>
</tr>
</tbody>
</table>

The NRVB plays an important role in the multi-barrier approach of this disposal concept; one of the main safety functions of the NRVB is to provide a high-pH environment around waste packages, which limits corrosion of containers and the solubility of many radionuclides. A significant body of experimental work has been undertaken to characterise the effectiveness of the chemical barrier provided by the NRVB in terms both of long-term pH-buffering behaviour (see section 11) and radionuclide solubility (see [14]) and sorption behaviour (section 12).

### 2.1.2 Swiss ‘Opalinus Clay’ concept for ILW/LLW

Nagra are proposing to site repositories for radioactive wastes in the Opalinus Clay of Northern Switzerland; one for SF, vitrified HLW and long-lived ILW and one for intermediate/low level waste (ILW/LLW) [15], and it is the latter that we focus on in this example.

The Swiss disposal concept for ILW/LLW involves the emplacement of waste containers within caverns in the host rock [16]. Rock bolts and a sprayed concrete lining (shotcrete with steel mesh reinforcement) will be used for structural support of the caverns. Drums and packages containing wastes pre-conditioned with either cementitious grouts or bitumen will be placed within concrete disposal containers and the spaces between the drums filled with a low viscosity mortar (M2). The lower parts of the caverns will be partitioned into disposal sections by reinforced concrete walls (bulkheads). The void space between containers in the lower cavern will be filled with M2 mortar. A high viscosity mortar (M1) will be used to fill void space between containers in the upper part of the cavern and between the concrete lining wall of the cavern and the container stacks. Cave access tunnels would be backfilled with mortar and closed with a concrete plug. The concept for the ILW/LLW cavern is shown schematically in Figure 3. In the reference design, each cavern would have a cross-section of 11.0 m by 13.2 m and be approximately 200 m long.
The main features of the safety barrier system for ILW/LLW disposal are set out in Nagra’s documentation [15] and those features relevant to cementitious materials are:

- the cementitious backfill (mortar) has favourable radionuclide retention properties and provides a chemical environment that promotes stability of the disposal containers;
- disposal containers restrict water inflow and retain radionuclides.

The cementitious backfill mortars (M1 and M2) used to fill voids around the waste drums and around the waste containers within the disposal caverns are formulated to have a low hydraulic permeability, thus the flow of water will be restricted. They will also buffer the porewater to alkaline pH values, which will favour the long-term stability of waste drums by limiting corrosion rates and will lower the solubility of many key radionuclides. In addition the mortars have a high sorption capacity which will support the retention of radionuclides. A further influence on the design of grouts is gas generation in the near field, particularly from corrosion. The mortars are designed to have a porosity of 0.3 to 0.35 (higher than most cements, but lower than NRVB, ~0.5 [12]), to reduce the potential for overpressurisation in the caverns.

The compositions of the M1 [17] and M2 mortars [18] are summarised in Table 3. The M1 material is characterised by a much higher silica content, and lower calcium and water contents than NRVB. Its major component is a quartz aggregate 2-3 mm in size. It is designed to be a highly porous material with a large pore size; porosity is about 0.27.

Nagra predict that the cement porewaters will be strongly alkaline. At the early stages, when the pH is controlled by sodium/potassium hydroxides, the pH values will be ~13.5. The pH will drop to
~12.5, controlled by the dissolution of calcium hydroxide, once the alkali-metal hydroxides have been leached away [19].

Table 3 Proposed compositions of Swiss M1 [17] and M2 [18] mortars

<table>
<thead>
<tr>
<th>Components</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M1</td>
</tr>
<tr>
<td>Portland Cement</td>
<td>1</td>
</tr>
<tr>
<td>Quartz Aggregate, 2-3 mm</td>
<td>5.33</td>
</tr>
<tr>
<td>Sand, &lt;1 mm</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>0.4</td>
</tr>
<tr>
<td>Water/cement ratio</td>
<td>0.4</td>
</tr>
<tr>
<td>Water/solid ratio</td>
<td>0.06</td>
</tr>
</tbody>
</table>

2.1.3 Belgian Supercontainer concept

In this concept, waste canisters of vitrified HLW would be placed within a larger container, termed a Supercontainer, which is designed to provide radiological shielding by means of a buffer which permanently surrounds the waste [20]. The basic design concept is that two waste canisters are placed within a carbon steel overpack surrounded by a concrete buffer which is contained within a stainless steel liner. The Supercontainer would be constructed above ground, transported to a GDF and emplaced in disposal galleries situated in a layer of Boom Clay approximately 230m below ground level. The arrangement of the near-field components is illustrated in Figure 4 and Figure 5.

![Radial cross-section of the Supercontainer design with OPC-based concrete buffer](image-url)
The concept design includes cementitious materials as buffer and structural components and potentially as gallery backfill. The gallery walls would be lined with pre-fabricated concrete blocks; the floor would be concrete; and the gap between the Supercontainer and the gallery lining could potentially be backfilled with cement.

One of the roles of the buffer within the Supercontainer is to isolate the contents of the waste package and to minimise migration of contaminants out of the near field. The exact composition of the buffer material has not yet been finalised, but a number of key requirements were identified initially [20]. An important one is that the buffer should be chemically compatible with the nearest components (i.e. the overpack and the clay). Further requirements include: stability under high temperature conditions (up to 100°C), a similar thermal expansion coefficient to the surrounding metal liner and a sufficient thermal conductivity to limit temperature gradients [20].

Two concretes are under consideration for use as the buffer; a high-pH concrete based on OPC and a neutral-pH buffer using inorganic phosphate cement (IPC)). OPC is the preferred option, because the high-pH buffer provides chemical conditions that are favourable to maintaining low corrosion of the overpack [21]. Modelling studies by ONDRAF/NIRAS have predicted that an OPC-based buffer will have porewater pH > 13 initially; this will be reduced to ~12.5 when alkali hydroxides are leached out [22]. The cementitious buffer material will also play an important role as a chemical barrier, limiting the solubility of chemical species and controlling transport processes (diffusion, sorption). The concrete buffer is also required to have a relatively high tensile strength (in view of the thermal stresses) and preferably sulphate-resistant qualities [21], qualities that

---

**Figure 5  Axial cross-section of the Supercontainer design [21]**
potentially could be achieved by a conventional construction concrete of strength class C30/37\(^1\). Finally, the concrete buffer material should be composed from a limited range of base materials that could be well-characterised; NIRAS/ONDRAF did not consider materials with a potentially more variable composition, such as BFS and PFA (which may vary with source and time - see sub-section 3.4), for the formulation [21].

The backfill outside the supercontainer fulfils a function different to that of the buffer. Its main purpose is to fill any gaps between the steel liner and the disposal gallery lining, and so provide long-term mechanical support for the gallery. This function could be provided by either a clay-based material or cement. Although the roles of buffer and backfill are different, it is possible that the same material could be used for both applications.

2.2 Structural cements

Arguably, all cementitious materials used in a GDF play some form of structural role in terms of supporting the excavated tunnels and vaults, buffer or backfill materials and the waste packages, either pre- or post-closure. Some cement components, however, have no specific safety functions post-closure, but play a key structural role in stabilising the excavations during the construction and operational phases of a GDF, enabling a safe working environment to be maintained. These structural cement components may include:

- grouts for rock and anchor bolts to fill the space between the rock and tensioned steel bolts (inserted into the rock to strengthen the walls) primarily to provide corrosion protection;
- vault and tunnel linings to support and seal the tunnel and vault walls;
- bulkheads to support load bearing apertures; and
- floors and roadways, to provide level, load-bearing surfaces.

In general, the main functional requirements for these materials are high compressive strength and stiffness.

These applications of cements in a GDF are conventional, in the sense that in the absence of GDF-specific functional requirements, it is expected that they would make use of conventional civil engineering techniques and materials for underground construction (mines, tunnels) in the chosen geological environment(s). This may be true in the upper levels (access tunnels) of a GDF far from the waste disposal areas. However, close to and within the waste disposal areas, the potential effects of interactions between the structural cements and other EBS materials need to be considered. In many disposal concepts, the only functional requirement placed on cement-based EBS materials post-closure is that they do not have a detrimental impact on other EBS components, most importantly the bentonite buffer in many HLW/SF disposal concepts. In some concepts involving the use of a bentonite buffer, the removal of roadways, tunnel linings and other structural cements is envisaged prior to sealing and backfilling of the access tunnels and shafts at facility closure [23]. This is designed to reduce the overall cement content of the facility and thereby minimise the formation of cementitious porewaters that could potentially impact on the bentonite buffer.

Therefore, with regard to structural cements, the principal interest in this report, is in the development of materials specifically for use in GDF environments.

2.2.1 Tunnel and vault linings

The primary function of tunnel and vault linings is to provide a safe environment during the operational phase of a GDF. Shotcrete is a generic name for mixes of cement, sand and fine aggregates that are applied pneumatically to the wall of excavation tunnel walls and drifts, with the aim of stabilising them structurally and reducing their permeability. The principal requirements of

\(^1\) Concrete is classified according to its compressive strength. The classification C30/37 refers to a concrete grade with characteristic cylinder and cube strengths after 28 days of 30 N mm\(^{-2}\) and 37 N mm\(^{-2}\) respectively.
shotcrete formulations are pumpability, a rapid set and the development of high compressive strength. Shotcreting the access tunnel and disposal vault walls is envisaged in most disposal concepts for facilities located in both hard-fractured and softer sedimentary rocks. In particular, the use of concrete for rock support is seen as a key issue for disposal concepts in clay formations to ensure the stability of the excavations.

In disposal concepts for HLW/SF that would include a clay-based buffer (such as the Swedish KBS-3 concept - see further details in sub-section 2.3.1), a particular concern is the possibility that high-pH plumes generated by cements may result in the degradation of the adjacent buffer [24] and host rock. Many OPC-based cementitious materials have porewaters of pH values in excess of 12 and such fluids are known to have detrimental effects on clay minerals (e.g. decrease in swelling pressure and mineral alteration – sub-section 10.5.1). For this reason, a key requirement for the cement-based components for use in clay-based buffered systems is that the equilibrium pH of the cement porewater should be less than pH 11, which has been shown to have a much-reduced impact on bentonite. Significant efforts have been made internationally to develop types of low-pH cement-based grouts and concretes to meet this requirement (see sub-section 3.7). Much of this development work has been carried out on the European ESDRED programme (Engineering Studies and Demonstration of Repository Designs), in a partnership involving the waste management organisations from Spain (ENRESA), Switzerland (Nagra), Finland (Posiva) and Sweden (SKB) [25].

Under Module 4 of the ESDRED project, trials have been conducted on low-alkali shotcrete for rock support, with formulations based on mixtures used in previous tests in Sweden and Switzerland. The functional requirements for these shotcretes are given in the ESDRED Module 4 technical report [26] and are reproduced in Table 4.

Table 4 Specification of mechanical properties for low-pH shotcrete for ESDRED trials [26]

<table>
<thead>
<tr>
<th>Property</th>
<th>Previous Nagra</th>
<th>Previous SKB/Posiva</th>
<th>New specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity</td>
<td>k ≤ 10^{-10} m·s^{-1}</td>
<td>Not specified</td>
<td>Not specified</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>≈ 10 MPa (8 hours)</td>
<td>≈ 10 MPa (8 hours)</td>
<td>≈ 10 MPa (36 hours)</td>
</tr>
<tr>
<td></td>
<td>≈ 25 MPa (7 days)</td>
<td>≈ 25 MPa (7 days)</td>
<td>≈ 20 MPa (7 days)</td>
</tr>
<tr>
<td></td>
<td>≈ 35 MPa (28 days)</td>
<td>≈ 35 MPa (28 days)</td>
<td>≈ 30 MPa (28 days)</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>Not specified</td>
<td>≈ 15 GPa (7 days)</td>
<td>≈ 15 GPa (7 days)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>≈ 20 GPa (28 days)</td>
<td>≈ 20 GPa (28 days)</td>
</tr>
<tr>
<td>Bonding</td>
<td>≈ 0.5 MPa (28 days, rock/clay)</td>
<td>≈ 0.9 MPa (7 days)</td>
<td>≈ 0.5 MPa (7 days)</td>
</tr>
<tr>
<td></td>
<td>≈ 1.0 MPa (28 days, concrete)</td>
<td>≈ 1.5 MPa (28 days)</td>
<td>≈ 0.9 MPa (28 days)</td>
</tr>
<tr>
<td>Durability</td>
<td>≥ 2 years (sulphate resistant)</td>
<td>≥ 2 years (sulphate resistant)</td>
<td>Not specified but sulphate resistant</td>
</tr>
<tr>
<td>Workability</td>
<td>≥ 2 hours</td>
<td>&gt; 2 hours</td>
<td>≥ 2 hours</td>
</tr>
<tr>
<td>Pumpability</td>
<td>&gt; 100m</td>
<td>~ 15m</td>
<td>&gt; 15m</td>
</tr>
<tr>
<td>Slump</td>
<td>15 – 20 cm</td>
<td>15 – 20 cm</td>
<td>15 – 20 cm</td>
</tr>
<tr>
<td>Peak hydration temperature</td>
<td>Not specified (&lt; 100°C)</td>
<td>~ 40°C-</td>
<td>Not specified (&lt; 100°C)</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>Dry: &gt; 0.5 W/m°C Saturated: &gt;1.2 W/m°C</td>
<td>Not specified</td>
<td>Not specified</td>
</tr>
</tbody>
</table>

It will be noted that although a low permeability (hydraulic conductivity) requirement was included in the original Nagra specification (for a GDF in Opalinus Clay), this has been relaxed in the final
specification for the ESDRED project. In the Swedish KBS-3 concept for disposal in a hard, fractured rock, the use of fracture injection grouts (see sub-section 2.3.1) effectively reduces the requirement for the tunnel lining to provide permeability reduction.

2.2.2 Rock bolt mortar

Rock bolt mortar is used to grout bolts and other possible anchors in rock. Rock bolts typically consist of a steel rod with a mechanical or chemical anchor at one end and a face plate and nut at the other that are inserted into holes drilled into the rock. They are always tensioned after installation. One of the primary reasons for rock bolt failure is corrosion and this can be mitigated by filling the space between the rock and the steel bolt with grout. To facilitate grout injection, hollow core rods may be used that allow air to bleed from the hole.

In the ONKALO excavation for a GDF for SF in Finland, rock bolts typically 3 m in length are being installed in the roof and walls [27]. These grouted rock bolts are considered permanent operational safety features and will not be removed from ONKALO. For this reason a low-pH grout would be the preferred material for rock bolt mortar. However, because the volume of bolt grout is small, it is assumed by Posiva that any possible pH plume will be local and not significant. Therefore other aspects, such as corrosion protection of bolts, are considered to be more important in the development programme.

The requirements for rock bolt mortars are compressive strength (≥ 45 MPa at 28 days) and sufficient cohesion to remain in place once injected into holes [27]. The rock bolt mortar should also be able to flow around the bolt to minimise its exposure to groundwater and air.

2.2.3 Structural cements in the Belgian Supercontainer concept

The Belgian supercontainer design (as illustrated in Figure 4, sub-section 2.1.3) includes a number of cementitious EBS components that provide structural support, in particular, the disposal gallery lining and the gallery floor. The gallery lining will be composed of concrete wedge blocks, which will be prefabricated from non-reinforced concrete. These wedge blocks will be placed against the excavated gallery wall in a ring. Key wedge blocks will be inserted last under a specified applied pressure that will provide the necessary expansion force to keep the ring elements in place. As the purpose of this lining is to provide structural support, concrete of a high strength is recommended (C50/60) according to the European standard, EN 206-1. Concrete used for the gallery floor is required to be of a strength class at least equal to that that specified for industrial floors or parking lots (C30/37) [21].

This is an example of a concrete application with no GDF-specific functional requirements at this stage of concept development, due to the compatibility of the structural cements with the preferred option of a high-pH cementitious backfill.

2.3 Sealing applications

Two principal sealing applications can be identified in GDF concepts:

- sealing of fractures that intersect the tunnels and vaults of a GDF;
- plugs for the sealing of vaults, tunnels, drifts and deposition holes once wastes have been emplaced and disposal areas backfilled.

In general, seals are designed to minimise the flow of groundwater through a GDF during construction, operation and/or post-closure. It is important to recognise that the scales of apertures requiring sealing varying widely from the tens of micron scale in fractured rock zones to the 5-metre scale for transverse plugs and seals for drifts and tunnels.

Cement-based seals are envisaged in most disposal concepts. Some examples of these applications and the special requirements of the sealing materials in a number of GDF concepts are illustrated in the following sub-sections.
2.3.1 Cement applications in the Swedish KBS-3 SF concept

Under the Swedish KBS-3 design [28], spent fuel waste is sealed in copper canisters that have iron inserts to provide mechanical strength. The copper canisters are emplaced in tunnels drilled in a fractured crystalline rock formation. The tunnels may be either vertical deposition holes (KBS-3V, the reference design adopted by SKB, Sweden) or horizontal drifts (KBS-3H an alternative design currently being investigated as part of a joint SKB/Posiva (Finland) project) [29], both illustrated in Figure 6. The canisters are surrounded by a bentonite buffer. The access tunnels are then filled with a bentonite based backfill.

KBS-3V is used as the illustrative geological disposal concept for HLW/SF in higher strength rocks in the UK Disposal System Safety Case (DSSC) [6]. However, owing to its tunnel geometry, a wider range of sealing applications are illustrated in the alternative KBS-3H design.

The main applications of cementitious materials in the KBS-3 design are:

- fracture grouting for groundwater inflow control;
- concrete roadbeds (that will be removed before GDF closure);
- shotcrete for lining of tunnels and drifts;
- grouting of support bolts, anchor bolts, fixing rings etc. into the rock; and
- the construction and grouting of seals and plugs.

Figure 6 The multi barrier KBS-3 concept showing both vertical deposition, KBS-3V (left), and horizontal deposition, KBS-3H, (right) designs [30]
A more detailed illustration of a single deposition drift tunnel in the alternative KBS-3H design is shown in Figure 7. In this design, multiple canisters containing spent fuel are emplaced in approximately 300 m long deposition drifts, slightly inclined towards the transport tunnel. Each waste canister with surrounding bentonite buffer is contained within a perforated steel shell, which, like in the Belgian concept, is also termed a supercontainer. The supercontainers are separated by bentonite spacing blocks, which are designed to provide hydraulic separation and thermal spacing. The drift may be divided into compartments to provide hydraulic isolation, in particular from regions of the tunnel with higher water inflows. This would be achieved by means of steel plugs designed to withstand the full hydrostatic pressure at tunnel depth (450-500 m). Once filled, the tunnels will be sealed with drift end plugs. Both compartmental and drift end plugs may include cementitious components. In this design [30], the main components of the system that ensure isolation of the spent fuel and containment of radionuclides are the canister, the bentonite buffer and spacing blocks and the host rock. Other system components have not been assigned specific safety functions, but are designed to be compatible with, and support the safety functions of, the canister, the buffer and the host rock. Therefore a key criterion in the choice of cements used in the KBS-3 design is to minimise any negative impact on the performance of the canister, buffer and host rock.

Figure 7  Details of the deposition drift of the KBS-3H design showing the inflow requirements of different parts of the drift ($Q_{\text{inflow}}$ is the rate of groundwater flow into the deposition drift)

2.3.2 Fracture grouts

Sealing of rock by means of grouting is a key method in restricting the in-flow of groundwater into excavations in a fractured hard rock such as those envisaged as host rocks for GDFs in Sweden, Finland and Canada, for example.

The performance of the KBS-3 design is sensitive to the groundwater flow into the drifts or deposition holes. Posiva and NUMO (Japan) have collaborated in developing and testing of injection grouts for the sealing of fractures to limit water flow [31]. In particular, the development of novel low-alkali fracture grouts has been necessary for the construction of the ONKALO facility in Finland. The required and desired properties of the fracture grouts developed by Posiva are summarised in Table 5. It should be noted that the requirements varied through the different trials. The principal requirement for this application, in addition to the low pH, is the penetrability of the grout into cracks, characterised in terms of the minimum fracture aperture through which the grout will flow, $B_{\text{min}}$, and $B_{\text{crit}}$, the critical aperture above which the grout will flow indefinitely.

SKB have specified the following in-flow requirements for the KBS-3H design:

- deposition hole  
  spot inflow: 0.1 L min\(^{-1}\)

- deposition tunnel  
  10 L min\(^{-1}\) per 300 m of tunnel; spot inflow: 1 L min\(^{-1}\)

- shaft and access ramp  
  10 L min\(^{-1}\) per 100 m of tunnel

- other underground facility parts  
  10 L min\(^{-1}\) per 100 m of tunnel.
SKB’s specifications for fracture sealing grouts are defined more qualitatively than those of Posiva, as follows [32]:

- only grout that gives a leachate with a pH $\leq 11$ may be used;
- superplasticisers and other additives may be used;
- there are no pre-set limits to the amount of materials that may be used, but in choosing between different approaches, the one giving the lowest material use is preferred;
- long-term durability (durability longer than 5–10 years) is not a requirement;
- grouting [injection] boreholes outside the tunnel periphery may be used; and
- grouting or other boreholes must not intersect deposition holes.

It is also envisaged by SKB that injection grouts will be used to improve the bond of rock bolts used for improving structural bearing capacity. Consequently, it is necessary for the grout to have a low hydraulic conductivity, good penetrability of very fine fissures, and physical and chemical compatibility with the host environment. There is also a requirements for the amount of cement and additives and the number of grouting holes used to be minimised.

### Table 5 Required and desired properties for low-alkali grout for injection of deep repositories (note that the requirements varied for different trials) [33]

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirement</th>
<th>Development</th>
<th>Field trials in Finland</th>
<th>Pilot tests ONALKO</th>
<th>Measuring method</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Required Properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>$\leq 11$</td>
<td>$\leq 11$</td>
<td>$\leq 11$</td>
<td></td>
<td>Leaching tests</td>
</tr>
<tr>
<td>Penetration-ability $b_{\text{min}}$</td>
<td>$\leq 80 , \mu\text{m at 60 min}$</td>
<td>$\leq 80 , \mu\text{m at 60 min}$</td>
<td>$\leq 80 , \mu\text{m at 30 min}$</td>
<td>Penetrability meter</td>
<td></td>
</tr>
<tr>
<td>Penetration-ability $b_{\text{crit}}$</td>
<td>$\leq 120 , \mu\text{m at 60 min}$</td>
<td>$\leq 120 , \mu\text{m at 60 min}$</td>
<td>$\leq 120 , \mu\text{m at 30 min}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>50 mPa s</td>
<td>Not used</td>
<td>50 mPa s</td>
<td></td>
<td>Rheometry</td>
</tr>
<tr>
<td>Yield value</td>
<td>$\leq 5 , \text{Pa}$</td>
<td>Not used</td>
<td>$\leq 5 , \text{Pa}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluidity</td>
<td>Not used</td>
<td>Not numerically set</td>
<td>45 s at 30 min</td>
<td>Marsh cone</td>
<td></td>
</tr>
<tr>
<td>Bleed</td>
<td>$\leq 10%$</td>
<td>$\leq 10%$</td>
<td>$\leq 2%$</td>
<td></td>
<td>Measuring glass at 2 hours</td>
</tr>
<tr>
<td>Workability time</td>
<td>$\geq 60 , \text{min}$</td>
<td>$\geq 60 , \text{min}$</td>
<td>$\geq 30 , \text{min}$</td>
<td></td>
<td>Determined by penetrability fluidity</td>
</tr>
<tr>
<td>Shear strength</td>
<td>$\geq 0.5 , \text{MPa at 6 h}$</td>
<td>More than about 2kPa at 6 h. Not numerically set</td>
<td>2 kPa at 8 h</td>
<td>Fall cone</td>
<td></td>
</tr>
<tr>
<td>Compressive strength</td>
<td>$\geq 4 , \text{MPa}$;</td>
<td>$\geq 8 , \text{MPa}$; 7 MPa also acceptable if other properties excellent. Not set numerically.</td>
<td>$\geq 4 , \text{MPa}$;</td>
<td>Uni-axial compressive strength at 28d</td>
<td></td>
</tr>
</tbody>
</table>

**2.3.3 Low-pH concrete plugs**

The ESDRED programme conducted trials of concrete formulations for tunnel and drift sealing plugs in disposal concepts incorporating a bentonite buffer [26]. These plugs are required either to limit groundwater flow or to provide temporary mechanical (and sometimes hydraulic) confinement to buffer and seal materials arranged around the waste containers.
Table 6  Functional requirements for shotcrete sealing plugs specified on different National GDF research programmes [26]

<table>
<thead>
<tr>
<th>Items</th>
<th>ENRESA</th>
<th>SKB</th>
<th>ANDRA</th>
<th>POSIVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity (k)</td>
<td>≤ 10^{-10} m·s^{-1}</td>
<td>≤ 10^{-10} m·s^{-1}</td>
<td>Depends on length L: ( \frac{k}{L} \leq 10^{-12} \text{ s}^{-1} )</td>
<td>≤ 10^{-10} m·s^{-1}</td>
</tr>
<tr>
<td>Final mechanical properties:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Young modulus</td>
<td>( &gt; 20000 \text{MPa} )</td>
<td>( &gt; 20000 \text{MPa} )</td>
<td>High strength is not required as such, but the requirements on durability lead to prescribe mix compositions corresponding to high performance concrete (= 60 MPa at 90 days)</td>
<td></td>
</tr>
<tr>
<td>- Poisson’s ratio</td>
<td>( 0.2 – 0.3 )</td>
<td>( 0.2 – 0.3 )</td>
<td></td>
<td>( &gt; 100 \text{MPa} )</td>
</tr>
<tr>
<td>- Tensile strength</td>
<td>&gt; 1 MPa</td>
<td>&gt; 1 MPa</td>
<td></td>
<td>( &gt; 10 \text{MPa} )</td>
</tr>
<tr>
<td>- Friction angle</td>
<td>( \geq 37^\circ )</td>
<td>( \geq 37^\circ )</td>
<td></td>
<td>( \geq 37^\circ )</td>
</tr>
<tr>
<td>- Cohesion</td>
<td>( \geq 2 \text{MPa} )</td>
<td>( \geq 2 \text{MPa} )</td>
<td></td>
<td>( \geq 2 \text{MPa} )</td>
</tr>
<tr>
<td>- Compressive strength</td>
<td>( \geq 10 \text{MPa} )</td>
<td>( \geq 10 \text{MPa} )</td>
<td></td>
<td>( \geq 10 \text{MPa} )</td>
</tr>
<tr>
<td>Durability</td>
<td>≥ 100 years</td>
<td>≥ 100 years</td>
<td>As high as possible (and sulphate resistant)</td>
<td>≥ 100 years</td>
</tr>
<tr>
<td>Workability</td>
<td>≥ 2 hours</td>
<td>≥ 2 hours</td>
<td>≥ 2 hours</td>
<td>≥ 2 hours</td>
</tr>
<tr>
<td>Pump ability</td>
<td>250 m</td>
<td>250 m</td>
<td>&gt; 100 m</td>
<td>250 m</td>
</tr>
<tr>
<td>Peak hydration temperature</td>
<td>≤ 40ºC</td>
<td>≤ 40ºC</td>
<td>≤ 30ºC</td>
<td>≤ 40ºC</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>1.2 W m(^{-1}) K(^{-1})</td>
<td>1.2 W m(^{-1}) K(^{-1})</td>
<td>Access drift plugs: not specified Disposal cell plugs: 1.75 W/m(^{2})</td>
<td>1.2 W m(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>Construction rate</td>
<td>1 m day(^{-1})</td>
<td>Not specified</td>
<td>Not specified</td>
<td>Not specified</td>
</tr>
<tr>
<td>Use of organic components (fibres or admixtures)</td>
<td>Not specified. To be studied</td>
<td>No. But if this is not possible, quantities and types of organic material must be described</td>
<td>No. But if this is not possible, quantities and types of organic material must be described</td>
<td>No. But if this is not possible, quantities and types of organic material must be described</td>
</tr>
<tr>
<td>Estimated pressure at the plug/buffer interface</td>
<td>7 MPa</td>
<td>15 MPa</td>
<td>Access drift plugs: 3 MPa Disposal cell plugs: 4.5 MPa</td>
<td>15 MPa</td>
</tr>
<tr>
<td>Length of plug</td>
<td>Not specified</td>
<td>As short as possible but it must be able to withstand the estimated pressure with a safety factor</td>
<td>Access drift plugs: not defined Disposal cell plugs: 4 to 6 m</td>
<td>As short as possible but it must be able to withstand the estimated pressure with a safety factor</td>
</tr>
<tr>
<td>Diameter</td>
<td>Not specified</td>
<td>1860 mm-1840 mm</td>
<td>Access drift plugs: 7 m Disposal cell plugs: 0.7 to 3.5 m</td>
<td>1860 mm-1840 mm</td>
</tr>
<tr>
<td>Drainage</td>
<td>Not specified</td>
<td>It must be possible to drain water through the plug during construction (including curing time) and to seal the drainage hole after construction of the plug</td>
<td>Not specified. However, piping might be needed for artificial water supply to buffer (to be eventually grouted)</td>
<td>It must be possible to drain water through the plug during construction (including curing time) and to seal the drainage hole after the construction of the plug</td>
</tr>
</tbody>
</table>
In Module 4 of the ESDRED project, a number of input parameters for the design of concrete plugs were agreed and fixed at the outset. These ‘input data’ or ‘fixed design criteria’ were associated with the properties of the host rock environment, the concrete specification and emplacement method; these were:

- the use of shotcreting as emplacement method: shotcreting was considered to be proven as an efficient and cost saving method for rock support in underground construction that could be applied also to plug construction;
- a concrete porewater pH equal to or below 11: a pH value \( \leq 11 \) (measured in porewater extracted by pore squeezing) was required for the shotcrete formulation;
- the mechanical properties of the host rock: the rock properties specified for the designs were: Young’s modulus, Poisson’s ratio, tensile strength, friction angle and cohesion; additionally, some rock-plug interface mechanical properties were specified: friction angle, cohesion and normal and shear stiffness;
- hydraulic conductivity of the host rock: the maximum hydraulic conductivity allowed through the shotcrete plug should be at least that of the host rock;
- groundwater composition: the durability of the shotcrete will depend on the aggressiveness of the underground water, which is a function of salinity and flow.

In addition, some flexible requirements (termed functional requirements) were identified [26], which tend to vary between national programmes. Some of these requirements are reproduced in Table 6.

### 2.3.4 Salt concrete seals

In the German salt dome concept for SF and HLW disposal, waste containers are placed in drifts excavated in evaporitic host rock and the drifts then backfilled with crushed salt [34]. After backfilling the drifts would be sealed. The functions and requirements of the drift seals are to hydraulically separate the disposal areas from the rest of the openings and potential pathways to the groundwater system (e.g. through mineral seams). A candidate material for these seals is salt concrete, a mixture of cement, crushed salt and PFA. Examples of the compositions of two such materials, developed in Germany for sealing operations in the Morsleben disposal facility, are given in Table 7. In terms of post-closure performance, the key property of the salt-concrete drift seals is their long-term permeability; a permeability of less than \( 10^{-18} \) m\(^2\) (corresponding to a hydraulic conductivity of approximately \( 10^{-11} \) m s\(^{-1}\)) is required [35]. The ability of salt concretes to achieve this requirement is supported by gas permeability measurements [36].

<table>
<thead>
<tr>
<th>Components</th>
<th>M2</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recipe (kg m(^{-3}))</td>
<td>Weight fraction (%)</td>
<td>Recipe (kg m(^{-3}))</td>
</tr>
<tr>
<td>High sulphate resistant cement</td>
<td>328</td>
<td>16.4</td>
</tr>
<tr>
<td>PFA</td>
<td>328</td>
<td>16.4</td>
</tr>
<tr>
<td>Water</td>
<td>267</td>
<td>13.4</td>
</tr>
<tr>
<td>Crushed rock salt, &lt;20mm</td>
<td>1,072</td>
<td>53.8</td>
</tr>
</tbody>
</table>

* Not to be confused with the Swiss M2 mortar.
3 Introduction to the structure and chemistry of cement systems

3.1 Introduction

Cements have been used for construction since prehistoric times to join masonry and brick units, to form foundations and floors, etc. Portland cement, so called because of its similarity to Portland stone, is a manufactured product developed during the nineteenth century as a fast-hardening cement with higher compressive strength than naturally available materials. Modern Portland cement (also known as ordinary Portland cement, OPC) has become the most widely used manufactured construction material; world production is estimated to exceed $2 \times 10^9$ tonnes per year. Almost all applications of cementitious materials in GDF designs are based on OPC.

There are different standards for classification of Portland cement. The two major current standards are the ASTM C150 [38] used primarily in the U.S. and the European EN-197 [39, 40]. EN 197-1 defines 5 classes of common cement that comprise Portland cement as a main constituent (which, confusingly, differ from the ASTM classes):

- CEM I Portland cement Comprising Portland cement and up to 5% of minor additional constituents;
- CEM II Portland-composite cement Portland cement and up to 35% of other single constituents;
- CEM III Blastfurnace cement Portland cement and higher percentages of BFS;
- CEM IV Pozzolanic cement Portland cement and up to 55% of pozzolanic constituents (volcanic ashes);
- CEM V Composite cement Portland cement, BFS or PFA and pozzolana².

Constituents that are permitted in Portland-composite cements are artificial pozzolans (BFS, silica fume, and PFA) or natural pozzolans (such as volcanic ash glasses, calcined clays and shale).

Although the term CEM I effectively replaces the term OPC, because much of the work described in this report has used OPC, the latter term will be used throughout for consistency with the original references.

It is important to recognise that further evolution of these standards is likely to occur before the commencement of GDF construction, operation and closure operations in the UK. Materials specifications for cement-based EBS materials will need to be considered throughout the development and operation of a GDF.

3.2 Composition of Portland cement clinker

Portland cement is supplied as a fine powder, typically having a surface area in the range 300-500 m$^2$kg$^{-1}$. Mineralogically, OPC is heterogeneous and its phase composition reflects the high temperatures used in its production. Table 8, compiled from references 41 to 43, describes the mineralogy, composition and origin of the phases. During grinding of the indurated product, termed clinker, other mineral additions are made. Principally, calcium sulphate (gypsum) is added to control set time but up to 5% filler or other supplementary materials, e.g. PFA, BFS or ground

² The name derives from volcanic ashes from Pozzuoli in Italy that were combined with lime to make a mortar that set under water. The term is used generically to refer to natural or artificial siliceous or siliceous aluminous materials that will react with lime (calcium hydroxide) and water to form a hardened product.
limestone are also permitted without special labelling; this is a distinct stepwise change permitted in recent years under EN-197, which departs from historic practice.

As Table 8 shows, the major clinker phases are tri- and di-calcium silicates. However, all the clinker phases are reactive with water and participate in the cementing reactions, albeit at different rates: tricalcium aluminate reacts rapidly while at the other extreme, the iron-bearing phase may react slowly, over months or years.

Table 8  Mineralogy of Portland cement clinker

<table>
<thead>
<tr>
<th>Clinker minerals</th>
<th>Phase/ substance designation</th>
<th>Approximate mass % in finished cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_3$SiO$_5$</td>
<td>Alite</td>
<td>50-60</td>
</tr>
<tr>
<td>Ca$_2$SiO$_4$</td>
<td>Belite</td>
<td>20-35</td>
</tr>
<tr>
<td>Ca$_3$Al$_2$O$_6$</td>
<td>“Aluminate”</td>
<td>3-10</td>
</tr>
<tr>
<td>Ca$_2$(Fe,Al$_2$)O$_5$</td>
<td>“Ferrite”</td>
<td>3-8</td>
</tr>
<tr>
<td>CaO</td>
<td>Lime</td>
<td>&lt;1-2</td>
</tr>
</tbody>
</table>

**Added to clinker in the course of grinding**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$S$_4$.nH$_2$O</td>
<td>Gypsum (or anhydrite)</td>
</tr>
<tr>
<td>Supplementary materials</td>
<td>Limestone, BFS, PFA</td>
</tr>
<tr>
<td>Grinding aids</td>
<td>Organic amines, such as triethanolamine (TEA)</td>
</tr>
</tbody>
</table>

No formal chemical specification exists for the chemical composition of Portland cement but, to meet strength gain and other targets without excessive grinding, the above mineral proportions are usual and set limits to the range of possible cement chemistries. Additionally, chemical and mineralogical composition limits are imposed on certain substances, for example a maximum free lime (CaO) content of ~3% (and preferably less than 2%) is imposed [44] with the result that despite having a typical bulk chemistry with 66-69 wt% chemical CaO, virtually all the “CaO” reported in the bulk analysis must be combined into calcium silicate, aluminate and aluminoferrite minerals.

The various types of cement supplied into the market are achieved mainly by (i) changing the grinding regime and (ii) altering the relative proportions of phases shown in Table 8: for example, the content of tricalcium aluminate is limited in “sulphate-resistant” Portland cement (SRPC). Since the introduction of EN-197-1, the inclusion of 5% “other” material in CEM I has broadened the range of commercially-available bulk compositions that can be marketed as “Portland cement” compared to previous standards (e.g. BS12 [45]).

Although cements are nominally inorganic materials, some organic content can be introduced in the course of manufacture. Thus, for example, gypsum used for set retardation may contain some minor organic impurities of natural origin. So called “grinding aids”, often organic amine derivatives such as TIPA (trisopropanolamine), may be added to facilitate clinker grinding in the mill; grinding machinery may contribute traces of lubricant, etc. Thus an as-supplied Portland cement is liable to contain on the order of 0.1% organic matter, the content and nature of which are variable.

Commercial Portland cement material, as supplied, will have been quality checked for certain aspects of performance including free lime content, surface area and particle size distribution, set time and strength gain. Thus if commercial cement is stored correctly, its quality is reasonably well assured for normal construction uses.
3.3 Hydration of Portland cement

3.3.1 General principles

Cement components can be dry blended to achieve the required cement solids mix. Hydration is initiated by mixing the blended powder with water. Thereafter, a period of workability is achieved usually lasting several hours. Subsequent setting and hardening occur spontaneously and (in most cases) irreversibly.

The cement mix components fall broadly into three types:

i) supplementary cementing materials (SCMs) intended to react with cement and eventually becoming part of the matrix;

ii) agents added to control the rheology of the fresh mix (chemical admixtures); and

iii) fillers.

The nominally inert “fillers” usually comprise naturally occurring or crushed and sized sand, gravel and rock. In the case of concretes, added inert “fillers” or aggregate may comprise 85% (or more) by weight of the hardened mass. For example, a “1:2:4” concrete contains 1, 2 and 4 parts cement, sand and coarse aggregate respectively by weight and is thus 1/7 cement, ~14%, on a dry basis.

The fresh mix can be emplaced into the desired shape by pouring, pumping, etc.; consolidation may be assisted by mechanical compaction or vibration. After a few hours, the fresh mix loses its fluidity, i.e., it “sets” and shortly thereafter, begins to gain strength. Strength gain is rapid in the first few days but continues for some months, albeit slowly, and it is common to measure strengths at 1, 3, 7 and 28 days. The setting and hardening occur by a series of chemical reactions which are irreversible and evolve considerable heat. The mass may undergo considerable self-heating, depending on the formulation, physical size, shape and opportunity for heat to escape.

Dimensional changes also occur, partly due to self heating but under isothermal conditions, shrinkage occurs in the course of hardening. This shrinkage, termed chemical shrinkage, arises from the reduction in absolute volume of the solids and liquids of the hydrating pastes and arises mainly as a consequence of converting liquid water to chemically-bound water with concomitant reduction in the specific volume occupied by water in the mix.

3.3.2 Nature of the hardening reactions

The reactions leading to set do not directly involve the inert aggregate, so for simplicity only reactions occurring in the paste fraction (cement plus water) will be described. The solid grains of cement are, as noted in Table 8, polymineralic, and are somewhat soluble. Within a few seconds of mixing with water, the pH of the aqueous phase rises to greater than 12; the aqueous phase becomes strongly alkaline and rapidly supersaturates. Precipitation of hydrated solids begins. The solid products of hydration initially accumulate both on the surfaces of solid grains, both clinker and aggregate, and in the interstitial water-filled spaces.

However, cases may arise where early hydration does not proceed normally; the wet mixture may stiffen too quickly and lose fluidity. This is known as either “flash set” or “false set”. If the fluidity can be restored by vigorous mixing, it is termed false. False set most commonly arises from overdosing with gypsum or other calcium sulphate source but is rare in commercial concrete formulations. Flash set is usually accompanied by considerable heat evolution and fluidity cannot be restored by further mixing. Flash set is often associated with the rapid reaction of aluminates if the proper amount or form of calcium sulphate is not available to control the calcium aluminate hydration. Flash set may be encountered in novel blended cements, e.g. amongst formulations with high slag contents. In general its occurrence is difficult to predict and so it is customary to conduct extensive trials on novel compositions prior to commencing cementation.

As normal hydration proceeds and the remaining clinker becomes surrounded by a tenuous film of hydrates; water has increasingly to diffuse through the film of reaction products to reach and
hydrate the remaining solids, with the result that the reaction slows. As the initially tenuous hydrate matrix densifies, strength gain begins. By 28 days, most (>90%) of the cement grains will have reacted in the course of normal (5-30°C) hydration. In the period beyond 28 days changes still occur but are slow and for this reason, many engineering properties such as strength are commonly measured at 28 days.

Most of the aqueous phase becomes chemically combined into solids in the course of hydration. Thus cements do not harden by drying; indeed, conservation of water for the full duration of the hydration process is important to optimise the properties of the hydrated product. The amount of water required completely to hydrate cement is subject to some uncertainties arising as a result of difficulties in distinguishing between “bound” and “free” water. But if we accept that chemisorbed water is essential to the constitution of solid phases such as C-S-H, the necessary water content for complete hydration, expressed as a weight ratio of water/cement (w/c) is in the range 0.32 to 0.36. Water in excess of this ratio remains trapped in pores and is termed “pore water”. Since most concretes are made to water cement ratios not less than 0.45, they trap water and thus aqueous chemistry concepts are applicable: for example, solid cements are still said to have a pH. This can be verified experimentally because pore water can be expressed at high pressures and subjected to analysis [46].

The hydrate phases that form are intimately mixed and are, in part, semi-crystalline. Table 9 shows the four main phases which comprise >95% of the hydrated cement. The three crystalline phases have compositions which are either fixed, as in the case of portlandite, or which vary over well-characterised limits. Their basic crystal structures are known. However ~65-70% of the solid is a poorly crystalline phase designated C-S-H (shorthand for Calcium, Silica and Water; dashes signify variable proportions). “Crystallinity” requires an operative definition, which is usually provided by the appearance of the powder X-ray pattern: the pattern of C-S-H contains a few broad, diffuse reflections which do not permit structure analysis, hence the usual classification of C-S-H as “amorphous” or “gel-like”. However, local environments within C-S-H are sufficiently well ordered over distances of a few nanometers to apply nuclear magnetic resonance with which to determine average Si (and Al) environments [47]. Thus C-S-H is essentially a rigid gel with short-range ordering. The short range order is similar to that found in two crystalline calcium silicate hydrate minerals, tobermorite and jennite and C-S-H is therefore sometimes referred to as “tobermorite gel”. Details of the supposed structural similarity are, however, still the subject of debate. For present purposes it is important to note that:

i) C-S-H has a variable composition, although C-S-H coexisting with portlandite is calcium-saturated, with Ca:Si ratio of at least 1.5;
ii) C-S-H structural units adhere strongly but contain nanopores; and
iii) the bonding of water within C-S-H ranges greatly in strength, from weakly bound to structurally incorporated, with some water being retained to >400°C upon heating in air.

Table 9 Phases present in hydrated Portland cement paste (0-30°C)

<table>
<thead>
<tr>
<th>Phase designation</th>
<th>Crystallinity and amount (wt%)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portlandite (CH)</td>
<td>Crystalline, 20-30%</td>
<td>Ca(OH)₂</td>
</tr>
<tr>
<td>C-S-H</td>
<td>Non crystalline, 50-65%</td>
<td>3CaO.2SiO₂.8H₂O</td>
</tr>
<tr>
<td>Ettringite, or AFt</td>
<td>Crystalline, 2-6%</td>
<td>6CaO.Al₂O₃.3SO₃.32H₂O*</td>
</tr>
<tr>
<td>AFm</td>
<td>Crystalline, 5-10%</td>
<td>4CaO.Al₂O₃.SO₃.12H₂O*</td>
</tr>
</tbody>
</table>

* Ignoring minor substitution of Al by Fe(III): the formula is idealised

Given the major changes in phases occurring during hydration (compare Tables 8 and 9), the overall chemical reactions result in remarkably little net volume change. Clinker has density of ~3.1 g cm⁻³ and many of the hydrates (AFt excepted) have densities in the range ~2.3-2.6 g cm⁻³ [48]. It is normal to obtain a little shrinkage in the course of setting and hardening but the formation
of low density AFt (ettringite has a density ~1.77 g cm\(^{-3}\)) serves to offset in part the chemical shrinkage. However precise control over dimensional stability of cements undergoing hydration has not been attained; too many variables, such as hardening temperature, affect the numerical values. So in many civil engineering applications a little shrinkage is preferred as it permits demoulding and simplifies the removal of formwork.

SCMs, including PFA and BFS added to cement, generally react more slowly than cement. It has been difficult experimentally to determine the rate of reaction, although recent calorimetric studies have been reported by Utton et al. [49]. In general, the rate of reaction depends in part on chemistry, mineralogy, granulometry and reaction temperature, as well as the amount of replacement; high replacement of cement by SCMs generally leads to a slower rate of reaction. The variable nature of these supplementary materials is important in this respect: whereas cement has relatively consistent composition and properties, those of slag and fly ash are much more variable. The additional uncertainties thus introduced about their long term performance are discussed below.

3.4 Blended Portland cement

Special requirements are often met by blending Portland cement with SCMs. The terminology applied to the blending agents is varied and imprecise but in the present context a “blending agent” or SCM is used to refer to substances that are themselves inert or poorly cementitious with water but, when activated by Portland cement, combine with cement and water to become an integral part of the binder. SCMs differ from “fillers” which are chemically inert in a cement matrix. As noted in sub-section 3.1, EN 197-1 recognises a number of distinct types of blended cements approved for use in civil engineering.

Both SCMs and fillers can affect the porosity and permeability of the cement product without excessive loss of compressive strength. However, any beneficial action of fillers is usually limited to, at most, a few weight percent, whereas SCMs can typically be used with benefit at much higher cement replacement levels.

Table 10 lists some commonly-used blending agents. Many of these materials are obtained as industrial by-products, for example PFA arises from combustion of pulverised coal while BFS refers to quenched iron blast furnace slag; silica fume arises as a vapour condensate in the course of ferrosilicon production. For this reason, the composition and mineralogy of SCMs is variable, most especially that of PFA; coals of different rank and geological province often give special ash compositions. More esoteric materials, both natural and man-made, e.g., metakaolin, made by calcination of naturally occurring kaolin, are also used as an SCM, but have not been used widely in cement compositions for GDF applications.

The materials shown in Table 10 have a significant historical use in Portland cement systems. BFS-cements have been used in continental Europe for over a century. PFA has been available in quantity for cement blending for perhaps 60 years and many UK coal-fired power stations built in the 1950-1960 period used PFA concrete to demonstrate the beneficial properties of PFA on mass concrete. Silica fume has been available, albeit in limited quantities, for a similar period.

Addition of SCMs influences the properties of fresh cement mixes. The addition of PFA, depending on its granularity, often results in a slight reduction in the amount of water needed to achieve a required slump\(^3\). In contrast, the addition of silica fume, with its high content of submicron-sized grains, sharply increases water demand and, unless mixtures are heavily plasticised (see sub-section 3.5.1), additions are usually limited to a maximum of 6-10% replacement. The ultrafine particulate matter resulting from addition of well-dispersed silica fume is, however, known to refine the pore structure with a consequent significant reduction in the permeability of hardened concrete.

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\(^3\) A slump test is a simple empirical test used to measure the workability of a fresh batch of wet cement or concrete. The test is carried out in accordance with BS EN 12350-2 [50].
Table 10 Supplementary Cementing Materials

<table>
<thead>
<tr>
<th>Designation</th>
<th>Constitution and characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash from coal combustion (PFA)</td>
<td>Heterogeneity in composition and microstructure, both within any one source as well as between sources.</td>
</tr>
<tr>
<td>Iron blast furnace slag, granulated and ground (BFS)</td>
<td>Differences between sources but any one supply tends to be homogeneous. High glass content. Notable for content of reduced sulphide sulphur.</td>
</tr>
<tr>
<td>Silica fume</td>
<td>Nearly pure (~95%) amorphous silica. Physically in sub micron size grains.</td>
</tr>
<tr>
<td>Zeolite</td>
<td>A family of hydrous crystalline aluminosilicates, natural as well as synthetic.</td>
</tr>
<tr>
<td>Clay and calcined clay, e.g. metakaolin</td>
<td>Layer-structured aluminosilicates, of which the 2:1 types (e.g. kaolin and halloysite) are the most important. Activated by heating to ~700°C, giving a solid which reacts readily with cement.</td>
</tr>
</tbody>
</table>

Both BFS- and PFA-based cements are commonly used as waste immobilisation grouts in the UK, and the nuclear industry has pioneered the use of grouts with high cement replacement levels, with potentially up to 75% replacement of cement by PFA and up to 90% by BFS [51, 52]. This has stemmed from concerns about the initial heat evolution of cement, and its consequential thermal excursion during initial set and strength gain. Cement blends containing these materials may potentially be used in other GDF applications. The UK nuclear waste programme has historically used almost exclusively, low-lime PFA (usually <5% CaO) for immobilisation of ILW, in contrast to materials with lime contents of up to 30% available elsewhere. The main reactive component of these ashes is an aluminosilicate glass containing small (usually <5% each) amounts of alkali, magnesia, iron oxide, etc. Significant crystalline matter may also be present. Thus PFA is not a single material but a variable mixture. At one time, most UK coal-fired power plants were tied to a particular coal source, usually local, and gave a relatively consistent ash. Increasingly, however, production at specific plants is no longer tied in this way, leading to greater variability in the chemistry and mineralogy of the PFA product. BFS materials have a high glass content. Materials from any one source tend to be relatively homogeneous, but the composition may vary significantly between sources, depending on the fuel and ore compositions.

In the short term, the properties of BFS and OPC blends are very much like those of Portland cement. This similarity results from the comparatively slow reaction of the supplementary materials: the Portland cement activator dominates the observed short-term behaviour. Long-term data on the evolution of properties are relatively lacking, although a number of studies have been reported on the composition and microstructure of OPC/BFS blends [53, 54].

### 3.5 Cement admixtures

Cement admixtures are used widely in the formulation of cements and concretes to improve key properties of the material relevant to their application and emplacement. Admixtures may be used to [55]:

- increase workability and reduce water demand of cements to optimise compressive strength;
- retard the rate of cement hydration and setting, especially in warm climates;
- accelerate the rate of cement hydration and setting, especially in cold climates;
- increase water repellency and impede water flow through hardened concrete, in water-retaining or below-water table structures;
- provide a very rapid set for sprayed concretes;
- inhibit corrosion of steel reinforcement;
• aid pumpability in long pump lines, especially where low-density aggregates are being used;
• control segregation (separation due to differences in particle size or density) and ensure mix cohesion of highly-fluid mixes for self-compacting concrete; and
• allow large volumes of air bubbles to be trapped in foamed concretes.

In general, admixtures are commercial products often with a fairly ill-defined chemical composition due to the presence of additional components (that are often unspecified) as well as their principal ones [56]. In many cases, admixture compositions are tailored to include components with complementary functions for particular applications (and such compositions are subject to commercial secrecy). As a result there is an enormous range of cement admixture products available in the market that could potentially be selected for GDF applications. However, due to their ill-defined nature, product consistency is a potential issue, as well as the extent to which the performance of any individual product is representative of any particular class of admixture.

Of the above applications, those of most relevance to cement-based materials used in GDFs are the use of so-called superplasticisers to reduce the water demand and/or to increase the workability of cement materials used in structural and sealing-type applications; and potentially the use of set modifiers to either retard or accelerate the hardening of fresh cements (e.g. shotcretes).

3.5.1 Superplasticisers

In general, the strength of concrete is inversely proportional to the amount of water added or the water-cement (w/c) ratio (see sub-section 6.2.1). However, the lower the water content, the less workable the mix (noting that w/c ≥ 0.32-0.36 is required for complete hydration of the cement component). Superplasticisers act as dispersants that adsorb to the surfaces of the cement particles and prevent their aggregation thereby maintaining workability at lower water contents.

The earliest types of cement plasticisers were manufactured from lignosulphonates (LS), a by-product from the paper industry [57]. These allow a reduction in water content of typically 10% (and also give some degree of set retardation). Since the 1960s, superplasticisers have been manufactured from sulphonated naphthalene condensate (SNF) or sulphonated melamine formaldehyde (SMF) and later from vinyl copolymers. These materials, which are also referred to as High Range Water Reducers, are used to give very high levels of workability or water reductions of up to 30%. A new generation of superplasticisers is based on polycarboxylate ether (PCE) branched comb polymers [58].

The repeating structures of the traditional types of plasticisers and superplasticisers are illustrated in Figure 8 [57]. It should be noted that lignosulphonates are composed of a variety of structurally-related monomers (of which one example is shown in the figure), which are polymerised irregularly into a macromolecule, and that the degree of polymerisation may vary, typically with molecular masses varying from several hundred to 100,000 Daltons [57]. All of these materials comprise polymer chains with appended, negatively-charged, sulphonate groups, through some of which the polymers may chemically bind to positively charged surface sites on cement clinker grains. The net effect is to confer a net negative charge to the cement particles, which maintains dispersion through electrostatic repulsion. Typically, SNF and SMF superplasticisers are used in the range 0.7-2.5% by weight of cement mix and can give water reductions of 16-30% [59]; typically LS plasticisers are used in the range 0.2-0.6% by weight to give up to 12% water reduction [60].
The structure of the repeating unit of a typical PCE is shown schematically in Figure 9. The structure is composed of a backbone of polymethacrylate (PMA) with hydrophilic polyethylene glycol (PEG) sidechains capped with methyl groups. The ratio of the PEG sidechains to free acrylate groups on the PMA backbone can be varied as can the length of both the PEG chains and the backbone through tailored chemical synthesis [58].

PCEs sorb to cement particles via the negatively-charged acrylate groups on the polymer backbone; cement dispersion arises by steric repulsion resulting from the interactions of the PEG sidechains on adjacent particles. This form of dispersion is more powerful in its effect than electrostatic repulsion alone and gives improved workability retention to the cementitious mix. With a relatively low dosage (0.5–1.5% by cement weight) a reduction in water content of up to 40%, can be achieved. Although PCEs can be relatively expensive on a cost per litre basis, their cost is off-set by their enhanced performance. PCEs are widely used in pre-cast concrete and are the principal superplasticiser type used in the production of self-compacting concrete [59].

Superplasticisers are an important component of low-pH cements being developed for use in GDF concepts that include a bentonite buffer [61]. SMF-, SNF- and PCE-based superplasticisers are all being considered. PCEs are used in the high-volume fly ash and silica fume cement (HFSC) formulation developed as a low-pH high-pozzolan OPC blend in Japan [62]. The main chemical admixture used to aid injection grout workability at ONKALO in Finland is a SNF-based superplasticiser [33].

Superplasticisers (e.g. SNF, 1-1.5% dosage) have been used in limited amounts in grouts to condition some UK ILW (e.g. 9G48/C, encapsulated skips and fuel cooling pond debris from Trawsfynydd) [63] and work is currently in progress to evaluate a PCE (ADVA Cast 551) for use in immobilisation grouts [64]. Additional work is in progress on the RWMD programme to consider the general usage of superplasticiser within a GDF. Some of this work has been concerned with the potential impact of these materials as complexants for radionuclides that may affect radionuclide solubility and sorption behaviour - see sub-section 12.7.2 for further details.
3.5.2 Accelerators

Accelerators are used to increase the rate of hardening of cement and concrete mixes. Originally used to accelerate setting in cold weather conditions, they are also important additives to concrete formulations, such as shotcrete (see below), that require a rapid set.

The most widely used accelerators are calcium salts, in particular calcium chloride and calcium formate; calcium nitrate and calcium thiosulphate are also used [65]. Calcium chloride is the most effective (and economic) accelerator for use in unreinforced concrete under winter conditions and its effects on concrete have been extensively studied (as summarised in reference 65 for example). So-called “chloride-free” accelerators are sometimes preferred in reinforced concretes due to concerns about corrosion arising from the potential presence of free chloride in the cement porewater. Recently, a novel calcium sulphoaluminate accelerator has been used for low-pH shotcrete mixes developed in Japan [66].

In general, the only properties of wet concrete that are affected by the addition of calcium chloride or calcium formate accelerators are the heat evolution (which is increased slightly) and the setting time (which is reduced); workability, mix stability and w/c ratio are unaffected [65]. In addition, the 28-day compressive strength of concrete is increased, typically by about 10% under ambient curing conditions by the addition of 1% by weight of calcium chloride [65].

3.6 Shotcrete

Shotcrete, also called ‘sprayed concrete’, is a well-known construction material that is applied by spraying onto a rigid surface (rock or soil), using a concrete pump and compressed air. The compressed air projects the concrete mix at high speed against the surface, so that it sticks. Once sprayed, the concrete starts to set immediately, thanks to an ‘accelerant’ additive, to form a self-supported layer. The setting speed determines both the self-supporting capacity and the rate of development of structural strength in the shotcrete layer, and is controlled by the dosage of accelerator and also by the shotcrete formulation. In normal conditions, the typical thickness of shotcrete layers ranges from 5 to 15 cm. Due to the characteristics of the formulations used and the spraying process, shotcrete is normally a high density and low permeability material, compared to an average standard concrete. It also shows lower surface cracking.

There are two basic types of shotcreting techniques, called ‘wet mix’ and ‘dry mix’, depending on whether water is added at the mix before the pump stage (wet mix), or at the end of the pipe, just before the spraying nozzle (dry mix) [67]. Nowadays, practically all shotcrete works are made using the wet mix system, as this provides a more uniform flow and therefore a more consistent quality in the final product. Shotcrete operation can be performed either manually or using articulated arms, commonly known as ‘robots’, that can perform some movements in automatic or semi-automatic mode. In galleries of small cross-section, like those planned in many GDF designs, the operation may need to be carried out manually, making the operation more difficult; at present, the dimensions of the robots existing in the market are made for larger spaces [67].
OPC is the most commonly used cementitious material in shotcrete formulation; however, blended cements can also be used to improve the properties required in either the plastic or hardened states. The addition of silica fume, in particular, improves pumpability, cohesiveness and adhesion, and is very commonly used in high-quality shotcrete mixes. The addition of silica fume enables the construction of thicker shotcrete layers in a single pass.

The grain size distribution of aggregates is a critical factor in the shotcrete formulation. It must comply with the curves specified in the applicable standards, to prevent particle-size segregation of the material along the pipe. Maximum grain size is usually 4, 8, or 16 mm, depending on the fineness of the shotcrete. In comparison with standard concrete, shotcrete requires a higher proportion of fines, especially if using a wet mix. Any type of aggregate can be used, but rounded, natural washed gravels and sands provide a better behaviour at the pumping stage. In general, selecting an adequate aggregate for each mix requires considerable experience and testing.

Steel and polymer fibres can be added to the shotcrete mix to meet particular requirements. Steel fibres improve the tensile and flexural strength of the hardened shotcrete and also reduce shrinkage and cracking. Polymer fibres have a similar effect in terms of reducing shrinkage, and also improve other properties such as ductility and fire resistance.

Shotcrete requires a number of admixtures, which vary from one mix to another, depending on the application and the specific requirements. The two most important are a superplasticiser and an accelerator. Other admixtures such as retarders, hydration control compounds and curing agents may also be required, depending on the application and the work site conditions. In particular, curing compounds may be relevant in a GDF application, as they prevent the evaporation of water from the mix, reducing shrinkage and cracking.

As noted previously, work on shotcrete formulations in GDF programmes to date has primarily been concerned with developing materials for use in SF disposal concepts that include a bentonite buffer, which have a requirement for a lower leaching pH for cement-based EBS materials. Further background on low-pH cements is provided in the following sub-section; the development of low-pH shotcretes for GDF applications is discussed in sub-section 13.3.

### 3.7 Low-pH cements

The development of low-pH cements for use in GDFs for radioactive waste has arisen from concerns over the potential for deleterious effects upon the host rock and other EBS materials (notably bentonite) under the high-pH conditions (pH > 12) of OPC pore fluids. Low-pH cement (also known as low-heat cement) was developed by the cement industry for use in large structures (e.g. dams) where the heat generated during the curing of large cement pours could lead to subsequent problems with cracking of the resulting structure. This type of cement was first applied in a GDF context by AECL in Canada who developed a low heat of hydration Portland cement (LHHPC) for use as a concrete plug in repository galleries [68]. In low-pH cements, the amount of cement is reduced by substitution of materials such as PFA, BFS, silica fume, and/or non-pozzolanic silica flour. It is necessary to use additives such as superplasticiser to improve the workability of low-pH cements.

Silica fume appears to be the most promising blending agent for low-pH grouts [31]. The fine particle size of silica fume can lead to difficulties in practice, however; issues include problems achieving physical mixing without agglomeration, unfavourable mix rheology, and excessive shrinkage in the immediate post-setting stage [69]. However, silica fume-OPC blends can achieve high compressive strengths and low permeabilities. Use of large amounts of silica fume (more than 40%) effectively reduces the pH of cement paste leachate, but high contents (more than 70%) lead to a loss of workability of fresh concrete due to an increase in its viscosity, since the particle size of silica fume is around 0.1 μm. To ensure workability, the maximum content of silica fume is therefore limited to 20%, fly ash being used for the balance as an alternative pozzolanic material [66].
The principal solid phase in low-pH cement is a low C/S (< 1.0) C-S-H gel. Production of low C/S C-S-H gel increases the average size of the silicate anions it contains, with a similar effect to that of carbonation [70]. With silica fume as the additive, the mean C/S ratio remains at about 1.5 for as long as any portlandite remains. If all the Ca(OH)$_2$ is consumed, then the C/S ratio decreases to around 1.0. A number of studies have shown that the addition of silica fume greatly accelerates the hydration of C$_3$S and that the C-S-H gel thus formed is highly polymerised, e.g. Groves and Rodger [71]. Groves and Rodger noted excellent bonding between the C-S-H gel and residual silica which suggests that such a system may be capable of developing high strength.

SKB, Posiva, Nagra, Andra and JAEA have all developed low-pH cements for use as grouts, plugs and shotcrete, with much of this research carried out jointly through the EC ESDRED programme [26, 31]. These developments are discussed in section 13. Some of the compositions considered are summarised in Table 11.

### Table 11 Low-pH cement compositions for GDF applications investigated worldwide [72]

<table>
<thead>
<tr>
<th>Country</th>
<th>Cement formulations†</th>
<th>Material developed</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada – AECL</td>
<td>OPC 50% - silica fume 50%</td>
<td>High strength concrete</td>
<td>[73]</td>
</tr>
<tr>
<td>Finland – Posiva Oy</td>
<td>OPC 60% - silica fume 40%</td>
<td>Injection grout</td>
<td>[74]</td>
</tr>
<tr>
<td>France – ANDRA, CEA, EDF</td>
<td>OPC 60% - silica fume 40%</td>
<td>High strength concrete</td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td>OPC 37.5% - silica fume 32.5% - PFA 30%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OPC 20% - silica fume 32.5% - BFS 47.5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OPC 33% - silica fume 40% - BFS 13.5% - PFA 13.5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Japan – JAEA, CRIEPI, NUMO</td>
<td>OPC 40% - silica fume 20% - PFA 40%</td>
<td>Shotcrete</td>
<td>[66, 76]</td>
</tr>
<tr>
<td>USA – ORNL</td>
<td>OPC 40% - BFS 30% - PFA 25% - silica fume 5%</td>
<td>Shotcrete</td>
<td>[77]</td>
</tr>
<tr>
<td>Spain – IETcc-CSIC, ENRESA</td>
<td>OPC 60% - silica fume 40%</td>
<td>Shotcrete</td>
<td>[78]</td>
</tr>
<tr>
<td></td>
<td>OPC 35% - silica fume 35% - PFA 30%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Switzerland - Nagra</td>
<td>OPC 60% - silica fume 40%</td>
<td>Shotcrete</td>
<td>[79]</td>
</tr>
</tbody>
</table>

† These formulations also include superplasticisers at up to few percent by weight of dry material and in some cases additional additives, such as an air entrainer and an accelerator in shotcretes [66, 78].
4 Introduction to the properties of cement systems

4.1 Introduction

This section is designed to provide a brief introduction to the physical properties of cements and the processes associated with the setting and curing of cement-water mixes. This sub-section introduces the flow properties and setting time of wet cement mixes, heat evolution during cement hydration, and the mechanical, thermal and mass transport properties of cured cements, which are then discussed in more detail in subsequent sub-sections. In dealing with these processes and the properties of cement systems, the approach taken herein is to offer some general principles, to describe the key factors influencing performance, and then to indicate how different cement types may influence performance.

Immediately after mixing cement and water, cement paste may be considered as a viscous fluid with solid particles in suspension. The flow properties of the grout (see sub-section 4.3.1) are important in relation to the ability to transport the grout (possibly over long distances in pipelines) and to enable the grout to flow, unaided in some situations, into relatively small spaces. The viscosity (sub-section 5.3) is also important in situations where gas generation from waste is occurring during placement.

During the period before setting, the cement paste is subject to bleed and settlement (sub-section 5.5). The solid particles, with specific gravities of up to about 3.15 (for Portland cement) settle under gravity leaving a top surface layer that has a lower cement content, and hence higher water/cement (w/c) ratio, than the material below. This weaker layer is known as laitance (see sub-section 4.3.1). The extent to which bleed and settlement will occur is determined both by the particle size distribution and w/c ratio which, in combination, determine the degree of cohesion of the grout, and by the setting time, which determines the period during which bleed and settlement can occur.

With time, the degree of fluidity progressively reduces, i.e. the viscosity increases. This is principally due to early hydration reactions and within hours the cement paste no longer exhibits fluid behaviour. If significant, loss of moisture will also affect the stiffening time. Setting (sub-section 5.4) is progressive and definitions are provided for initial set and final set as the resistance to penetration using a standard test. Typically, setting occurs within hours of mixing and is affected by the cement type, the temperature and any chemical admixtures that have been used.

The hydration reaction (sub-section 5.6) of cement with water is exothermic and the rate of heat evolution is most rapid within the first few days. While the rate of heat generation exceeds the rate of heat dissipation (determined by the geometry of the element and its thermal properties) the temperature will rise. As the rate of heat evolution progressively reduces, the rate of heat dissipation becomes dominant and the bulk temperature will then begin to drop.

As hydration proceeds the compressive strength (sub-section 6.2) and stiffness (modulus of elasticity – sub-section 6.3) of the grout increases. The ultimate strength is determined primarily by the w/c ratio, with lower strength at higher w/c ratio. The type of cement will also affect the ultimate strength and the rate at which strength development occurs.

Any temperature rise (sub-section 5.6) during hydration will cause the rate of hydration and hence the rate of development of the mechanical properties to accelerate but may also lead to a change in the ultimate strength as a result of a change in the nature of the hydration products formed at different temperatures.

The internal moisture content of the cement paste will also change as free water is used up in the hydration reaction. At the same time moisture may be lost to the environment through drying.
Changes in moisture content will lead to dimensional changes (sub-section 5.8). Autogenous shrinkage (sub-section 5.8.2) occurs as a result of self-dessication as hydration proceeds. Drying shrinkage (sub-section 5.8.3) occurs when water is lost to the environment and if wetted, swelling may occur. If the dimensional changes are restrained, e.g. by waste packages in a backfill, then stresses are developed. Restraint to contraction leads to tensile stresses which, if exceeding the tensile strength (sub-section 4.3.4(b)) of the grout, will cause cracking.

Under sustained loading cement systems continue to deform, or creep (sub-section 6.4), beyond the initial elastic deformation which occurs when the load is first applied. When the load is strain induced, the stresses developed initially are proportional to the modulus of elasticity of the grout, but creep will lead to a relaxation in these stresses. Creep continues at a reducing rate over many years and is increased at elevated temperature.

Deformation is also caused by changes in temperature. The coefficient of thermal expansion (sub-section 5.8.1) of the grout will determine the magnitude of thermal strain associated with a particular change in temperature. This property is influenced by the moisture content of the grout. The change in the temperature will itself be determined by the thermal properties of the materials, in particular the specific heat capacity (sub-section 4.3.5(a)), the density and the thermal conductivity (sub-section 4.3.5(b)).

The properties of cement systems continue to develop over weeks, months and sometimes years. For a given cement system, a slower rate of hydration will, as a general rule, lead to higher ultimate compressive strength (sub-section 6.2) and vice versa. This is because more stable and dense hydration products are achieved under these conditions.

The mass transfer properties (sub-section 4.3.6) are in part related to the mechanical properties of cementitious systems as both are related to the porosity and pore connectivity. Hence systems with low w/c ratio will tend to have high strength, lower porosity and low permeability (sub-section 4.3.6(a)). However, the mass transfer properties are also determined by cement chemistry and will evolve through interactions with air (i.e. carbonation due to reaction with carbon dioxide) and water (i.e. through reactions with groundwater mineral components – see section 9).

The inherent variability of cementitious materials, the fact that they may be combined in different proportions, and the added variability that is introduced by the use of inert fillers, makes it difficult to predict with a high degree of reliability the properties that will be achieved for any particular combination. Furthermore, there have been no systematic studies to compare the physical performance or the mass transfer properties of the variety of cements used in GDF applications. Generally the cement has been selected for its chemical characteristics (pH, binding, etc) and the proportions of the components of the mixture have then been adjusted to give the required characteristics for both the fresh and the hardened material. An inherent part of the development of any cementitious combination has therefore been trial mixes to ensure that the various requirements for the fresh and hardened material are met. Such an approach was adopted for the NRVB [12].

### 4.2 Cement types

Numerous cementitious materials are proposed for use in GDF designs. These include a range of Portland cements (sub-section 3.1) and their combination with SCMs such as PFA, BFS and silica fume (sub-section 3.4). In addition, calcium aluminate cement (CAC, formerly high alumina cement) has been used in the development of low-alkali cement for backfill. Ultrafine cement is also used in grout required to fill narrow cracks.

When comparing the properties of cement types it is important that the basis of comparison is clear. For example, if comparisons are made using cement pastes at the same w/c ratio, the differing particle size distributions may lead to mixes at the same w/c ratio having considerably different rheological properties. If comparison is made on the basis of mixes with the same flow characteristics it is very likely that the w/c ratios will be different.
When dealing with mortar and concrete the issue of comparison becomes more complex as the sand or aggregate also has a significant impact on both the fluid and the hardened properties.

In construction, concrete is classified by its strength class, the compressive strength being the most important criteria for structural integrity. The strength class is defined by tests on a standard cube or (2:1) cylinder at an age of 28 days after curing in water at constant temperature (20°C in the UK). In addition, the workability is specified to ensure that the concrete may be properly placed and compacted. When different cements are used this inevitably leads, therefore, to changes in the mix proportions.

4.3 Typical properties

4.3.1 Flow properties

Grouts, mortars and concrete may be designed with a wide range of flow properties from very low viscosity, high flow materials (virtually self levelling) to very dry materials that require a high degree of mechanical compaction. The higher the w/c ratio, i.e. the lower the volume of solids, the higher the flow achieved. The flow properties are also determined by the physical characteristics of the cement, i.e. the particle size distribution and the particle shape.

The majority of cement-bases grouts and concretes are non-Newtonian in their flow behaviour. That is, they have a yield stress which must be exceeded before the material will flow and thereafter the viscosity of the mix may change with the rate of shear applied. This is referred to as Bingham flow (see sub-section 5.3.1).

Increasing the w/c ratio for a given cement type will tend to increase the extent to which settlement and bleed occur. As the cement particles have specific gravities that are much higher than water, some bleed is inevitable. The magnitude of bleed and settlement that occurs is a function of the particle size and size distribution and the setting time. Particle systems that have a continuous grading tend to exhibit less bleed than systems which have single sized particles or gaps in the grading. In addition, the rate at which setting occurs will determine the period over which bleed and settlement can occur. The magnitude of bleed may vary from a fraction of a percent to several percent, measured as the head of bleed water above a column of grout. The extent of bleed may be limited by adopting a low water to solids (w/s) ratio and by ensuring that the particle size distribution has a continuous grading and high surface area.

Bleed is not necessarily a problem. In fact, in general construction, some bleed is advantageous particularly in a drying environment. Provided the rate of bleed exceeds the rate of evaporation, plastic shrinkage cracking of the surface is avoided. However, when bleed is high, this can lead to a weak surface layer (laitance). Where a good bond is required, the laitance may have to be removed before subsequent layers are cast.

In the context of the GDF, when placing grout in horizontal spaces, e.g. between two waste packages stacked one above the other, the effect of bleed may be to leave a gap at the top of the grout where bleed water has collected and then been re-absorbed into the grout after setting. Differential settlement (which occurs, for example, where the vertical thickness changes) may also lead to cracking when more settlement occurs in the deeper section.

4.3.2 Workability loss and setting time

To transport and place the grout, the flow properties must be maintained and the setting time delayed until the grout is in place. Typically cement paste takes a few hours to set and this varies with the cement type and temperature. At elevated temperatures stiffening and setting times are reduced and vice versa. The chemistry of the cement is more influential, however, than the physical properties of the cement in determining the rate at which the fluidity is lost. Although the physical properties of the powder will determine the amount of water needed to provide adequate flow properties, the subsequent rate at which workability is lost is primarily due to the cement hydration reaction.
Chemical admixtures may also be used to delay the set [55]. Their use is common in construction in hot climates and the setting time may be delayed by several hours [55].

### 4.3.3 Heat of hydration

The hydration reaction of cement is exothermic, generating heat; typically, OPC generates 300–400 kJ kg\(^{-1}\) during hydration. The type of cement has a significant effect on both the rate of hydration and the ultimate heat generated (see sub-section 5.6).

In the early stages of hydration the rate of heat generation is high and, depending upon the element size, this may exceed the rate at which heat is dissipated, resulting in a rise in temperature. In typical structural concrete sections, walls, beams, slabs etc, which commonly have cement contents of 300–400 kg m\(^{-3}\), the temperature rise may be as high as 50°C depending on the cement content and type and on the geometry of the element as this affects the rate of heat loss. Grouts have much higher cement content than concrete (without the benefit of dilution by inert sand and aggregate). A grout comprising OPC and water only (with w/c = 0.4) will have a cement content of about 1400 kg m\(^{-3}\) (i.e. about 4 times that of concrete) and the temperature rise may be potentially much higher, reaching 100°C or more.

The effect of the early temperature rise is both to accelerate the rate of strength development and, for some cements, to impair the rate of strength development in the longer term, leading to a lower ultimate strength compared with that achieved by curing at lower temperature.

In addition to the effect on the strength development, thermal stresses in the finished structure may also result in cracking. Thermal stresses arise from differential thermal expansion and contraction in different parts of an element or from the thermal deformation of the element being subject to external restraint, e.g. by more rigid waste packages.

### 4.3.4 Mechanical properties

The mechanical properties affect the performance of grout, mortar and concrete in relation to structural integrity and the response to imposed loads and restrained deformations.

**(a) Compressive strength**

The compressive strength, \(f_c\), of grout, mortar and concrete is generally defined by the 28-day value achieved under ideal curing conditions, i.e. stored in water at 20°C. The value achieved is therefore the potential strength, as these ideal curing conditions are rarely achieved in practice. Furthermore, the small specimens used for testing will often have been prepared under ideal laboratory conditions enabling complete compaction, while in a structure full compaction may not be achieved. However, strength will continue to develop over periods longer than 28 days.

BS EN 13791 [80] requires that \textit{in-situ} strength should be at least 85% of the strength of standard specimens. However, a study by the Concrete Society [81] found that 85% may not also be applicable. For elements containing CEM 1 subjected to a high early-age peak temperature (in excess of ~60°C), the \textit{in-situ} strength of core samples was found to be only 65% of the cube strength. Nevertheless, continued strength development resulted in \textit{in-situ} strength achieving 85% of 18-day cube strength after one year.

Grouts, mortars and concrete used in construction may be designed to achieve a wide range of compressive strength from a few MPa to values in excess of 100 MPa. The principal determinant of compressive strength is the w/c ratio. Higher strength is achieved with low w/c ratio. To achieve high strength, the w/c ratio may be in the range of 0.3–0.4. The low strength NRVB, requiring a maximum strength at any age of 10 MPa (see Box 1, sub-section 2.1.1), requires a w/c of 1.37\(^4\).

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\(^4\) The NRVB specification requires a maximum strength at any age of 10 MPa to enable the possible retrieval of waste packages after backfilling. Alternative backfilling strategies that did not require retrievability might not require a low strength material (c.f. the Swiss M1 and M2 mortars, which have lower w/c and higher strength – see Table 3 and section 5.1).
The cement type will influence both the rate of development of compressive strength and the ultimate strength achieved. However, recognising this, the w/c ratio and cement content may be adjusted to achieve a wide range of compressive strength for any particular cement combination.

Other mechanical properties are related to the compressive strength, although not always in direct proportion.

(b) Tensile strength
Cement paste is weak in tension. The direct tensile strength, \( f_t \), is generally in the order of 5-7% of the compressive strength [82]. Hence values of tensile strength may be less than 1 MPa increasing for low w/c grouts to values in excess of 7 MPa.

When subject to tension, the risk of cracking is therefore high. It is for this reason that structural concrete uses steel reinforcement. The steel does not prevent cracking, but will support the tensile stress when a crack occurs and limit the crack width.

(c) Flexural strength
The flexural strength, \( f_b \), measured in bending (also referred to as the modulus of rupture) is generally in the range from 10-15% of the compressive strength [82]. Hence values of tensile strength may be less than 1 MPa increasing for low w/c grouts to values in excess of 15 MPa.

(d) Modulus of elasticity
The modulus of elasticity, \( E_c \), defines the extent to which a material deforms elastically under load. Stronger concrete or grout tends to have a higher modulus of elasticity and for a given load will exhibit less deformation. The relationship between compressive strength and modulus of elasticity differs however, for grout, mortar and concrete. For grout, the modulus of elasticity may be approximately proportional to the compressive strength. However, for mortar and concrete, the aggregate, generally being much stiffer than the cement paste, begins to dominate the modulus of elasticity, while the strength is limited by the cement paste matrix. In this case, the modulus of elasticity is less sensitive to changes in compressive strength, \( f_c \), and is often represented by a relationship of the form \( E_c = a f_c^b \), where \( b \) is in the range 0.3 to 0.5 [82]. The relationships between the modulus of elasticity and compressive strength, and the effects of cement type, are discussed in more detail in sub-section 6.3.

(e) Creep
Creep is the deformation of a material under a sustained load. In cement-based materials creep will continue for many years but at a progressively reducing rate. As creep occurs to a much greater extent in cement paste than in sand or aggregate, the creep of cement paste is much greater than the creep of mortar or concrete [83].

Creep is beneficial in relieving stresses that are strain-induced [84].

(f) Shrinkage and swelling
Large shrinkage deformations may occur if grout is allowed to dry out. Such shrinkage of bulk material, if restrained, can lead to tensile strains within the grout that may lead to cracking. If the grout is subsequently re-wetted, swelling will occur reducing tensile strain.

4.3.5 Thermal properties
Temperature changes caused by either heat of hydration or within the waste will be determined by the thermal properties of the cementitious material.

(a) Specific heat capacity
In combination with the density, the specific heat capacity determines the temperature change associated with a gain or loss of heat. Materials with high specific heat capacity exhibit a lower
change in temperature for a given heat gain or loss. The specific heat capacity of the mix is determined by the specific heat capacities of the individual components, the extent of hydration and the proportion of pore water. Because the specific heat capacity of free water is much higher than that of water used in hydration, the temperature rise during hydration will be lower for higher values of w/c ratio.

(b) Thermal conductivity
Thermal conductivity defines the rate at which heat flows through a material. In concrete, the thermal conductivity is determined primarily by the thermal properties of the sand and aggregate type that, in combination, comprise about 70% of the volume.

(c) Coefficient of thermal expansion
The coefficient of thermal expansion (CTE) defines the deformation associated with a unit change in temperature and is usually expressed in units of microstrain per °C (με °C⁻¹). In concrete, the CTE is determined primarily by the sand and aggregate type that, in combination, comprise about 70% of the volume. The CTE of aggregate varies, but is generally lower than that of cement paste. Hence concrete and mortar generally exhibit lower values of CTE than cement paste.

4.3.6 Mass transport properties
(a) Water permeability
The permeability is a measure of the ease with which fluids can flow through a porous medium. The permeability to water is a key property for a number of applications of cements in a GDF. Seals and grouts require low permeability to restrict water flow whereas backfills for ILW concepts require high permeability to enable the development of homogeneous conditions and to allow gas to escape. For a particular cementitious system, the permeability to water will be determined primarily by the w/c ratio. Low w/c ratio will lead to low permeability.

(b) Gas permeability
Gas will be generated in a GDF for ILW from the corrosion of metal wastes and containers and from the degradation of organic materials [85]. The gas permeability of the GDF backfill must be sufficiently high to permit gas release. The gas permeability is also related to the w/c ratio, but the moisture content is also a critical factor. In a fully saturated system the gas permeability will be limited by the rate at which the water may be driven through the system and by the gas diffusion through the porewater.

(c) Porosity
The porosity is the fraction of the volume of a solid that is occupied by void space. Three types of matrix pores can be distinguished [86]:

- isolated pores that are not connected to other pores and so do not contribute to mass transfer processes within a solid;
- transport pores through which fluids (water, gas, NAPLs) may flow and which determine the permeability of a porous solid; and;
- dead-end pores that when saturated with water are accessible to solutes only by diffusion and into which (or out of which) net diffusive transport only occurs under transient conditions.

Together, the transport porosity and the dead-end porosity comprise the connected porosity.

When the porous medium is saturated with water, the solute-accessible porosity will comprise part or all of the connected porosity. Ion exclusion, particularly of anions, from part of the water-connected pore space may occur when pore dimensions are similar to the length scales of electrostatic interactions in aqueous solutions, and this is observed in cementitious materials due to fine-scale porosity that is present (see sub-section 8.1.3). Ion exclusion is particularly important in low ionic strength waters, but is less significant at higher ionic strengths due to the shorter range of electrostatic interactions [87].
The solute accessible porosity of a cement backfill is important in providing access to the internal surface area of the solid to which solutes can sorb.

**(d) Diffusion coefficient**

The intrinsic diffusion coefficient is a measure of the diffusive flux of a solute through a porous medium under stagnant conditions compared to that through an equivalent volume of water. The diffusion coefficient is influenced both by the accessible transport porosity and by the tortuosity of the pore network. For a partially-saturated cement, the diffusion coefficient will depend on the moisture content. In general, higher diffusion coefficients are associated with higher w/c ratios and, in this case, a higher degree of saturation through which the species can migrate.

### 4.3.7 The relationship between cement type and the fresh and hardened properties of grout, mortar and concrete

Even with detailed knowledge of the cement chemistry and the mix proportions it is difficult to predict the mechanical performance of the resulting grout, mortar or concrete with a high degree of reliability. For this reason, empirical relationships exist to help to aid the process of concrete mix design [88]. For structural concrete, the starting point is the w/c ratio, which is the dominant factor influencing the compressive strength; relationships exist between w/c ratio and strength for various cements and combinations. Having established the w/c ratio, the water content (litres per cubic metre of concrete) required to provide an adequate level of workability is determined, again based on empirical data for different types of aggregate and sand. With these two parameters, the cement content (kg m\(^{-3}\)) may then be estimated. With the water content and the cement content established the amount of sand and aggregate required to provide each cubic metre of concrete can be determined.

The constituent materials, while meeting the minimum requirements of the appropriate British or European standards will, nevertheless, vary from source to source, and be subject to variability within a source over time. Hence, even with a long history of the use of concrete and empirical guidance on mix design, trials still form an accepted part of the mix design process. With regard to the physical properties of the fresh and hardened concrete, the approach adopted in this report has therefore been to present available information and to identify the way in which specific properties may be influenced by the range of cements available.
5 Emplacement of cement materials as backfill

5.1 Requirements

The emplacement behaviour of cement backfills is not only critical to the backfilling strategy but also has implications for backfill performance in the longer term. As indicated in Box 1 in section 2, the flow characteristics must be such that the backfill can be pumped over long distances (possibly 250 metres for the NRVB specification) and must be free flowing and close to self levelling within a GDF. When in place, the backfill should exhibit limited bleed and settlement to minimise the formation of plastic cracks and potential leak paths, e.g. beneath packages. It must also have dimensional stability to minimise the extent of cracking in its hardened state and may also be required (Box 2) to avoid achieving excessive strength to enable retrieval of the embedded waste packages if required in the future.

In conventional concrete it is often necessary to achieve both high strength and high flow, with conflicting requirements in relation to the w/c ratio. In general, high flow requires a high water content, while a high water content (in relation to cement) also leads to lower strength. To overcome this incompatibility it is common to use chemical additives in concrete to enhance the workability and to reduce the water demand, thus enabling high flow, high strength mixes.

The NRVB, however, has a specific requirement for low strength to enable future retrieval of the waste packages, hence a high water content is consistent with both the workability and strength requirements. The specific requirement is that the compressive strength should not exceed 10 MPa within 50 years [12]. For the NRVB, this led to the use of a mix with a very high w/c ratio which, on its own would have resulted in an unstable mix with excessively high bleed. To stabilise the mix and achieve less than 2% bleed, both hydrated lime and limestone flour were added. The former also provided long term chemical buffering. The constituents of NRVB are given in Table 2 (sub-section 2.1).

A similar requirement for low strength was adopted for the backfill composition for the horizontally-accessed annular void space around the Belgian HLW supercontainer (Figure 4), developed as part of the ESDRED project [89]. A dry pre-mix backfill was developed by BASF Construction Chemicals, Belgium, which requires only the addition of water at w/s = 1.30 to 1.35, i.e. similar to the NRVB. This backfill comprised cement clinker, calcium carbonate powder (limestone flour), fine sand and a limited addition of a polycarboxylate ether-based superplasticiser. Specific proportions of the solid materials and admixture were not reported however.

The Swiss GDF concept for ILW/LLW located in Opalinus Clay requires two mortar backfill materials [16]. Mortar M2 is described as a low viscosity material which is placed between and around the waste packages. Mortar M1, described as high viscosity, is designed to fill the space between the encapsulated waste packages and a shotcrete lining to the vault. M1 has a low w/c of 0.40 and appears to rely on not being compacted to achieve a relatively low strength of 5.4 MPa at 7 days. With full compaction the strength is about 35 MPa.

M2 is reported to have a mean strength of 15.5 MPa in its non-compacted state.

Aspects of backfill development and testing programmes concerned with the engineering performance of candidate backfill materials are reviewed in this section. Topics covered include:

- backfilling strategy;
- flow properties;
- setting time;
- plastic settlement and bleed;
- heat of hydration;
- early strength development; and
- early dimensional stability.
This section draws heavily on work in the UK concerned with the engineering performance of the NRVB, because this is the backfill material for which most information is readily available in the open literature. The principal sources of information are the NRVB Current Status Report to 1994 [12] and references therein. More recent work on the cracking of NRVB [90-92] is also discussed.

The discussion of the emplacement behaviour of specific backfills is placed in the wider context of the behaviour of different cement types, including blended Portland cements with SCMs. Blended Portland cements are not currently under consideration as cementitious backfill formulations, but are being used in the development of low-pH grouts and concretes for structural and sealing applications in disposal concepts for HLW/SF that would include a bentonite buffer (see section 13).

5.2 Backfilling strategy

5.2.1 Assumptions

Various applications for cement-based materials as backfill have been outlined in sub-section 2.1. A logistical study for the backfilling, sealing and closure of a cement based GDF for UK ILW/LLW has outlined an approach to backfilling [93]. However, at the current stage of concept development, the strategy and procedures have yet to be determined in detail. Therefore, in studies concerned with the properties of the backfill post-closure [e.g. 92] numerous assumptions have had to be made about the backfilling strategy and the filling procedure. Assumptions need to be made in the following areas:

i) the vault dimensions and operating environment;

ii) the waste package design and stacking arrangements (e.g. Figure 10);

iii) the backfilling strategy;

iv) heat generated by the waste packages; and

v) the properties of the backfill.

Items i), ii) and iii) determine the rate at which the backfill flows into the vault and how it fills the spaces between the waste packages.

Items iv) and v) determine how the properties of the backfill change during and after the filling process.

The set of assumptions adopted in recent studies concerned with backfill cracking [92] are given in Table 12.

<table>
<thead>
<tr>
<th>Item</th>
<th>Details</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAULT GEOMETRY</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cross section</td>
<td>Base case</td>
<td>16 x 16m</td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>20 x 20m</td>
</tr>
<tr>
<td></td>
<td>Minimum</td>
<td>5 x 5m</td>
</tr>
<tr>
<td>Length</td>
<td></td>
<td>300m</td>
</tr>
</tbody>
</table>

Table 12 Summary of assumptions used in a recent study of backfill cracking and its effects on groundwater flow and chemistry in the near field [92]
<table>
<thead>
<tr>
<th>Item</th>
<th>Details</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>WASTE PACKAGES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500 litre drums, 0.8 mm dia x</td>
<td>1.2 m high 4 per stillage.</td>
<td>Stillages 1.665 x 1.665 x 1.245m high</td>
</tr>
<tr>
<td>3m³ boxes 1.72 x 1.72 x 1.225m</td>
<td>high</td>
<td>SL box 1.665 x 1.665 x 1.245m high will also be used</td>
</tr>
<tr>
<td>3m³ drums 1.72 m dia x 1.225m</td>
<td>high</td>
<td></td>
</tr>
<tr>
<td>MBGWS boxes 1.85 x 1.85 x 1.37m</td>
<td>high</td>
<td></td>
</tr>
<tr>
<td>Contents</td>
<td>Variable</td>
<td></td>
</tr>
<tr>
<td>Stacking</td>
<td>Each column will comprise a single type of package.</td>
<td>Consider staggering rows longitudinally (see Figure 10)</td>
</tr>
<tr>
<td>Spacing</td>
<td>0.23m between stillages</td>
<td>The capping layer will be 500mm</td>
</tr>
<tr>
<td></td>
<td>0.35m between 3m³ boxes and drums</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.29m between stillages and boxes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Approx. 1m between packages and side wall</td>
<td></td>
</tr>
<tr>
<td>VAULT ENVIRONMENT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>Variable 25-35°C</td>
<td>To be considered in relation to the rate of stiffening of the fluid</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>Variable 70-85%</td>
<td>NRVB and subsequent property development</td>
</tr>
<tr>
<td>Air velocity</td>
<td>Variable Up to 10 km h⁻¹</td>
<td></td>
</tr>
<tr>
<td>BACKFILLING STRATEGY</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start of backfilling</td>
<td>After 50 years vault operation and a further 50 years care and</td>
<td>Subsequently updated to a period of up to 300-400 years operation before</td>
</tr>
<tr>
<td></td>
<td>maintenance</td>
<td>backfilling</td>
</tr>
<tr>
<td>Filling procedure</td>
<td>Full width layers cast in sections daily until one layer complete,</td>
<td>Layer thicknesses to be investigated. Consider staggering horizontal</td>
</tr>
<tr>
<td></td>
<td>then layers repeated until full height complete.</td>
<td>joints</td>
</tr>
<tr>
<td>Volume of backfill</td>
<td>Ratio of volume of waste to volume of backfill = 1:1</td>
<td></td>
</tr>
<tr>
<td>Rate of filling</td>
<td>20 m³ hr⁻¹</td>
<td></td>
</tr>
<tr>
<td>Transportation</td>
<td>By pump from backfill gallery</td>
<td>Distance may be 250m and take up to 2 hours from mixing</td>
</tr>
<tr>
<td>Heat generation from</td>
<td>It is assumed that the majority of heat will arise from the backfill and</td>
<td></td>
</tr>
<tr>
<td>waste packages</td>
<td>that the packages will have little effect on the peak temperature</td>
<td></td>
</tr>
<tr>
<td>Item</td>
<td>Details</td>
<td>Comments</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>----------------------------------------------</td>
<td>---------------------------------------------------</td>
</tr>
<tr>
<td>NRVB PROPERTIES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleed /Settlement</td>
<td>1.7%</td>
<td></td>
</tr>
<tr>
<td>Setting time</td>
<td>4 hours at 40°C</td>
<td>Will increase at lower temperature</td>
</tr>
<tr>
<td>Heat of hydration</td>
<td>46°C rise under adiabatic conditions</td>
<td>Actual temperature rise will depend on placing rate, geometry and heat loss to air and waste packages</td>
</tr>
<tr>
<td>Density</td>
<td>Wet -1730 kg m⁻³</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oven dried – 1095 kg m⁻³</td>
<td></td>
</tr>
<tr>
<td>Compressive strength</td>
<td>7 days – 4.95 MPa</td>
<td>Cured at 40°C</td>
</tr>
<tr>
<td></td>
<td>28 days – 5.95 MPa</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90 days – 6.26 MPa</td>
<td></td>
</tr>
<tr>
<td>Gas permeability</td>
<td>Dry - 2 x 10⁻¹⁵ m²</td>
<td>It is assumed that in the saturated state, flow is determined by the water permeability.</td>
</tr>
<tr>
<td></td>
<td>Saturated – 5 x 10⁻¹⁷ m²</td>
<td></td>
</tr>
<tr>
<td>Water permeability</td>
<td>1 x 10⁻¹⁸ m²</td>
<td></td>
</tr>
</tbody>
</table>

Figure 10 Staggering of stacks to minimise propagation of cracks
5.2.2 Reference case

For the reference case adopted in the recent study of backfill cracking [92], backfilling was assumed to be in layers. This would involve placing backfill over the full width of the vault to a predetermined length and thickness achievable in 24 hours. At a proposed production rate of 20m$^3$ h$^{-1}$, the relationship between the selected length of a 24 hour pour and the layer height is shown in Figure 11 for a number of vault cross sections, e.g. 5m x 5m. The relationship between length and rate of filling in mm h$^{-1}$ is shown in Figure 12. The ratio of backfill to waste package volume was assumed to be one to one [92].

![Figure 11](image1.png)

**Figure 11** The relationship between the selected length of a 24-hour pour and the layer height for a number of vault cross sections, e.g. 5m x 5m

![Figure 12](image2.png)

**Figure 12** The relationship between the selected length of a 24-hour pour and the rate of filling (mm h$^{-1}$) for a number of vault cross sections, e.g. 5m x 5m

An assessment of three examples is given in Table 13 for bay lengths of 50m, 100m and 150m with layer thicknesses of 1200mm, 600mm and 400mm respectively [92].
Table 13  Examples of different pour sizes (assumes 300m long vault, 25°C, 20m³ h⁻¹ production rate and 2 h transportation from mixing to placing in the vault)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Examples</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Length (m)</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Depth (mm)</td>
<td>1200</td>
<td>600</td>
</tr>
<tr>
<td>Rate of filling (mm h⁻¹)</td>
<td>12.5</td>
<td>25</td>
</tr>
<tr>
<td>Fluid head (mm)</td>
<td>364</td>
<td>182</td>
</tr>
<tr>
<td>Potential settlement (mm)</td>
<td>8.74</td>
<td>5.3</td>
</tr>
<tr>
<td>Period between layers (h)</td>
<td>120</td>
<td>48</td>
</tr>
<tr>
<td>Rate of bleed (kg m⁻² h⁻¹)</td>
<td>1.46</td>
<td>0.73</td>
</tr>
<tr>
<td>Risk of plastic cracking</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Temperature rise in single layer (°C)</td>
<td>39</td>
<td>30</td>
</tr>
<tr>
<td>Temperature rise after multiple layers (°C)</td>
<td>39</td>
<td>30</td>
</tr>
<tr>
<td>Risk of early-age thermal cracking</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

Based on the cracking analysis in reference 92, the preferred approach would be to cast thin large area layers up to the penultimate layer, with the final layer cast as thicker, smaller area pours.

5.3 Flow properties
5.3.1 Rheology of solid suspensions

The flow properties of grout are critical for the transportation and placing of the materials. Pumping may be required over long distances (250m or more for the NRVB) and the grout may be required to flow unaided to fill relatively small spaces with no additional agitation. At the estimated rate of filling for the NRVB, the material may not be deposited in the vault until two hours after mixing, and will still be required to be free flowing.

The fluid behaviour of grout, mortar or concrete may be defined by the general equation [94]:

\[ \tau = \tau_o + a \gamma^n \]  

where \( \tau \) is the rate of shear stress; \( \tau_o \) is the stress required to induce strain and hence initiate flow (i.e. the intercept on the shear stress axis of the stress-strain relationship); \( \gamma \) is the rate of shear strain; and \( a \) and \( n \) are constants. Most cement pastes may be represented by the simplest form of
equation 1 in which \( n = 1, \ \alpha = \mu, \) the plastic viscosity and \( \tau_o = \tau_y, \) the yield stress. This is defined as Bingham behaviour [94], (Figure 13) where:

\[
\tau = \tau_y + \mu \dot{\gamma}
\]  

(2)

**Figure 13 Bingham flow behaviour**

The relative flow properties of different cementing materials may be assessed therefore by comparing the yield stress and the plastic viscosity.

These properties are generally measured using a rotational viscometer, and provide a clear description of the fluid behaviour. This method is very useful at the development stage of a new cementitious material. However, for practical purposes simpler tests are commonly used [95] including:

- flow cones – measure the time for grout to flow from the aperture in a cone of defined dimensions;
- flow troughs – measure the distance over which grout travels along a trough when released from a wide mouthed funnel located at one end;
- penetrability meters – measure the aperture size through which the grout will flow under pressure;
- immersion test – measures the time for a torpedo shaped plunger to fall through a column of grout;
- consistometer – measures the torque on a stirring frame when the grout is rotated.

These tests are empirical but are useful in controlling consistency during production.

Numerous factors have been found to influence the flow characteristics of cement paste, some physical and some chemical. The most significant is the w/s ratio by volume. For example, the effect of increasing the w/c ratio for Portland cement pastes [96] is shown in Figure 14. Both the yield stress (the intercept) and the viscosity (the gradient of the yield stress/strain rate relationship) are significantly reduced by increasing the w/c ratio.

In mortar and concrete, a similar relationship applies, with the plastic viscosity \((\mu)\) having been shown to be related to the relative solids concentration, this being the ratio of the actual solids concentration in the mix \((\Phi)\) to the maximum achievable solids concentration when fully compacted.
A reducing solids concentration represents greater separation of the solid particles and a higher water content. The relationship between $\mu$ and $\Phi/\Phi^*$ is defined by the expression [97]:

$$
\mu = \exp \left[ 26.75 \left( \frac{\Phi}{\Phi^*} - 0.7448 \right) \right]
$$

(3)

Figure 14 Bingham flow curves for OPC paste at different w/c ratios

Results from tests on low-pH grouts by Posiva are presented in Figure 15 [98] showing the viscosity at various w/c ratios. The results are compared with values of viscosity for OPC paste derived from the results in Figure 14. The viscosity is presented on a logarithmic scale, indicating the very significant effect of w/s ratio.

Figure 15 The relationship between viscosity and water to solids ratio for low-pH grouts with OPC/silica fume=0.3 compared to OPC

It should be noted that in construction, the mix constituents are presented as weight proportions, as this is how they are measured in practice. However, cementing materials have varying specific gravity from about 2.2 for silica fume to 3.15 for Portland cement [99]. The same w/c ratio by weight therefore leads to different solids concentrations by volume and it is the latter which is the
critical factor. When comparing systems using different cements or combinations this should therefore be taken into account.

The NRVB has a w/c ratio of 1.37 but a w/s ratio of 0.55 (Table 2). All of the materials used in the NRVB have a fineness similar to that of OPC and hence the w/s ratio should be used when assessing the rheology. Limestone and hydrated lime are less dense than OPC and hence for a given weight will occupy a larger volume. Comparing the NRVB with an OPC grout on the basis of w/s ratio by volume, the equivalent w/OPC ratio for the NRVB is 0.48. Assuming that the relationship between w/c and viscosity for OPC applies, the viscosity of the NRVB is estimated to be about 50 mPa s.

The development of the NRVB used Marsh flow cone measurements to establish a sufficiently fluid mix [12]. Empirical relationships between results from the flow cone and viscosity have been reported [100] and an example is shown in Figure 16 for OPC grout. With values of 12 seconds immediately after mixing and 14 seconds after one hour [12], the plastic viscosity of NRVB would be expected to be about 200 mPa s (based on Figure 16). This is higher than the figure of 50 mPa s estimated using the relationship with w/s ratio above, but it is clear from Figure 15 that at the value of effective w/OPC ratio of 0.48, a large change in viscosity can occur for a relatively small change in w/c ratio and this may explain the discrepancy between the two approaches.

![Graph showing relationship between flow time and plastic viscosity for OPC grout](image)

**Figure 16** The relationship between flow time (from the Marsh cone) and plastic viscosity for OPC grout [100]

During the initial development of the Posiva low-pH injection grouts for large fractures [101], there was a similar requirement for a viscosity of \( \leq 0.05 \text{ Pa s} \) (50 mPa s) at 60 minutes, although the method of measurement later changed to the Marsh cone and no specific limits were set.

With regard to fluidity, the Belgian supercontainer backfill studied under the ESDRED project requires “sufficient fluidity to be pumpable over > 30 m and remain [SIC] sufficient fluidity after pumping to allow mixing for \( \geq 5 \) h (operational objectives for the full-scale mockup test)”. Unfortunately no details have been provided either of the specific mix details or of the method of testing used to either develop or control the grout during large scale tests [89].

While the simplest way to increase fluidity is to reduce the solids content (i.e. increase the w/c ratio) this also leads to a lower strength and an increase in the bleed and settlement. Low strength is consistent with the requirements for the NRVB but there is also a requirement to limit bleed (<2%) and this increases with w/c ratio. Reference 12 describes how the mix development process for the NRVB addressed these conflicting requirements.

Factors other than w/s ratio will also affect rheological properties, including the particle size distribution as discussed in sub-section 4.3.1.
5.3.2 Effect of cement composition

(a) Effect of OPC chemistry

Typical relationships between the rate of shear stress, \(\tau\), and the rate of shear strain, \(\gamma\), are shown in Figure 17 (based on data presented by Kucharska [102]), illustrating the effect of cement chemistry on the range of flow characteristics at a single w/c ratio of 0.4. In reference 102, cements were tested with a range of C_3A contents and the results showed a tendency for a higher viscosity as C_3A increased. The results also showed a tendency for higher viscosity in cements with higher C_3S/C_2S ratios. This is consistent with the higher rate of early hydration associated particularly with C_3A and also with C_3S.

Other studies [103, 104] showed a similar effect of C_3A content and of the effects of sodium equivalent alkali content, (Na_2O)_e, and the level of sulphate. For example, the shear stress was reported to more than double with an increase in (Na_2O)_e from 0.3% to 1%. Providing the cement offers the appropriate chemistry for buffering, selecting low-alkali cement with a low C_3A will therefore offer benefits of reduced viscosity and increased fluidity for the NRVB.

![Figure 17](image_url)  
Figure 17 Typical flow behaviour for cement paste using Portland cement with w/c = 0.4 (solids by volume = 44%), based on data presented by Kucharska [102], showing the effect of C_3A content on shear stress

(b) Effect of PFA

The addition of PFA generally improves the workability of cementitious sytems, with the finer material being most effective [99]. PFA particles less than 50 \(\mu\)m are generally spherical while the larger particles tend to be more irregular. The smaller particles therefore optimize packing as well as acting as ‘ball-bearings’ to improve workability. This can lead to a reduction in water demand when using PFA. For this reason the British Standard for PFA limits the percentage retained on a 45 \(\mu\)m sieve to 12%.

A similar effect of fineness was reported following tests on cement pastes in which the finer of two PFAs (surface area 309 m\(^2\) kg\(^{-1}\) and 332 m\(^2\) kg\(^{-1}\)) was demonstrated to have ‘a much stronger liquefying effect’ when tested in a rotary viscometer [105]. Tests on water reductions in mortars also demonstrated improved rheological performance with increasing fineness and percentage addition of PFA [106]. With a mean particle size of 6\(\mu\)m the water reduction was in excess of 10%, reducing to about 7% and 4% for mean particle sizes of 9 \(\mu\)m and 27 \(\mu\)m respectively.
(c) Effect of BFS

Particles of BFS are angular and glassy but the particle size distribution and fineness is similar to that of OPC. In concrete, a small reduction in water demand is achieved with BFS or, at the same water content, the workability is increased [107].

As with all cements the fineness may be varied by the grinding process and often BFS may be finer than typical OPC. Using a rotating viscometer to assess rheological behaviour of grouts, it has been reported that increasing the BFS content up to 40% led to a reduction in both the shear stress and the plastic viscosity [108]. In this case the BFS was reported to be much finer than the OPC (although specific values were not given).

(d) Effect of silica fume

Compared with other cementing materials silica fume is very fine. Its particle size is typically less than 1 μm and it has a fineness of about 15,000 m² kg⁻¹ or greater (compared with 300-500 m² kg⁻¹ for OPC). However, as supplied, silica fume forms agglomerates [109] with particle sizes in the range 10-100 μm (i.e. similar to that of OPC) as shown in Figure 18. To fully benefit from the use of silica fume these agglomerates must be broken down. This is achieved in practice using chemical admixtures (superplasticisers) which cause the agglomerates to break down during the mixing process [99]. Without these admixtures, silica fume will cause a significant reduction in workability, or increase in water demand.

The effect of sonification to break down the agglomerates in silica fume for testing is shown in Figure 18 [109]. As received, the material was coarser than OPC but, when fully dispersed, was considerably finer.

![Particle size distributions for OPC and silica fume in various stages of agglomeration](image)

**Figure 18** Particle size distributions for OPC and silica fume in various stages of agglomeration [109]

In tests using a co-axial viscometer, increasing the proportion of silica fume caused a significant increase in the yield stress [110]. However, the change in plastic viscosity associated with an increase in silica fume was found to be dependent upon the superplasticiser, of which two were tested. Using a naphthalene sulphonate-formaldehyde condensate the plastic viscosity increased with silica fume content. However, using a polyacrylate with grafted polyether chains the plastic viscosity reduced with silica fume content. The latter is therefore better suited for high flow materials.
A major study of the rheology of grouts containing high proportions of silica fume was undertaken as part of the Posiva programme to develop low-pH cementitious grouts for the sealing of large fractures [101]. To achieve the required pH (≤ 11), the silica fume/OPC ratio was 0.69 [101] but in original studies the combination of strength and fluidity could not be achieved. Further tests using superplasticisers were therefore carried out and a range of grout mixes that met the flow and strength requirements were identified [98].

(e) Comparative performance

Compared with OPC alone, the workability is generally improved to the greatest extent by partial replacement with PFA. A smaller improvement is achieved using BFS. Using silica fume will cause a significant reduction in workability unless used with a superplasticising admixture. However, the extent to which the workability is affected will depend on many factors including the particle size distribution and the amount of OPC that is replaced. PFA and BFS also slow the rate of setting (see sub-section 5.4) and are therefore likely to maintain the workability of the cement for longer.

5.4 Stiffening and setting time

Setting time is important in relation to the backfilling process, providing a measure of the rate at which the cement begins to stiffen. This is particularly important if the material is being pumped and is relied upon to be almost self-levelling. The setting time of cement is measured using the Vicat penetration test [111] and is typically 3-5 hours at 20°C for OPC, reducing at higher temperatures. The NRVB has a setting time of about 4 hours [12]. In mortar or concrete, setting time may also be assessed using a penetration test or, more commonly by observing the change in the fluidity over time [94].

The fluidity reduces with time due to a combination of factors. In grout this is primarily due to early hydration reactions but in mortar or concrete, absorption of water by the sand and aggregate (if not fully saturated before mixing) also contributes to loss of fluidity. Reactions between the cement and any chemical admixtures will also have an effect.

The w/c ratio is a primary factor in determining the rate of loss of fluidity. Some typical results of tests to measure the gain in shear stress with time are shown in Figure 19 [112]. The shear stress increases logarithmically with time. For the data presented it appears that the shear stress increases by a factor of 10 over a period of about 170 minutes at each of the four levels of w/c ratio.

![Figure 19 The change in shear stress with time for OPC pastes at different w/c ratios][112]
As part of the development of the Posiva low-alkali grouts for sealing large fractures, a fall cone test was used to determine the extent to which the grout had set after 6 hours [113]. The test is more commonly used for soils. The minimum shear strength, estimated using the fall cone test, was required to be ≥ 500Pa.

The cement type may have a significant effect on the stiffening and setting time. Both PFA and BFS lead to an increase in the setting time, the effect being greater with higher proportions of PFA or BFS [114]. Silica fume has little effect on the setting time when used at levels up to about 5% (typical for structural concrete) but at higher levels the setting time is extended [115, 116].

The setting time is also influenced by chemical admixtures. The high-pH cementitious buffer for the Belgian supercontainer design developed under the ESDRED programme comprises cement clinker, calcium carbonate powder, fine sand and a polycarboxylate ether-based superplasticiser [89]. The w/c was about 1.35. Despite being provided in a pre-blended form so that only water needed to be added, a considerable difference in the setting behaviour of the backfill was observed between two large-scale placing trials undertaken at 2/3 and full scale [89]. While the 2/3-scale test was successful and cores were extracted for testing, in the full-scale test the backfill had not set after 5 months. When exposed, the surface did harden on exposure to the atmosphere, suggesting that this may have been due to carbonation as beyond about 20mm from the surface the grout remained plastic.

The need to use superplasticising admixtures for low-pH grout can also delay setting (e.g. [101]).

5.5 Plastic settlement and bleed

5.5.1 Mechanisms and consequences

Settlement of the solids prior to setting leads to bleed on the surface and a weaker layer on the surface as a result of the higher w/c ratio [94]. Settlement can lead to cracking under the following conditions:

- there is a sufficient head of fresh backfill for the magnitude of settlement to be significant;
- there is restraint to the downward movement of the backfill;

however, the bleed water prevents rapid drying of the surface that may lead to plastic cracking.

Bleed measured in the NRVB was 1.7% [12]. For the reference case the maximum head developed before setting of the backfill is likely to be about 122 mm [92]. This could increase if the transportation time is reduced but will reduce at temperatures above 25°C which will reduce the setting time. The maximum extent of bleed is therefore likely to be about 2mm.

A particular condition in which bleed and settlement needs to be considered is where the backfill meets the underside of a horizontal surface, i.e. the solid base of a drum or a box. In this case the backfill in contact with the surface will settle but will not be covered by a new layer of backfill. Under such circumstances a layer of bleed water will form below the surface as shown in Figure 20.
As the backfill hydrates, any bleed water will be absorbed back into the backfill leaving an air gap until resaturation commences [92].

5.5.2 Effect of cement type

Bleed and settlement may be reduced by reducing the w/s ratio. Bleed and settlement may also be reduced by improving the particle packing. This can be achieved either with a continuous particle size distribution and/or by the introduction of finer particles (e.g. as SCMs) [94].

Cements with a fineness greater than OPC will generally be expected to reduce bleed. The most marked effect is with silica fume which effectively fills the gaps between OPC and other similar sized particles of BFS of PFA. Tests for Posiva using silica fume in the ratio of 0.69:1 to OPC (about 40% of the cementitious material) for the injection of large fractures reported no bleed over a 2 hour period [101]. Both PFA and BFS are effective when the fineness is controlled to a sufficiently high level.

In concrete there can be increased bleed with BFS when used at fixed w/c ratio, but when the w/c ratio is reduced to achieve a similar strength the effect is much less apparent [114]. Furthermore, very high levels of BFS (90%) have been used successfully for waste encapsulation grouts [117], usually with relatively low w/c ratios of the order of 0.35.

5.6 Heat of hydration

5.6.1 Portland cement

An adiabatic heat generation curve for OPC is shown in Figure 21. This is an upper 90 percentile based on tests on a range of UK cements [118]. Values of heat output may range from 300 to 400kJ kg$^{-1}$ and if heat of hydration is considered to be critical to the performance of the materials, testing should be undertaken as it is difficult to reliably predict the heat output from the chemical and physical properties of the cement.
5.6.2 The NRVB

The NRVB contains 450 kg m\(^{-3}\) OPC and the estimated adiabatic temperature rise (i.e. with no heat loss) based on the heat generation for OPC alone (Figure 21) is shown in Figure 22 [119]. This assumes a placing temperature of 25°C, a specific heat capacity of 2.1 kJ kg\(^{-1}\) K\(^{-1}\) and a bulk density of 1730 kg m\(^{-3}\).

Using the adiabatic temperature curve, the temperature rise and fall may be predicted for various volume pours and geometries in different locations. Examples are given in Figure 23 showing the effect of different geometries. In each case, the temperature rise has been calculated for an isolated volume of backfill (shown in yellow) in the void space between 4 drums in a waste stillage or stack. The large volume between 3 m\(^3\) drums will result in a higher temperature rise (estimated to be 35°C) than occurring between the smaller 500l drums within a stillage (18°C) because the heat has further to travel and dissipates more slowly. Estimates have been made using the thermal model described in CIRIA report C660 [120].
Space between 500 l drums within a stillage
Effective thickness = 146 mm

Space between 3 m³ drums
Effective thickness = 726 mm

Estimated temperature rise = 18°C
Estimated peak temperature = 43°C

Estimated temperature rise = 35°C
Estimated peak temperature = 60°C

Figure 23 Estimated temperature rise in the NRVB at different locations in relation to the waste packages

As the cement is the source of heat, changing the cement type will have a significant effect on the early-age temperature rise. Different sources of OPC may exhibit different heat generating characteristics. As a general rule, heat is generated more rapidly from cement with higher levels of fineness, C₃A and C₃S [44].

5.6.3 PFA and BFS

PFA and BFS are commonly used in UK construction and comprehensive testing on various combinations with OPC [118] has provided a database for use with a thermal model presented in CIRIA report C660 [120]. Some results are shown in Figure 24 using levels of PFA and BFS adopted for waste encapsulation grouts [117, 121, 122]. Compared with a typical value of about 350 kJ kg⁻¹ for OPC, the heat generated by both PFA and BFS is significantly lower, with values less than 200 kJ kg⁻¹ when high proportions of PFA (50%) or BFS (75%) are adopted. For this reason these materials are commonly used in mass concrete construction to avoid early age thermal cracking [120].
Figure 24  Heat generation and resulting estimated temperature rises for cement blends with either a) BFS (ggb – ground granulated BFS) or b) PFA

5.6.4 Silica fume

Silica fume is not commonly used in concrete in the UK. The principal application is to achieve high strength concrete (about 80 MPa or greater) without the need for an excessively high cement content with the additional benefit of reduced heat generation. This can be achieved because silica fume has a much higher cementing efficiency than OPC. Where silica fume is used in concrete, additions rarely exceed 10% of the cement by weight, although in some proprietary grouts a higher proportion may be used. At the low levels used in concrete, silica fume is assumed to have little effect on the heat of hydration of the cement mix [99]. CIRIA report C660 [120] recommends, conservatively, that silica fume should be assumed to contribute the same heat as OPC. Nevertheless, lower temperature rises have been reported in high strength, low w/c mixes with relatively high proportions of silica fume [123, 124]. At levels of silica fume in excess of about 10%, this is attributed to insufficient Ca(OH)$_2$ being produced by the hydration of Portland cement to support the pozzolanic reaction so that much of the silica fume acts as an inert, but very effective, pore filler.
5.7 Early strength development

5.7.1 Prediction of the strength of concrete

Maturity methods have been used extensively in recent years to predict the strength of concrete [125]. These methods use the concept of equivalent age derived from temperature history. The Arrhenius method is commonly used for deriving the rate at which the properties of concrete develop and this includes the temperature dependence of the rate of strength development. The rate of strength development is defined as the reciprocal of the time taken (from the time of the onset of strength development) for the concrete (in standard cubes) to reach 50% of its ultimate strength [126]. The rates of strength development determined at different curing temperatures are used to determine a so-called “apparent activation energy” for the strength development process.

The maturity method provides an equivalent age function which converts the chronologic curing age $t$ of a concrete cured at a temperature $T$ [°C] to an equivalent age $t_e$ for a specimen cured at a specific reference temperature $T_r$ according to the expression:

$$t_e(T_r) = \int_0^t \exp \left( -\frac{E}{R} \left( \frac{1}{273 + T} - \frac{1}{273 + T_r} \right) \right) dt$$

(4)

where $t_e$ is the equivalent age at curing temperature $T$ [°C],

$T_r$ is the reference curing temperature [°C],

$E$ is the apparent activation energy [J mol$^{-1}$],

$R$ is the molar gas constant, 8.314472 J mol$^{-1}$K$^{-1}$.

This model assumes that the ultimate hydration, and hence the ultimate strength, is independent of the curing temperature. However, it has been recognized for many years that while the early age strength is increased at a higher curing temperature, the long term strength development may be adversely affected [127, 128]. In a recent study by Abdel-Jawad [129], this effect has been quantified and then used to predict more reliably the strength gain of concrete from early age through to late life.

The modification initially involves deriving a value of apparent activation energy $E$ as affected by the curing temperature and w/c ratio using the expression:

$$E = 38 \left( \frac{T_r - T}{T - T_o} \right)^{1 - \frac{w/c}{\beta}}$$

(5)

where $T_o$ is the datum temperature (-10°C) below which it is assumed that hydration ceases and $\beta$ is a coefficient defined by the expression:

$$\beta = 1.1 - 0.004T$$

(6)

To estimate the strength $f_c(T,t)$ after curing, the following empirical expression is then applied:

$$f_c(T,t) = f_c(T_r,t_e) \left[ 0.01 \left( 1 - e^{-0.05t_e} \right) \right]$$

(7)

where $f_c(T_r,t_e)$ is the compressive strength of the concrete at equivalent age $t_e$ and cured at reference temperature $T_r$.

5.7.2 Performance of the NRVB

Strength data were obtained for the NRVB as part of the development programme [12]. The results were obtained for cubes cured at 40°C and are given in Table 14 together with estimates of
the equivalent age and adjusted strength for curing at 20°C, based on the following parameters [119]:

- from Equation (6), for curing at 40°C, $\beta = 0.94$;
- using Equation (5), with $w/c = 1.37$, $\beta = 0.94$, $E = 37.25$ at 20°C.

**Table 14 Measured strength of NRVB cubes cured at 40°C [12] and their estimated strength at 20°C [119]**

<table>
<thead>
<tr>
<th>Age (days)</th>
<th>Measured at 40°C</th>
<th>Estimated for 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Strength (MPa)</td>
<td>Equivalent Age (days)</td>
</tr>
<tr>
<td>7</td>
<td>4.95</td>
<td>18.6</td>
</tr>
<tr>
<td>28</td>
<td>5.95</td>
<td>74.4</td>
</tr>
<tr>
<td>90</td>
<td>6.26</td>
<td>239.1</td>
</tr>
</tbody>
</table>

The lower curing temperature leads to a longer equivalent age compared with the test results at 40°C and it is necessary therefore to extrapolate the data to estimate the strength development at shorter times. This extrapolation has been achieved using the age coefficient $\beta(t)$ defined in EN1992-1-1 [130]. This applies to concrete cured at 20°C and is of the form,

$$
\beta(t) = \exp\left\{ s \left[ 1 - \left( \frac{28}{t} \right)^{0.5} \right]\right\}
$$

where $t$ is the time in days; and

- $s$ is a coefficient which depends on the type of cement:
  - $s = 0.20$ for class R – rapid hardening
  - $s = 0.25$ for class N – normal
  - $s = 0.38$ for class S = slow hardening

The cement combination used in the NRVB is CEM I (Portland cement) plus lime, which will also contribute to the hydration process. Strength development curves for each of the three basic cement types are shown in Figure 25 compared with the strengths estimated for the NRVB cured at 20°C [119].

The curve generated for the slow hardening cement provides a reasonably close fit to the estimated strengths of NRVB with age while curves for normal and rapid hardening cement both underestimate the strength gain in the longer term. Equation (8) has therefore been used to provide a reference curve at 20°C with $s = 0.38$.

Having established the reference curve for strength development at 20°C curing, the Arrhenius method with the modification by Abdel-Jawad [129] has been used to derive curves at different curing temperatures. These are shown in Figure 26 [119].
Figure 25 Strength development curves derived using the age relationship of EN1992-1-1 for slow, normal and rapid hardening cement compared with NRVB (open symbols) [119]

Figure 26 Estimated strength development curves for the NRVB at different curing temperatures compared with laboratory data (open symbols) [119]

Having established a model for estimating the rate of strength development for the NRVB under conditions of constant curing temperature, this may then be developed into a model for estimating the strength development under conditions of thermal cycling (i.e. through the cycle of self-heating due to cement hydration followed by cooling). Results obtained are shown in Figure 27 [119].
Over the plan area of the vault the NRVB varies in thickness depending upon the way in which the waste packages are stacked. Hence the local rise in temperature will vary also, resulting in a variation in the rate of strength development and the ultimate strength. Two conditions are illustrated, representing the space between four 3 m$^3$ drums and the space between four 500 dm$^3$ drums within a stillage. These provided the upper and lower limits of peak temperature estimated as part of the NRVB cracking study [92].
5.7.3 Effect of cement type

Cement type not only affects the early temperature rise but also the way in which temperature history affects the strength development. This is reflected in differences in the so-called apparent activation energy that is used to parameterise the effect of temperature on the rate of strength development. For example, it has been reported that the apparent activation energy parameter increases with the use of BFS [126] from about 34 kJ mol\(^{-1}\) for OPC to about 60 kJ mol\(^{-1}\) with 70% BFS. PFA appears to have a much less significant effect on the apparent activation energy resulting in, on average, a small reduction.

Results are included in Figure 28 from several sources indicating how the apparent activation energy parameter changes in relation to OPC as the percentage of either PFA or BFS is increased [126, 131-135]. Limited data for silica fume suggests that the apparent activation energy parameter increases by about 10% when the silica fume comprises 10% of the cementitious material [131, 136].

![Figure 28](image)

**Figure 28** The relative effects of PFA and BFS content on the apparent activation energy parameter that is used to characterise the effect of temperature on the rate of strength development

5.8 Dimensional stability

Dimensional changes will occur as a result of changes in either temperature or relative humidity. Some (autogenous) shrinkage may also occur due to the hydration reaction but this will be small compared with other dimensional changes and is only significant when the w/c ratio is very low (less than about 0.4). Backfill materials tend to have w/c ratios substantially higher than 0.4, although encapsulation grouts and sealing grouts may have lower w/c ratios. The potential magnitude of dimensional changes is considered in sub-sections 5.8.1, 5.8.2 and 5.8.3. Excessive contractions can lead to cracking.

5.8.1 Thermal deformation

The coefficient of thermal expansion (CTE) of mature cement paste is about 18-20 με °C\(^{-1}\) but develops over time as hydration proceeds [137]. The results in Figure 29 are for saturated cement pastes, some of which contain PFA. The slower hydration of the PFA is consistent with the slower development of CTE but after 28 days the difference is small.
The CTE is also affected by the moisture content with a maximum value occurring at a relative humidity of 50-70% [138, 139]. This is due to swelling pressures associated with changes in temperature. Published results are shown in Figure 30, with results for the NRVB [140].

In mortar and concrete, the thermal deformation of the cement paste is restrained by the sand and aggregate, which typically have a lower CTE than cement paste and are less sensitive to variations in moisture content. The effect of increasing the volume of sand in a mortar is shown in Figure 31 [138].
In concrete, which comprises about 70% sand and aggregate by volume, the CTE will be determined primarily by the type of aggregate. Some typical values are given in Table 15 [141].

Table 15  Values of coefficient of thermal expansion for aggregate and concrete

<table>
<thead>
<tr>
<th>Aggregate rock group</th>
<th>Thermal expansion coefficient (microstrain °C⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rock</td>
</tr>
<tr>
<td>Chert or flint</td>
<td>7.4 - 13.0</td>
</tr>
<tr>
<td>Quartzite</td>
<td>7.0 - 13.2</td>
</tr>
<tr>
<td>Sandstone</td>
<td>4.3 - 12.1</td>
</tr>
<tr>
<td>Marble</td>
<td>2.2 - 16.0</td>
</tr>
<tr>
<td>Siliceous limestone</td>
<td>3.6 - 9.7</td>
</tr>
<tr>
<td>Granite</td>
<td>1.8 - 11.9</td>
</tr>
<tr>
<td>Dolerite</td>
<td>4.5 - 8.5</td>
</tr>
<tr>
<td>Basalt</td>
<td>4.0 - 9.7</td>
</tr>
<tr>
<td>Limestone</td>
<td>1.8 - 11.7</td>
</tr>
</tbody>
</table>

In a study to measure the effect of moisture content on CTE, various concretes prepared from OPC and from OPC in combination with either PFA or BFS were tested. No effect of cement type was observed [142].

5.8.2  Autogenous shrinkage

Autogenous shrinkage is a volume change that occurs as a result of self-dessication during cement hydration - water is drawn from already hydrated cement gel to enable the hydration reaction to progress. It occurs to a significant extent when the w/c is low. Some typical values of autogenous shrinkage after 7 days and 1 year for Portland cement paste are shown in Figure 32 [143, 144]. Deformations may exceed 0.1% when the w/c is below about 0.35, i.e. values typical of...
encapsulation grouts, but at the much higher w/c ratios used for backfill (e.g. w/c = 1.37 for NRVB) autogenous shrinkage will be negligible. The results presented in Figure 32 indicate that autogenous shrinkage will approach zero when the w/c approaches about 0.8.

![Figure 32 Autogenous shrinkage for cement paste in relation to the w/c ratio](image)

When the cement paste is combined with inert sand and aggregate, autogenous shrinkage will be reduced. EN1992-1-1 for structural concrete [130] provides guidance on autogenous shrinkage and an expression to estimate its magnitude in relation to the strength class. Even for very high strength concrete (100 MPa) the design value is less than 0.02%, i.e about 20% of the value for cement paste.

EN1992-1-1 [130] does not account for the use of different types of cement but there is evidence that the cement type may have a significant effect. A review of published data is presented in Appendix 4 of CIRIA Report C660 [120], and the results are shown in Figure 33. Addition of either BFS or silica fume appears to cause an increase in autogenous shrinkage relative to OPC, whereas addition of PFA leads to a reduction. It should be noted, however, that the results summarised in Figure 33 were all obtained from concretes or cement pastes with w/c ratios of 0.4 or less and for combinations using proportions of PFA (up to 60%), BFS (up to 80%) and silica fume (up to 10%) typical of those used in structural concretes. The effects of very high levels of silica fume that have been used to achieve low-alkali cement have not been investigated.
5.8.3 Drying shrinkage and swelling

Shrinkage occurs when moisture loss occurs from cementitious systems but much of the shrinkage may be recovered (by swelling) if the material is re-wetted. Results from tests on the NRVB [90], using small specimens (75 x 75 x 285 mm) stored at low humidity (RH = 30%) and a temperature of 43°C are shown in Figure 34. The ultimate drying shrinkage, measured after oven drying was about -3000 με (microstrain). Specimens were rewetted after different periods of drying and in each case the swelling was about +1400 με, regardless of the amount of shrinkage prior to rewetting.

The effect of relative humidity was also investigated and desorption isotherms established [92] as shown in Figure 35. At a temperature of 30°C and 70%-85% relative humidity the reported drying shrinkage was in the range from about -2000 to -2500 με.
The effect of cement type on drying shrinkage is not significant compared with other factors such as the w/c ratio and relative humidity. A comprehensive review of published results concluded that the effect of BFS was to increase shrinkage by 3% compared with OPC concrete and that this was due largely to the increased paste volume [145]. Similarly, tests on mortar with increasing proportions of silica fume (up to 30%) showed no difference in drying shrinkage over the long term, although there was an increase at 28 days [146]. In tests on cement paste with increasing levels of PFA up to 75% [147] the shrinkage was shown to increase by up to about 7% with levels of PFA up to about 30% and to reduce from this peak as the PFA level increased further, with a reduction of about 15% when the PFA content was 75% as shown in Figure 36.

![Figure 35 Desorption isotherms for the backfill at 30°C [90]](image)

**Figure 35** Desorption isotherms for the backfill at 30°C [90]

At the levels of PFA used in concrete, typically up to about 40%, the effect on drying shrinkage would be expected to be small and when used in concrete the effect will be diluted by the presence of sand and aggregate. In studies on concrete the only effect attributable to PFA is that which results from any change in the paste volume resulting from the reduction in water demand and the lower specific gravity of PFA compared with OPC [148].

![Figure 36 The effect of PFA on the shrinkage of cement paste at w/c = 0.30](image)

**Figure 36** The effect of PFA on the shrinkage of cement paste at w/c = 0.30
5.9 Key points

- A wide variety of materials is available for the production and emplacement of cementitious backfill systems with the range of properties required in the fluid, the hardening and the hardened states. The process of designing a cementitious backfill is to balance the various requirements which may often be conflicting. For example, a higher value of water/solids ratio is required for fluidity while a lower value is needed to minimise bleed and settlement and subsequent drying shrinkage.

- Specific requirements for fluidity, bleed, setting time, and heat of hydration will be dependent on the backfilling strategy, including the required rate of backfill production, the distance to be transported, the method and rate of placement and the array of waste packages. However, based on the results of completed and ongoing studies, sufficient knowledge is available to provide at least an initial basis for mix design. It is important to recognise however that there are no unique models for predicting the performance of a particular system, although substantial empirical data has enabled critical parameters to be identified and general relationships to be established.

- The critical properties of cements in relation to the emplacement process are summarised in Table 16. The key factors influencing the in-place mechanical performance of cements are summarised in Table 17. While trends in performance may be derived, it is difficult to predict precisely the properties that will be achieved for a particular combination of materials as there may be several influencing factors, both chemical and physical. For this reason, an essential part of the development of any mix of grout, mortar or concrete is undertaking trials.

Table 16 The critical properties of cements in relation to emplacement and the key influencing factors

<table>
<thead>
<tr>
<th>Property</th>
<th>Influencing factors</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluidity</td>
<td>Water/solid ratio</td>
<td>Fluidity increases with w/s ratio.</td>
</tr>
<tr>
<td></td>
<td>Particle size and distribution</td>
<td>As a general rule, for a given w/s ratio, fluidity reduces as the specific surface area increases. Fluidity is increased by partial replacement of OPC with PFA or BFS and reduced by addition of silica fume.</td>
</tr>
<tr>
<td>Cohesion</td>
<td>Water/solid ratio</td>
<td>Cohesion is higher at low w/s ratio.</td>
</tr>
<tr>
<td></td>
<td>Particle size and distribution</td>
<td>Cohesion is increased by finer particles.</td>
</tr>
<tr>
<td>Stiffening and setting time</td>
<td>Cement chemistry and fineness</td>
<td>Stiffening and setting occurs more rapidly in OPC with higher levels of C₃A, C₃S and alkalis and with higher specific surface area. The use of PFA and BFS tends to extend the stiffening and setting time of blended cements. Silica fume is generally used with a plasticising admixture which itself may extend stiffening and setting time.</td>
</tr>
</tbody>
</table>
Table 17  The key properties of cements during emplacement and the related factors which affect their in-place mechanical performance

<table>
<thead>
<tr>
<th>Property</th>
<th>Influencing factor</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleed and settlement</td>
<td>Water/solids ratio</td>
<td>Bleed and settlement are increased at higher w/s ratio.</td>
</tr>
<tr>
<td></td>
<td>Particle size distribution</td>
<td>Bleed and settlement are lower when finer particles are used and when there is a continuous grading curve for optimal particle packing. The use of PFA reduced bleed while BFS may increase bleed. Silica fume significantly reduced bleed.</td>
</tr>
<tr>
<td>Heat of hydration</td>
<td>Cement content</td>
<td>The amount of heat developed is approximately proportional to the cement content.</td>
</tr>
<tr>
<td></td>
<td>Cement type</td>
<td>Heat of hydration tends to be higher in OPC with higher C3A and C3S. Heat development is more rapid in finer cement.</td>
</tr>
<tr>
<td></td>
<td>Replacement of OPC with SCM</td>
<td>Both heat of hydration per unit weight of cement and the rate of heat generation are reduced by replacing OPC with either PFA or BFS.</td>
</tr>
<tr>
<td>Thermal deformation</td>
<td>Cement type</td>
<td>For cement paste the coefficient of thermal expansion (CTE) is 18-20 microstrain °C⁻¹.</td>
</tr>
<tr>
<td></td>
<td>Aggregate type and content</td>
<td>In concrete, with a high volume of aggregate (including sand), the CTE is determined primarily by the thermal properties of the aggregate. Aggregates have a lower CTE than cement paste hence the CTE is lower in concrete with a higher volume of aggregate.</td>
</tr>
<tr>
<td></td>
<td>Moisture content</td>
<td>The CTE is highest when the internal humidity is in the order of 60-80%.</td>
</tr>
<tr>
<td>Autogenous shrinkage</td>
<td>Water/cement ratio</td>
<td>Only significant when the water/cement ratio is less than about 0.45.</td>
</tr>
<tr>
<td></td>
<td>Cement type</td>
<td>Evidence of a reduction in autogenous shrinkage when partially replacing OPC with PFA, but an increase when using BFS or silica fume.</td>
</tr>
<tr>
<td>Drying shrinkage</td>
<td>Water/cement ratio</td>
<td>Drying shrinkage increases with the water/cement ratio.</td>
</tr>
<tr>
<td></td>
<td>Cement content</td>
<td>Drying shrinkage increases with the cement content.</td>
</tr>
</tbody>
</table>

- While some early work has been undertaken on the backfilling strategy for the UK ILW/LLW concept in higher strength rock, the backfilling strategy adopted will be dependent on the design of the GDF and the closure requirements specified both during and at the end of operations (e.g. any specific requirements concerning the early closure of individual disposal vaults). The backfilling procedures and the timescales over which backfilling may take place will be dependent on the strategy adopted. Development and testing of the backfilling procedures is likely to go hand-in-hand with refinement of the requirements for the cement-based backfill.
6 Mechanical performance of cements

6.1 Critical properties

Assessment of the long term performance of cementitious backfill and sealing materials in a GDF requires knowledge of the mechanical performance of the grouting materials, including their structural integrity and dimensional stability. This section deals with the mechanical properties of a range of cementitious systems, recognising that various applications require different properties.

For backfill materials, the requirement for compressive strength is low compared with that which is achievable generally using cementitious materials. The issue here is ensuring that the strength does not grow over the long term thereby making retrievability difficult. For example, the NRVB has a requirement for a maximum strength of 10 MPa, while normal structural concrete has a value typically 3 or 4 times higher; and high performance concrete and grout may achieve compressive strengths in excess of 100 MPa.

Other mechanical properties are important in relation to the way in which the material responds to loading. The modulus of elasticity, \( E \), determines the stress and strain generated by a particular load. Materials with a high \( E \) exhibit high stress but low strain and vice versa. Considering the long periods over which loads may be generated in a GDF and the long periods over which these loads may be sustained, creep is also significant in determining the extent to which continued deformation or stress relaxation occurs. Where the initial strain is load induced, and the load is maintained, high creep will lead to increased deformations. Where load is strain induced (e.g. by thermal stresses or shrinkage), high creep will result in a greater relaxation of the stresses generated and a reduced risk or extent of cracking.

In general, the loads induced in a backfill will be strain-induced through changes in temperature and moisture state. In this case, a low \( E \) value and high creep material is desirable to minimise the risk and/or extent of cracking.

Deformations, when restrained, lead to stresses and a risk of cracking. Deformations are induced primarily by changes in temperature (at early age from cement hydration and in the longer term by heat generated by the waste) and by shrinkage due to drying. The extent of the deformation is influenced heavily by the moisture content, which affects the CTE. If drying is inhibited, shrinkage will be minimised. The magnitude of stresses developed will be determined by the potential magnitude of the deformation, the level of restraint, the modulus of elasticity and creep. Whether or not cracking occurs will depend on the ratio of the tensile stress to the tensile strength.

6.2 Compressive strength

6.2.1 Effect of w/c ratio

As a general rule, for a particular cement type, a lower compressive strength is achieved by increasing the w/c ratio. However, at a given w/c ratio, changing the cement type may lead to a significant change in strength at a particular age.

Different practical applications require different grout properties and it is often properties other than strength which drive the mix design. Waste encapsulation grouts are of relatively low w/c, typically 0.3 to 0.6, and hence have relatively high strength (up to about 75 MPa). In the case of backfill materials, if retrievability were a requirement, a relatively lower strength (typically less than 10 MPa) would be needed and this would be achieved by using a much higher w/c ratio. For example, the NRVB has a w/OPC ratio of about 1.35, in common with a backfill grout developed on the ESDRED programme for the Belgian supercontainer concept (see sub-section 2.1.3 and Figure 4) [89].
It is difficult to make direct comparisons between the various materials used because the range of applications is so diverse, the material combinations vary significantly and the age at which testing is carried out is not consistent. In construction, standard tests are carried out after 28 days curing under standard conditions (in water at 20°C) but published results for backfill, encapsulation and sealing grouts are obtained over periods up to one year.

Some typical results showing the relationship between strength and w/c ratio are given in Figure 37. The following results are included in the figure (compositions from the same study that differ only in w/c ratio are joined by curves as an aid to the eye).

- **Stripa grouts for borehole, shaft and tunnel sealing** [149]. Grouts used for sealing major fracture zones and disturbed zones around sealed shafts used a combination of OPC and silica fume. The cement was relatively finely ground cement, with a surface area (Blaine) of 600 m² kg⁻¹ and would be considered rapid hardening. OPC is typically about 400 m² kg⁻¹ but may range from about 300-500 m² kg⁻¹. Also shown in Figure 37 is the benefit in terms of increased strength when using silica fume, particularly at the higher w/c ratios. At w/c = 0.7 the effect of 10% silica fume was to increase the compressive strength from 20 MPa to 50 MPa.

- **SKB concrete for borehole sealing plugs at Åspö** [150]. The cement was a combination of white OPC and silica fume in the ratio 1:1 with additional finely ground α-quartz and cristobalite forming the matrix. Aggregate was 0-8mm ballast. Varying w/s ratios were tested (7%, 9% and 21%) with water/reactive powder ratios of 0.32, 0.41 and 0.96.

- **NRVB** [12]. The NRVB has a w/c ratio of 1.35 and comprises a combination of OPC, Limestone flour and hydrated lime.

- **UK encapsulation grouts** [117]. These grouts comprise blends of OPC with high proportions of either PFA or BFS. Results are presented at ages of 28 days and 360 days.

- **OPC grout by Padevet et al.** [151]. These tests were not part of any of the radwaste programmes and are included as an illustration of the performance of grouts containing OPC only.

- **Posiva low-alkali injection grouts** [98]. These grouts all have a silica fume/OPC ratio of 0.69 and some include small amounts of CAC (1.5 wt% CAC relative to OPC).

- **ESDRED shotcrete plugs for LLW and ILW** [26]. Four concrete mixes were tested for temporary shotcrete plugs. The mixes comprised combinations of either CAC or OPC and silica fume or OPC, silica fume and PFA. In all cases the silica fume comprised at least 20% of the cementitious material. Results are also included from the development phase, covering a wider range of w/c and strength [152].

- **ESDRED backfilling grout for HLW** [89]. High pH backfill for the annular gap around a horizontal cylindrical supercontainer for HLW. The mix comprised cement clinker, calcium carbonate powder and fine sand, although the proportions were not given. The w/c ratio was 1.3 – 1.35.

- **Swiss M1 mortar backfill for an ILW/LLW GDF in Opalinus Clay**. Trials were undertaken at four w/c ratios. The mix comprised sulphate-resisting cement and quartz sand [17], with w/c = 0.4, the strength was also assessed at different degrees of compaction, described qualitatively as non-compacted, compacted and highly compacted.

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6 Included for illustrative purposes only. Encapsulation grouts are outside the scope of this review.
Figure 37  The relationship between compressive strength and w/c ratio

The general trend for higher strength at lower w/c is apparent but the differences in cement and age at test result in a high level of variability. This is due to the cement type having a significant impact on the rate of strength development.

6.2.2 Effect of cement type

Compared with OPC, the cement type has a significant impact on the rate of strength development, which may continue over many years, and hence affect the ultimate strength. In studies of concrete used for nuclear application, continued strength development has been measured up to 25 years [153] as shown in Figure 38, with an increase of about 40% from 28 days to 25 years.
Figure 38  Long term strength development of concrete used in nuclear power stations

As a general rule the replacement of OPC with PFA or BFS will result in slower early strength gain (i.e. within the first few weeks) but enhanced strength development over the medium and long term. An example is shown in Figure 39 for three concretes designed with the same compressive strength at 28 days [154]. While the early strength develops more slowly, the enhanced long term strength development associated with the use of PFA and BFS is clear.

Figure 39  Compressive strength development (in MPa) up to 1 year for standard cured cubes for concrete with cement combinations using PFA and BFS [154]

The requirement for relatively low compressive strength for retrievability is one of the reasons why neither PFA nor BFS were used in the NRVB. While the early strength may be sufficiently low, over the very long term a substantial increase in strength may occur. For example, concrete mass fill, using a mix with 100 kg OPC and 100 kg PFA achieved a strength of about 14 MPa at 28 days but after 18 months was almost 40 MPa [155].
The strength development of concrete containing silica fume is generally more rapid at early age compared with OPC concrete using the same w/c ratio. An example is shown in Figure 40 [156]. This is due partly to the pozzolanic reaction and partly to the pore-filling effect of the very fine particles of silica fume. In terms of strength enhancement, most benefit is achieved at levels of silica fume up to about 10%. This is due to the pozzolanic reaction with the silica fume exhausting the supply of calcium hydroxide from hydration of the OPC. In this situation, the unreacted part of the silica fume acts as an inert filler.

![Figure 40](image)

**Figure 40  Strength development of silica fume concrete with w/c = 0.45 [156]**

Beyond 28 days the strength gain of concrete containing silica fume is similar to that using OPC alone. Results from 1 month to 155 months (almost 13 years) are shown in Figure 41 [157]. In each case the strength continues to grow at significant rate up to about 1 year but thereafter the increase in strength is, on average, only about 6%.

![Figure 41](image)

**Figure 41  Long-term strength development of concrete with OPC and with 10% silica fume [157]**
6.2.3 Summary of factors affecting compressive strength

For a particular cementitious combination the principal factor influencing the compressive strength is the w/c ratio.

Compared with the use of OPC alone, other cements will have the following effects on compressive strength when compared at the same w/c ratio:

- PFA and BFS will slow the early rate of strength gain but enhance long term strength development such that the ultimate strength may be higher;
- silica fume will increase the rate of early strength development (up to about 28 days) but the rate of longer term strength development is unlikely to be affected.

6.3 Modulus of elasticity

6.3.1 Relationship between modulus of elasticity and compressive strength

In general, the modulus of elasticity, $E_c$, has not been specified in the requirements for cementitious systems for most GDF applications. However, for concrete plugs for temporary sealing applications ENRESA, SKB and POSIVA specify a minimum value of 20 GPa to provide support [158].

In the design of conventional concrete structures, the modulus of elasticity is related to the compressive strength and the aggregate type [130]. The latter comprises about 70% of the volume of concrete and therefore has a predominant effect. Typical relationships between compressive strength and $E_c$ are shown in Figure 42 for concrete with different aggregate types. Results obtained for shotcrete for the ESDRED temporary sealing plug and for the Swiss M1 mortar for backfilling the ILW/LLW GDF concept in Opalinus Clay are also shown as individual points in Figure 42; both materials exhibit compressive strength-$E_c$ relationships that are broadly consistent with EN1992-1-1 [130]. A single result for NRVB is also shown.

For general comparison, Figure 42 also shows typical results (yellow points) for a range of commercially available grouts, obtained from a range of technical literature. Although there is some scatter (most probably due to the various formulations), the results presented indicate approximate proportionality between $E_c$ and strength $f_c$, with $E_c$ (in GPa) = 0.4337 x $f_c$ (in MPa) (shown by the fitted black straight line).
Figure 42 Relationships between modulus of elasticity and compressive strength for grouts and concrete

The difference in the relationships between $E_c$ and $f_c$ for concrete and grout is due to the presence of aggregate. At relatively low strength, the aggregate is much stiffer than the cement paste and dominates the value of $E_c$. Hence for a given compressive strength, $E_c$ for concrete is much higher than that for grout. However, for cement paste with higher strength, the stiffness of the grout approaches and, depending upon the aggregate type, may exceed the stiffness of the aggregate.

6.3.2 Effect of cement type

In a review of concretes used in nuclear applications, it was found that those concretes containing PFA exhibited higher values of modulus of elasticity [153]. Furthermore, a relationship was observed between $E_c$ and the volume of Portland cement paste only (i.e. ignoring the PFA) as shown in Figure 43. This would be consistent with the assumption that the component of hydrate associated with the PFA is stiffer than that of the hydrate associated with Portland cement only and is effectively acting as a stiff aggregate.
Other studies have found an increase in $E_c$ with PFA. Bamforth measured the properties of concrete subject to in-situ heat cycles and reported an increase in $E_c$ of about 5 GPa (15-25%) for concretes of the same strength [159]. An investigation of PFA in foamed concrete yielded similar findings [147]; the ratio of compressive strength to elastic modulus increased with the PFA/OPC ratio. At a ratio of 3:1 the elastic modulus had increased by about 65% in relation to the compressive strength compared with a mix with OPC only.

In some studies however, no difference in the elastic modulus (relative to compressive strength) has been observed [148]. A Concrete Society review of the properties of concrete using PFA [114] concluded that the elastic modulus of concrete containing PFA is generally equal to or slightly in excess of that for OPC concrete of the same strength but not to the extent that it affects the relationship between elastic modulus and strength used for design purposes.

Similar effects on elastic modulus have been reported for BFS, with an increase in $E_c$ for a given strength. The greatest difference compared with OPC concrete appears to be associated with concrete subject to heat cycling [114, 159]. Again, the Concrete Society review [114] concluded that while concretes containing BFS develop a higher elastic modulus in relation to compressive strength compared with OPC concrete, the difference is not significant in design.

Silica fume, used in proportions up to about 10% of the cement, appears to have little effect on the relationship between elastic modulus and strength. Reported results are shown in Figure 44 [160, 161]. The difference between OPC concretes and those with up to 10% silica fume exhibit relationships which are almost identical. However, at high levels of silica fume (15% and 20%), the results are consistently at the low end of the range, although still broadly consistent with values estimated using EN-1992-1-1 [130]. Also included in Figure 44 are the results obtained as part of the ESDRED development programme for concrete plugs in which 40% silica fume was used to achieve a low-alkali cement [158]. In this case the values of elastic modulus are significantly lower. Indicating either a very soft aggregate (the values are consistent with a weak sandstone or a lightweight aggregate) or an effect of the silica fume. The aggregate used was either crushed granite or siliceous gravel, neither of which would be expected to yield a low modulus and the effect is therefore most likely due to the presence of the high proportion of silica fume.
Creep

It is not common to specify creep as a requirement for concrete structures. In most cases it is assumed for design purposes that the long term deformation will equal the initial elastic deformation. However, for some structures, where excessive deformations may be critical, knowledge of the potential magnitude of creep may be essential. This was the case for the design of pre-stressed concrete pressure vessels for nuclear power stations, and extensive testing was undertaken to provide the designer with information of long term load behaviour [162]. A particular feature of these structures was that they would not be subject to loading for perhaps years and a feature of the testing programmes was to assess the effect of loading age. The effect of temperature was also investigated (see section 7).

The results demonstrated the following:

- creep reduces with age at loading;
- creep increases with temperature;
- both PFA and BFS cause a reduction in creep in moisture stable concrete; and
- creep reduces as the proportion of aggregate or sand is increased (Figure 45).
Figure 45 Relative creep of concrete mortar and cement paste [83]

The deformation of the concrete under load may not be critical in many applications. However where the material is used to support the cavern both strength and stiffness may need to be specified. As linings will generally represent a relatively small proportion of the cementitious material within a vault and will have a very specific structural role, conventional concrete or shotcrete is likely to be used with limited chemical requirements. In this case the designer may adopt conventional design practice.

6.5 Mortar M2 for the Swiss ILW/LLW concept in Opalinus Clay

Various cementitious materials are to be used in the proposed Swiss concept for ILW/LLW disposal in Opalinus clay including two backfill mortars with differing flow characteristics [16]. The differing applications of these materials are illustrated in Figure 3 (see sub-section 2.1.2). Waste packages are placed in prefabricated concrete containers and the void spaces within the containers are filled with a free-flowing mortar designated M2. The containers are stacked in the repository and the space between and around them is backfilled, also with a high viscosity mortar M2. Although, in common with the NRVB, the Swiss backfills have a requirement for a high porosity and gas permeability, the Swiss specification does not require a low compressive strength to allow package retrievability.

The backfill mortar M2 was designed to achieve a fresh density of about 1990 kg m\(^{-3}\) but as no compaction would be applied in practice, tests were undertaken to establish the likely range of density that would occur \textit{in situ} [18]. This involved filling a mould, shown in Figure 46, from the top. Cores were then extracted from the top, middle and bottom sections to measure density, compressive strength and elastic modulus at 28 days and at 150 days.
Three mixes were tested, all using the same high sulphate-resisting cement with the same cement content of 474 kg m\(^{-3}\), but variations were made in the w/c ratio (0.75 and 0.88) and the source of the sand (both with a maximum particle size <1mm but of different fineness). In addition, the mortar was modified by the addition of varying amounts of finely-divided aluminium powder (0.1% and 0.3% wt of cement). This was added to generate hydrogen gas to form voids within the mortar to achieve a high porosity and high gas permeability. Results are shown in Figure 47 and Figure 48.

A linear relationship was observed between the density and the compressive strength at both 28 days and 150 days. However, the strength had increased significantly between 28 days and 150 days without a significant change in density. A similar relationship between elastic modulus and strength was applicable at both ages.

Much of the variability observed was due to the location within the test block. Samples from the bottom section yielded the highest values of density, compressive strength and elastic modulus, while the lowest values were achieved in the top section. On average, the density, compressive strength and elastic modulus were respectively about 20%, 50% and 60% lower in the top section compared with the bottom section. This indicates that while the mortar would be free flowing, it is not self compacting and so the properties through the vault would vary significantly. It was suggested [18] that the cause of this inhomogeneity was the weight of the mortar compressing the air bubbles in the lower section of the test block reducing the total porosity but increasing density and compressive strength. It should be noted that due to the in situ generation of hydrogen in these trials, this is a rather different system to a self-compacting backfill mix such as the NRVB.

Figure 46 Configuration of the mould used to test the flowability of Swiss mortar M2 (dimensions in mm) [18]
6.6 Key points

- It is clear that a wide range of mechanical properties may be achieved for cementitious systems, from very low strength backfill material where retrievability is a requirement, to very high strength material where load bearing capacity and stiffness is critical. While the strength and the stiffness are related, the relationship is not universal and will be affected by the amount and type of aggregate and/or sand that is used and by the cement type itself. To a large degree it is therefore possible to customise a concrete mix to meet a wide range of specification requirements.

- In the case of a vault lining, the loads on the concrete will depend very specifically upon the design (geometry, size, etc) and on the geology (e.g. rock creep in the host rock). Limiting values would therefore have to be developed as part of the design process. However, based on the knowledge available it is clear that a wide range of mechanical properties may be achieved through appropriate selection of cement type, aggregate type and mix proportioning (in particular the w/c ratio).
7 Effects of temperature on cement materials

7.1 GDF temperatures

7.1.1 Ambient GDF temperature

The ambient temperature of the host rock surrounding a GDF will be determined by the local geothermal gradient and the depth of the facility. In general, the temperature of the rock mass increases linearly with depth, and can be represented by an expression of the form:

\[ T = T_s + x d \]  \hspace{1cm} (8)

where \( T \) is the temperature (°C), \( T_s \) is the annual mean surface temperature, \( x \) is the local geothermal gradient (°C m\(^{-1}\)) and \( d \) is the depth below surface (m). As an example, at Sellafield in the UK, where \( x \) has been evaluated to be 0.022°C m\(^{-1}\), and \( T_s \) is 10°C [163], the ambient temperature at a depth of 650m was predicted to be about 25°C [164]. According to the British Geological Survey [165], the mean value of \( x \) in the UK is 0.026°C m\(^{-1}\), so that for a UK GDF located at a depth between 200m and 1000m, the ambient temperature would be expected to lie between 15 and 36°C.

7.1.2 Heat generation in a GDF

During the construction and operational period, and throughout the early post-closure period, a number of near-field processes will generate heat leading to an increase in the temperature of the EBS and the surrounding host rock. The most significant heat generating processes are radioactive decay and cement hydration (sub-section 5.6). Other processes, such as corrosion and microbial action, may also generate some heat but are much less significant in terms of the total heat generated.

Heat produced due to radioactive decay is most significant for HLW, spent fuel and to a lesser extent plutonium wasteforms. Thermal modelling of GDF designs for spent fuel undertaken by Nagra [166] and SKB [167] suggests that radiogenic heating may be significant for a few thousand years after disposal, while short-lived radionuclides decay. Although thermal modelling calculations have yet to be published for illustrative concepts for UK HLW and spent fuel, it is likely that heat generation will be significant over similar timescales.

As discussed in sub-section 5.6, cement hydration proceeds via a range of exothermic (heat releasing) chemical reactions, some of which occur rapidly, releasing significant quantities of heat. In the case of an EBS for ILW/ILW backfilled with large quantities of cementitious materials, cement hydration can cause a significant temperature increase that may persist for a few years to several tens of years (depending on the backfill strategy) [168].

NDA’s current Technical Specification for a GDF [169] provides the following guidance on temperature limits.

For planning purposes, a guidance value of less than 50°C for all (ILW) waste packages following closure shall be assumed. The consequences of any period when this target is exceeded (e.g. in response to backfill curing should a cementitious backfill be used) shall be considered. In ILW disposal designs that incorporate a cementitious backfill, waste package temperatures of up to 80°C shall be acceptable for a period of 5 years.

Disposal of graphite wastes shall consider the potential for Wigner energy release to affect disposal facility temperatures.

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\(^7\) The authors understand that a package of work is in progress on the NDA RWMD programme.
For planning purposes, the design of the HLW and spent fuel disposal modules shall be based on a temperature limit of 100°C on the external surface of the disposal canister at any time following emplacement.

Recent thermal modelling for the illustrative UK ILW/LLW concept for a higher strength host rock at a depth of about 630m, with an initial ventilated vault temperature of 25°C, found that peak temperatures in the disposal area within a 50 year transient after backfilling with NRVB would be less than 48°C (covering the wasteform, the container and the backfill) [170]. Thus, the maximum temperature rise due to hydration of the NRVB would be less than 23°C; the peak temperature would be reached about 1 year after the start of backfilling (assumed to take 142 days). After 50 years the vault temperature would have decreased to about 38°C, maintained above the ambient temperature of the host rock by radiogenic heating from the waste packages. Ventilation during the operational phase (over several decades) strongly influences the temperature distribution in the local host rock. If ventilation is maintained during backfilling it would draw a significant part of the backfill exotherm heat loading out of the facility. If the temperature of the ventilation system was increased or ventilation was stopped during backfilling then the local temperatures in the packages may be affected.

Nevertheless, an alternative ILW disposal concept and/or a geological location (i.e. disposal depth) could be selected in which peak vault temperatures could exceed 48°C. Therefore for the purpose of this review, the current guidance limits for both ILW and HLW/SF disposal will be used as the context for considering temperature effects.

The effect of heat of hydration on the short and longer term development of mechanical properties have been dealt with in sub-section 5.6. This section deals with the effect of temperature per se on the properties of mature cementitious systems.

7.2 Mineralogical changes in Portland cement and concrete

7.2.1 Background

The impact of elevated temperature on cement backfill performance has been described in a previous review [171]. That review summarised the work undertaken up to 1997 on the hydrothermal alteration of cement phases and the resulting changes, and concluded that temperature perturbations post-closure may change cement mineralogy and that these changes may not be reversible; the nature of the phases formed is not well characterised. Experimental work on freshly prepared C-S-H phases show that hydrothermal treatment gave rise to changes in the mineral phases. At higher C/S ratios (>2) portlandite was formed by hydrothermal treatment at 80°C to 200°C, at C/S ratios less than 1.7, tobermorite was the principal phases detected.

The situation is more complicated in real cement systems where other elements are available to form cement phases. In the CaO-SiO₂-CaCO₃-H₂O system, at 85°C crystallisation of C-S-H to afwillite and tobermorite occurred, but CaCO₃ remained the only carbonate detected. In the CaO-Al₂O₃-SiO₂-H₂O system treatment at 85°C lead to the formation of tobermorite, portlandite, siliceous hydrogarnets, gehlenite hydrate, zeolite P and gibbsite. For the CaO-Al₂O₃-CaSO₄-H₂O system, monosulphoaluminate was found to be the most stable phase at temperatures greater than 50°C, for sulphate levels typical of most cements. However, ettringite becomes more stable at enhanced sulphur levels which may occur from ingress of groundwater.

The previous review [171] concluded that it is unlikely that changes in mineral phases caused by temperature perturbations will affect the pH-buffering capacity of NRVB post closure, because it has a portlandite content, which persists across the range of predicted temperatures.

The impact of prolonged elevated temperature on cement has impinged on civil engineering in three ways:

- the use of cement in deliberately heat-cured products which subsequently find use at normal or near normal temperatures;
in the course of the transient thermal excursion arising from retention of heat during the initial set reactions of large masses of concrete; and

- exposure to fire.

The latter is outside the scope of this report. Neither of the other two situations is directly applicable to EBS cements in GDF; they are experienced at early stages of setting and hardening and are relatively brief whereas in the post-closure period for storage facilities, raised temperature may be experienced for extended periods. Experience of these thermal effects on cement materials is outlined below.

In autoclaved, heat-cured products, fresh Portland cement is mixed with silica, preferably quartz, and water. After fabrication to the desired shape at ambient temperature, the product, usually with a low w/s ratio, is cured in saturated steam at 160-190°C for 12-16 hours; this permits a daily production cycle. The bulk composition of the mix is important for strength development. To generate strength, it is important that the reaction products have approximately the same density as normal cement hydrates, about 2.3-2.4 g/cm³. The Portland cement has a C/S ratio ~2.6-2.9 and the product of crystallisation, dicalcium silicate hydrate, 2CaO·SiO₂·H₂O, is considerably denser than the target figure with the result that much open pore space develops in the autoclaving and the resulting product has poor strength. However two crystalline phases that have low densities and give good mechanical strengths are xonotlite (Ca/ Si=1.5) and tobermorite (C/S~0.83). The amount of added silica is therefore sufficient to bring the mean C/S ratio of the mixture close to that of the desired crystalline phases. To achieve rapid reaction, silica is usually ground to micron size, ~1000 cm²g⁻¹. The efficiency of processing is relatively high: most commercial products contain little (1-5%) free silica after autoclaving: C-S-H, while present, is usually a minor component. Experience has been that slag and fly ash are not satisfactory substitutes for quartz, probably because their high concentrations of oxides other than silica adversely affect the product(s) of reaction. Thus quartz remains the choice for silica additions.

The system CaO-SiO₂-H₂O has been well studied with respect to providing support for the autoclaving process and also in the Yucca Mountain repository where projection showed that cement might be exposed to temperatures as high as 200°C [172, 173]. Thus phase relations are well established in the range 120-200°C at saturated steam pressure. It was shown that, contrary to belief, many reactions in this system were reversible on a laboratory time scale (weeks, months). The main phases generated by autoclaving persist indefinitely at ambient temperature, as shown in natural occurrences.

Another body of experience, mainly in the range below 100°C, is provided by experience of large concrete pours. The resulting heat evolution has been described elsewhere in this report (see sub-section 5.6). In massive constructions, heat escapes only slowly with the result that the cement hydration reactions occur in part at elevated temperatures. Two opposing consequences may result from the thermal excursion:

- hardened cement, like most materials, has a positive coefficient of thermal dilation and so contracts with decreasing temperature; and
- the mineralogy of cement paste is sensitive to temperature and may be altered, both on increasing and decreasing temperature, with the result that the molar volume of the stable solids tends to increase on decreasing temperature.

Mineralogical change may dominate and cause significant long-term expansion with cracking. Thus the combination of these two impacts does not generally cancel, partly because they occur on different time scales (response to thermal dilation is rapid whereas mineralogical transformations are slow). The most important of these, involving the re-formation of ettringite at lower temperatures (delayed ettringite formation) has been described, for example, in a symposium proceedings [174]. Delayed ettringite formation may be physically disruptive.
7.2.2 Processes affecting cement performance

Table 18 summarises the potential impact of elevated temperatures on cement components and the potential impacts affecting cement performance, on the assumption that peak temperatures do not significantly exceed 80°C.

<table>
<thead>
<tr>
<th>Materials affected</th>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>Lower water content, even at high RH. Increased density and porosity with shift of porosity to larger mean size: sorptive properties may change, possibly irreversibly.</td>
</tr>
<tr>
<td>C-S-H</td>
<td>Unaffected, so pH conditioning performance during early stages of pH evolution would be unchanged†.</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>Possible, but no supporting evidence.</td>
</tr>
<tr>
<td>Crystallisation of slag and C-S-H</td>
<td>Probably reduce or disappear with formation of siliceous hydrogarnet: increase in porosity, owing to increasing solids density in the course of reaction.</td>
</tr>
<tr>
<td>Minor phases (AFm, Aft)</td>
<td>The matrix is modified by cement-aggregate interactions resulting in chemical combination of portlandite with decrease in pH. Possible dimensional instability.</td>
</tr>
</tbody>
</table>

† See sub-section 11.3 for discussion of the different stages of pH evolution.

The detailed course of reaction depends on the formulation used and for this reason, Table 18 considers a range of formulations. NRVB is not expected to have high strength and is deliberately formulated to be very porous, so it is unlikely that the thermal excursions changes will significantly affect performance except for altering the sorptive contribution attributed to C-S-H which is likely to be affected by annealing and crystallisation. Some data on the sorption of radionuclides to aged NRVB samples has been reported and also onto fresh samples of NRVB at elevated temperatures, and these data are discussed further in sub-sections 12.5 and 12.11.1.

Paul [175] reported on the mineralogical reconstitution of a Portland cement following initial set and 28 day cure at ~20°C with subsequent curing for 8 years at 100% RH and 85°C. At the conclusion of the elevated temperature exposure, AFm and AFt phases were absent. While C-S-H persisted, its C/S ratio had decreased to 1.5 or less. Ca(OH)₂ persisted and it was thought this was an equilibrium persistence. However after heat treatment much of the aluminium was in the form of siliceous hydrogarnet, formation of which increased the cement porosity. The pH of these cements was controlled by Ca(OH)₂ which persisted, probably even increasing in amount as the C/S ratio of C-S-H decreased. Thus, the pH remained high, >12 at 20°C. No crystalline calcium silicates were detected.

A companion study, on a 40% fly ash-60% Portland cement blend, has been reported by Gordon [176]. The blended cement had received 28 days hydration at approximately 20°C before the high temperature exposure. Reaction was far from complete at 85°C, after 8 years at 100% RH. Characterisation of reaction products was handicapped by the incomplete and localised nature of reaction, although free portlandite had been consumed, a wide spread of C-S-H compositions persisted. The mean C/S ratio for the C-S-H was ~1.2, showing that portlandite reaction with C-S-H had influenced the C-S-H composition. However, it was considered from the chemical and microstructural data that reaction was incomplete. Morphological relicts of fly ash were seen and
these were locally high in silicon and aluminium but low in lime. Both strätlingite (C$_2$ASH$_8$) and siliceous hydrogarnet (C$_3$AS$_{0.8}$H$_{4.4}$) were abundant and it was conjectured that their formation was ongoing; had reaction time at 85°C been extended, more of these phases would have formed. It is noteworthy that when the samples were examined after an additional 4-5 years cure at ambient temperature, no evidence was found that the high-temperature state had reverted back to the lower temperature state.

A 10-year project on the hydrothermal ageing of NRVB and two typical waste encapsulation grout formulations (OPC/PFA and OPC/BFS blends) is in progress on the NDA RWMD programme [177]. By mid-2011 data was available for individual samples and grout samples in contact with NRVB that have been aged at various temperatures for two years. In general, little change in the composition and microstructure has been observed, although temperature appears to increase the rate of reaction of BFS, and Ca(OH)$_2$-rich material was observed to diffuse from NRVB into the blended cement grouts.

7.2.3 Role of mineral aggregates

When the system contains mineral aggregates, the possibilities for reaction increase. Where the amount and composition of the aggregate materials has not been specified it is difficult to make generic statements. Calcite has only a minor impact on paste mineralogy and much of this impact will be achieved prior to the thermal excursion, in the course of setting and hardening [178].

With regard to cement-aggregate reactions, their importance cannot be neglected especially given that the total aggregate content of a concrete may comprise >80-85% of the total mass. As noted in Table 18, while pure calcium carbonate aggregates are essentially inert with cement other carbonates, such as dolomite, CaMg(CO$_3$)$_2$, are reactive [179]. The main problems are, however, anticipated to occur as a consequence of using siliceous aggregates. There is evidence of the frequent occurrence in modern concrete of deleterious reactions between silica and/ or silicate minerals and Portland cement. This process, termed “Alkali–Aggregate Reaction”, or AAR, affects structures worldwide, including many in the UK, and the process is well characterised [180]. The high hydroxyl content of cement leads to slow hydrolysis of Si-O-Si bonds in, for example, quartz. In a second step, the resulting Si-OH bonds imbibe water and the aggregate swells; this leads to physical expansion and cracking. Thus three conditions are necessary for AAR: susceptible aggregates, high concentrations of hydroxyl ions and the availability of water. The time to onset of damage by AAR is markedly reduced by temperature, with the result that accelerated tests are often made at temperatures up to ~80°C.

Criteria for the identification and rejection of deleterious aggregates are not well agreed. Moreover screening criteria thus far proposed are relevant to concretes intended for service at ambient temperature, and are unlikely to be applicable to service at elevated temperature.

To keep the hazard assessment of AAR in perspective, we know that ancient concretes occur but show no signs of reaction between the cementitious components and quartz or other siliceous aggregates. Of course their moisture history is unknown and it is unlikely that they have ever been exposed to high temperature while wet. On the other hand, we have the evidence of hydrothermal curing where extensive, nearly complete reaction occurs between silica and cement in <24 hours at ~160°C. But much of the reaction occurs while the cement is still capable of plastic response, and in any event, the matrix undergoes complete recrystallisation, giving the opportunity for relief of stresses.

7.3 Mechanical properties

7.3.1 Structural performance of cementitious materials at elevated temperature

Long term studies of the effect of prolonged exposure to elevated temperature on cementitious systems are rare. One of the few areas in which this topic has been covered is in relation to nuclear power station construction. Nuclear reactors operate over a range of temperatures similar to those expected in the GDF and the concrete used, having been cast as massive pours, will have undergone early age thermal cycles also.
As part of the UK development of concrete for use in nuclear applications, extensive testing was undertaken over a range of temperatures up to 95°C and some specimens used in the original studies were maintained at elevated temperature for periods of up to 25 years before testing. A review of concretes used in five UK nuclear power stations [181] concluded that under prolonged storage in a moisture stable state, temperatures up to 95°C were not detrimental to compressive strength. At all storage temperatures the strength continued to develop such that after 25 years the strength was almost double that achieved after 28 days. Results were available for concrete using either OPC of a combination of OPC/PFA. The long term strength gain was marginally higher for the latter.

The same study [181] reported on compressive strength after exposure to rapid changes in temperature. A strength loss was observed and this was attributed to internal stresses caused by the differential thermal expansion of the cement paste and the aggregate. Such stresses would not be expected in a grout. The rate of temperature change was 20°C per hour and heating from 20°C to 80°C was found to reduce the strength by less than 5%. Heating to 120°C caused a more significant reduction of up to 20%. The significant additional damage was attributed to the combination of differential thermal expansion of cement paste and aggregate and drying shrinkage of the paste which increased markedly when the temperature exceeded 100°C. As the temperature in the backfill is not expected to exceed 80°C, elevated temperature is not expected to cause significant detriment to strength.

The stiffness of concrete is affected by temperature. As the temperature increases so the modulus of elasticity reduces. Further tests on concretes for nuclear applications [162] showed an approximately linear reduction in the elastic modulus of about 30% when heating specimens at an age of 100 days at a range of temperatures from 20°C to 95°C. A similar reduction (about 33% over the range from 20°C to 100°C) was reported for concretes loaded at late life (ages from 12.5 to 24.5 years) [182].

Creep (deformation under sustained loading) is also increased significantly at elevated temperature to a much greater extent than the elastic strain occurring under initial loading. For example, for concrete loaded at an age of 100 days, a difference in temperature when loaded (from 20°C to 95°C) caused the elastic strain to increase by about 50% but the total deformation under sustained loading for 100 days (elastic plus creep) to increase by about 100%.

Similar findings with regard to the effect of temperature on the mechanical properties of concrete are reported elsewhere, e.g. [183].

In terms of structural behaviour, therefore, elevated temperature in a GDF is not expected to have a detrimental effect on strength but will reduce the stiffness (lower modulus of elasticity and higher creep). Lower stiffness is beneficial as the stresses associated with a given strain change are lower also, and the risk of cracking is reduced. Load induced stresses are also more readily redistributed, achieving a more uniform stress state.

7.3.2 Thermal behaviour at elevated temperature

The thermal expansion coefficient is necessarily measured over a temperature range and any deviation in the temperature-strain relationship from linearity would indicate an effect of temperature. In tests on concrete in the range from 20°C to 50°C [184] linearity was observed over the full range. In tests on concrete up to much higher temperatures it was reported that in the range from 20-120°C the variation was not large [185]. It may be assumed therefore that the coefficient of thermal expansion will not change significantly over the range of temperatures experienced within a GDF.

In tests on concrete, changes in both the coefficient of thermal conductivity and the specific heat capacity have been observed [186]. With increasing temperature over the range from 0 to 80°C, the thermal conductivity decreased linearly by about 10%, whereas the specific heat capacity increased linearly by a similar amount. The combined effect was a reduction in the thermal diffusivity with increasing temperature by about 20% over the same temperature range.
Similar findings are reported in a review prepared for the US Nuclear Regulatory Commission [187].

ILW vaults will operate at temperatures generally up to about 50°C but temperatures up to 80°C are permissible when using a cementitious backfill. To model reliably the temperature change within a cement-based near field, account should be taken of the change in thermal properties that may occur with temperature.

7.4 Key points

- The temperature in the near field of a GDF is expected to rise significantly above ambient during the early post-closure period. In the case of HLW and spent fuel, radiogenic heating may be significant for several thousand years while short-lived radionuclides decay; the current technical specification allows temperatures to reach up to 100°C on the surfaces of waste containers. In the case of cement-based vaults for the disposal of ILW/LLW, heat generated by cement hydration on emplacement of the backfill may be significant for tens of years and the current technical specification allows for the temperature to rise up to 50°C generally and up to 80°C in the short term. As a result, cement materials within a GDF will be exposed to elevated temperatures for varying durations during curing and the resaturation of the GDF with groundwater.

- In terms of mineralogical changes, heat treatment of OPC at 85°C (a temperature above that expected in an ILW vault), appears to have negligible effect on the Ca(OH)\textsubscript{2} content but may lead to changes in aluminium-containing phases with some lowering of the C/S ratio of C-S-H phases. Potentially the most significant mineralogical change associated with temperatures above ~60°C is the delayed formation of ettringite on cooling to lower temperatures, which is associated with a significant increase in solids volume that potentially can be physically disruptive. These reactions are slower than thermal contraction and thus will have an additional impact.

- For NRVB, which has a significant Ca(OH)\textsubscript{2} content (Table 2), the impact of the thermal cycle at lower temperatures is not expected to be significant. Work is ongoing on the RWMD programme to study the hydrothermal ageing of NRVB at a number of temperatures over a 10 year period.

- With regard to the physical properties of cementitious systems, the temperature \textit{per se} is unlikely to have a significant effect. In terms of structural behaviour, therefore, the elevated temperature in a GDF is not expected to have a detrimental effect. Elevated temperatures will, however cause a reduction in the stiffness (lower modulus of elasticity and higher creep). This is potentially beneficial because the stresses associated with a given strain change would be lower and would be more readily relieved by creep, thus reducing the risk of cracking. In addition, load-induced stresses are more readily redistributed achieving a more uniform stress state.

- Based on testing of concrete, the coefficient of thermal expansion is expected to remain constant over the operating temperature range. Changes in thermal conductivity and specific heat capacity may result in a reduction in the thermal diffusivity of about 20% at the high end of the temperature range.
8 Mass transfer performance of cement backfills

In this section, the mass transfer properties and behaviour of cementitious backfill materials are discussed. It is likely that backfill materials will have a significantly higher permeability than cementitious material used for sealing. In particular, this is the case for NRVB. Its specification includes a requirement [12] for a permeability that is sufficient to promote homogenous aqueous chemistry and to facilitate the migration of gas generated by corrosion and microbial activity away from the waste. This is to avoid the build up of excessive pressure, which could lead to damage both to the facility and to a zone of rock around the facility. The M1 backfill considered by Nagra (and used in particular in the COLEX experiment [188]) also has a relatively high permeability. However, it is possible that a low permeability backfill might be used in some circumstances to reduce flows of water in the immediate vicinity of the waste packages. This would be likely to mean that some mechanisms for package degradation would be less effective, and also to reduce fluxes of radionuclides away from the waste.

The mass transfer behaviour of the cementitious backfill may affect the following processes within the EBS:

- the resaturation of a GDF (see sub-section 8.3.1);
- the flow of groundwater through a facility after resaturation, which may affect corrosion, and hence the lifetime of waste containers and gas generation; it may also affect the release of contaminants from the facility and hence their impacts;
- diffusion of contaminants dissolved in groundwater out of a facility;
- the flow of gas out of a facility, which will affect the pressure that develops within the facility and the radiological and other hazards associated with gas;
- migration of non-aqueous phase liquids (NAPLs) from the facility.

However, apart from the third bullet point above, the properties of the host rock rather than the properties of the backfill may be the key controls on these.

8.1 Mass transfer properties

The processes above are affected by the following mass transfer properties of the backfill (and similar properties of the rocks around the facility).

- The permeability (or intrinsic permeability). The permeability is a measure of the ease with which fluids can flow through a porous medium. The specific discharge $q$ (the ratio of the volume flow rate crossing an area to the area) is given by

$$q = \frac{k}{\mu} (\nabla P - \rho g), \quad (9)$$

where:

- $k$ is the permeability of the medium;
- $\mu$ is the viscosity of the fluid;
- $P$ is the pressure;
- $\rho$ is the density of the fluid;
- $g$ is the gravitational acceleration.

- The porosities accessible to fluids (water, gas, NAPLs) and solutes (cations, anions and molecular species).
• The two-phase water-gas properties: the relative permeability for water; the relative permeability for gas; and the capillary pressure.

• The three phase water-gas-NAPL properties: the relative permeability for water; the relative permeability for gas; the relative permeability for NAPL; the NAPL-water capillary pressure; and the gas-NAPL capillary pressure.

• Diffusion properties: the intrinsic diffusion coefficients for solutes including dissolved gases.

8.1.1 Permeability

Permeabilities have been measured for various potential cementitious backfill materials. The permeability for NRVB is about $10^{-16}$ m$^2$ [12], which is at the upper end of the range for concretes. The permeability of the Swiss M1 mortar used in the Nagra programme (and in the COLEX experiment, in particular) is $4 \times 10^{-10}$ m$^2 \pm 3 \times 10^{-10}$ m$^2$ [188], which is also relatively high. For comparison, typical values of concrete permeability lie in the range $10^{-21}$ m$^2$ to $10^{-15}$ m$^2$ [189], and in the EC FORGE project, values of about $5 \times 10^{-17}$ m$^2$ have been measured for concrete [190]. The concrete composition$^8$ was that of concrete intended for the construction of disposal cells in which waste containers would be placed in the Spanish El Cabril disposal facility. This would probably not be a composition used for a backfill.

It is possible that a low permeability cementitious backfill might be used. The permeability of structural concrete, which might be used for vault floors for example, would be expected to be towards the lower end of the range for concretes.

It is noted that at low pressure, the apparent permeability of a porous medium to gas is higher than the permeability to water. This is because of ‘slippage’ at the walls of the pore space when the mean free path of the molecules in the gas becomes comparable to the dimensions of the pores. Klinkenberg [191] suggested that the gas permeability is related to the water permeability as follows:

$$k_g = k_w \left(1 + \frac{B}{P_m} \right)$$

where

- $k_g$ is the gas permeability [m$^2$];
- $k_w$ is the water permeability [m$^2$];
- $B$ is the Klinkenberg parameter, a constant for a given porous material and a given gas [Pa]; and
- $P_m$ is the mean pressure of the gas [Pa].

Bamforth [192] has derived the following empirical relationship between the Klinkenberg parameter and the water permeability

$$B = 1.657 \times 10^{-3} k_w^{-0.5227}$$

The backfill permeabilities given above are for uncracked backfill. However, it is expected that shortly after backfill emplacement, cracks may develop as a result of plastic settlement, early-age thermal contraction and expansion of the waste packages as a result of corrosion, (see section 5 and [92]).

$^8$ The concrete has a water/cement ratio of 0.43 and its composition is:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aggregate 4/16</td>
<td>1023 kg</td>
</tr>
<tr>
<td>Sand 0/4</td>
<td>634 kg</td>
</tr>
<tr>
<td>Sand 0/2</td>
<td>203 kg</td>
</tr>
<tr>
<td>Cement I 42,5R/SR</td>
<td>400 kg</td>
</tr>
<tr>
<td>Melcret-222 additive</td>
<td>6.5 kg</td>
</tr>
<tr>
<td>Water</td>
<td>175 L.</td>
</tr>
</tbody>
</table>
The crack pattern that is expected to develop in NRVB is discussed in reference 92. The cracks contribute to the effective permeability of the backfill. For central values of parameters, the effective permeability of the cracked NRVB is estimated to be about $4 \times 10^{-13}$ m² [92]. The permeability is anisotropic with slightly different values in different directions because the cracks with different orientations are expected to have slightly different spacing and aperture [92].

For NRVB, the contribution to the effective permeability from the cracks is therefore expected to dominate the contribution from the uncracked matrix. Groundwater will therefore flow predominantly through the cracks. It would therefore be expected that the two- and three-phase flow properties (see sub-section 8.1.4) would be dominated by the contribution from the cracks.

However, the case of the Swiss M1 mortar is rather different and there is no published information on the expected pattern of cracking in this material. If the pattern were similar to that in NRVB, then the contribution from the cracks to the effective permeability of the cracked M1 mortar would be similar to that for the NRVB. However, in the case of the M1 mortar, the contribution to the effective permeability from the uncracked matrix dominates. Therefore, it would be expected that the two- and three-phase flow properties of M1 mortar (see sub-section 8.1.4) would be dominated by the contribution from the uncracked matrix, with the following exception. It is possible that the gas entry pressure for the cracks might be less than that for the matrix, and so gas might be able to enter the cracks and migrate through them more readily than it could enter and migrate through the backfill matrix.

Further, the pattern of cracking for M1 mortar could differ from that of NRVB, because of their different strengths and coefficients of thermal expansion in particular. Similarly the pattern of cracking could be different for a different cementitious backfill. Whether or not the contribution from the cracks to the effective permeability dominates that from the matrix can only be determined on a case by case basis.

### 8.1.2 Porosity

Porosities have been measured for various potential cementitious backfill materials. The porosity for NRVB has been measured to be about 0.5 using a combination of mercury intrusion porosimetry for large pores and nitrogen desorption for small pores [12]. Mercury intrusion porosity shows that the pores are generally less than about 800 nm in radius with a distribution that peaks at about 500 nm. However, mercury intrusion porosimetry cannot measure pores below about 2 nm. Nitrogen desorption was used to measure the distribution of the smaller pores. There is an upper limit of about 60 nm on the pores that can be investigated using nitrogen desorption. Used together the two approaches provide the whole distribution. However, it is noted in reference 12 that the measurements generally involve drying the samples, which tends to increase the porosity. The value above may therefore be an overestimate. It is noted that a lower value of around 0.16 has been found for the water accessible porosity of NRVB in through-diffusion experiments using tritiated water [193]. The porosities accessible to anions and cations are discussed in sub-section 8.1.3.

The porosity of the Swiss M1 mortar (used in the COLEX experiment) was estimated to be about 0.27 [188] on the basis of a correlation between porosity and bulk density [194]. A similar estimate was obtained from the bulk density of the mortar and its true density, taking into account chemical shrinkage during hydration. In reference 188 it is noted that direct measurements were not made because drying leads to damage to the microstructure (see also reference 190).

In his textbook, Neville [189] reports a porosity of 0.28 for cement paste.

The discussion above addresses the porosity of the backfill matrix. However, as discussed in the previous section, it is considered that in the NRVB flow would be predominantly through cracks rather than the matrix. The pore volume associated with the cracks can be estimated from the apertures and spacing of the cracks and is much smaller than the total pore volume of the uncracked matrix.
In reference 193, an average surface area of 28,000 m²kg⁻¹ is also presented for NRVB. Although this is not a measured value of porosity, it is reported in this sub-section because it potentially provides information about the nature of the pore space. In particular, it indicates that the typical pore size is of the order of nanometres.

### 8.1.3 Diffusion properties

In the Nirex programme, diffusion properties were measured for NRVB and various other cementitious materials [193]. Intrinsic diffusion coefficients and capacity factors were determined from through-diffusion experiments for non-sorbing solutes and from depth profiling following in-diffusion for solutes with significant sorption. The latter technique was used because the solutes would not diffuse through samples on a practicable timescale. Intrinsic diffusion coefficients were also estimated from formation factors determined from measurements of the electrical conductivities of samples [193]. The values of the intrinsic diffusion coefficients and capacity factors are summarised in Table 19 and Table 20 respectively. The capacity factor is given by

\[
\alpha = \phi + \rho K_d
\]

where
- \(\phi\) is the (matrix) porosity [m²];
- \(\rho\) is the density [kg.m⁻³]; and
- \(K_d\) is the sorption distribution coefficient [m³.kg⁻¹].

The intrinsic diffusion coefficient is often expressed as

\[
D_i = \frac{\phi_{acc} D_0}{\tau}
\]

(or an equivalent form) where
- \(\phi_{acc}\) is the porosity accessible to the solute;
- \(D_0\) is the free-water diffusion coefficient for the solute;
- \(\tau\) is the tortuosity for the solute.

#### Table 19 Best estimates of the intrinsic diffusion coefficients for various cementitious materials (from [193]); ranges are not provided for cases in which only one measurement was available

<table>
<thead>
<tr>
<th>Material</th>
<th>(D_i) for ions of differing ionic charge (10⁻¹³ m² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-1</td>
</tr>
<tr>
<td>Sulphate-resistant Portland Cement mortar*</td>
<td>70 ± 35</td>
</tr>
<tr>
<td>Sulphate-resistant Portland Cement mortar</td>
<td>20 ± 5</td>
</tr>
<tr>
<td>BFS/OPC mortar†</td>
<td>2 ± 2</td>
</tr>
<tr>
<td>BFS/OPC concrete</td>
<td>3 ± 2</td>
</tr>
<tr>
<td>PFA/OPC concrete‡</td>
<td>4 ± 4</td>
</tr>
<tr>
<td>Preliminary grout^</td>
<td>1700 ± 600</td>
</tr>
<tr>
<td>NRVB</td>
<td>340 ± 70</td>
</tr>
</tbody>
</table>

Notes:
* SRPC mortar had fine aggregate < 2.5 mm, aggregate/cement = 2 and w/c = 0.6.
† BFS/OPC = 4, fine aggregate < 2.5 mm, aggregate/cement = 2 and w/c = 0.6.
‡ PFA/OPC = 3, fine aggregate < 2.5 mm, aggregate/cement = 2 and w/c = 0.475.
^ The composition of the preliminary grout is 2:1 lime/OPC with w/c = 0.9.
Table 20  Best estimates of the capacity factors for various cementitious materials (from [193])

<table>
<thead>
<tr>
<th>Material</th>
<th>Tritiated water</th>
<th>Iodide</th>
<th>Caesium</th>
<th>Strontium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate-resistant Portland Cement mortar*</td>
<td>0.12±0.08</td>
<td>7±5</td>
<td>2±1</td>
<td></td>
</tr>
<tr>
<td>Sulphate-resistant Portland Cement mortar</td>
<td>0.10±0.03</td>
<td>3±2</td>
<td>0.65±0.02</td>
<td></td>
</tr>
<tr>
<td>BFS/OPC mortar†</td>
<td>0.02</td>
<td>0.4±0.1</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>BFS/OPC concrete</td>
<td>8</td>
<td>0.9±0.4</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>PFA/OPC concrete‡</td>
<td>0.002</td>
<td>0.11±0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Preliminary grout^</td>
<td>0.24±0.04</td>
<td>0.2±0.1</td>
<td>0.2±0.1</td>
<td></td>
</tr>
<tr>
<td>NRVB</td>
<td>0.16±0.01</td>
<td>0.1</td>
<td>0.45</td>
<td></td>
</tr>
</tbody>
</table>

Notes: see notes below Table 19.

These results appear to indicate that there is anion exclusion in NRVB, that is, the porosity accessible to anions is less than that accessible to neutral species and cations, with the porosity accessible to iodide being about half that accessible to tritiated water. This is relevant to the diffusion of radionuclides that may be present as anionic species, in particular Cl⁻, I⁻ and Tc-99 as pertechnetate.

### 8.1.4 Two-phase properties

Bate et al. [195] carried out a brief review of the two-phase flow properties of cementitious materials. The properties in question are the capillary pressure and the relative permeability (see sub-section 8.3.6 for a discussion of these properties). They depend on the saturations $S_w$ and $S_g$, which are the fractions of the pore space occupied by the two fluids (here considered to be water, $w$, and gas, $g$). Of course,

$$S_w + S_g = 1$$  \hspace{1cm} (14)

so only one saturation is independent. The independent saturation is usually taken to be the water saturation. The two-phase flow properties are commonly represented using functions (of water saturation) characterised by a small number of parameters. The functions are obtained by fitting to the available experimental data. The functions are then used in numerical modelling of two-phase flow.

### (a) Capillary pressure

Various methods can be used to measure capillary pressures, as discussed for example in reference 196. The methods have their own advantages and disadvantages. One approach [196] is to inject mercury into a dried sample in steps of gradually increasing pressure and measure the volume of mercury that has entered the sample at each step. The capillary pressure curve derived for mercury in this way is then converted to a water-gas curve using the appropriate interfacial tensions and contact angles for water and mercury. The method is rapid, but has the disadvantage of leading to a sample contaminated with mercury and requires the indicated conversion. In the case of cement and concrete, the required drying also leads to damage to the microstructure (see section 8.1.2), so the derived capillary pressure curve may be severely biased.

Another approach [196] is to mount a saturated porous plate with a high gas entry pressure on one side of a sample and to supply gas to the other side of the sample. The porous plate allows the water to pass out of the sample, but not the gas. The sample is left until an equilibrium is reached. The water content of the sample is then measured. The process is repeated for several steps of
increasing gas pressure. This method avoids the problems associated with the mercury intrusion approach, but is very time-consuming.

Other approaches can be used such as a dynamic method involving the injection of two fluids simultaneously into a sample, with one being produced behind a semi-permeable membrane, a transient approach and a centrifuge approach [196].

One form that is commonly used for the capillary pressure is that introduced by van Genuchten [197]:

\[ p_c = p_a \left( S_{sw}^{1/m} - 1 \right)^{1-m} \]  

(15)

where

\[ S_{sw} = \frac{S_w - S_{wr}}{1 - S_{wr}} \]  

(16)

\[ S_{eg} = \frac{S_g - S_{gr}}{1 - S_{gr}} \]  

(17)

and

- \( p_a \) is the "apparent" gas entry pressure [Pa];
- \( m \) is a parameter related to the pore-size distribution of a porous medium that controls the shape of the capillary pressure function;
- \( S_{wr} \) is the residual saturation of the water phase [–].
- \( S_{gr} \) is the residual saturation of the gas phase [–].

Here, the residual saturation is the saturation at which the phase becomes mobile9. \( p_a \), \( m \), \( S_{wr} \) and \( S_{gr} \) are parameters that are derived by fitting to experimental data.

In recent work by Baroghel-Bouny et al. [198] and Mainguy et al. [199], \( m \) was taken to be 0.5. This form is also consistent with a model of the two-phase properties of concrete used by Senger et al. [200].

The gas entry pressure depends on the pore-size distribution. The pressure required for gas to displace water from a pore \( (p_a) \) increases as the size of the pore decreases. For example, for gas to displace water from a cylindrical capillary, the pressure in the gas has to be greater than the pressure in the water at the gas-water interface by:

\[ p_a = \frac{2\gamma}{a} \]  

(18)

where

- \( a \) is the radius of the capillary;
- \( \gamma \) is the surface tension of water.

It is noted that if the pores are smaller, the permeability will tend to be smaller. Therefore, it would be expected that the gas entry pressure will tend to be higher for media with lower permeability.

Ibrahim et al. [201], Pihlajavarra [202] and Ingram et al. [203] examined the possible relationship between the gas entry pressure and the permeability. Ibrahim et al. derived an empirical correlation between the gas entry pressure and the permeability for various porous media. Subsequently, Pihlajavarra carried out further measurements for concrete and concluded that the correlation of Ibrahim et al. consistently overestimated the gas entry pressure (see Figure 49).

\footnote{If water occupying a medium is displaced by flowing gas, not all of the water will be displaced (and vice versa). The residual saturation of water (or gas) represents the fraction of the porosity occupied by water (or gas) that cannot be displaced.}
Figure 49 Plot of gas entry pressure against permeability based on experimental measurements; the curve labelled (1) is the threshold displacement pressure curve, as presented by Ibrahim et al. [201]; the shaded area labelled (2) shows the experimental range for concrete obtained by Pihlajavaara [202] in 23 different tests (two scales for the permeability are provided to aid comparison with experimental results).

Ingram et al. reanalysed the data of Ibrahim et al., which were for a variety of porous media, and suggested the following generic correlation for the gas entry pressure ($p_a$) with permeability ($k$):

$$p_a = 5.874 \left(\frac{1}{k}\right)^{0.33}$$

see Figure 50. It should be noted that there is considerable uncertainty about the value of the gas entry pressure. For low permeability values, the correlation only gives the gas entry pressure to within about a factor of five either way.

Using the correlation in equation (19) and assuming $S_{wr} = 0.25$; and $S_{gr} = 0$, Bate et al. [195] derived a value of 0.35 MPa for the gas entry pressure of NRVB.

Various other functions are used to represent the capillary pressure. For example, the capillary pressure of the Swiss M1 mortar was described using a model proposed by Narasimhan [204]:

$$P_c = -P_0 \left(\frac{1 - S_w}{S_w - S_{w0}}\right)^{1/\eta}$$

where $P_0$, which is related to the gas entry pressure, $S_{w0}$, and $\eta$ are parameters.

In general, it will be possible to obtain acceptable fits for various functional forms to the limited data that are likely to be available for a particular cementitious material. Thus there will be uncertainty...
about the form of the function as well as about its parameters. The different functional forms generally have similar behaviour over most of the range of saturation, but have different behaviour as the ends of the range are approached. In some cases, the differences will have little effect on the behaviour of the system of interest, but in other cases, the differences may have significant effects. For example, the behaviour of the capillary pressure for very small gas saturations may have a significant effect on the ability of gas to begin to migrate through a potential barrier and hence on the pressure that builds up behind the barrier (see sub-section 8.3). The extent to which the uncertainty about the functional form will be addressed in practice depends on the nature of the calculations undertaken. For illustrative or scoping calculations, it may be sufficient to carry out calculations for one particular form, but for a detailed analysis in which the uncertainties are examined, it may be necessary to carry out a range of calculations in which the uncertainty about the form of the functional form is examined as well as the uncertainty about its parameters.

![Figure 50 Plot of threshold (capillary) displacement pressure against intrinsic permeability for a wide range of undifferentiated lithologies, including shale, limestone and anhydrite, based on in situ measurements (Ingram et al. [203] based on the data compilation of Ibrahim et al. [201])](image)

(b) Relative permeability

Relative permeabilities are measured using either a steady-state or a transient technique. In the steady-state method, water and gas are driven simultaneously though a sample until a steady state is reached. Then the saturation and the effective permeability are determined (from the pressure across the sample). From this, the relative permeability for the saturation can be calculated. In the
transient method, gas is injected into a sample, and the relative permeability determined from the fluxes of water and gas out of the sample.

As well as the form for the capillary pressure discussed in the previous sub-section, van Genuchten [197] also proposed the following forms for the relative permeability functions:

\[
k_{rw} = S_{ow}^{\eta} \left[ 1 - \left( 1 - S_{ew}^{1/m} \right)^m \right]^2
\]

\[
k_{rg} = S_{og}^{\zeta} \left[ 1 - \left( 1 - S_{eg}^{1/m} \right)^m \right]^{2m}
\]

where the exponents \( \eta, \zeta \) are parameters for the water and gas phases respectively. Van Genuchten suggested that values of 0.5 for the exponents would be typical of porous media.

It was suggested by Baroghel-Bouny et al. [198] and Mainguy et al. [199] that the forms above could be used for cementitious materials. Monlouis-Bonnaire et al. [205] used a value of \( m \) of the order of 0.5 for the exponent in the van Genuchten expression for the capillary pressure, they suggest:

\[
\zeta = 5.5 \left( = \eta \right)
\]

This was based mainly on their attempt to fit the relative gas permeability data as \( S_{ow} \to 0 \).

Jason [206] argues that while this fit is correct at small saturations,

\[
\zeta = 3.5 \left( = \eta \right)
\]

is more appropriate for intermediate saturations (i.e. \( 0.3 < S_{ow} < 0.5 \)).

Harris et al. [207] observed that the gas permeability of the NRVB was reduced by about two orders of magnitude as the NRVB saturated. This observation supports the choice:

\[
\zeta = 0.5 \left( = \eta \right)
\]

The gas permeability would be reduced by much more if the exponent were larger. The choice of an exponent of order 0.5 is also consistent with the model of the two-phase properties of concrete used by Senger et al. [200].

Other forms can be used for the relative permeabilities. One form that is often used is that of Corey, in which the relative permeability for water is expressed as a power of the water saturation, and the relative permeability for gas is expressed as a power of the gas saturation.

For the Swiss M1 mortar [188], the relative permeabilities were taken to be linear functions of the corresponding saturation.

Similar remarks to those made about the various functional forms for the capillary pressure models in the previous sub-section apply to the various functional forms for the relative permeability.

(c) The two-phase flow properties of cracks

In the discussion above, the two-phase flow properties of uncracked backfill are discussed. However, in some cases, such as that of NRVB, see sub-section 8.1.1, the dominant contribution to the permeability will come from cracks that develop shortly after backfill emplacement. In such cases, the two-phase flow properties would be dominated by the contribution from the cracks. For fractured media, the capillary pressure is often taken to be zero (see references 195 and 208) because gas is expected to be able to enter fractures relative readily. The relative permeabilities of fractured media are often taken to be equal to the corresponding saturation [195, 208], because it is expected that there will be little interference between the different phases.
Even if the contribution from the cracks is not the dominant contribution to the effective permeability of the backfill, the cracks may play an important role in the migration of gas (and NAPLs – see sub-section 8.3.5) through the backfill, because the gas entry pressure for the cracks will be low. Therefore, gas may be able to enter the cracks and migrate through them more readily than it can through the matrix of the backfill. Whether this is the case or not needs to be assessed on a case by case basis.

8.2 Evolution of the mass transfer properties

The mass transfer properties shortly after emplacement of the backfill are discussed in the previous section. The properties will evolve over time and their expected evolution is discussed in this section. The discussion builds on the discussion in [12] and understanding of the evolution of the system and its likely consequences for the behaviour of the backfill.

As a result of the resaturation of a GDF (see sub-section 8.3.1), the stress distribution within the backfill would change significantly. In particular, the pressure in the water in the pores and fractures in the backfill would change by an amount equal to the hydrostatic pressure associated with a column of water of height equal to the depth of a GDF. This would be a significant stress change and would lead to changes in the mass transfer properties of the backfill. It would be expected that the increase in the pressure of the water in the pores and cracks would lead to pore sizes and fracture apertures increasing. The former would lead to an increase in the permeability of the backfill matrix. The latter would lead to an increase in the contribution of cracks to the effective permeability.

It should also be noted that some low permeability host rocks exhibit substantial creep (see for example reference 209). This would lead to an increasing stress on the backfill, which would tend to lead to fracture apertures and pore diameters decreasing, and hence to reductions in the porosity and permeability.

After closure, the pattern of cracking would evolve over time from the initial pattern of cracking resulting from curing and and shrinkage of the backfill. The backfill itself would also evolve. Consequently the mass transfer properties and behaviour of the backfill will evolve. At early times after closure, the evolution of the pattern of cracking will be mainly affected by expansion as a result of corrosion within packages containing reactive waste (such as Magnox and aluminium) (see reference 12). The extent of corrosion, and hence cracking, will be reduced if there has been significant corrosion of the reactive waste before disposal. The extent of cracking is likely to be greater if the vaults have open crown spaces (see Figure 2). Heterogeneity in the expansion throughout a vault of a GDF could lead to the development of localised tensile stresses, which would lead to the development of additional cracks if the tensile strength of the backfill at the time is exceeded. It should be noted that the tensile strength and hence the pattern of cracking for backfills other than NRVB may be significantly different from those for NRVB, for which the design specification includes a requirement of low strength. The changes in the stress pattern would also lead to changes in the apertures of cracks created in the period immediately after emplacement of backfill.

The corrosion would also generate gas (see references 85 and 210, and sub-section 8.3.2). If the gas cannot migrate away from the vaults sufficiently readily, the pressure in the gas would rise and could reach a level where it leads to additional cracks developing in the backfill. It would also lead to changes in the apertures of existing cracks.

The pattern of cracking could also be affected by shrinkage resulting from carbonation of the cementitious backfill [11, 189]. This could result from carbon dioxide generated by microbial processes [85].

The backfill matrix will also evolve over time, leading to changes in its mass transfer properties. The main changes will be associated with the leaching of cement components by groundwater flowing through the backfill (see sub-section 9.2). It is also expected that there would be precipitation of secondary minerals resulting from interactions of cement with groundwater. The
precipitation of secondary minerals could occur mainly on the surfaces of cracks through which groundwater is predominantly flowing. This could lead to ‘armouring’ of cracks or to healing of cracks [11].

The leaching out of the portlandite and then the C-S-H gels from the backfill will lead to an increase in its porosity over time, which might be counteracted by precipitation of secondary minerals. The increase in porosity will result in an increase in the permeability of the backfill. It would also be expected that there would be changes to the two- and three-phase relative permeabilities and capillary pressures and to the tortuosity (see sub-section 8.1.3). There is considerable uncertainty about these changes.

The time scale for leaching for cement components and the associated changes to the mass transfer properties will depend on the rate of groundwater flow through the GDF (see section 8.3.3). This will depend on the effective permeabilities of the host rock, the backfill and possible vault liners and the possible presence of open crown spaces to the vaults. The time scale will be very long for a low permeability rock such as a clay, shale or mudstone. For a fractured host rock, if transmissive features have been grouted to reduce inflows, the grouting may lose its effectiveness over time (see sub-section 13.2), leading to increasing flow through a GDF and shorter time scales for the changes discussed.

Over time, minerals within the cement might become more crystalline. Although this might have a significant effect on sorption (see sub-section 12.5), it is not expected to have a big effect on the mass transfer properties. However, there is no quantitative experimental information on the mass transfer properties of aged cementitious backfill.

8.3 Mass transfer behaviour

8.3.1 Resaturation

In this section, the resaturation of a GDF post-closure is discussed. The discussion builds on the discussion in Bate et al. [195, 211]. See also reference 11.

The pressure in open parts of a GDF after its construction would be at atmospheric. This is much less than the pressure that would have been in the groundwater at the position of the GDF, which would have been of the order of the hydrostatic pressure at the depth of the GDF. Groundwater would therefore flow into a GDF driven by the difference between the pressure in the groundwater in the surrounding rocks and the pressure in the GDF.

As groundwater flows into a GDF, the pressure in the rocks immediately adjacent to the GDF would drop and a region of drawdown (i.e. reduced pressure) would develop in the host rock around a GDF. The size of this region would increase with time, and as it does, the pressure gradients driving flow into the GDF would fall and hence the flow into a GDF would fall. The drawdown and the rate of inflow will tend to a nearly steady-state (neglecting seasonal fluctuations).

Superimposed on the flow toward a GDF would be very local flows driven by differences in groundwater head between different parts of a GDF, as a result of their different elevations.

For a fractured host rock, most of the inflows to a GDF would be associated with individual features. It would be expected that the layout of a GDF would be designed to avoid major features, and it would be expected that, if a GDF intersected features carrying significant flow, these would be grouted to reduce inflows to the GDF.

For an environment in which the host rock does not have very low effective permeability, such as a fractured higher strength rock, a liner with lower permeability than the host rock could be constructed. This would reduce the inflow into the GDF and the magnitude and extent of the drawdown region. Alternatively, or in addition, individual fractures/features in the host rock might be grouted to reduce their transmissivity in the vicinity of the GDF. This would also reduce inflows into the GDF.
It would be expected that the tunnels, vaults and shafts of a GDF would be sealed at appropriate locations. The seals would be constructed of materials such as structural concrete and bentonite and would have low effective permeability overall. The seals would be designed to ensure that there would not be a continuous high permeability path along which water could flow through a GDF post-closure.

It would be expected that prior to closure, the water flowing into the GDF would be removed by a suitable drainage system. It would also be expected that some water in the host rock would evaporate, migrate into the air within a GDF and be removed in the ventilation system.

After closure, water will no longer be removed in the drainage or ventilation systems. Water would therefore start to build up within the GDF and fill voids, such as a possible open crown space, and open porosity within the backfill. That is, the GDF would resaturate.

The resaturation of a GDF could lead to saline water being drawn up into the GDF from greater depths (so-called ‘saline upconing’). The saline water could affect various processes such as gas generation as a result of corrosion.

Water could also be drawn by suction pressure into backfilled parts of the GDF. These could include vaults for ILW and deposition holes for HLW/SF in some concepts. Thus for example, deposition holes that had been backfilled prior to final closure of the GDF, might resaturate before the GDF is closed.

Immediately after closure, the air within the open parts of the GDF (e.g. an open crown space) would be at atmospheric pressure. As water flows into the GDF, some of the air would dissolve, but most would remain as a gas, and would gradually be compressed. The pressure would also rise as a result of gas generation (see sub-section 8.3.2). As the pressure within the GDF rises, the rate of water inflow would reduce, because the difference in the pressure from that in the surrounding rocks would reduce. However, only when the inflowing water has filled most of the void space would the pressure have risen sufficiently to reduce the water inflow rate significantly.

If the design of the GDF is such that there is an open crown space after closure, then it would be expected that the backfill would resaturate before the crown space because water would be drawn into the backfill by the capillary forces (see also reference 211) and by gravity.

The resaturation of the GDF is coupled to the processes of gas generation and migration from the GDF (see sub-section 8.3.2) and potentially depends on the effective permeabilities of the backfill, the host rock, and possible features such as vault liners or a vault floor (which would probably be constructed of cementitious materials).

For a GDF backfilled with a higher permeability cement-based material, such as the NRVB, the key controls on the time for a GDF to resaturate (i.e. for most of the void space to become filled with water) would be the effective permeability of the host rock and the possible presence of a low-permeability liner. For a host rock with very low permeability (such as a clay) it could take thousands of years to resaturate. However, for a host rock with higher permeability, such as a fractured higher strength rock, it might only take a few decades. Because of its relatively high permeability, which would be increased by cracking, the NRVB would not be expected to have a significant impact on the resaturation time.

The NRVB was not designed to have low permeability and thereby reduce water flows past the waste. Rather it was designed specifically to be sufficiently permeable to promote the development of a homogeneous water chemistry in the near field and to enable gas migration (sub-section 2.1.1). However, an alternative approach might be adopted in which the cementitious backfill is designed to restrict water flows past the waste and, therefore, requires a much lower permeability than NRVB. This might have two potential benefits: the backfill would restrict fluxes of radionuclides out of the near field of a GDF because it would restrict water flows past the waste; it would also reduce the rate of gas generation by corrosion, because less water would contact the waste. However, it would be more difficult for generated gas to migrate away from the waste and
so gas pressures could build up to high values. The potential benefits and disadvantages of a particular backfill would need to be considered carefully.

As indicated, it is possible that a cementitious backfill with a lower permeability than NRVB could be used. As discussed in sub-section 8.1.1, typical values of concrete permeability lie in the range $10^{-21}$ m$^2$ to $10^{-15}$ m$^2$, whereas the permeability of NRVB is around $10^{-16}$ m$^2$. Typical permeabilities for fractured higher strength rock at depth are around $10^{-17}$ m$^2$ to $10^{-16}$ m$^2$ (e.g. [212, 213]) and values an order of magnitude lower or perhaps two orders of magnitude higher are possible.

It is possible, therefore, that for some combinations of a cementitious backfill and a fractured higher strength host rock, the effective permeability of the backfill might be lower than that of the host rock. In this case, the effective permeability of the backfill would affect the resaturation time and the subsequent groundwater flow through a GDF.

8.3.2 Gas migration through the backfill

Gas would be generated in a GDF. It would be mainly generated by corrosion of metals and by microbial processes [85, 210]. Metal corrosion would generate hydrogen, which would form the bulk of the generated gas. Microbial processes would generate methane and carbon dioxide. Radiolysis would also generate small volumes of gas. The overwhelming majority of the generated gas would be non-radioactive, but a very small fraction would be radioactive.

Although water flowing into the GDF would be drained during the period when the GDF is open, some water could be available to support corrosion, microbial processes and radiolysis. There could be some porewater initially within waste packages, and some of the water flowing into the GDF might contact the packages before it is removed by the drainage system. Therefore, some gas might be generated during the period that the GDF is open. This gas would be removed by the ventilation system.

Once the GDF is backfilled, sealed and closed, over time, more water would become available to support corrosion, microbial processes and undergo radiolysis. The gas generation rate could therefore be higher than before closure. Gas generated after closure would no longer be removed by the ventilation system, but would remain within the GDF and contribute to the increasing pressure within the GDF.

The gas generation and migration from the GDF would be coupled initially to the resaturation of the GDF (see sub-section 8.3.2), and after resaturation, to the groundwater flow through the GDF (see sub-section 8.3.3). The generation and migration would potentially depend on the permeabilities of the backfill, the host rock and possible features such as vault liners or vault floors, and on the two-phase flow properties of these. It is likely that vault liners or floors would be constructed of cementitious materials.

For a GDF backfilled with NRVB, the permeability and two-phase flow properties of the backfill are expected to have little effect on gas generation and migration. This is because NRVB has a relatively high permeability. Further, it is expected to crack after closure, which will increase the effective permeability. The flow of water into a GDF during resaturation and the subsequent flow of water through the GDF (which will affect the gas generation) will therefore be controlled by the effective permeability of the host rock and of possible features, such as low-permeability vault liners. However, a different cementitious backfill with low permeability would have a significant effect on the flow of water into and through a GDF and hence on the gas generation and migration, at least for a GDF in a fractured higher strength rock.

For a host rock with very low permeability (such as a clay, shale or mudstone), it might take a very long time to generate significant volumes of gas, because the gas generation might be limited by the available water and the rate of water flow into the GDF would be very low for such rocks. For a host rock with higher permeability (such as a fractured higher strength rock) it might still take a long time to generate significant volumes of gas if a cementitious backfill with a low permeability was used (rather than NRVB) to reduce the flow of water to the waste packages.
NRVB is also expected to have relatively little effect on the migration of gas from a GDF, mainly because it is expected to be cracked after closure. This means that the gas entry pressure will be small. The gas entry pressure is the excess pressure in the gas over that in the water that is required for gas to be able to enter a medium that is initially saturated with water. Generated gas would therefore readily be able to enter and migrate through cracks in the NRVB.

However, for a different cementitious backfill which has low permeability and is not fractured, gas can only enter and migrate through the backfill once the gas entry pressure is exceeded. Gas would therefore build up at increasing pressure behind the backfill. It is possible that the pressure might rise sufficiently high as to fracture the backfill before the gas can migrate through the pores in the backfill. Gas would then be able to migrate through the fractures relatively easily.

A low-permeability cementitious vault liner would have a similar effect. Gas would only be able to enter and then migrate through the liner once the excess pressure in the gas builds up sufficiently. Similarly, gas would only be able to enter and migrate through a low permeability cementitious vault floor once the pressure built up sufficiently. However, such a floor would only provide a barrier to flow out of part of a vault surface, and would therefore not prevent migration of gas out of a vault.

It should be noted that, even if gas is able to migrate through the backfill, the host rock could also provide a barrier to gas migration if it has low permeability and a high gas entry pressure. In such circumstances, the host rock would be the main barrier to migration of gas away from a GDF.

8.3.3 Groundwater flow through a GDF after closure

Once a GDF has largely resaturated (see sub-section 8.3.1), there will no longer be a net flow of groundwater towards the GDF, but there will be groundwater flow through the GDF. The flow may affect corrosion, and hence gas generation (see sub-section 8.3.2) and also the lifetime of waste containers. It may also affect the release of contaminants from the facility and hence their impacts (see sub-section 8.3.4).

The flow will depend on the effective permeability of the host rock, the effective permeability of the material within the GDF and on the design of the GDF. The flow will also be affected by gas migration from the GDF.

An important aspect of the design is whether or not the vaults have open crown spaces. If this is the case, and the vaults are not lined then the effective permeability of the vault in the direction along its axis will generally be much higher than that of the host rock in the same direction. Consequently, on the upstream side of the vault, groundwater flow in the host rock in the direction in question will be drawn into the vault and on the downstream side the flow will spread out again. The flow through the vault is therefore greater than the flow that, if the vault were not present, would have passed through the space occupied by the vault [214]. The flow enhancement factor, that is, the ratio of the flow that occurs in the presence of the vault to that in its absence, depends on the geometry of the vault and can be significant. This flow will be through the open crown space and will bypass the backfill and waste. However, in an assessment of post-closure performance, this bypassing might conservatively be neglected.

However, if the vaults have a liner (which could be cementitious) with sufficiently low permeability, then this flow enhancement would not occur, even if the vaults have open crown spaces. The necessary low permeability would depend on the permeability of the host rock.

If the vaults have structural concrete floors these would probably have lower permeability than a fractured higher strength rock. They would therefore divert flow in the vertical direction around them, leading to a small region immediately above the floor that is partly shielded from the vertical flow. However, a floor would have little effect on the flow across a vault or the flow along the axis of a vault.

If the vaults do not have open crown spaces, do not have low permeability liners and the backfill has a permeability significantly higher than that of the host rock (which would probably be the case...
for the NRVB or the Swiss M1 mortar), then the flow through the vaults in the direction along the axes of the vaults would still be enhanced. The enhancement depends mainly on the geometry of a GDF rather than on the permeability of the backfill if this is significantly higher than that of the host rock. In this case, the enhanced flow would pass through the backfill.

If the backfill (which could be cementitious) has permeability significantly lower than that of the host rock, then rather than flow being focused through the vaults, flow would be diverted around them. This case would only occur for a low permeability cementitious backfill and a relatively high permeability host rock, which would probably be a fractured higher strength rock.

In general, the total flow through the host rock in the vicinity of a GDF would be partitioned between the host rock, possible vault crown spaces, the backfill, possible grout within the waste packages and the waste itself. The partitioning would depend on the effective permeabilities of the host rock, possible vault liners, possible open crown spaces (which effectively have unlimited permeability), the backfill, possible grout within waste packages and the state of integrity of the waste packages. The partitioning would also depend on the geometry of a GDF and on the direction of the flow.

Similar remarks, on different length scales, would apply to different disposal concepts, such as those involving the use of disposal holes rather than disposal vaults.

### 8.3.4 Migration of dissolved contaminants out of a GDF

The migration of dissolved contaminants out of a GDF would depend to some extent on the mass transfer properties of the backfill. The migration would depend on the flow of groundwater through the GDF (see sub-section 8.3.3) and in particular in the distribution of the total flow through a GDF between possible open crown spaces to vaults, the backfill, possible grout within the waste packages and the waste itself. However, in a post-closure performance assessment, the partitioning might conservatively be neglected with all the flow being taken to pass through the waste. The migration of dissolved contaminants out of a GDF would also depend on the diffusion and sorption properties of the backfill (see section 12). For a host rock with sufficiently low permeability, the flow through a GDF would be negligible and migration would be dominated by diffusion.

In the case of a GDF backfilled with NRVB in a fractured higher strength rock, it would be expected that the flux of groundwater through the GDF would have very little dependence on the properties of the NRVB, but would be controlled by the properties of the host rock (see sub-section 8.3.3). As discussed in sub-section 8.1.1, it is expected that the flow through the NRVB would be predominantly through cracks. Diffusion between the water flowing in the cracks and water moving more slowly within the matrix of the NRVB would potentially be very important in providing access to the porosity within the matrix of the NRVB and to sorption sites within the matrix. The latter could be very important in terms of leading to lower concentrations and retarding the migration of dissolved contaminants out of the GDF.

If a different higher permeability cementitious backfill were used that would not have significant fracturing, then groundwater flow would be through the matrix porosity of the backfill, and its diffusion properties would not be important. However, if the permeability of the backfill or the host rock were sufficiently low that flow through the backfill would be negligible, migration through the backfill would be dominated by diffusion.

### 8.3.5 Migration of non-aqueous phase liquids (NAPLs) from a GDF

Small volumes of NAPLs will be disposed in a GDF. Contaminants may preferentially dissolve in NAPLs. NAPLs that are less dense than groundwater (Light- or L-NAPLs) will tend to migrate vertically upwards as a result of buoyancy effects and may travel faster than groundwater. It is likely that gas will be migrating from a GDF at the same time as NAPLs. It may therefore be necessary to consider the coupled flow of NAPLS, gas and groundwater from a GDF. This is normally represented as three-phase flow (see sub-section 8.3.6).
NAPLs behave in a very similar way to gas (see sub-section 8.3.2), albeit with different values of the properties. As is the case with gas and water, the capillary pressure represents the overall behaviour of the interfaces between the phases (in particular it accounts for the effects of hydrophobic NAPLs).

For many NAPLs and media, water will preferentially wet the medium and so a NAPL will only be able to displace water from an initially saturated medium if the pressure in the NAPL exceeds the appropriate entry pressure. One difference between NAPLs and gas is that NAPLs have much higher viscosity than gases and therefore flow rates are much smaller than the flow rates for gas.

8.3.6 Two- and three-phase flow

(a) Flow of gas and water

In general, gas as well as groundwater will flow in a GDF and the rocks in its vicinity. The gas will comprise a mixture of air present in the GDF at closure and gas generated by corrosion and microbial processes.

The flow of groundwater and gas (in a cementitious material or a rock) is normally represented as two-phase flow in a porous medium. For the standard model of such a flow, each phase behaves as if it is flowing through a porous medium with reduced porosity $\phi_S$ and reduced effective permeability $k_{rS}$, where: $\phi$ is the porosity; $S_i$ is the saturation of the phase in question, that is the fraction of the pore and void space occupied by the phase; $k$ is the permeability; and $k_r$ is the relative permeability.

The relative permeability is a function of the saturations. Only one saturation (generally taken to be the water saturation) is independent, because the saturations sum to 1. Typically, $k_r$ behaves like a moderate power law in the saturation of the phase in question (see sub-section 8.1.4). For flow through fractures, the relative permeability is often taken to be a linear function of the saturation [195, 208].

The behaviour of the flow also depends on the capillary pressure. Different pores in the medium will contain different phases. As a result of capillary forces, the interfaces between the different phases will be curved, and there will be pressure differences across the interfaces, with the pressure being lower in the phase that preferentially wets the pore surfaces. This phase is water in the case of water and gas, but it is not water in all cases. The pressure difference is greater for interfaces with greater curvature, which occur in smaller pores. The capillary pressure is the average difference between the pressures in the different phases. The capillary pressure depends on the distribution of pore sizes and the connectivity of the pores.

Capillary pressure curves generally have the form shown in Figure 51, with the capillary pressure increasing rapidly as the saturation of the wetting phase decreases. The reason is that the wetting phase tends to remain in the smaller pores because the suction pressure required to drain the wetting phase out of the smaller pores increases with decreasing pore size.

Capillary pressure curves generally exhibit hysteresis (as shown in Figure 51). That is, there are different curves for the saturation of the wetting phase increasing and the saturation of the wetting phase decreasing. However, hysteresis is seldom represented in practical modelling.

Because of the capillary pressure, the pressure in the gas (the non-wetting phase) has to be greater than the pressure in the water (the wetting phase) in order to displace the water from the medium. The amount by which the gas pressure has to exceed the water pressure (the gas entry pressure) depends on the capillary pressure curve and hence ultimately on the distribution of pore sizes within the medium and can be very large in low permeability media with very small pores, such as clays, shales or mudstones (see sub-section 8.1.4) or low permeability cementitious materials. The gas entry pressure is not particularly low for NRVB because of its relatively high permeability. Further, NRVB is expected to be cracked and the gas entry pressure for typical...
cracks is small, and so it would be expected that gas would be able to enter the cracks and migrate through them.

Figure 51  Typical capillary pressure curve

In the COLEX experiment [188], gas was injected at the base of a long vertical column of the M1 mortar. The pressures and saturations were monitored at several points along the column and the flux of gas out of the top of the column was monitored. Numerical modelling based on the standard two-phase flow model with appropriate parameters gave a good match to certain aspects of the experiment. However, some aspects of the experiment were not reproduced by the model. Experimentally, it was found that the release of gas occurred in pulses, whereas the model predicted a smoothly varying release. Given this discrepancy, it was suggested that the model might be extended to take into account the presence of isolated “passive” gas bubbles, which could provide an explanation for the observed oscillatory behaviour. The isolated bubbles would be compressed as the pressure in the fluid increased but then expand when the pressure decreased, for example, on gas breakthrough. Such rapid changes in local gas pressure could drive water back into transport channels. The pressure would then build up again, and so on.

(b) Flow of NAPL, gas and water

In some cases (see sub-section 8.3.5), it may be necessary to consider the combined flow of groundwater, gas and NAPL through the GDF and the surrounding rocks. This is normally represented as three-phase flow in a porous medium. This is described in terms of three relative permeabilities (for water, gas and NAPL) and two capillary pressures (water-NAPL and NAPL-gas, say), which are functions of two independent saturations (the saturation of water and NAPL, say). It is very difficult to measure the three-phase properties over the full ranges of saturation, and so in practice the three-phase properties are usually derived by interpolation and extrapolation from two-phase properties. There are various approaches for this (e.g. [215, 216]). The approach of Stone [215] to the interpolation and extrapolation is widely considered as the standard approach.
8.4 Key points

- It is expected that the mass transfer properties of the backfill matrix (porosity, permeability, two- and three-phase flow properties and the diffusion properties) will evolve over time as cement components (initially portlandite and subsequently C-S-H phases) are leached out of the cement, and as secondary minerals form. There is significant uncertainty about these changes.

- The time scale for changes to the properties of the backfill would depend primarily on the groundwater flow through a GDF.

- The flow will depend on the permeability of the host rock, the presence of a possible low permeability liner (which could be cementitious) to vaults and the backfill. For a host rock with very low permeability (such as a clay, shale or mudstone) the flow would be low and the time scale would be long. The flow would also be low and the time scale long if vaults have a low permeability liner, or the backfill itself has low permeability.

- In the case of a backfill with relatively high permeability (such as NRVB or the Swiss M1 mortar), it is expected that the flow through a GDF will not depend significantly on the permeability of the backfill, but only on the permeability of the host rock, the possible presence of a low permeability liner to vaults and on the design of the GDF (for example, on the arrangement of the vaults, their number, width, height, length and spacing).

- In the case of NRVB, it is expected that the backfill will be cracked shortly after emplacement as a result of plastic settlement, early-age thermal cracking and expansion of waste packages as a result of corrosion.

- In the case of NRVB, it is expected that the contributions from the cracks will dominate the effective permeability of the backfill and will determine the two- and three-phase flow properties.

- A different cementitious backfill would have a different pattern of cracking and might not be significantly cracked. Even if there is some cracking, this might not contribute significantly to the permeability and two- and three-phase flow properties.

- It is expected that the pattern of cracking of cementitious backfills will evolve over time and therefore the contributions to the effective permeability and the two- and three-phase flow properties will evolve.

- The migration of contaminants out of a GDF will depend on the groundwater flow through the GDF and the mass transfer properties of the backfill. If the flow is sufficiently low (because the host rock has low permeability, or there is a low permeability liner to vaults, or the backfill itself has low permeability) then migration through the backfill may be diffusion dominated. In this case the migration of contaminants out of the GDF would depend on the intrinsic diffusion coefficient for the backfill for each radionuclide species.

- In the case of a backfill, such as NRVB, that has cracked to the extent that the permeability is dominated by the contribution from the cracks, then diffusion between the water flowing in the cracks and the water in the backfill matrix would potentially play a very important role in ensuring that solutes migrating in water and gas flowing through the cracks access the porosity and sorption sites within the backfill matrix. This could be very important in terms of leading to lower concentrations and retarding the migration of dissolved contaminants out of a GDF.

- If the groundwater flow through the GDF is low, then the rate of gas generation will be low.

- Gas is expected to be able to enter and migrate readily through the cracks in NRVB.

- For a different cementitious backfill with low permeability that is not cracked, there could be a significant gas entry pressure barrier to overcome before gas could enter and migrate through the backfill. This could lead to the development of high gas pressures with the potential for significant fracturing of the backfill.
9 Interactions of cements with groundwater and the host rock

9.1 Introduction

Where cementitious materials are present in significant quantities, they are expected to strongly influence the chemistry of the near field. This is particularly the case for geological disposal concepts in which a cementitious backfill is specified to provide the main controls on the near field chemistry, such as maintaining an alkaline environment. However, most of these effects will only occur following resaturation of the disposal facility, because the major reactions of the cements with waste components, encapsulants and structural materials are mediated by the groundwater. In their chemical interactions, the cement phases and the groundwater have significant effects upon each other leading to chemical conditioning of the groundwater, and to changes to the mineral assemblage present in the cements. The composition of each of these components is expected to evolve as groundwater continues to flow through the near field. These chemical changes can have very significant effects such as altering:

- the rates of radionuclide release and migration for elements whose solubilities or sorption values vary with the evolving conditions;
- the groundwater flow paths and flow rates in the near field, where precipitation or dissolution reactions lead to changes to the porosity.

The chemical conditioning of the porewater by cementitious materials can also facilitate the reaction of the cementitious materials with the host rock around the waste disposal vaults.

In this section, the following aspects of the interactions of cements are discussed:

- the impact of the groundwater on the cementitious materials present;
- the impact of the groundwater on the host rock;
- the impact of the cementitious materials on the groundwater;
- modelling of cement-groundwater interactions.

9.2 Impact of groundwater on cement

The evolution of cementitious materials in GDFs is strongly dependent on the chemistry and flow rate of the groundwater, and consequently on the chemical and physical properties of the host rock. Specifically:

- the groundwater chemistry (together with any interaction with waste components) will govern the range of cement mineral phase alteration products;
- the groundwater flow rate will govern the timescales over which the cementitious materials evolve.

This evolution also depends on the initial chemistry of the cementitious solids. For high-calcium backfills, the major components are expected to include calcium hydroxide, calcium silicate hydrate phases and calcium aluminate or calcium aluminosilicate hydrate phases [22, 217].

The major chemical processes arising from groundwater interactions with the initial cementitious materials are summarised below.
9.2.1 Dissolution of the alkali metal oxide cement components

Most freshly-cured cement materials, including OPC-based systems, have a significant alkali metal oxide (Na$_2$O, K$_2$O) component retained after curing. These components are highly soluble and on saturation of the cement by groundwater their rapid dissolution tends to raise the pH (above that due to equilibration with portlandite). Although this has been considered a transient feature of the near field in UK hard rock concepts [11, 12], it can persist for significant periods for disposal facilities located in very low groundwater flow geologies, e.g. clays [218].

9.2.2 Leaching of cementitious materials

Groundwater flow through cementitious materials will tend to dissolve any cementitious components that are undersaturated with respect to the groundwater composition. Since most of these components dissolve to form ionic aqueous species, this process is usually enhanced for higher ionic strength groundwaters [219]. However, where (for example) the calcium and silicon groundwater components are present at higher concentrations, the rate of dissolution of C-S-H phases is expected to be lower. Leaching of calcium from portlandite, and preferential leaching of calcium from high C/S C-S-H and calcium aluminosilicate hydrate (C-A-S-H) phases will lead to more silicon-rich and aluminium-rich phases over time. This process leads to a decrease in the pH of the porewater, from around pH 12.5, once the excess calcium hydroxide in the backfill has dissolved (see sub-section 11.3). Due to the importance of C-S-H phases in buffering the pH of cementitious systems, their solubility and leaching behaviour has been the focus of significant effort, as described below.

(a) Dissolution of C-S-H gels

The dissolution of C-S-H gels into deionised water has been studied in a wide range of solubility experiments [220-222] and dynamic leach tests [223-225]. The leaching studies have demonstrated the incongruent dissolution of the high C/S ratio C-S-H systems. Incongruent dissolution occurs when the molar ratio of the calcium and silicon dissolved in solution is different from that in the solid phase resulting in changes to the stoichiometry of the solid. In the reported studies, incongruent dissolution occurred towards a congruent end point with a solid phase C/S ratio in the range 0.7 to 0.9 [220, 225, 226]. Recently a detailed study under the NDA research programme [227] has provided improved data for low C/S C-S-H systems. This has indicated that, for C-S-H gels with initial C/S solid ratios from around 0.3 to 0.7, silicon is preferentially leached leading to an increase in C/S ratios towards a similar endpoint to that found for the high C/S systems. For gels with a C/S ratio of 0.25 or lower, progressive leaching lowers the solid C/S ratio towards that of silica.

The effects of salinity on C-S-H gel dissolution has been studied by Glasser et al. [228] and under the NDA’s research programme [229]. Enhanced calcium ion concentrations (above those expected for the ionic strength effect) were measured for higher sodium chloride concentrations, and these were consistent with an ion exchange process between sodium and calcium ions [230]. In further work [231], similar effects were observed for other group 1 metal (lithium and potassium) ions. Experiments equilibrated at temperatures of 25°C and 45°C showed decreases in dissolved calcium concentration and pH with increasing temperature that are broadly similar to the behaviour of calcium hydroxide. The temperature dependence of pH in such systems is discussed in sub-section 11.2.

(b) Dissolution of cementitious backfills

The leaching studies have been extended from C-S-H gel systems to the more complex dissolution of NRVB in deionised water and in a simulated saline groundwater [232]. This showed a more rapid decrease in pH for the saline water than for deionised water. Earlier studies on the leaching of a structural concrete by tap water and simulated groundwater showed that this type of material is a relatively poor pH buffer and is sensitive to the formation of surface layers. In contrast, high porosity backfills were found to be more difficult to occlude and provide a more robust pH buffer [233]. Where leaching occurs into groundwaters or simulated groundwaters the chemistry of the system is significantly more complex and may lead to the formation of a wide range of other solid
phases by precipitation or alteration. Some of the more important reactions are discussed in sub-section 9.2.3 below.

(c) Low-pH cements - leachate requirements and characteristics

International agencies (e.g. SKB, Nagra, Posiva, JAEE) have defined a pH limit $\leq 11$ for leachates from low-pH cement grouts (e.g. [31]). The rationale for this precise limit is unclear, but in general the aim is to avoid or lessen adverse effects of high pH, such as reducing the alteration of clay mineral phases in buffer materials. Clearly, OH$^-$ concentrations can be expected to be reduced by two orders of magnitude between pH 13 and pH 11 (from a nominal 1700 mg dm$^{-3}$ to 17 mg dm$^{-3}$), but the pH 11 limit does not appear to be linked to a specific ‘function indicator’ (e.g. [234]). An alternative pH limit would be that defined by the change in aqueous speciation of silicon (pH = 10), above which uncharged silica species dissociate to produce silicate anions, and thus increase the solubility of silicate minerals (e.g. Figure 52). However, it may be difficult to produce a cement grout with pH $\leq 10$, due to the low C/S ratio of C-S-H gels that, in principle, would be required.

![Figure 52 Variation of silicon speciation and quartz solubility (in terms of the activity, a, of dissolved silica) with pH (from Savage and Benbow [319])](image)

To attain a low pH in leachates, blending agents must comprise at least 40 wt % of dry cementitious components (Table 11). Because low-pH cement has little, or no free portlandite, the cement consists predominantly of calcium silicate hydrate (C-S-H) gel with a C/S ratio $\leq 0.8$. Consequently, low-pH cements supply approximately 50% less hydroxyl ions than conventional OPC for a given volume of cement. Low-pH cement has a high strength and low hydraulic conductivity, making it suitable for use in the GDF environment [235] but greater proportions of silica fume may lead to slower gain of strength, lower ultimate strength, and greater sensitivity to curing conditions [69].

Harris et al. [225] have published experimental data describing the leaching of C-S-H gels of variable C/S ratio in pure water under both ‘static’ and ‘sequential’ leaching conditions. Results of some of their experiments are shown in Figure 53. It may be seen from Figure 53 that to achieve a pH less than 11, then the C-S-H gel must have a C/S ratio less than 0.81. Unlike gels with a greater C/S ratio, gels of C/S $\sim 0.81$ do not show dramatic incongruent dissolution behaviour. In
other words, leaching of these gels produces a fluid with a broadly constant C/S ratio with
time/volume throughput (i.e. dissolution is congruent).

Low C/S C-S-H gels show preferential leaching of silicon, which is in marked contrast with gels of
greater C/S ratio. Unlike the higher C/S ratio gels, those with C/S ≤ 0.81 show a C/S ratio
increasing towards a congruent composition as leaching proceeds. This implies preferential
leaching of silicon from the gel, which contrasts with gels of higher C/S ratio that show the
preferential removal of calcium. A high silicon solubility is also associated with gels of lower C/S
ratio (up to 2.2 mmol dm⁻³, according to Harris et al. [225]).

More recent leaching experiments [227] on a wider range of low C/S C-S-H gels (0.2-0.6) have
confirmed that a congruent dissolution point around C/S = ~0.8 and pH close to 11, is approached
for all gels with C/S ≥ 0.3. These results again apply to leaching into deionised water, and indicate
a silicon concentration close to 1 mmol dm⁻³ at congruent dissolution under controlled temperature
conditions. Groundwaters with calcium concentrations above 1 mmol dm⁻³ are expected to
suppress the silicon solubility, potentially affecting the pH of congruent dissolution (and whether the
C-S-H gels around C/S = 0.3 approach the congruent point). Overall, however, the confirmation of
congruent dissolution being reached for a wide range of low C/S C-S-H gels, helps to provide
confidence in the understanding of the long-term pH behaviour of low-calcium cements under
leaching conditions. This conclusion applies so long as sufficient C-S-H remains and is accessible
to equilibrate with the porewater.

![Figure 53 Variation of pH during leaching of C-S-H gels of variable C/S ratio in pure water](from Harris et al. [225])

Leachates from low-pH cements typically have lower alkali metal contents due to their removal by
sorption on C-S-H. C-S-H gels with low C/S ratios develop a negative surface charge, thereby
increasing the efficiency to bind alkali metals. The binding process may be most effective when the
C/S ratio is between 1.2 and 0.85 [236].
9.2.3 Reactions with groundwater components

Cementitious phases can chemically react with many major groundwater components. Over time such reactions lead to changes to cementitious mineral assemblage which in turn affect the conditioning of the porewater as well as the structural properties of concretes present. The implications of the chemical evolution for the pH of the near-field porewater are further discussed in section 11.

(a) Reaction with chloride ions

Chloride, as sodium chloride, somewhat enhances the solubility of cementitious phases. The effect is most marked up to about 0.5 mol dm⁻³ NaCl: increased concentrations, up to around several molar, have less impact. For example, Table 21 shows the solubility of portlandite, Ca(OH)₂, in sodium chloride at different temperatures reported in reference 228. The solubility of portlandite decreases with increasing temperature but increases with rising NaCl concentration so that its solubility at 85°C in 1.5 mol dm⁻³ NaCl is not greatly different than in pure water at 25°C.

Table 21 Solubility of Ca(OH)₂ in aqueous sodium chloride (after Glasser et al. 1990)

<table>
<thead>
<tr>
<th>NaCl (mol dm⁻³)</th>
<th>Temperature (°C)</th>
<th>Ca solubility (mmol dm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>12.6</td>
</tr>
<tr>
<td>0.5</td>
<td>25</td>
<td>27.7</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>21.9</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>20.9</td>
</tr>
<tr>
<td>1.0*</td>
<td>25</td>
<td>20.4</td>
</tr>
<tr>
<td>1.5</td>
<td>25</td>
<td>26.6</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>21.7</td>
</tr>
</tbody>
</table>

* Not determined at 55°C and 85°C

C-S-H shows very similar trends with respect to its solubility in NaCl [228]. The pH of saline water is conditioned to high pH; the presence of NaCl makes little difference to the pH conditioning ability of Ca(OH)₂, relative to pure water.

When chloride migrates into cement, the cement substances sorb and/or ion exchange some chloride. For example, the AFm phase normally contains hydroxide ions and sulphate ions as interlayer charge balancing ions but at pore solution chloride above ~5 millimolar, increasingly AFm exchanges chloride for other anions, converting to Friedel’s salt, Ca₂Al(OH)₆Cl·nH₂O [237] (and see also reference 238). The C-S-H phase also sorbs chloride although quantitative data on the strength of sorption are scarce but, owing to the abundance of C-S-H in cement, it is nevertheless a major sink for chloride. Such retardation processes increase the uncertainty in the time taken for chloride to diffuse through cover concrete to steel reinforcements and initiate accelerated corrosion [239]. However empirical experience is that (i) resistance to corrosion is proportional to the thickness of cover concrete and (ii) low permeability concretes give superior protection.

Honda et al. [240] have shown that the formation of Friedel’s Salt due to reaction of cement with saline groundwaters can increase the ambient pH of cement pore fluids to > 13. The pH increase is attributed by them to the generation of hydroxide ion accompanying the precipitation of Friedel’s
salt from the reaction of portlandite and hydrogarnet \((C_3A_H_6)\) with chloride ions from saline groundwater:

\[
\begin{align*}
\text{Ca(OH)}_2(s) + 3\text{CaO.Al}_2\text{O}_3.6\text{H}_2\text{O}(s) + 2\text{Cl}^- + 4\text{H}_2\text{O} & \rightarrow 3\text{CaO.Al}_2\text{O}_3.\text{CaCl}_2.10\text{H}_2\text{O}(s) + 2\text{OH}^- \\
\text{portlandite} & \quad \text{hydrogarnet} \\
& \quad \text{Friedel's salt}
\end{align*}
\]

(b) Reaction with sulphate ions

Sulphate is a common component of groundwaters where the charge balancing ions are mainly calcium, magnesium and to a lesser extent sodium. The relatively poor resistance of Portland cement to sulphate attack has been known for over a century; sulphate attack results in a physical expansion, often accompanied by cracking and spalling. This allows other aggressive agents, if present, to penetrate to greater depths, so reaction is progressive. This form of attack is designated \textit{external sulphate attack} and may also arise from uptake of sulphate from waste components. \textit{Internal sulphate attack} may also occur due to delayed ettringite formation, in which the amount of sulphur in the cement remains constant, but its distribution changes as a function of temperature (see sub-section 7.2.1). A symposium in 2002 [174] addressed the causes, identification and analysis of sulphate attack as well as possible preventative actions.

Empirical exposure testing continues to dominate specification, as is shown in Table 22.

<table>
<thead>
<tr>
<th>Severity of conditions</th>
<th>Total soil/ rock (\text{SO}_4^{2-}) (%)</th>
<th>(\text{SO}_4^{2-}) in soil extract (g dm(^{-3}))</th>
<th>(\text{SO}_4^{2-}) in water (g dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderate</td>
<td>0.2-0.5</td>
<td>1.0-1.9</td>
<td>0.3-1.2</td>
</tr>
<tr>
<td>Severe</td>
<td>0.5-1.0</td>
<td>1.9-3.1</td>
<td>1.2-5.0</td>
</tr>
<tr>
<td>Very Severe</td>
<td>1.0-2.0</td>
<td>3.1-5.6</td>
<td>2.5-5.0</td>
</tr>
</tbody>
</table>

Note: the soil extract is from a 1:2 weight of soil/ aqueous extractant

Waters containing <0.3g sulphate dm\(^{-3}\) are regarded as innocuous.

Similarly, in unsaturated conditions, structures exposed to wicking (i.e. cycles of water transport and evaporation) can experience higher concentrations of sulphate than that in the groundwater.

One approach to the problem of coping with sulphate attack is to use sulphate resisting Portland cement (SRPC). SRPC is frequently specified where Table 22 indicates moderate or severe sulphate exposure and is formulated to prevent sulphate attack by reducing the supply of tricalcium aluminate. Tricalcium aluminate reacts rapidly with both water and sulphate ions forming mixtures of AFm and AFT. AFT continues to form within hardened concrete. In practice, however, trials show that SRPC gives highly variable performance; the expected benefit is sometimes, but not always obtained in laboratory simulations [174].

Another approach to the problem is to use blended cement formulated with relatively high replacement levels of OPC by BFS and/ or PFA.

The most common product of sulphate attack is ettringite, formed from the reaction of sulphate in water with portlandite when aluminium is available. The reaction may cause swelling and cracking due to solid volume changes associated with the conversion of portlandite and C-S-H gel to ettringite and /or gypsum. Ettringite formation requires 3 moles of sulphate and 2 moles of aluminium, and thereby consumes 6 moles of portlandite (or the equivalent amount of calcium from C-S-H gel):

\[
6\text{Ca(OH)}_2(s) + 2\text{Al}^{3+} + 3\text{SO}_4^{2-} + 26\text{H}_2\text{O} \rightarrow \text{Ca}_9\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}.26\text{H}_2\text{O}(s)
\]

portlandite ettringite
The net solids volume increase for this reaction is around 350%. Although, the rate of formation of ettringite may be limited by the supply of aluminium in groundwater (the solubility of Al in groundwater at neutral pH is relatively low, ≤ 5 x 10⁻⁶ mol dm⁻³). However, many cementitious materials, have a significant aluminium oxide component, including NRVB at around 1% by mass, that may be available for reaction; aluminium would also be present at more significant levels in cementitious encapsulation grouts, and also in some wastes.

Alternatively, cement could degrade to gypsum during sulphate attack, if there is not enough Al for the stabilisation of ettringite:

\[
\text{SO}_4^{2-} + \text{Ca(OH)}_2(s) + 2\text{H}_2\text{O} = \text{CaSO}_4\cdot2\text{H}_2\text{O}(s) + 2\text{OH}^- \\
\text{portlandite gypsum}
\]

This reaction involves an increase in solids volume of around 230%, so that sulphate attack could lead also to a large increase in solids volume and physical cracking of cement and concrete. Sulphate concentrations greater than 5 mmol dm⁻³ are required to precipitate gypsum (Figure 54). However, it is envisaged that groundwaters in, and adjacent to, Permo-Triassic sedimentary basins in the UK can contain as much as 30 mmol dm⁻³ sulphate (e.g. [241]). Consequently, gypsum may be much more likely as an alteration product of cement in sulphate-rich groundwaters in the UK. At high ionic strengths, anhydrite (CaSO₄) will form instead of gypsum (CaSO₄·2H₂O).

Most of the interest in sulphate attack has been driven by its effects on the structural performance of concrete. For cementitious geological disposal concepts, the effects on the pH-buffering performance need also to be considered (see sub-section 11.4).

![Figure 54 Phase relations in the system CaO-Al₂O₃-SO₄-H₂O at 25 °C; each axis is proportional to the fifth root of concentration (from [242])]
carbonate being furnished by calcium carbonate [243]. However the extent of these reactions is limited because the cement solids usually become saturated at low (1-3%) content of calcium carbonate. This results from the low carbonate activity achieved by calcium carbonate in the presence of portlandite. Additional carbonation can occur in unsaturated systems when carbon dioxide reaches the cement (such as during resaturation), or in saturated systems due to reaction with dissolved carbon dioxide or bicarbonate ions.

![Figure 55 Role of water films in facilitating the carbonation process](image)

In air carbonation due to atmospheric carbon dioxide is progressive. However, gaseous CO₂ does not react, except very slowly, with cement solids but the reaction is facilitated by condensing a thin film of water onto cements and this film dissolves carbon dioxide (as shown schematically in Figure 55). The water film contacts cement which is slightly soluble and this solubility conditions the water to high pH; hydroxide ions also accelerate the dissolution process and promote ionisation of CO₂ to carbonate. The pores in cement allow condensation of a film to begin at ~30-40% relative humidity (RH). By about 70% RH, the pores completely fill and the apparent surface area available for transport decreases. Thus, for any given set of conditions, carbonation is most rapid in the range 30-70% RH. Once carbonation commences, and the surface becomes carbonated, the rate at which carbonation progresses inwards is proportional to the square root of the time. Modelling of the evolution of carbonation under these unsaturated conditions [243] has shown the development of distinct zones during the course of carbonation, as shown in Figure 56.
The scale at the bottom of the figure shows the amount of CO₂ reacted per 100g cement paste while the scale near the top of the figure shows the aqueous pH conditioning power of the solids and its evolution in the course of carbonation.

The carbonation of NRVB by carbon dioxide in unsaturated systems has been studied by Harris et al. [244]. The carbonation capacity of NRVB was determined as 5,200±100 mol m⁻³, and was assumed to be associated with the calcium hydroxide and calcium silicate hydrate components. For drier material (less than about 90% relative humidity), well-defined kinetics were determined, whereas in more saturated systems the reaction was slower and less well defined. In further studies [245], a maximum carbonation level of 80% was achieved with NRVB at a relative humidity of 75%. By contrast a 3:1 BFS/OPC encapsulation grout material achieved a maximum carbonation level of around 4%, in experiments performed at 75% and 100% relative humidity, and typically over an 18-day period. This reflected a much lower rate of carbonation for 3:1 BFS/OPC than for NRVB.

Carbonation under fully saturated conditions proceeds slowly such that the film of (mainly) calcium carbonate is stable over a wide range of groundwater chemistry. However this stability is not always ensured. For example, degradation of organic materials can lead to products that attack the cement (see sub-section 10.4.1). Also, certain acidic natural waters are notably undersaturated with respect to carbonate and under these conditions, attack may progress rapidly. Figure 57 shows an empirical approach typical of the guidance given [246, 247]. In general, aggressivity increases as total dissolved CO₂ exceeds that which is speciated as bicarbonate, corresponding to more acidic groundwater. Very aggressive conditions can result from total CO₂ concentrations as low as ~1mmolar.
Figure 57 Aggressivity map of groundwater compositions

Where dissolved CO₂ dominates the speciation the dissolution of the calcium carbonate layer becomes the most significant process:

\[ \text{CO}_2(g) + \text{CaCO}_3(s) + \text{H}_2\text{O} = \text{Ca}^{2+} + 2\text{HCO}_3^- \]

whereas in bicarbonate-dominated waters calcium carbonate formation is favoured:

\[ \text{HCO}_3^- + \text{Ca(OH)}_2(s) = \text{CaCO}_3(s) + \text{OH}^- + \text{H}_2\text{O} \]

Modelling calculations support the general approach summarised in Figure 57 [248] and enables quantification, so the arbitrary divisions between regions of differing aggressivities shown in Figure 57 disappear.

(d) Reaction with magnesium ions

The solubility of brucite, Mg(OH)$_2$(s), decreases rapidly with increasing pH. Consequently, under alkaline conditions, magnesium ions in the groundwater are likely to precipitate on entering a cementitious near field.

\[ \text{Mg}^{2+} + \text{Ca(OH)}_2(s) = \text{Ca}^{2+} + \text{Mg(OH)}_2(s) \]

However, the long-term stability of brucite in cementitious systems is uncertain and the magnesium may be taken up into other secondary mineral phases such as sepiolite or hydrotalcite.

9.2.4 Evidence from natural analogue sites

At the Maqarin natural analogue, the presence of relatively sulphate-rich groundwaters (up to 15 mmol dm$^{-3}$) has led to the development of ettringite-thaumasite (solid solution) alteration of the host rock (biomicrite limestone) [249, 250].

Further understanding of the long-term effects of carbonation has been derived from studies of natural systems. The degree to which cementitious materials undergo carbonation processes will be dependent upon the geological environment of the GDF, and more specifically the ambient partial pressure of carbon dioxide ($PCO_2^{10}$) of the groundwater [251]. For example, it has been

\[^{10}\text{The } PCO_2 \text{ is the partial pressure of carbon dioxide that would be in equilibrium with a groundwater of a given composition, pH and temperature. It does not necessarily imply the presence of a CO}_2 \text{ containing gas phase.} \]
observed that $P_{CO_2}$ of groundwater in sedimentary basins is higher than groundwaters in fractured hard (basement) rocks [252, 253]. This difference is illustrated in Figure 58 where it may be seen that although $P_{CO_2}$ levels in groundwaters in both environments increase with increasing temperature, at a given temperature, $P_{CO_2}$ values in groundwaters in fractured hard rocks are 2-3 orders of magnitude lower than those in sedimentary rocks. These different trends are ascribed to different mineral-fluid buffering reactions, with clays, micas and carbonates dominating in sedimentary rocks, whereas feldspars, zeolites and carbonates dominate in fractured hard rocks [252].

Higher $P_{CO_2}$ values and lower activities of $SiO_2(aq)$ increase the likelihood of cement carbonation reactions, and thus these reactions tend to occur at the interface between cements and sedimentary host rocks (Figure 59). This interfacial carbonation has been inferred to occur in modelling studies of reactions between mudstones and cement/concrete, but notably, has been observed in industrial analogues at the interface between cement/concrete and mudstone (e.g. the Tournemire analogue [254, 255] and at the Bure site in France [256, 257]). Although the carbonation reaction has been observed to decrease the porosity of the mudstones at the interface and thus reduce mass transfer [255], diffusion of alkali cations may reach beyond the zone of carbonation into the sediment [254]. The Tournemire analogue suggest that this perturbation may be of the order of 1-2 cm after 100 years.

Figure 58 Groundwater $P_{CO_2}$ values (log values in bars) versus temperature for different rock types (redrawn from [252]); data from sedimentary rocks are shown as circles, those from fractured hard rocks as inverted triangles, and those from fractured hard rocks adjacent to sedimentary basins as squares
Figure 59  (A) Macroscopic photomicrograph showing a well-defined zonation in mudstone from the Tournemire Tunnel at a contact with concrete and the occurrence of carbonates at the interface (zone 1);  (B and C) SEM photomicrographs of the first millimetres beyond the contact, showing the precipitation of calcite as a crust; (B) fibrous gypsum and idiomorphic calcite (C);  (D) SEM photomicrograph showing a cm-wide zone characterised by intense precipitation of honeycomb neoformed clays and calcite;  (E and F) SEM photomicrographs showing the final cm-wide zone characterized by high calcite precipitation (E) and feldspar overgrowths (F) (from Tinseau et al. [254])

Investigations of carbonation of C-S-H gels and minerals at the Scawt Hill site in Northern Ireland has shown that rims of carbonate minerals are produced around hydrated low-temperature calcium silicate (C-S-H) minerals. These carbonation zones enclose residual cores of primary high-temperature metamorphic calcium silicates and calcium aluminates (dominated by larnite, and often accompanied by wollastonite, spurrite, paraspurrite, brownmillerite, bredigite, andradite-grossular) with carbonation proceeding progressively from the outer margins of the nodules [258]. Calcite and scawtite are the dominant secondary calcium carbonate minerals, but vaterite and aragonite have also formed. The carbonation process produces dense, low-porosity carbonate
rims. This is associated with a reduction in volume, accompanied by shrinkage and microfracturing of the underlying residual poorly crystalline C-S-H gel and its silica-rich alteration product, which has created significant secondary porosity in the altered material. Although some secondary calcium carbonate reaction products may partially mineralise the fractures, they do not seal the fractures completely, allowing further ingress of CO₂/bicarbonate [258].

Cement carbonation, especially in saline/brine solutions is of considerable interest to the burgeoning CO₂ sequestration industry, where cement well seals are a key link in the performance of CO₂ storage systems [259]. There are numerous studies in this field. As an example, Kutchko et al. [260] have described the degradation of ‘Class H’ cements (as defined in American Petroleum Industry specification 10A [261]) under geological storage conditions, highlighting the occurrence of alteration zones. They report that in contact with supercritical CO₂, cement is converted to calcite (CaCO₃) at a single reaction front. In CO₂-saturated brine, they identified three reaction zones (Figure 60) that form as a result of the following processes: portlandite (Ca(OH)₂) dissolution; calcite precipitation; calcite dissolution; and leaching of C-S-H gel to form amorphous silica (SiO₂(am)). The depth of alteration was found to vary as a function of cement curing conditions, with reported values ranging from 0.59 to 0.22 mm.

In contrast to the experimental system, the SACROC borehole core data [262] provide insights into well seal stability over longer timescales. Cement exposed to CO₂-rich brine for over 30 years, at a temperature of 50 °C, resulted in an alteration depth ranging from 1 to 10 mm [262].

![Figure 60 Schematic representation of zones of cement alteration in the experimental system of Kutchko et al. [260] (from Wilson et al. [259])](image)

### 9.3 Impact of cement on the host rock

This issue has been studied extensively, especially from a UK perspective, by Nirex in the 1990s. A full description of this issue is beyond the scope of this report, but a number of reviews of this topic are available, considering experimental, modelling, and analogue evidence [250, 263-266].

In summary, groundwater that has reacted with cement will migrate and potentially react chemically with the enveloping rock and groundwater. Alteration can be viewed as consisting of two main components, described below.
- A zone closest to the cement/concrete where there may be mineral alteration. The principal reactions will be the dissolution of rock-forming minerals and the precipitation of secondary solids. These may be amorphous and/or crystalline. Some modification of the physical properties of the rock (porosity, permeability) may occur as a result.

- A zone further from the cement/concrete where pH is still elevated from its unperturbed value, but lower than that in the zone of mineral alteration. In this zone, ion exchange dominates and mineral alteration reactions occur at a much slower rate, so that physical property changes are less likely to occur. The elevated pH will have an impact on processes such as ion exchange, sorption of radionuclides, clay swelling pressure, the activity of microbes and the mobility of colloids.

A schematic view of alkaline alteration and the migration of a hyperalkaline fluid is shown in Figure 61. The following issues need to be considered with regard to the assessment of the impacts of any alkaline disturbed zone (ADZ):

- the scale and spatial extent;
- its longevity and stability;
- coupled processes leading to modification of radionuclide transport and retention properties of the host rock (this includes the effects of porosity and permeability modification);
- the impact on rock matrix diffusion behaviour, and the sorption/uptake of radionuclides;
- the interaction with colloids, bacteria, and naturally-occurring organic materials.

![Figure 61 Schematic illustration of rock alteration by cement pore fluids (after Savage [263]). A zone of perturbed fluid composition (elevated pH, Na, K, Al and Si) where ion exchange reactions dominate, migrates ahead of a zone of mineral dissolution and growth. Calcium concentrations in the migrating cement pore fluid decrease relatively close to the cement/concrete due to precipitation in C-S-H solids through reaction with the host rock. Similarly, Al and Si concentrations in the migrating fluid increase with distance due to dissolution of host rock/buffer minerals. Secondary minerals which form as a result of these interactions reflect the composition of the fluid, such that calcium silicate hydrates (C-S-H) form nearest the cement, whilst zeolites form further away. With time, this mineral sequence evolves as the fluid migrates.](image-url)
Zones of pore fluid perturbation and rock alteration develop around masses of cement/concrete in response to chemical reactions which titrate hydroxyl ions in migrating cement pore fluids. The mechanisms of hydroxyl ion titration can be envisaged to consist principally of:

- dilution and groundwater mixing;
- ion exchange and surface complexation;
- aqueous speciation;
- mineral hydrolysis; and
- mineral growth.

The relative role of each of these processes is a site (rock)-specific issue, but details of the respective mechanisms are described by Savage [266].

9.4 Impact of cement on porewater chemistry

The interaction of groundwater with cementitious materials is a two-way process so that, at any given state of evolution, the cementitious solids present will strongly affect the composition of the conditioned porewater. This may occur either in local environments or on the vault scale (in the case of cementitious backfills). The most significant effects of groundwater interactions with cementitious solids on the porewater chemistry are summarised below.

9.4.1 pH of the porewater

Cementitious materials generally have alkaline properties but their precise effect on the pH of the porewater depends on a number of factors. The most important of these are the initial mineralogy of the cement and the changes to this mineralogy due to interactions with the groundwater and other components of the disposal facility. The temperature of the system also has a significant effect on pH, as described in sub-section 11.2. For high-calcium systems, the main influences on the pH are the initial dissolution of the alkali metal oxides typically raising the pH into the region pH 13 to 14, equilibration with the portlandite constrained the pH to around pH 12.5, and a subsequent fall in pH with equilibration with C-S-H and C-A-S-H phases (and potentially with other mineral phases formed by reaction of the initial mineral assemblage). The pH evolution of the porewater is discussed in more detail in sub-section 11.3, in the context of the performance of disposal facilities.

Low-pH cements are designed to have minimal alkali metal oxide components and much lower calcium content; formulations are designed to allow complete reaction of any lime with SCMs to form C-S-H of lower C/S, leaving no portlandite. This results in porewaters with pH values below 11 (see section 13).

9.4.2 Concentration of major groundwater ions

The calcium concentration of porewaters in equilibrium with high-calcium cements is constrained by equilibration with portlandite. Whilst the pH is elevated by alkali metal dissolution, the calcium concentration will be suppressed [12] to values around $4 \times 10^{-3} \text{ mol dm}^{-3}$. Once these materials have been flushed away, portlandite equilibration will maintain the calcium concentration around 2 to $4 \times 10^{-2} \text{ mol dm}^{-3}$. The magnesium concentration will be reduced to very low values ($< 10^{-7} \text{ mol dm}^{-3}$) due initially to its precipitation from solution as brucite, Mg(OH)$_2$. Sodium and potassium ion concentrations in the groundwater are not expected to be strongly affected by cements, other than by the early dissolution of their oxides from the cements described above.

The concentration of carbonate is expected to be largely controlled by equilibration with calcite, in combination with the calcium concentration in the porewater. Consequently, it is also dependent on portlandite equilibration, for high-calcium cements. At pH 12.5, the high calcium concentration is expected to suppress the carbonate to around $10^{-5} \text{ mol dm}^{-3}$ (maintaining equilibrium calcite), although this effect will be reduced at higher pH during the early period of alkali metal dissolution. Once the portlandite component is exhausted, the carbonate concentration is expected to increase (as the calcium concentration falls). Below pH 10.3, bicarbonate will be the major form of
carbonate in solution. The concentration of sulphate may be lowered from that of the groundwater due to formation of phases such as gypsum, monosulphate and ettringite. For saline groundwaters, chloride concentrations are not expected to be strongly affected, although small amounts may be taken by the formation of Friedel's salt.

9.4.3 Redox potential
The redox potential of the porewater will depend on the composition of the groundwater entering the vaults and on the redox properties of the backfill, buffer, waste and encapsulation materials that the groundwater contacts. Portland cement-based backfills such as NRVB tend to have much weaker effects on the redox potential of the pore water than certain waste components and encapsulation grouts such as those based on BFS [11].

9.4.4 Precipitation of humic materials
Under the high-pH and high-calcium conditions of a cement-based near field, naturally-occurring humic materials associated with some groundwaters tend to precipitate [267]. This would help to reduce the mobility of radionuclides bound by these polymeric organic complexants.

9.5 Modelling
9.5.1 Thermodynamic database for cementitious mineral phases
In recent years (2007-2009), CEMDATA, a database for thermodynamic data, has been developed based on work carried out at the Swiss research institute EMPA [268]. This database is relevant to hydrated solids in the Portland cement system (CaO·Al₂O₃·SiO₂·CaSO₄·CaCO₃·Fe₂O₃·MgO·H₂O)). Solubility data have been generally calculated based on a critical review of the available experimental data and on additional experiments to derive missing data or to verify the existing data from which fundamental thermodynamic data have been derived. The resulting data base CEMDATA2007 covers hydrates commonly encountered in Portland cement systems in the temperature range 0-100 °C, including C-S-H, hydrogarnet, hydrotalcite, AFm and AFt phases and their solid solutions. The database includes solids potentially formed by interaction with major groundwater elements. It forms the most thoroughly reviewed and self-consistent thermodynamic data set for the modelling of Portland cement systems for applications in radioactive waste disposal and elsewhere.

The database is based on a series of published articles. Some of these (e.g. [269, 270]) include modelling demonstrations of the application of the database, including fitting of experimental data.

9.5.2 C-S-H systems
In principle, the interpretation of the data for C-S-H systems using thermodynamic modelling is not applicable because they are not thermodynamically stable solids, but less-polymerised metastable precursors of crystalline tobermorite or jennite [271]. They tend to convert into more polymerised forms with time or at elevated temperatures. However, assumptions about the rate of ageing of the C-S-H phases have allowed thermodynamic methods to be applied to develop a more detailed understanding of the behaviour of these solids. Modelling of the solubility of C-S-H phases has been the subject of an NEA review [271]. These are mostly based on application of a solid solution model to each of the regions above and below congruent dissolution (such as references 222 and 272). Approaches involving ideal solid solution (e.g. Kulik and Kersten [270]) have the advantages that they are based on the formation of an ideal solid solution (and therefore has fewer fitting parameters), and that they can be extended to include the uptake of other elements without the introduction of many (semi-empirical) interaction parameters associated with non-ideal solid solutions [273].

The solubility of C-S-H gels in deionised water has been modelled [232] using the empirical approach of Berner [226] and has been extended to sodium chloride solution by the addition of an ion exchange reaction between sodium and calcium ions [230]. For the modelling of saline systems it is important to use of an appropriate model of aqueous activity coefficients such as employing the
Pitzer approach coefficients or using specific interaction theory, 'SIT' [274]. Low-pH cement systems have received little attention thus far regarding the development of models for the chemical evolution of pore fluids.

9.5.3 Application to near-field evolution

Thermodynamic modelling has been applied to the interaction of cementitious backfills with ingressing groundwaters to predict the evolution of the pH of the near field. This is described in more detail in sub-section 11.5.

For cementitious disposal facilities, coupled chemistry and transport models have been applied to the evolution of near-field cementitious materials [275, 276]. Recent work on the UK ILW/LLW concept has included the development of a powerful multidimensional reactive transport model that predicts the groundwater interactions with cementitious backfill and waste packages and the evolution of the porewater pH and chemistry [277]. It also allows for the changes in porosity and transport associated with evolving solid phase assemblages.

9.6 Key points

- The impact of the groundwater on cements is strongly dependent on the groundwater composition and flow rate, and can affect the structural properties of concretes and, over long timescales, reduce the ability of cementitious backfills to chemically condition the porewater.

- Groundwaters low in calcium and silicon can lead to an increased rate of dissolution of the cementitious materials, whereas components of saline and high-$P$ CO$_2$ groundwaters can chemically react with the cementitious phases:
  - carbonation depends upon the geological environment – groundwater in sedimentary basins have much higher PCO$_2$ than those in fractured hard rocks, leading to much greater degrees of carbonation at cement-rock interfaces.
  - salinity effects can lead to decreased pH due to interaction with Mg-SO$_4$ brines, but pH may be increased due to the increased solubility of portlandite with increasing concentrations of NaCl in groundwater ('salting-in' effect). Chloride ions may be bound in Friedel’s Salt potentially consuming some of the calcium hydroxide component of the backfill.
  - reaction with sulphate may lead to the formation of ettringite or gypsum which can increase solid volumes, potentially leading to cracking.

- For cementitious geological disposal concepts, the cement backfill is designed to have a strong influence on the ingressing groundwater; high-calcium cements provide a high-pH low-carbonate near-field environment.

- The impact of cement on the rock is mediated by the groundwater leading to changes in physicochemical properties of the rock, and is a site-specific issue.

- Improvement to solid solution models for representing calcium silicate hydrate phases and the recent development of a database for cementitious mineral phases have provided the tools for modelling many of the processes affecting the evolution of cements interacting with groundwaters.
10 Interactions of cements with waste, wasteform and other EBS materials

10.1 Introduction

Due to their alkaline nature, cements will react with a wide range of acidic and amphoteric materials in wastes, wasteforms and EBS materials. In most cases such reactions will be mediated by the near field porewater, following re-saturation. Some of the important reactions of cements can be beneficial reactions, such as the adjustment of the porewater to conditions that lower the solubilities of some key radionuclides. However, the reaction of backfill cements with other materials tends to consume alkaline component and reduce the effects of porewater conditioning in long-term. In this section, the focus of the review is on the impacts of such interactions on the cements (rather than the waste and EBS materials), and particularly on cementitious backfills.

10.2 Interaction with encapsulants and vitrified waste

10.2.1 Cementitious grouts

Cementitious grouts are widely used to encapsulate a range of intermediate level wastes. These materials will be significantly different in composition to high-calcium cementitious backfills. This difference in composition may provide a driving force for a pozzolanic reaction between the grouts and the backfill, potentially altering the mineralogy and behaviour of both. This reaction would result in the formation of additional C-S-H gel from the higher silica content in the grouts and the higher calcium content of NRVB. The chemistry of the pozzolanic reaction has been widely studied for the reaction between silica and dissolved calcium in pozzolanic cements. A similar reaction between encapsulation grouts and NRVB may occur, based on the inhomogeneous distribution of silica and calcium between the materials and the long time-scales available for reaction. The extent of this reaction is uncertain and some of the silica may not be reactive even on the time-scales considered in performance assessment calculations. Such processes have been included in reactive transport modelling studies of near field evolution [277] (and sub-section 11.5). These calculations indicated that a pozzolanic reaction is likely to occur between cementitious backfills and encapsulation grouts of lower calcium-silicon molar ratio. The volume increase associated with this reaction may form a seal that prevents or reduces further reaction, but this has not been confirmed experimentally. Where the reaction does occur, it is likely to reduce the capacity of the cement for buffering at a high pH, but the calcium silicate hydrate phases formed may enhance such buffering at less alkaline pH values.

10.2.2 Vitrified wasteforms

Vitrification is under consideration for the immobilisation of certain ILW wastes in the UK, because it may provide a volume reduction and greater durability and reduced waste reactivity compared with cement encapsulated materials, under certain conditions [278- 281]. If such wastes are disposed of in cementitious vaults, their potential effects on the chemical performance of the near field would need to be considered. Such effects could be included in the treatment of processes affecting pH-buffering performance described in sub-section 11.4.

A review of published information on the durability of glassy materials in a high-pH environment has been carried out [282]. It was concluded that the high-pH environment envisaged in the cement-based ILW/LLW concept is likely to lead to more rapid dissolution of vitrified ILW placed into the GDF compared with emplacement of the same vitrified product in a non-cementitious environment. However, the effect of such dissolution on the pH-buffering capacity of the cement is not apparent from the literature. An experimental programme [283] was subsequently undertaken to address the knowledge gaps highlighted by the review, concerning:

- the initial rate of vitrified ILW dissolution in a calcium-rich alkaline environment;
• the nature of the colloids, alteration product and gel layer formed by dissolution of different ILW glasses in a calcium-rich alkaline environment;

• whether the assumption of a residual dissolution rate for long-term glass dissolution due to the formation of a protective glass gel-layer [284] holds for the alkaline environment of the backfill.

The results of these experiments suggest that the presence of dissolved calcium may be a significant factor controlling the performance of waste glasses in high-pH environments. It seems probable that the presence of calcium mitigates the effects of high-pH conditions that tend to reduce glass durability due to reaction with the glass and formation of a protective layer of C-S-H phases on the glass surface as observed in the scanning electron micrographs shown in Figure 62.

Reduction in glass dissolution rates have also recently been reported in calcium-rich solutions at pH 9 (in a confined medium reaching apparent saturation state) [285]. The calcium effect on the alteration kinetics was again explained by the presence of a protective layer.

![Image of simulant ILW glass particle before and after dissolution](image-url)

Figure 62 Surface of simulant ILW glass particle (a) before reaction and (b) after dissolution at 90°C for 28 days in saturated and buffered Ca(OH)₂ solution (from [283])

10.2.3 Polymer encapsulants

Organic polymeric resins are potential encapsulants for some intermediate level wastes. Several of these possible encapsulants have been shown to be relatively stable over laboratory timescales. Experimental studies to examine their stability have been performed under aqueous alkaline conditions (in the presence of calcium hydroxide) and have included investigation of the effects of elevated temperature (80°C) and radiation doses up to 10 MGy [286].

In the thermal leach tests, total organic carbon released from the resin was found to be enhanced when compared with tests at ambient temperature. For vinyl ester styrene (VES), gas chromatography – mass spectrometry results suggested that a significant contributor to this could have been dimethyl aniline (a component in the manufacture of VES) rather than a degradation product. The VES was found to be the most resistant to radiation with its mechanical properties almost unaffected after a dose of 10 MGy, whereas two epoxy resins were more affected. One epoxy resin was heavily degraded, whereas the other retained its compressive strength at this dose, but its flexural strength was reduced by 80%. It is not clear whether calcium hydroxide had been significantly consumed during these experiments, because an excess of calcium hydroxide ensured that the pH remained high. Tests using deionised water did show a significant decrease in pH.

Despite the stability of some of the resins over laboratory timescales, the possibility of degradation over very long periods cannot be excluded (e.g. due to potential alkaline hydrolysis of the ester...
groups in VES), particularly if slower kinetic or diffusion-limited reaction steps are involved in the degradation. For example, VES may potentially react with the hydroxide component of the backfill:

\[ RCOOR' + OH^- = RCOO^- + R'OH \]

where R and R' represent the (polymeric) organic chains linked by the ester group. The ether linkages in epoxy resins, by contrast, are much less susceptible to hydrolysis.

### 10.3 Interaction with container materials

The corrosion of steel container materials is the major process affecting the lifetime of the physical containment of the associated waste packages. Cementitious alkaline conditions play an important role in determining the rates of corrosion of container materials to cementitious disposal concepts. These effects have been reviewed [287-289] and summarised [9] in detail elsewhere, for aerobic and anaerobic conditions. It is noted that in a cementitious environment, corrosion rates in the aerobic period will be significantly reduced due to the high pH, particularly in the case of re-saturation by saline groundwaters. Beyond the aerobic period, general corrosion occurs through the reduction of water.

The direct impact of the corrosion interactions on the chemical properties of cements is expected to be small because the corrosion reactions do not consume calcium or hydroxide ions, e.g.:

- **aerobic**: \( 4\text{Fe(s)} + 3\text{O}_2(g) = 2\text{Fe}_2\text{O}_3(s) \)
- **anaerobic**: \( \text{Fe(s)} + 2\text{H}_2\text{O(l)} = \text{Fe(OH)}_2(s) + 2\text{H}_2(g) \)

However, there may be the potential for the reaction products to be incorporated into cementitious phases due to reaction with \( \text{Ca(OH)}_2 \) or calcium aluminate species. Alternatively, reaction with \( \text{Ca(OH)}_2 \) to form higher aqueous hydrolysis species of iron would reduce the pH-buffering capacity of the backfill [219]:

- e.g. \( \text{Fe(OH)}_2(s) + 0.5\text{Ca(OH)}_2(s) = \text{Fe(OH)}_3^- + 0.5\text{Ca}^{2+} \)
- \( \text{Fe(OH)}_3(s) + 0.5\text{Ca(OH)}_2(s) = \text{Fe(OH)}_4^- + 0.5\text{Ca}^{2+} \)

However, the significance of this process is not known. It will depend on the groundwater flow rate and the solubility, and crystallinity, of the corrosion products formed.

### 10.4 Interaction with wastes

A cementitious backfill has been specified in disposal concepts for ILW and LLW in the UK and elsewhere. The associated waste streams tend to be chemically diverse and often complex. This is particularly the case in the UK, because of the legacy of nuclear energy development in this country. Consequently, there is a huge range of potential waste component reactions that may affect the evolution and performance of cementitious backfills.

The major classes of backfill-consuming reactions are reviewed in sub-section 11.4 and are summarised in Table 23.
### Table 23 Summary of major classes of backfill consuming reactions with waste components (based on information in Heath et al. 2009 [219])

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degradation of organic materials</td>
<td>e.g. $\text{RCOOR}^- + 0.5\text{Ca(OH)}_2(s) = \text{RCOO}^- + \text{R'}OH + 0.5\text{Ca}^{2+}$</td>
</tr>
<tr>
<td>Reaction with cellulose-like organic waste components</td>
<td>e.g. $\text{C}<em>6\text{H}</em>{10}\text{O}_5 + 3\text{Ca(OH)}_2(s) = 3\text{CO}_3^{2-} + 3\text{CH}_4(g) + 2\text{H}_2\text{O} + 3\text{Ca}^{2+}$</td>
</tr>
<tr>
<td>Reaction with reactive metals</td>
<td>e.g. $\text{U(s)} + 4\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2(s) + 3\text{H}_2(g)$</td>
</tr>
<tr>
<td>Conversion of metal oxides and hydroxides to mixed calcium-metal solids</td>
<td>e.g. $2\text{UO}_2(\text{OH})_2(s) + \text{Ca(OH)}_2(s) = \text{CaU}_2\text{O}_7(s) + 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Hydroxide formation from metal salts</td>
<td>e.g. $\text{Mg}^{2+} + \text{Ca(OH)}_2(s) = \text{Mg(OH)}_2(s) + \text{Ca}^{2+}$</td>
</tr>
<tr>
<td>Reaction of protonated forms</td>
<td>e.g. $\text{HCO}_3^- + 0.5\text{Ca(OH)}_2(s) = 0.5\text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Reaction of unprotonated anions</td>
<td>e.g. $5\text{Ca(OH)}_2 + 3\text{PO}_4^{3-} = \text{Ca}_3(\text{PO}_4)_2\text{OH}(S) + 9\text{OH}^-$</td>
</tr>
<tr>
<td>Reaction of silicates and aluminosilicates</td>
<td>e.g. $\text{Na}_6(\text{AlO}_2)\text{Si}_3\text{O}_10\cdot24\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Formation of higher aqueous hydrolysis species</td>
<td>e.g. $\text{Fe(OH)}_3 + 0.5\text{Ca(OH)}_2 = \text{Fe(OH)}_4 + 0.5\text{Ca}^{2+}$</td>
</tr>
</tbody>
</table>

#### 10.4.1 Reaction with organic wastes

Organic wastes that include acidic groups such as carboxylic acids or protonated forms of amine groups are expected to undergo rapid neutralisation reactions with alkaline cementitious materials. Such reactions have been studied for a range of short chain carboxylic and hydroxy-carboxylic acids with NRVB [290]. In experiments with enhanced levels of organic acid, disintegration of the cementitious material occurred, consuming the calcium hydroxide and C-S-H components of the NRVB. The hydroxyl-carboxylic acids did not react with calcium aluminate phases in NRVB over the experimental timescale. However, where such wastes are chemically conditioned with cementitious encapsulation grouts during packaging, neutralisation by the grout rather than the backfill is expected.

Polymeric organic materials in the waste are also expected to degrade. For cellulosic wastes, the chemical degradation with cements has been investigated in detail in the UK and elsewhere (see for example the reviews in references 291 and 63). Such reactions proceed primarily by alkaline hydrolysis but may also be enhanced by radiolytic degradation [292]. The products of such reactions include isosaccharinic acid, which is a strong complexant for some radionuclides. Its effects on radionuclide solubility and sorption, and implications for performance assessments, is of importance and is discussed in sub-section 12.7.

There have been few studies of the degradation of other polymers under the alkaline, reducing chemical conditions anticipated in a cement-based near field. Some experiments on their alkaline
Degradation (and radiolysis) have been performed by investigating the effects of the degradation leachates on plutonium solubility. For most of the typical synthetic organic polymers present in radioactive waste there is little evidence of any effect of degradation on laboratory timescales [63]. However, where organic polymers are irradiated at elevated temperatures, a significant enhancement of degradation rates can be observed due to radiation/thermal synergy [293]. A relatively modest increase in temperature of tens of degrees Celsius during irradiation can generate significantly higher degradation rates than would be expected by applying the thermal and radiation environments sequentially.

Degradation of chlorinated organic wastes such as poly(vinylchloride) is likely to result in the production of hydrochloric acid via an unzipping reaction [294]. From the backfill pH-buffering performance point of view, such degradation processes are detrimental because acidic products such as HCl consume some of the calcium hydroxide or C-S-H components (see sub-section 11.4.3). The rate of degradation of such polymers (and consequent calcium hydroxide consumption) is strongly dependent on the presence and type of plasticisers and additives in the organic material [295-297].

Further degradation of the organic materials in the waste is possible. Complete degradation to carbon dioxide and methane may occur, particularly if the conditions allow microbial activity. Any carbon dioxide or carbonate species that are formed by such processes may contribute to the carbonation of cements (see sub-section 9.2.3).

10.5 Interaction with other backfill and buffer materials

10.5.1 Bentonite

(a) Background

The use of cement grouts and tunnel plugs in a GDF for SF/HLW, together with the potential co-location of ILW, may affect the long-term stability and performance of bentonite used as a buffer and in tunnel backfills. This topic is of importance for geological disposal concepts that involve bentonite and has been reviewed in detail recently for NDA RWMD [298] so the emphasis here is to provide a brief summary of the key points and to focus on issues regarding different cement types, especially low-pH varieties.

Cement-clay interactions have been studied extensively in the last ten years, through laboratory experiments (e.g. [299-306]), computer simulations (e.g. [307-312]), and a number of analogue investigations (e.g. [254, 313-315]). However, most of these studies have considered the interaction of OPC-type cement with bentonite, and not other formulations. There are some useful reviews, especially from a performance assessment perspective (e.g. [264, 266, 316-320]).

(b) Key reactions

The most important processes in defining the spatial and temporal extent of cement-clay interactions are as follows [298].

- Diffusion of cement pore fluids into bentonite, with mixing and reaction of pore fluids. Gradients in the porewater pH and saturation with respect to CO₂ across interfaces encourage the growth of solid carbonates, leading to a decrease in porosity.
- Fast exchange of cations in cement pore fluids for cations in interlayer sites in montmorillonite, leading to a decrease of swelling pressure. These reactions advance in front of dissolution-precipitation reactions.
- Fast protonation-deprotonation reactions at clay edge sites.
- Slow dissolution of montmorillonite and other minerals. These lead to an increase in porosity and may decrease clay swelling pressure.
- Precipitation of secondary minerals, forming in a zonal fashion (Figure 63).
Figure 63  Schematic diagram of the potential sequence of secondary mineral formation due to the migration of hyperalkaline pore fluids through bentonite. As the composition of cement pore fluids evolves with time, sodic-potassic phases will be replaced by more calcic varieties (from Savage et al. [319]).

Previous studies have highlighted that cement-bentonite interactions are strongly non-linear, with a complex interplay between fluid transport, clay ion exchange and dissolution, secondary mineral growth, and consequent changes in physical properties of the bentonite (Figure 64). This complexity makes it difficult to extrapolate the results of laboratory experiments to the timescales of interest for the safety case. Reactive transport models have been applied to predict the evolution of mineral assemblages in bentonite (for example, see the next sub-section on modelling interactions with low-calcium cement porewater). However, there are many uncertainties associated with the data available for such modelling, such as the growth rates of mineral alteration products.

These reactions can result in the following changes to bentonite properties.

- **Porosity.** Porosity decreases in clay, regardless of pore fluid type due to the precipitation of secondary solids [321].

- **Hydraulic conductivity.** Since porosity is predicted to decrease with time due to cement-clay reactions in diffusive transport conditions, similar changes to hydraulic conductivity are to be expected.

- **Swelling pressure.** A reduced swelling pressure in bentonite (30-80% lower than initial) has been measured due to exchange of Ca for Na in smectite interlayers in laboratory experiments where compacted bentonite has been contacted with cement or cement pore fluids (e.g. [322, 323]).

- **Mineralogical composition.** Data from computer simulations show similar mineral alteration sequences (Figure 63); and evidence from a 125 year-old industrial analogue of clay-cement (OPC) interaction at Tournemire shows a sequence of calcite, gypsum, C-S-H, and K-feldspar with increasing distance across a 2-3 cm zone of claystone adjacent to a cement contact [254, 255].

Testing of these models and associated understanding is difficult due to the extremely slow kinetics of bentonite reaction in low-alkali cement leachates. Consequently, laboratory studies show little or no mineralogical change. However, the on-going Cyprus Natural Analogue Project [324] aims to develop understanding of the long-term impacts of alkaline groundwaters (in the approximate range pH 10-11) on clay, from sites that include bentonite and associated clay-rich sediments. Progress to date [325] has shown that: the groundwater chemistries are relevant to low-alkali cement leachates; identified evidence of clay reaction; and built confidence in a site conceptual model.
The potential deleterious interactions of OPC-derived pore fluids with clay engineered barriers described above are managed by (e.g. [320]):

- limiting the amounts of cements through design choices; and
- using alternative cement compositions, including low-pH cements.

This latter option is considered in more detail below.

(c) Reactions of low-pH cements with bentonite

Owing to the potential for deleterious effects of alkaline conditions (pH > 12) of standard cement pore fluids upon bentonite, 'low-pH' cements are being considered as a potential alternative material (e.g. Garcia Calvo et al. [326]). However, the interaction of low-pH cements with bentonite has only been addressed in modelling studies.

Watson et al. [310] compared the evolution of a bentonite sample under the influence of several cement pore waters over a pH range from 10 to 13.2. The pore water compositions were taken from published C-S-H gel leaching experiments and published cement-bentonite modelling studies. The simulations suggested that the amount of degradation that is likely to be observed when low-pH cement water interacts with bentonite is likely to be much less than when OPC water is the permeating fluid. Below pH 11 there was no observable montmorillonite dissolution front which would tend to support the pH 11 target for cement pore fluids suggested by NUMO, Posiva and SKB.
Lehikoinen modelled the interaction of bentonite with cement pore fluids at a range of pH [327]. A feature of all the simulations was the clogging of the pore space at the interface between the bentonite and the rock fracture carrying the alkaline water. Depending on the pH considered in the calculations for the plume (pH 12.17, 11.60 or 9.70), the clogging occurred after 10, 18 or 5,900 years, respectively, following the onset on interaction. In each case, the mineralogically-altered zone was confined close to the interface, as illustrated in Figure 65.

Low-pH cement grouts produce pore fluids relatively rich in silicon, compared with natural groundwaters (e.g. Savage and Benbow [319]). For example, the concentrations of dissolved silicon measured by Harris et al. [225] in C-S-H gel leaching experiments for compositions relevant to those of low-pH cements were up to 2.2 mmol dm$^{-3}$, which is equivalent to the solubility of amorphous silica at neutral pH at 25 °C. Most natural groundwaters contain dissolved silicon equivalent to that of chalcedony (0.2 mmol dm$^{-3}$ at 25°C) or quartz (0.1 mmol dm$^{-3}$). Potentially, the higher silicon concentrations associated with low-pH grout pore fluids could destabilise montmorillonite. According to the phase relation diagram shown in Figure 66, higher silicon concentrations could theoretically destabilise montmorillonite to form albite (Na-feldspar), which could lead to embrittlement of the bentonite and a loss of swelling properties.
There is evidence for reactivity of montmorillonite in the pH range 9-10 at the Searles Lake analogue in California, USA [315]. Appreciable dissolution of montmorillonite is inferred to have occurred, with the precipitation of illite, K-feldspar and analcime. These observations are in contrast with the results of the modelling studies described above, probably due to:

- advection being the primary mode of fluid transport in the Searles Lake diagenetic system; this would have contributed to the reactivity of montmorillonite observed;
- reactant fluids at Searles Lake being (it is thought) essentially calcium-free, so that reaction would not have been minimised by formation of porosity-filling C-S-H solids, which contribute to the cessation of reaction predicted in computer simulations.

(d) Effects of bentonite on cements

Most of the work on cement-bentonite interactions has focused on minimising the deleterious effects of cements and associated alkaline plumes on bentonite stability and performance (discussed above). Little work has been reported on the effects of bentonite on cement performance. Any effect on cementitious materials is likely to be mediated by groundwater. If the bentonite is separate but upstream from the cement, it is unlikely to provide the major control on the conditioning of the porewater, because the main flow is expected to be through more permeable materials (i.e. around bentonite). Where bentonite-conditioned porewater meets cements the effects are expected to fall within the ranges of those described for groundwater interactions (see section 9).
10.5.2 Crushed rock

Crushed rock has been considered as a potential backfill material for ILW disposal concepts [328, 329]. The effects of such backfills on cementitious materials are expected to fall within the range of those described for groundwater/host rock interactions (see section 9). However, the crushing of the rock and its close proximity to the cements present may increase the rate of such interactions.

10.6 Effects of radiation on cement materials

A great deal of work has been done to investigate the effects of radiation on the physical properties of cements used in nuclear reactors. However, it is difficult to relate results from these studies to the behaviour of materials in a geological disposal facility because of the significant differences between the conditions. In reactor studies, most data are for combined effects of neutron and gamma irradiation and are probably not directly comparable to radiation effects in a GDF.

Work on programmes for geological disposal has tended to focus on grouts used to encapsulate materials in waste packages. The grouts are, in many ways, similar to a backfill cement; the main constituents being OPC with either BFS or PFA. The behaviour of these grouts may therefore be used as a guide to the effects of irradiation on backfill materials. However, dose rates used in experiments on encapsulation grouts are generally in the order of 1 Gy s⁻¹ to simulate conditions within waste packages. Dose rates in backfilled areas of a geological disposal facility would be significantly lower than this. From UK inventory information, an average dose rate at the surface of an unshielded ILW waste drum has been calculated as 6 x 10⁻⁴ Gy s⁻¹ in year 2060, decreasing to 1 x 10⁻⁴ Gy s⁻¹ by 2160 [330]. For shielded ILW packages and LLW packages, the dose rates would be considerably lower. Dose rates around HLW and SF containers are not expected to be significantly higher owing to the shielding provided by the package. As part of the Swedish SR-Can assessment a maximum dose rate outside of the canister of 1 x 10⁻⁴ Gy s⁻¹ (500 mGy hr⁻¹) derived mostly from Cs-137 (half-life ~30 years) has been calculated [331]. The buffer used with HLW and SF containers would likely be clay-based and so dose rates to cement materials beyond the buffer would be significantly lower.

A number of studies have looked at the effects of radiation on the physical properties and mineral composition of grouts. Wilding et al. [332] investigated the effects of gamma radiation on BFS/OPC grouts. This study concluded that there was no significant deterioration of physical properties caused by gamma irradiation doses up to 12 M Gy at dose rates up to 3 Gy s⁻¹, although at the higher dose rate, some cracking and spalling was detectable due to high rates of radiolytic gas production. Richardson et al. [333] examined samples of BFS/OPC irradiated at 50°C. Gamma doses of 3 to 80 M Gy were used over a period of 2 years (~1 Gy s⁻¹). Little in the way of changes in the microstructure were detected and C-S-H phases remained unaltered in composition and morphology. Some differences in the cement phases present were observed, with calcium trisulphoaluminate being present in only the irradiated samples. In a study by Wilding et al. [334], irradiated fuel hulls were encapsulated in a 3:1 BFS/OPC grout of w/c = 0.35. The alpha irradiation dose rate was approximately 0.002 Gy s⁻¹ and the beta/gamma 0.2 Gy s⁻¹. The samples remained in good physical condition with no measurable dimension changes. These studies indicate that at the dose rates expected within waste packages, the effects of radiation on the physical properties of cements are minimal. At the lower dose rates experienced by the backfill and sealing grouts, it is reasonable to assume that in general other effects such as interaction with groundwater will be more important in the alteration of physical properties.

Another important consideration is gas generation caused by radiolysis of porewaters. Radiolysis of water results in the production of a several primary species, including: OH⁻, H⁺, e⁻, H₂O₂, H₂ and HO₂⁻. The release of hydrogen and oxygen from BFS/OPC grout under gamma irradiation in air has been measured [332]. The results suggest that some of the minor constituents of the grout may have an impact on gas release, for example the presence of nitrates suppressed H₂ evolution. Under the reducing conditions expected in the near field, oxygen is expected to be consumed, so that the main gas released would be hydrogen. It is suggested in reference 332 that some of the cracking seen in the grouts under irradiation may be due to pressure from the build up of gas in the
pores. This is unlikely to be an issue in NRVB, firstly because of the lower doses rates, but also NRVB has a higher permeability than encapsulation grouts. For the ILW/LLW concept, it is expected that overall the contribution of porewater radiolysis to gas generation will be minimal compared to that produced by corrosion of reactive metals in the waste inventory (about three orders of magnitude higher) [210]. Once reactive metals have corroded, gas generation by radiolysis will be comparable to the rate of gas generation produced by anaerobic steel corrosion, until around 10,000 years, by which time the radiation field is reduced [210].

Organic additives are often included in cement formulation to improve flow and setting properties and under irradiation these may break down to release H$_2$ and CO$_2$ or low-molecular-weight hydrocarbons. The current formulation for NRVB [11] excludes these organic additives, but they may be used in the sealing grouts. Gas releases from 3:1 BFS/OPC grout with various organic admixtures have been compared by Palmer et al. [335]. The pure admixtures were shown to release H$_2$ and CO$_2$ under gamma irradiation with doses of up to 9 MGy. Hydrogen releases per unit mass of admixture were at least an order of magnitude lower when incorporated in grout. CO$_2$ yields were unchanged for a sulphonated melamine admixture, but sulphonated naphthalene produced more CO$_2$ when irradiated in grout. The authors of reference 335 suggest that the higher CO$_2$ yield may be due to a chemical effect, with the high pH of the grout weakening carbon-to-carbon bonds. However, the difference may be due to a combination of chemical and radiolytic effects.

It is known that organic additives can give rise to soluble species which form aqueous complexes with radionuclides, so altering their solubility and sorption behaviour. The radiolytic degradation of these additives will alter their complexing behaviour. For example, superplasticisers used in cements have been shown to increase the solubility of plutonium and uranium, but this effect is reduced by gamma irradiation, probably due to the strongly-complexing ligands being broken down [336].

Another potential effect of the radiolysis of porewater is the alteration of redox conditions. Radiolysis of water leads to the production of some oxidising species, such as OH$^-$, H$_2$O$_2$, HO$_2^-$. However, consideration of the impact has concluded that redox potential within the near field is likely to be dominated by corrosion of iron and steel [330].

A small amount of work has been done to investigate the effects of radiation on the sorption properties of minerals. Gamma radiation doses of $10^5$ to $10^6$ Gy may affect the surface area [337] and so increase the number of sorption sites. However, a study of the sorption of lithium, caesium and strontium onto magnetite found doses of ~6 x $10^4$ Gy to have very little effect on sorption [338]. These doses compare with an estimated total dose of the order of $10^7$ Gy in a GDF for UK ILW/LLW [9].

The impact of alpha irradiation will be limited to materials inside the containers until these are breached. After breach, alpha emitters are likely to be concentrated in the immediate vicinity of the container for a very long period of time, because actinides tend to be strongly sorbing (see section 12). Therefore, the distribution of alpha radiation in the backfill will be limited so that, even if there was an effect, overall the bulk properties should be unaffected.

### 10.7 Key points

- Interaction of cements with other materials consumes alkaline component, Ca(OH)$_2$ (portlandite), and such processes can reduce pH-buffering performance of cementitious backfills in the long-term.
- Reaction mechanisms of hyperalkaline cement pore fluids with bentonite include cation exchange, montmorillonite dissolution and precipitation of secondary minerals; such reactions may result in changes in bentonite porosity, swelling pressure, hydraulic conductivity and sorption capacity.
• Bentonite-cement interactions include complex, non-linear processes, making it difficult to extrapolate the results of laboratory experiments to the timescales of interest for the safety case.

• Reactive transport models may be used to predict the evolution of mineral assemblages in bentonite, but there are many uncertainties associated with the data available for such modelling, such as the growth rates of mineral alteration products.

• Reactive transport models may be used to predict the evolution of cementitious mineral assemblages, including the reaction of cementitious backfills with encapsulation grouts, but there are uncertainties associated with the data available for such modelling.

• Other international agencies are in the process of adopting low-pH cement/concrete as their preferred material for fracture grouts, shotcrete and tunnel plugs in repositories for HLW/SF to counteract these potential deleterious interactions; moreover, some GDF designs aim to reduce the amounts of cement/concrete left in the system at closure.

• Low-pH cements may result in less aggressive chemical conditions, and modelling studies indicate little or confined smectite alteration. However, it is still possible that such alteration may occur in alkaline environments (pH 9-11), albeit much more slowly than at pH 13. Currently, there are no experimental studies available investigating the reaction of bentonite with low-pH cements.

• There is little evidence of significant changes in the physical properties of cements induced by radiation at the dose rates expected to the backfill, sealing grouts and structural materials.

• In situ gas generation due to the radiolysis of porewater in grouts has been suggested as the cause of some of the cracking observed in these lower permeability materials under irradiation. However, this is considered unlikely to be an issue for a high permeability backfill, such as the NRVB, in which dose rates will also be lower.

• Radiolysis of water has the potential to produce oxidising species in solution, but this is expected to be counteracted by the low redox potential brought about by corrosion reactions of steels in the GDF.
11 pH-buffering performance of cementitious backfills

11.1 Introduction

The chemical environment of the near field is a key factor affecting the overall performance of a radioactive waste disposal facility. It controls processes such as the degradation of waste canisters and waste-forms, the solubility of radionuclides in the porewater and the retardation of radionuclides migrating through the near field. Many chemical parameters affect these processes, but for cementitious disposal facilities, the single most important parameter is the pH of the porewater [11].

In many concepts for the disposal of low-level [339] and intermediate-level wastes (e.g. in UK [11], Switzerland [15], France [340], Japan [341]), cementitious backfill materials have been specified largely because of their ability to condition the pH of the associated porewater. Cementitious backfills are also selected for their high sorption capacity, ease and effectiveness of backfilling, and because they can be designed with high porosities, facilitating gas release and promoting greater homogeneity. The selection of a cementitious formulation provides an alkaline, low-carbonate porewater, and these chemical conditions lower the solubility of many important radionuclides. Although there is some uncertainty concerning certain aspects of the cement-curing processes, the conditioning of the porewater in saturated systems and the cementitious solid phase responsible for this are well understood. Research into the interaction of such backfills with groundwater components and other waste components is also improving our understanding of the longer-term pH conditioning of near-field porewaters, as described in sub-section 9.5.

In this section, the focus is on the performance of high-calcium cementitious backfills. Low-calcium cements, by contrast, are not considered because they are designed to avoid generating highly alkaline environments.

11.2 pH-buffering performance criteria and temperature dependence

To carry out performance assessment calculations it is necessary to assign values (and their uncertainties) for a range of chemical parameters, such as radionuclide solubilities and sorption distribution coefficients. This assignment requires the definition of the ranges of conditions to which the values will be applied, and includes the range of near-field pH values that will be encountered over the period represented in such calculations. In the ILW concept in the UK, a pH greater than pH 9 has been assumed to persist for a period of one million years in the elicitation of chemical parameters (see for example reference 342). In earlier work [343], it was reported that this pH conditioning requirement would be met if:

“the hydroxyl molality in the porewater is maintained above $10^{-5}$ mol kg$^{-1}$ to provide chemical retention in the repository near field.”

It was further noted that the value for the hydroxyl concentration was calculated from the water dissociation reaction at 25°C (and this corresponds to pH 9 at this temperature)\(^{11}\). In practice the pH requirement should be met if the backfill provides pH-buffering through the dissolution of calcium hydroxide and calcium silicate hydrate gel from a material based on Portland cement [11],

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\(^{11}\) This requirement is preferred to a subsequent one based on the persistence of pH buffering provided by the dissolution of magnesium hydroxide, due to uncertainty over the long-term stability of this solid in the near-field environment, and which requires a significant magnesium concentration in the groundwater.
over the million year period. It is noted that mineral phases formed by interaction of the backfill cement with groundwater and waste components may also contribute to the longer-term pH buffering.

The temperature dependence of pH results from the increased dissociation of water molecules at elevated temperatures. However, for alkaline systems in equilibrium with calcium hydroxide the effect of this increased dissociation on the concentration of hydroxide ions is small. Calculations of the hydroxide ion concentration in NRVB-equilibrated waters [12, 171] predict a decrease from $3.6 \times 10^{-2} \text{ mol dm}^{-3}$ (pH 12.4) at 25°C to $2.6 \times 10^{-2} \text{ mol dm}^{-3}$ (pH 10.7) at 80°C. It is the hydroxide ion concentration that is important in determining the solubility of the oxides and hydroxides of radionuclides at high pH.

In the discussion of pH values in the sub-sections below, a temperature of 25°C is assumed.

11.3 Description of pH evolution

11.3.1 Initial mineralogy

The pH conditioning of the porewater at the time of resaturation depends on the formulation of the backfill and the extent of curing processes at this stage. For high-calcium backfills, the major components include calcium hydroxide, C-S-H phases and aluminate phases such as hydrogarnet or C-A-S-H. In addition, significant quantities of sodium and potassium oxides/ hydroxides are initially present (see section 3).

11.3.2 Mineralogy of NRVB

For NRVB, the early-stage mineralogy has been reviewed by Holland and Tearle [217] based on a detailed literature search of the general use of lime and limestone additives in cement and concrete formulations and on consideration of specific experimental studies of the hydrated backfill. Resulting from this study, three model compositions of the hydrated NRVB were recommended for consideration:

- short-term high temperature model (80°C) based on the mineral assemblages: calcium hydroxide, C-S-H gel, hydrogarnet and calcium carbonate;
- long-term restricted sulphate ingress model (delayed ettringite formation) based on the mineral assemblages: calcium hydroxide, C-S-H gel, hydrogarnet, monocarboaluminate, ettringite and calcium carbonate;
- long-term unlimited sulphate ingress model based on the mineral assemblages: calcium hydroxide, C-S-H gel, ettringite and calcium carbonate.

The first of these model compositions, shown in Table 24, was considered the most appropriate for use in studies in the early post-backfilling era of the disposal facility, and has been applied as the initial mineralogy in modelling of the backfill-groundwater interactions, described below.

Table 24 Mineral assemblage in NRVB - short-term high temperature model (80°C) taken from Holland and Tearle 2003 [217] (model ‘H’)

<table>
<thead>
<tr>
<th>Component</th>
<th>Abbreviation</th>
<th>Content in dry NRVB (mol m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portlandite</td>
<td>CH</td>
<td>3704</td>
</tr>
<tr>
<td>Calcium silicate hydrate</td>
<td>C-S-H</td>
<td>758</td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>C$_3$AH$_6$</td>
<td>311</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>4950</td>
</tr>
</tbody>
</table>
11.3.3 Main features of pH evolution

Leaching experiments on high-calcium cementitious systems and associated modelling studies have allowed an understanding of the changes in the cement mineralogy arising from interactions with the groundwater to be developed. The following stages in the associated pH evolution have been identified [11, 339]:

Stage 1  pH > 12.5 arising from the dissolution of sodium and potassium oxides, with the pH value dependent on the amounts of alkali metal oxides and on the porosity of the backfill;
Stage 2  pH ~ 12.5 buffered by equilibration of the ingressing groundwater with the calcium hydroxide component of the backfill;
Stage 3a pH falling from 12.5 to ~ 9.8 controlled by the incongruent dissolution of calcium silicate hydrate phases;
Stage 3b pH ~ 9.8 controlled by congruent dissolution of calcium silicate hydrate phases (or secondary mineral phases giving additional buffering at other pH values);
Stage 4  pH < 9 once exhaustion of the pH-buffering cementitious phases has occurred, with pH determined by the groundwater and remaining phases such as calcite.

This simple picture is summarised in Figure 67. Similar pH calculations have been performed in the context of disposal facilities in a variety of geologies. These show the same main stages but the timescales vary considerably with the groundwater flow rate through the waste vaults, and with the groundwater chemistry. For the Swiss concept for ILW disposal, pH evolution in potential disposal facilities sited in marl (Wellenberg) and in Opalinus Clay has been considered. For the Wellenberg site, the study by Neall [344] indicated that the cementitious near field of the disposal concept will be in Stage 1 of cement degradation for a few thousand years and, for a very much longer time, in Stage 2. The time spans may be even longer for an ILW repository based in Opalinus Clay [19] as diffusion is the dominant transport process in this host rock [345].

![Figure 67 Schematic representation of the evolution of pH in the backfill porewater during groundwater leaching](image-url)
The effect of pH evolution under diffusion control has been demonstrated clearly under the French programme for a clay-based disposal facility located in Callovo-Oxfordian argillites. In this case the cement material is a type CEM V composite (OPC/BFS/PFA) concrete used as a tunnel coating for structural support. For a concrete hydrolysis model by Bourbon [346] (summarised in Dossier 2005 [340]) a sequence of degradation stages almost identical to those in Figure 67 are presented. However, under such conditions, the timescales of cement degradation and pH evolution are much longer and the pH results are presented as spatial pH profiles at different stages in the evolution of the relevant vaults, as shown in Figure 68.

Figure 68 Schematic representation of the of the progressive degradation of a type CEM V concrete coating / support of an ILW (B-waste) disposal cell [340]
The hydraulic disposal conditions are characterized by low water fluxes within the Callovo Oxfordian and within the structures. These lead to a slow chemical degradation of the cement-based materials occurring over hundreds of thousands of years. The propagation of the front relating to the altered condition of the concrete would reach less than one metre in one million years.

By contrast for the near surface, unsaturated LLW disposal facility at Dessel, Stage 3 is conservatively estimated to end after around 35,000 years, although the same overall pH profile is expected [339].

For the flow rates considered in performance assessments for the UK [347-349], Stage 2 would be expected to last for a period of tens of thousands of years. The pH-buffering performance criteria discussed above imply that Stage 3b needs to extend beyond one million years. In practice, Stage 3 may be strongly affected by equilibration with secondary mineral phases (such as ettringite, hydrotalcite) formed by backfill interaction with the groundwater or waste components. These processes are discussed in sections 9 and 10.

11.4 Reactions of the backfill

The pH buffering of the porewater by the cementitious backfill is primarily provided by the calcium hydroxide and calcium silicate hydrate phases, and results in pH profiles like that shown in Figure 67. However, a wide range of reactions can consume a proportion of these phases and reduce the duration of the various pH buffers. Consequently, such reactions affect pH-buffering performance and potentially the performance of the near-field chemical barrier to radionuclide migration. The pH-buffering phases may react with chemical components of the groundwater, the waste or the encapsulant materials, or may dissolve slowly into the groundwater.

11.4.1 Backfill reactions with groundwater

Backfill reactions with the groundwater are discussed in section 9. These reactions and dissolution of the backfill are expected to occur rapidly in comparison with the rate of groundwater flow. Consequently, the extent of these reactions is proportional to, and limited by, the groundwater flow rate. In addition, the various reactions are dependent on the concentrations of the major elements in the groundwater. In general, low salinity groundwaters lead to more rapid dissolution and leaching, whereas higher salinity waters lead a variety of Ca(OH)₂-consuming reactions. For example, the importance of carbonate in reducing the period of high-pH buffering has been demonstrated in BFS/OPC and SRPC leaching experiments in a clay groundwater [223]. A summary of these reactions and their expected effects on the pH buffering is given in Table 25.

11.4.2 Backfill reactions with encapsulants

For cementitious grouts with lower calcium contents, the pozzolanic reaction may potentially consume the calcium hydroxide component of the backfill, as discussed in sub-section 10.2.1. This reaction would reduce the period of buffering at around pH 12.5, in Stage 2. However, the additional C-S-H formed may increase the period of the longer-term pH buffer in Stage 3b.

Reaction of the backfill with polymer encapsulants is discussed in sub-section 10.2.3. Such reactions may potentially reduce both the pH buffering at around pH 12.5 and the longer-term pH buffering.

11.4.3 Backfill reactions with waste components

The reactions of backfill with waste components are many and varied, owing to the diverse range of ILW. The major groups of these detrimental reactions are discussed in sub-section 10.4 and summarised in Table 23. In each case, the detrimental reactions with waste components are expected to shorten the periods of pH buffering by calcium hydroxide or the longer-term pH buffer depending on the timescale of the reactions involved.
Reaction of the waste components is expected to result in a loss of backfill available for pH buffering, whether the reactions consume hydroxide ions or calcium ions. In the case of reaction with hydroxide ions, the loss of pH buffering is clear. Reactions that consume calcium ions, whether directly from the backfill or from the porewater, will result in an increased dissolution of the calcium hydroxide component of the backfill. Over time, the dissolved hydroxide ions will be flushed from the vaults (or undergo further reaction), reducing the backfill’s pH-buffering capacity.

Table 25  Summary of effects of major groundwater components on pH-buffering performance (based on information in reference 219)

<table>
<thead>
<tr>
<th>Component</th>
<th>Reaction</th>
<th>Effect on pH buffer duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bicarbonate ions</td>
<td>Rate of conversion of calcium hydroxide to calcite increases with bicarbonate concentration</td>
<td>Reduces the period of both the Ca(OH)₂ and long-term pH buffers</td>
</tr>
<tr>
<td>Magnesium ions</td>
<td>Rate of precipitation of magnesium hydroxide (and associated consumption of calcium hydroxide) increases with magnesium concentration</td>
<td>Reducing the period of the Ca(OH)₂ buffer Increased amount of precipitation of magnesium hydroxide causes an increase in the long-term pH buffer</td>
</tr>
<tr>
<td>Calcium ions</td>
<td>pH buffering by calcium hydroxide is reduced with increasing calcium ion concentration (weak effect)</td>
<td>Slightly increases the period of Ca(OH)₂ buffering</td>
</tr>
<tr>
<td>Calcium and silicate ions</td>
<td>The dissolution rate of C-S-H phases increases with decreasing calcium and silicon concentrations</td>
<td>Reducing the period of longer-term pH buffering</td>
</tr>
<tr>
<td>Sulphate ions</td>
<td>Incorporation into ettringite and monosulphate</td>
<td>Reduces the period of the Ca(OH)₂ buffer Likely to contribute to longer-term buffering</td>
</tr>
<tr>
<td>Chloride ions</td>
<td>Possible incorporation into Friedel’s salt</td>
<td>Reduces the period of the Ca(OH)₂ buffer due to Ca(OH)₂ consumption in forming Friedel’s salt However, it is likely to contribute to the longer-term buffering at lower pH; like many secondary phases formed in cement mineral assemblages, Friedel’s salt is unstable at lower pH values and its onward reaction is expected to contribute to pH buffering</td>
</tr>
<tr>
<td>Salinity</td>
<td>Higher salinities result in a small increase the rate of dissolution of the main pH-buffering solid phases owing to their increased solubility at higher ionic strengths</td>
<td>Small reduction in the periods of both the Ca(OH)₂ and long-term pH buffers, but is a relatively weak effect compared with the others listed above</td>
</tr>
<tr>
<td>Various</td>
<td>Processes that lead to shorter periods of Ca(OH)₂ buffering reduce the precipitation of magnesium hydroxide</td>
<td>Tends to shorten the period of longer-term pH buffering</td>
</tr>
</tbody>
</table>

Note: the period of Ca(OH)₂ buffering extends to the end of Stage 2, and the longer-term buffer persists to the end of Stage 3b as indicated in Figure 67.
11.5 Modelling

Reactive transport modelling has been applied to the evolution of pH in two main areas associated with disposal concepts that apply a cementitious backfill. This work has involved the development and application of:

- research tools for investigating the detailed spatial and temporal variation in pH as the groundwater reacts with the backfill and waste-forms; and
- simplified models for investigating the backfill requirement for meeting specified pH-buffering criteria, taking into account the detrimental reactions described above.

11.5.1 Detailed pH evolution modelling

Early models of the evolution of pH of the near-field porewater [343, 350] used a ‘one box’ model to represent a cementitious vault. For example CHEQCONC (a version of the chemical transport program CHEQMATE [351] with an in-built cement model) was applied to model the interaction of a specified groundwater as it flowed through a vault. This approach implicitly treated the vault as a chemically homogeneous region, taking no account of variations across the region. However, the method allowed the main stages of the pH evolution to be identified and their duration to be estimated. In another study a one-dimensional model was applied, with the vault represented as a small number of cells [275]. The resulting predictions of near-field pH evolution are difficult to validate because of the extremely long timescales involved. However, accelerated leach tests have been performed on cementitious materials, in which they are equilibrated with groundwater before the aqueous phase is removed and replaced with fresh groundwater. Simulation of such tests on SRPC and BFS/OPC leaching into a synthetic groundwater based on a composition found in an Oxford clay [351] gave reasonable agreement for the period of pH 12.5 buffering. However, agreement was not so good once the pH started to fall or for experiments using PFA/OPC. Similarly, in the simulation of leaching experiments performed on NRVB with a simulated groundwater [232], the observed fall in pH occurred at a smaller degree of leaching than was predicted, possibly due to carbonation effects or omission of important backfill-groundwater interactions in the model.

More recently, two and three-dimensional reactive transport programs (such as PHAST [352] and TOUGHREACT [353]) have been applied in developing more detailed modelling studies. These studies have investigated the detailed mineralogical changes associated with the pH evolution. For example, Small et al. [276]) demonstrate the potential for using PHAST for two-dimensional calculations of reactive flow through vaults and around waste packages. This approach has been extended by Baston et al. [277] using TOUGHREACT. Each of these approaches applied a solid solution model to represent the calcium silicate hydrate phases and investigated the evolving chemistry and flow in and around the waste packages in the vaults. The TOUGHREACT model allowed the evolving porosity of the backfill and waste-forms to feed back into groundwater flow parameters. This feature allowed the prediction to be made that the pozzolanic reaction between the backfill and encapsulation grouts would seal the regions around the associated waste packages once their containers had degraded. Similarly, mineral precipitation at the upstream end of the vault was predicted either to reduce the groundwater flow significantly, or to seal the NRVB, preventing further groundwater ingress depending on the groundwater composition. An example of the output from such modelling, for the pH evolution and porosity changes over a 50,000 year period, is given in Figure 69.
Figure 69  Illustrative modelling results (from reference 277) for the evolution of near-field pH and porosity over a 50,000 year period resulting from groundwater flow (with the composition of Sellafield RCF3 DET5 groundwater) around a wasteform (i.e. with no metal container) conditioned with 3:1 BFS/OPC grout; the flow corresponds to a specific discharge of $9 \times 10^{-11}$ m s$^{-1}$ (based on values used in Nirex 97 [347])

11.5.2 Backfill requirement models

Simplified models for pH evolution have been developed for the assessment of the amount of backfill required to meet specified pH-buffering performance criteria. In the UK, these models have been developed as spreadsheet tools that include the following features:

- detrimental reactions with waste components and encapsulants are pessimistically assumed to go rapidly to completion, reducing the amount of calcium hydroxide in the backfill subsequently available for porewater conditioning;
a groundwater model is applied to predict the duration of the calcium hydroxide and long-term pH buffers, taking into account time-dependent detrimental reactions with groundwater components;

an iterative approach is applied to include detrimental reactions that involve both waste and groundwater components, such as ettringite formation.

The groundwater model has been developed from fitting the results of a series of reactive transport simulations with varying initial calcium contents in the backfill. Such models have been developed for four alternative groundwater compositions, covering a range of ionic strengths, and clay and hard rock mineralogies.

The initial spreadsheet model for pH-buffering performance was developed for vault and disposal facility scale calculations [343] and included only the detrimental reactions with major waste components and with encapsulation grouts. Subsequently the model was extended to consider the effect of polymeric encapsulants [354]. The approach has also been extended to allow calculations performed at the package scale, providing a tool for the assessment of the post-closure performance of specific waste packages [219]. This model allows the inclusion of the wide range of detrimental reactions shown in Table 23 (section 10). The pH calculation results are compared with those performed on the vault-scale to help highlight wastes that may cause pH-buffering performance issues.

For specific waste encapsulation concepts, simple ‘one box’ reactive transport models can give a good indication of the effects of varying options. Figure 70 shows the results of the pH evolution calculation for encapsulating some major waste-streams in magnesium phosphate [355].

Figure 70 Example of reactive transport modelling results for the prediction of near-field pH (effect of magnesium phosphate encapsulant) [355]
11.6 Key points

- Cementitious backfill materials have been selected in a number of disposal concepts for LLW and ILW, because (among other reasons) the resulting alkaline low-carbonate porewaters impose low solubility limits on some important radionuclides.

- Cementitious backfills provide controls on the main aspects of near-field chemistry, such as pH, that are generally well understood.

- In the UK cementitious concept for ILW, a backfill performance criterion corresponding to maintaining pH 9 or above for one million years has been specified.

- A large range of potentially detrimental reactions of the backfill with waste and groundwater components is likely; spreadsheet tools have been developed to assess their impact on pH-buffering performance both for individual packages (considering all components) and at the vault scale (considering major waste and wasteform components).

- Applications of reactive transport programs have demonstrated a methodology for prediction of the spatial and temporal pH evolution in cementitious vaults, and the associated mineralogical changes.
12 Sorption properties of cement backfills

12.1 Introduction

A cement-based backfill acts as a chemical barrier to the migration of radionuclides by maintaining a high pH, thus lowering the solubility of a number of key radioelements and also by providing an excellent sorbing substrate for most radioelements, thereby retarding their migration from the near field. The high-pH conditions may also retard the migration of key chemotoxic species by similar mechanisms.

'Sorption' is a generic term that covers the processes of absorption, physical adsorption and chemical adsorption. Sorption mechanisms depend on the chemical speciation of the sorbing species, and the chemical and physical properties of the sorbent. The most important reactions of cement with radionuclides are those that lead to binding, i.e. a chemical interaction [356]. The term 'sorption' however generally excludes precipitation of a solid phase where the solution species exceeds its solubility limit. This topic is discussed further in the next sub-section.

In the UK, considerable work on sorption has been undertaken with radionuclides, firstly with 'conventional' cement formulations such as SRPC and BFS/OPC [357-360] before work was concentrated more on NRVB [361, 362]. The effects on sorption of alkaline degradation products of organic materials, especially cellulose, has also received much attention [363]. Extensive modelling studies have been undertaken looking at both perturbed and unperturbed conditions (e.g. [364]). Chemotoxic species such as beryllium, cadmium and chromium have received much less attention.

Most countries with nuclear power programmes have contributed data on sorption onto cements. Researchers in Switzerland have covered a great deal of this subject in depth, including the behaviour of cellulosic degradation products [365]. In addition, much attention has been focussed on sorption mechanisms (e.g. [366]). High quality data, suitable for use in performance assessments, have also come from French laboratories [367]. Countries such as Sweden and Japan have also made significant contributions (e.g. [368, 369]).

Cementitious materials are complex mixtures of hydrated minerals, and the properties of such materials will evolve over time. The near-field porewater chemistry affecting radioelement solubility and sorption, and the facility for cements to sorb radioelements, will change over time. In Belgium, ONDRAF/NIRAS recently commissioned two reviews of data for radionuclide sorption onto cementitious materials [339, 370] involving several internationally recognised experts. In these reviews, cement ageing was an important aspect, with sorption data being split into four states where the pH was controlled firstly by the dissolution of alkali metal hydroxides (pH 13.5), then by calcium hydroxide (pH 12.5), followed by C-S-H-gel phases (pH 12.5 – pH 10) and finally calcite / groundwater pH (see sub-section 12.5).

Most experimental data have been obtained using the batch sorption technique with crushed cement samples [339]. Data are normally reported in the form of $R_d$ values, proportional to the ratio of amount sorbed on the solid phase to the amount remaining in solution. Relying on batch sorption data implies these data are representative of radioelement sorption onto intact cement samples. The limited experimental evidence [371, 372] that is available suggests this may be true for some radioelements, and some cement types. However, even where differences have been observed [372] they appear to be no greater than approximately an order of magnitude.

12.2 Sorption mechanisms

The removal of dissolved chemical species from a solution requires interaction with solid phases. Two broad process types can be distinguished: precipitation (including substitution in existing solids) and sorption. Precipitation requires the formation of new solids, into which chemical species removed from solution are transferred. Changes in solute concentrations due to
Precipitation depend on the amount of precipitated solid. Precipitation occurs when the concentration of solute species rises above its solubility limit. Sorption processes, by contrast, do not involve the formation of new solids; the species removed from solution are taken up on existing mineral surfaces, so that changes in solute concentrations are proportional to the exposed surface area of the mineral [373].

The concepts of sorption and precipitation are usually differentiated. Sorption experiments are usually designed to avoid conditions under which the sorbing element will precipitate. However, despite such attempts, it is possible that coprecipitation or uptake into existing solid phases will occur, particularly in complex systems. Therefore, care is therefore, required in inferring sorption mechanisms from simple batch sorption data. Evidence from spectroscopic studies of the structure of sorbed species can help, however, in demonstrating the sorption/uptake mechanism (e.g. [374]).

A typical summary of the definition of sorption and other uptake mechanisms is shown in Table 26. Co-precipitation is a special case of precipitation. It occurs whenever foreign solutes are trapped in the body of a precipitating solid of stoichiometric composition.

Precipitation, where the radionuclide species is above its solubility limit, is considered a retardation mechanism but, as mentioned above, it is not normally regarded as sorption [339, 373]. Furthermore, sorption values traditionally used by performance assessments refer strictly to sorption processes that are linear, reversible, and obtained under equilibrium conditions. A detailed literature review of retardation mechanism studies has been published recently [356]. The author summarised his findings from the literature in Table 27. The table includes all retardation mechanisms and not just those regarded as purely sorption. The table includes a number of key chemotoxic elements (e.g. cadmium, chromium and mercury) as well as radioelements.

<table>
<thead>
<tr>
<th>Retention Type</th>
<th>Mechanisms</th>
<th>Description</th>
</tr>
</thead>
</table>
| **Sorption**                                        | Specific adsorption or chemisorption | The uptake of dissolved species on a mineral surface through specific chemical interactions between sorbate and sorbent surface groups and or formation of covalent bonds.  
*(For charged species an electrostatic component to the interaction with the surface will also contribute to the interaction.)* |
|                                                     | Ion exchange                        | The uptake of ions on a mineral surface with the simultaneous displacement of previously adsorbed ions.  
*(Primarily by electrostatic interaction but with no net change in charge.)* |
|                                                     | Physical adsorption                 | The uptake of molecules to a mineral surface through Van der Waals forces.  
*(Rather weak in this context.)* |
| **Co-precipitation and uptake into existing phases** | Isomorphous replacement (solid solution) | The incorporation of foreign ions in crystal lattice sites usually occupied by a major ion of the solid. |
|                                                     | Incorporation in crystal defects     | Incorporation of foreign ions, atoms or molecules outside the crystal lattice positions (e.g. in vacancies or dislocations). For an amorphous compound, any incorporation at atomic scale. |
|                                                     | Non-uniform incorporation            | The trapping of discrete particles (e.g. colloids) in a growing solid. |
Table 27  Summary of binding mechanisms (from reference 356)

<table>
<thead>
<tr>
<th>Species</th>
<th>Solid Studied</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1</td>
<td>C-S-H</td>
<td>Electrostatic sorption</td>
</tr>
<tr>
<td>Group 1</td>
<td>C-S-H</td>
<td>Electrostatic sorption to silanol</td>
</tr>
<tr>
<td>Al</td>
<td>C-SH</td>
<td>Substitution for Si</td>
</tr>
<tr>
<td>Am</td>
<td>Concrete</td>
<td>Mineralogical control</td>
</tr>
<tr>
<td>Am</td>
<td>Concrete</td>
<td>Surface area control</td>
</tr>
<tr>
<td>Am</td>
<td>OPC</td>
<td>Via hydroxide species</td>
</tr>
<tr>
<td>As</td>
<td>OPC</td>
<td>Sorption onto C-S-H</td>
</tr>
<tr>
<td>As</td>
<td>OPC</td>
<td>SO$_4^{2-}$ substitution in ettringite</td>
</tr>
<tr>
<td>As</td>
<td>OPC</td>
<td>Ca-As compound formation</td>
</tr>
<tr>
<td>Ba</td>
<td>C-S-H</td>
<td>Substitution for Ca</td>
</tr>
<tr>
<td>C (org)</td>
<td>Mortar</td>
<td>Electrostatic sorption</td>
</tr>
<tr>
<td>Cd</td>
<td>C-S-H</td>
<td>Immobilisation within C-S-H structure</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>HCP</td>
<td>Formation of CaO-CaCl$_2$-H$_2$O</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>Concrete</td>
<td>Chemisorbed layer on the surface of C-S-H</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>C-S-H</td>
<td>Chemisorbed on hydrated C$_3$S surface</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>(Synthetic) C-S-H</td>
<td>Friedel's salt formation</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>C-S-H</td>
<td>Incorporation in C-S-H</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>HCP</td>
<td>Precipitation</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>Cement</td>
<td>Adsorption on colloids</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>HCP</td>
<td>Electrostatic adsorption onto a positive site</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>Hydrogarnet</td>
<td>Incorporation by hydrogarnet</td>
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<td>Cr(III)</td>
<td>C-S-H</td>
<td>Si substitution in C-S-H</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>C-S-H</td>
<td>Al substitution in Ca aluminate hydrate</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Aluminate</td>
<td>Ion-exchange with OH$^-$</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>OPC</td>
<td>SO$_4^{2-}$ substitution in ettringite</td>
</tr>
<tr>
<td>Cs</td>
<td>C-S-H aluminate</td>
<td>-</td>
</tr>
<tr>
<td>Cs</td>
<td>C-S-H</td>
<td>Electrostatic sorption</td>
</tr>
<tr>
<td>Cs</td>
<td>C-S-H</td>
<td>-</td>
</tr>
<tr>
<td>Cs</td>
<td>C-S-H</td>
<td>Breakage of silicate chain</td>
</tr>
<tr>
<td>Cs</td>
<td>Cement</td>
<td>Inside agglomerated silica particles</td>
</tr>
<tr>
<td>Cu</td>
<td>CCF</td>
<td>Precipitation</td>
</tr>
<tr>
<td>Eu</td>
<td>C-S-H</td>
<td>Adsorption</td>
</tr>
<tr>
<td>Eu</td>
<td>C-S-H</td>
<td>Surface complexation or precipitation</td>
</tr>
<tr>
<td>Hg</td>
<td>Ettringite</td>
<td>-</td>
</tr>
<tr>
<td>I$^-$</td>
<td>Alumina cement</td>
<td>Replacement of OH$^-$</td>
</tr>
<tr>
<td>I$^-$</td>
<td>C-S-H</td>
<td>Electrostatic sorption</td>
</tr>
<tr>
<td>I$^-$</td>
<td>OPC</td>
<td>Electrostatic sorption</td>
</tr>
<tr>
<td>I$^-$</td>
<td>OPC</td>
<td>Incorporation</td>
</tr>
<tr>
<td>Mo(VI)</td>
<td>HCP</td>
<td>CaMoO$_4$ and Mo-substituted AF$_m$ phase</td>
</tr>
</tbody>
</table>
Table 27 (continued) Summary of binding mechanisms (from reference 356)

<table>
<thead>
<tr>
<th>Na</th>
<th>C-S-H</th>
<th>Substitution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>C-S-H</td>
<td>Ion exchange</td>
</tr>
<tr>
<td>Ni</td>
<td>C-S-H</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>C-S-H</td>
<td>Co-precipitation or surface complexation</td>
</tr>
<tr>
<td>Ni</td>
<td>HCP</td>
<td>Co-precipitation or surface complexation</td>
</tr>
<tr>
<td>Ni</td>
<td>HCP</td>
<td>Formation of LDH</td>
</tr>
<tr>
<td>Np</td>
<td>OPC</td>
<td>Sorption followed by reduction</td>
</tr>
<tr>
<td>Pb</td>
<td>C-S-H</td>
<td>Linked to silica tetrahedra in ferrite</td>
</tr>
<tr>
<td>Pb</td>
<td>C-S-H</td>
<td>Formation of Si-O-Pb bonds</td>
</tr>
<tr>
<td>Pb</td>
<td>CCF</td>
<td>Precipitation</td>
</tr>
<tr>
<td>Pb</td>
<td>OPC</td>
<td>Precipitation</td>
</tr>
<tr>
<td>Pb</td>
<td>C-S-H</td>
<td>Sorption of Pb(OH)$_3^-$</td>
</tr>
<tr>
<td>Pb</td>
<td>CCF</td>
<td>Substitution for Ca</td>
</tr>
<tr>
<td>Pu</td>
<td>Concrete</td>
<td>Preferential on cement paste over aggregates</td>
</tr>
<tr>
<td>SeO$_4^{2-}$</td>
<td>Ettringite</td>
<td>Formation of CaSeO$_3$</td>
</tr>
<tr>
<td>SeO$_3^{2-}$</td>
<td>Ettringite</td>
<td>Electrostatic sorption</td>
</tr>
<tr>
<td>SeO$_4^{2-}$</td>
<td>Ettringite</td>
<td>Substitution for SO$_4^{2-}$ in ettringite and monosulphate</td>
</tr>
<tr>
<td>Sn</td>
<td>C-S-H</td>
<td>Ca-stannate formation sorption at lower concentrations</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>C-S-H</td>
<td>Surface sorption</td>
</tr>
<tr>
<td>Sr</td>
<td>C$_3$AH$_6$</td>
<td>Substitution for Ca</td>
</tr>
<tr>
<td>U(VI)</td>
<td>OPC</td>
<td>Formation of solubility-limiting phases with Ca and Si</td>
</tr>
<tr>
<td>U(VI)</td>
<td>OPC</td>
<td>Inner sphere interactions</td>
</tr>
<tr>
<td>U(VI)</td>
<td>OPC</td>
<td>Formation of oligomeric surface complexes or precipitates</td>
</tr>
<tr>
<td>U(VI)</td>
<td>HCP/C-S-H</td>
<td>Calcium uranate precipitate</td>
</tr>
<tr>
<td>U(VI)</td>
<td>C-S-H</td>
<td>Sorption</td>
</tr>
<tr>
<td>VO$_2^+$</td>
<td>OPC</td>
<td>SO$_4^{2-}$ substitution in ettringite</td>
</tr>
<tr>
<td>Zn</td>
<td>C-S-H</td>
<td>Linked to Si tetrahedra in C-S-H</td>
</tr>
<tr>
<td>Zn</td>
<td>CCF</td>
<td>Precipitation</td>
</tr>
<tr>
<td>Zn</td>
<td>Ferrite</td>
<td>Formation of Fe-O-Zn bonds in ferrite</td>
</tr>
<tr>
<td>Zn</td>
<td>C-S-H</td>
<td>Precipitation of zincate phases</td>
</tr>
</tbody>
</table>

Notes:
All mechanisms as reported or invoked by original authors. Where the entry is ‘-’, no mechanism was suggested by the original authors.

C-S-H = calcium silicate hydrate
OPC = Ordinary portland cement
HCP = Hardened cement paste
CCF = Crushed concrete fines
12.3 Sorbing minerals in cementitious materials

Solid phases in concrete normally comprise hydrated cement solids and calcite aggregates. The major cement solid phases are crystalline portlandite (Ca(OH)$_2$) and amorphous C-S-H. Minor phases include ettringite (aluminoferrite trisulphate, AFt), monosulphate (aluminoferrite monosulphate, AFm), hydrogarnet and hydrotalcite [339]. All these solids provide potential sorbing surfaces for dissolved radionuclides. C-S-H phases display sorption behaviour where both cations and anions can be sorbed, although the mechanism may not always be known. Anion immobilisation onto hydrotalcite, AFm, and AFt phases has been reported [375]. Calcite, initially present as aggregates and/or generated as a newly formed phase owing to cement carbonation, may also sorb radionuclides [376].

Different sorbing cement minerals have a characteristically high surface area. For example, in one study, hardened cement paste (HCP) had a surface area >50,000 m$^2$kg$^{-1}$, portlandite had a surface area of ~6,000 m$^2$kg$^{-1}$, while C-S-H phases are reported to have very high surface areas (e.g. 148,000 m$^2$kg$^{-1}$ [377]). Large surface area combined with high sorption capacity results in high surface densities of sorption sites. From a qualitative point of view, differences in sorption values for different cement or natural minerals such as calcite may be related to differences in surface area and nature (intrinsic charge) of the surface. From a more quantitative point of view, surface area information may also be used in calculating sorption values, for example by means of surface complexation models [378] or ion exchange models [379]. One detailed study [380] looked at the sorption of Th, U, Np, Pu and Am onto OPC and also the sorption of Th, U, Pu and Am onto C-S-H gels (Ca:Si = 1.65, 0.9 and 0.65), tobermorite, ettringite, monosulphate, hydrotalcite, portlandite and calcite at 'natural' pH values ranging from 12.7 for C-S-H (1.65) to 9.1 for hydrotalcite. In addition, sorption onto C-S-H gels (Ca:Si = 0.9 and 0.65), tobermorite, ettringite, monosulphate, hydrotalcite and calcite was studied at pH ~12.6. Sorption was generally strong except for U as U(VI) onto portlandite, and also ettringite, monosulphate and calcite at above pH 12.5.

12.3.1 Portlandite (Ca(OH)$_2$)

Portlandite is relatively rarely studied as a sorbing solid. The hydroxyl functional groups on the surface of portlandite have potential to bind strongly sorbing metal ions, or sorb anions such as the halides, chloride and iodide, through substitution with hydroxyl [381]. Binding of anions and oxyanions is presumably weak, although it has been reported that certain oxyanions (such as those of arsenic, chromium, molybdenum, antimony, selenium, vanadium and tungsten) may have some affinity to cement minerals [382].

12.3.2 C-S-H phases

C-S-H gel is nearly amorphous to X-ray diffraction and on that account, is often referred to as "cement gel". Despite its low crystallinity there is a microscale structural resemblance to two crystalline calcium silicate hydrates, tobermorite and jennite. The structures of both are known – and consist of corrugated sheets or layers of alternating (Ca-OH) and silicate units. In tobermorite the silicate sheets are incomplete and much of the silica is dimeric, whereas in jennite, the dimeric units are bridged by additional silicate tetrahedra forming pentameric or higher molecular weight units. From NMR studies, it appears that these polymer units are organised into platelets [339]. The individual platelets adhere strongly giving rise to a nanoporous bulk gel. The high surface area measured by gas sorption arises from the poor packing of platelet substructures. This nanoproperty-scape substructure is responsible for the low crystallinity reported by XRD. The low crystallinity and imperfect "structure" of C-S-H can be expected to give rise to a high density of sorption sites for both cations and anions [383]. The "structure" of C-S-H also makes it impossible to distinguish in any fundamental way between "surface" and "bulk" processes. The main feature, which seems to dominate C-S-H sorbent properties, is the presence of a relatively high volume fraction (several %) of nanopores. A recent spectroscopic study [374] has shown that europium is incorporated into the crystal structure of the crystalline C-S-H phases, tobermorite and xonolite.

C-S-H also exhibits a zeta potential which affects the electrostatic contribution to sorption by a surface complexation mechanism. When contacted with deionised water, the zeta potential is dependent on the C/S ratio: C-S-H with high C/S molar ratio has a positive charge and thus tends
to sorb anions. It has been demonstrated that C-S-H of high C/S ratio is a better scavenger for iodide than C-S-H of lower C/S ratio [384]. As the C/S ratio decreases as a result of cement degradation, the surface charge becomes less positive, passing through the point of zero charge at C/S of about 1.2, and turns negative at lower C/S ratio. Thus, in terms of electrostatic sorption, C-S-H with a low C/S ratio is a better sorbent for cationic species. When in contact with more complex groundwaters or high concentrations of dissolve alkali metals, the surface charge may be strongly affected by the sorption of groundwater ions, even leading to reversal of the sign of the electrostatic charge.

12.3.3 AFt phases e.g. ettringite

AFt is calcium aluminosulphate hydrate with some iron substituted for aluminium, with ettringite being the most important AFt phase. It has a very open structure and presents several possibilities for crystal chemical incorporation. Many contaminant ions may substitute for the essential ionic components of ettringite – calcium, aluminium, and sulphate. Sorption mechanisms on ettringite have been summarised [381]: divalent cations such as Sr$^{2+}$ and Ni$^{2+}$ may substitute for calcium; trivalent metal ions replace aluminium, and anions such as CO$_3^{2-}$, Cl$^-$ and IO$_3^-$ exchange with sulphates. Ettringite surfaces exhibit a net negative charge so incorporation of anions in the bulk is probably more important than surface adsorption [382]. Strontium has been found to be structurally incorporated into AFt [385].

12.3.4 AFm phases e.g. monosulphate

This phase forms in the presence of limited sulphate availability or at elevated temperature. Its structure is tolerant of substitution and can sorb many contaminants through ion substitution. AFm is known to sorb di- and trivalent heavy metal ions and diverse anions. The formation of solid-solution with AFm may cause a stronger sorption of oxyanions on AFm as compared to ettringite. AFm phases bind iodide better than AFt phase [374]). Based on anticipated chemically similar behaviour between Cl$^-$ and I$^-$, AFm phase should have the potential to sorb Cl$^-$ as shown by formation of Friedel’s salt (3CaO.Al$_2$O$_3$.CaCl$_2$.10H$_2$O), a chloride-containing AFm phase. Strontium has also been found to be structurally incorporated into AFm [385].

12.3.5 Hydrogarnet

Sorption may happen on hydrogarnet through ion substitution, e.g., Cr(III) may replace Al in hydrogarnet [386]. Strontium has also been found to be structurally incorporated into hydrogarnet [385].

12.3.6 Hydrotalcite

Hydrotalcite has a layer structure and can incorporate many di- and trivalent cations, e.g., Ni$^{2+}$, and Co$^{2+}$ in place of Mg$^{2+}$, Cr$^{3+}$ in place of Al$^{3+}$, etc. Anions such as CO$_3^{2-}$, Cl$^-$, and NO$_3^-$ may also substitute for OH$^-$ and SO$_4^{2-}$ [339]. Sorption of lead onto hydrotalcite has been studied although sorption was dominated by C-S-H gel phases [387].

12.3.7 Calcite

Calcite will be present as aggregate and newly generated by cement carbonation. Calcite is highly crystalline and has a much smaller reactive surface area and much simpler structure than the sorbing cement materials. It therefore exhibits lower sorption potential than most other cement phases. Distribution ratios for sorption of 24 elements onto carbonate minerals including calcite have been reviewed recently [388].

12.4 Thermodynamic chemical modelling

Modelling of sorption processes in cementitious systems is useful because:

- it helps to demonstrate an understanding of the important processes and mechanisms that lead to retardation of radionuclides in the near field;
• it can facilitate the prediction, or support the estimation, of sorption values in cases where data are missing, providing the sorption mechanism is understood (this may include values for radionuclides, evolved cementitious materials or chemical conditions that have not been studied experimentally).

Such a mechanistic understanding of the sorption processes can be used to support the derivation of sorption data for studying the performance of a GDF. However, cementitious systems are complex and deriving detailed mechanistic sorption models is far from straightforward. Some of the main issues involved are:

• understanding which cementitious solid phases are the major phases responsible for radionuclide sorption or uptake;
• understanding how the cementitious phases and their surfaces interact with one another;
• identifying the key sorption or uptake mechanisms;
• ensuring that experimental data are taken from systems that have reached equilibrium (or at least a steady state in which the evolution of the solid phases is minimal), if thermodynamic modelling tools are to be applied.

Modelling tools in standard geochemical modelling programs such as PHREEQC [389] are available to implement each of the major sorption and uptake mechanisms identified. These are summarised below.

<table>
<thead>
<tr>
<th>Radionuclide fate</th>
<th>Mechanism</th>
<th>Process modelled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uptake or co-precipitation as major component of new phase or surface phase</td>
<td>Single phase solubility</td>
<td>Equilibration of mineral phase containing radionuclide with aqueous radionuclide species</td>
</tr>
<tr>
<td>Co-precipitation (as minor component) in new phase or substitution into existing cementitious phase</td>
<td>Solid solution Solubility</td>
<td>Equilibration of solid solution containing radionuclide with aqueous radionuclide species</td>
</tr>
<tr>
<td>Ion exchange of radionuclide ions with simple ions present in cementitious phase</td>
<td>Ion exchange</td>
<td>Ion exchange formulations (e.g. Gaines Thomas) allowing equilibration with aqueous radionuclide species with no build up of interlayer or surface charge</td>
</tr>
<tr>
<td>Sorption onto surface sites by specific chemical interaction</td>
<td>Surface complexation</td>
<td>Equilibration of surface complexes containing radionuclide with aqueous radionuclide species. Electrostatic models include a non-specific electrostatic interaction between sorbed ions and charged surfaces</td>
</tr>
</tbody>
</table>

Early modelling work under the Nirex/NDA research programme assumed that C-S-H phases provided the main sorbing surfaces and that these would be conditioned by equilibration with excess portlandite [390]. A surface complexation model was applied to fit zeta potential data and caesium and iodide sorption onto C-S-H phases of varying C/S ratio. More recently a similar surface complexation approach has been applied to fit zeta potential data for hydrated cement pastes as a function of C/S ratio [391]. Surface complexation models have also been applied to fit sorption isotherm data for ISA on NRVB [364] and hardened cement paste [392], and for carbon-14 (as carbonate) onto OPC cement pastes [393]. Ion exchange models have been applied to the uptake of strontium [394], and sodium [230] ions onto C-S-H phases, and for radium uptake by C-S-H phases and hardened cement pastes [377].
Data from a detailed experimental study of actinide sorption onto single cementitious mineral phases were tested against surface complexation and surface precipitation models [390]. However, the method to identify the major mechanism was based purely on fitting batch sorption data. More recently, identification of sorption mechanisms has been studied in some detail, particularly under the Swiss research programme. This includes application of spectroscopic techniques to identify the environment of the immobilised radionuclide, such as for Nd(III) uptake by amorphous calcium silicate hydrates [366], for selenium [395], cobalt [396] and curium [397] uptake by hardened cement pastes, and for nickel in cement systems [398]. In the latter case, evidence was presented that a solid-solution aqueous-solution system involving nickel may account for the behaviour of nickel in cement systems. In some cases the data have been interpreted using modelling techniques. This includes modelling the uptake of zinc onto C-S-H phases [273] and lanthanides onto calcite, each by a solid solution mechanism [399].

Where a sorption model has been developed, thermodynamic modelling is particularly useful for explaining or predicting the effects of perturbations to the system such as the presence of organic complexants. Such modelling applications have included the effect of organic ligands on the uptake of anionic radionuclides onto degraded cement pastes [400], the effect of gluco-isosaccharinate on caesium, nickel, promethium, and thorium sorption on cement [368].

### 12.5 Effects of ageing on sorption properties

As mentioned earlier, in the reviews carried out for ONDRAF/NIRAS [339, 370], cement ageing was an important aspect, with sorption data being split into four states. It should be mentioned however that timescales of evolution may be very different dependent on groundwater/ surface water flow rate and composition.

Four states of cement and concrete degradation are considered in reference 339, corresponding to the four stages of pH evolution discussed in sub-section 11.3.3.

**State I:** pH > 12.5. The pH is controlled by the dissolution of Na₂O and K₂O. Even though the duration of this state is relatively short, the very alkaline conditions typical of this state might affect the sorption of certain radionuclides such as caesium and strontium.

**State II:** pH ~12.5. The pH is controlled mainly by the dissolution of portlandite (Ca(OH)₂). The main phases present, portlandite and C-S-H gel phases, are strongly sorbing. However, the high solution concentration of calcium can compete with the sorption of cations such as strontium and radium.

**State III:** pH falling from 12.5 to ~9.8. This state is the most complex. The pH and concentrations of cement component elements in solution (except Na and K) are controlled by a sequence of dissolution and precipitation reactions of the C-S-H, AFm and AFt phases. This state ends when these phases are no longer present, i.e. after depletion of the last phase characteristic for cement, the tobermorite-like end member of the C-S-H phases. After this, sulphate and silicon concentrations are no longer controlled by the cement minerals, but by the infiltrating water. The C-S-H phases are strongly sorbing.

**State IV:** pH < 9. The pH is now determined by the groundwater and remaining phases such as calcite. Calcite is generally weakly sorbing as it is often relatively crystalline with a small surface area.

Which state is the strongest sorbing does vary from radionuclide to radionuclide, but generally State IV is the weakest sorbing of the four states.

During this ONDRAF/NIRAS study, there was an exhaustive literature search followed by evaluation of the data and a series of expert panel meetings. Best estimate $R_d$ values were drawn up along with recommended upper and lower limits. The best estimate values fell in the order shown in Table 29. It was noted that there were few data for some states; shown by values in parentheses or omitted if they were not selected by the panel.
Table 29  Order of best estimates for strength of sorption for each radioelement onto cements at different stages of degradation (States I to IV) [339, 370]

<table>
<thead>
<tr>
<th>Radioelement</th>
<th>Strength of sorption for each cement degradation state (best estimates)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am</td>
<td>I = II = III = IV</td>
</tr>
<tr>
<td>Ca</td>
<td>IV &gt; III &gt; I &gt; II</td>
</tr>
<tr>
<td>C (inorg)</td>
<td>II &gt; I = III</td>
</tr>
<tr>
<td>Cs</td>
<td>III &gt; II &gt; I</td>
</tr>
<tr>
<td>Cl</td>
<td>II &gt; I = III &gt; (IV)</td>
</tr>
<tr>
<td>H</td>
<td>I = II = III = IV (= 0)</td>
</tr>
<tr>
<td>I</td>
<td>II &gt; I = III &gt; (IV)</td>
</tr>
<tr>
<td>Mo (ettringite present)</td>
<td>I = II = III &gt; IV</td>
</tr>
<tr>
<td>Mo (ettringite absent)</td>
<td>I = II &gt; III = IV</td>
</tr>
<tr>
<td>Np(IV)</td>
<td>I = II = III &gt; IV</td>
</tr>
<tr>
<td>Ni</td>
<td>II = III &gt; I &gt; (IV)</td>
</tr>
<tr>
<td>Nb</td>
<td>I = II = III &gt; (IV)</td>
</tr>
<tr>
<td>Pb</td>
<td>III &gt; II &gt; IV &gt; I</td>
</tr>
<tr>
<td>Pu</td>
<td>II = III &gt; I &gt; IV</td>
</tr>
<tr>
<td>Pa</td>
<td>I = II = III &gt; IV</td>
</tr>
<tr>
<td>Ra</td>
<td>III &gt; I &gt; II &gt; (IV)</td>
</tr>
<tr>
<td>Se(IV)</td>
<td>I = II = III &gt; IV</td>
</tr>
<tr>
<td>Se(VI) (ettringite present)</td>
<td>I = II = III &gt; IV</td>
</tr>
<tr>
<td>Se(VI) (ettringite absent)</td>
<td>I = II &gt; III = IV</td>
</tr>
<tr>
<td>Sn</td>
<td>I = II</td>
</tr>
<tr>
<td>Sr</td>
<td>I = III &gt; II &gt; IV</td>
</tr>
<tr>
<td>Tc(IV)</td>
<td>I = II = III</td>
</tr>
<tr>
<td>Tc(VII)</td>
<td>I = II = III = IV</td>
</tr>
<tr>
<td>Th</td>
<td>I = II = III = IV</td>
</tr>
<tr>
<td>U(IV)</td>
<td>I = II = III = IV</td>
</tr>
<tr>
<td>U(VI)</td>
<td>II = III &gt; I &gt; IV</td>
</tr>
<tr>
<td>Zr</td>
<td>III &gt; II</td>
</tr>
</tbody>
</table>

Studies were undertaken to measure the sorption of neptunium, zirconium, tin and uranium(VI) onto leached and hydrothermally aged samples of NRVB [401, 402]. Sorption experiments were carried out on three types of simulated 'aged' backfill and on untreated NRVB for comparison. The three treatments used to simulate the effects of backfill ageing were: progressive leaching over 541 and 1272 days, and progressive leaching over 536 days followed by hydrothermal treatment at 80°C for a further 1183 days. The total calcium lost was measured from the leached samples and amounted to 9-10% of the mass of NRVB. The final C/S ratio was not measured. These ageing treatments have been shown previously to alter the mineralogy of the NRVB, primarily by the removal of portlandite. However, this study found that these alterations had very little effect on sorption capacity of the NRVB for neptunium(IV), zirconium and tin. Sorption of these three radionuclides onto the unaged and aged NRVB was found to be strong in all cases. The most likely explanation for these findings is that even after the 'ageing' treatments, C-S-H gel constitutes a large fraction of the NRVB mineralogy and it is C-S-H gel that provides the bulk of the sorption capacity. In the first study [402], the mineralogy was investigated and some alteration of the mineralogy in the aged cements was seen, the absence of portlandite being the most significant and X-ray diffraction identified some Ca-Al-Si, Ca-Al and Ca-Si minerals formed. Analysis by
electron microscopy showed ageing to have given rise to some crystallisation in all samples, but significant quantities of amorphous material were also present in all samples. The study suggested that the alteration of NRVB caused by such leaching with or without later hydrothermal ageing would have only a small, if any, effect on the sorption properties.

In earlier work for Nirex [403], the sorption properties of cementitious materials typical of those that might be present in a GDF were studied. The aim was to identify the hydrate phases in these materials after curing at different temperatures relevant to their ageing in a GDF, to synthesise these phases and then use sorption tests to identify which phases were responsible for sorption of the different radionuclides. A comparison between the sorption properties of real cement blends and pure synthetic hydrate phases for caesium, plutonium, chlorine, iodine and nickel isotopes was made using the batch sorption technique. Six cement blends representing encapsulating matrices for intermediate-level waste and possible backfill grouts including NRVB were investigated. These blends were characterised to identify qualitatively and where possible quantitatively, the hydrated phases present. Phase-pure samples of the hydration products identified were then synthesised and batch sorption tests carried out using the same five elements. Comparison of the sorption properties of the cements, and of their individual hydrate phases, identified which phases were largely responsible for sorption in the cements. The conclusions reflected the importance of calcium silicate hydrate gel (C-S-H gel), present in all cements, as the main sorbent. Amongst the radionuclides considered, sorption ranged from high (for plutonium and nickel) to low (for caesium and chloride). Unexpectedly, some iodide sorption was indicated in NRVB which contains C-S-H gel of high Ca:Si ratio. However, in most cases the variation in sorption coefficient of any particular element was relatively insensitive to the type of cement blend or to the particular C-S-H phase present.

NDA have however recognised that the bulk of sorption data are for fresh cements rather than aged or altered ones [10]: “However a limitation of the current dataset is that the majority of the measurements have been made onto freshly prepared cements. Data relevant to aged or leached material are more scarce.”

12.6 Effects of carbonation

Carbonate ions in groundwater flowing into a GDF [404] can react with calcium hydroxide to form calcium carbonate (CaCO₃) [12], as discussed in sub-section 9.2.3(c)). In addition, carbon dioxide generated through microbially mediated reactions will react with the cementitious materials present. This is a process (carbonation) that could affect the ability of cements to buffer the pH of the near-field porewater and to sorb radionuclides. Carbonation of cements can affect the sorption properties of the cements. The sorption properties of carbonated cements, essentially calcium carbonate, may differ significantly from uncarbonated cements where the important sorbing mineral phases are calcium hydroxide and C-S-H gels. There are very few reports on studies examining sorption onto carbonated cements [405, 406] but sorption has been shown to be lower than onto fresh cement [405]. There are also limited data concerning sorption onto calcium carbonate forms such as calcite e.g. [407, 408], and sorption is reported to be weak.

12.7 Effects of organic complexants on sorption to cements

12.7.1 Cellulosic materials

In terms of the impact on radioelement chemistry, the chemical degradation of cellulosic materials under alkaline anaerobic conditions is believed to be the most important source of organic complexants in the near field [63, 409]. Studies of the effect of the degradation of non-cellulosic polymers on radionuclide solubility under cementitious conditions have shown that any effect is generally small compared to that of cellulose [e.g. 410- 414]. An in-depth review of cellulose degradation has very recently been carried out [415]. This report reviewed the current understanding regarding alkaline cellulose degradation and the associated impacts of radiolytic and microbial processes. Conceptual and mathematical models developed to describe alkaline cellulose degradation were also outlined and discussed.
Data, largely from the Nirex programme, are available for the effect of the presence of cellulosic degradation products on the sorption onto cementitious materials of plutonium [410, 411, 416, 417] uranium [417], americium [411], nickel [418], zirconium [419, 420] and niobium [419, 360]. Much work has also been undertaken in Switzerland on this topic e.g. [365, 421, 422].

Sorption of cellulose degradation products themselves onto cement has also been observed to occur and has been measured in the case of ISA sorption to cementitious materials including NRVB (e.g. [423-425]).

12.7.2 Superplasticisers

As noted in sub-section 3.5.1, concrete admixtures or plasticisers are used for improving the workability of cement, to influence physical properties, such as compressive strength, durability or setting time, and to confer certain beneficial effects to the material. A particular concern with the use of superplasticisers in GDF applications is the potential of the superplasticiser itself, other chemical components of commercial products or their degradation products, to form chemical complexes with radionuclides and thereby both increase radionuclide effective solubilities in near-field porewater and reduce their tendency to sorb onto the backfill (e.g. [426, 427]). For this reason, the use of superplasticers was excluded from the specification for the NRVB (see sub-section 2.1.1). However, superplasticisers are important components of cement materials being developed for use in other EBS applications, and their potential impacts on post-closure performance and their acceptability for use in a GDF are being assessed.

Experimental studies have been undertaken on the UK [336, 428-430] Japanese [431], Swedish [432] and Swiss [426] programmes to investigate these potential impacts on the chemical/sorption barrier of the EBS and work in this area was reviewed by Posiva Oy in 2005 [56].

The effects of two Japanese superplasticisers: HS100, a mixed SNF/LS-based additive; and HS700, a PCE-based additive; on the solubility of technetium(IV), uranium(IV), plutonium12 and americium(III) were studied at pH 12 by Greenfield et al. [431]. The experiments found that both additives, when present in solution at concentrations typical of dose concentrations used in a cement mix, could enhance the solubility of radionuclides (by 4-5 orders of magnitude for plutonium and americium), compared to cement-equilibrated water. Dilution of the additives by a factor of 100 significantly reduced the effect, although radionuclide concentrations were still higher by 1 to 2 orders of magnitude than in the absence of additives. Similar effects on plutonium solubility at high additive concentrations in water at high pH were observed in studies of four candidate superplasticisers, both SNF and vinyl co-polymer-based, studied in the UK programme in the 1990s [428, 429] and more recently for the PCE-based ADVA Cast 551 [336].

However, it is recognised that such experiments with free additive solutions are not representative of the solutions in a cementitious porewater; in a hardened cement, the additive will be distributed between sorbed material, incorporated material and material in solution. Solutions prepared by short-term leaching of cement blocks containing superplasticisers were not found to enhance plutonium solubility [429]. Work is in progress in Japan to extract porewaters from hardened cement pastes containing a PCE-based superplasticiser, characterise their organic content [433] and to study the effects of such porewaters on radionuclide solubility, however, the latter studies have yet to be published.

The effect of a number of admixtures on the sorption properties of nickel, europium and thorium onto cements was investigated in a Swiss study [426]. Although some of the concrete admixtures investigated (including LS, SMF, SNF and PCE-based) were shown to be strong complexants, no adverse effect on the sorption of the radionuclides tested could be observed under realistic conditions. Strongly adverse effects on the sorption of the radionuclides tested were observed only in single cases, and under extreme conditions. However, in another study [432], the sorption of

12 The oxidation state of plutonium is less certain but was predicted to be Pu(IV) by thermodynamic modelling.
europium onto standard portland cement was found to be significantly reduced by the presence of cement additives, spent organic adsorbent resins and some organic cleaning agents.

12.7.3 Other organic materials

One study [434] investigated the potential impacts of picolinate, and the leachate from the alkaline, anaerobic degradation at 80°C of a strongly-basic anion-exchange resin on the sorption behaviour of nickel, plutonium and americium in the near field. Nickel sorption onto a C-S-H gel was reduced slightly. High sorption values suggested that the impacts of picolinate or the anion-exchange resin leachate on the sorption of plutonium or americium onto NRVB were unlikely to be important.

12.8 Effects of competing inorganic ions and complexants on sorption to cements

Inorganic complexants can have two separate effects on sorption processes:

- ionic strength effects – giving competition for sorption sites and also reducing electrostatic interactions (an example would be high chloride concentrations reducing iodide sorption);
- complexation of radionuclides in solution:
  - at the high pH values associated with high-calcium cements, the aqueous speciation of most elements is dominated by hydrolysis products, therefore most common groundwater ions have little effect on radionuclide sorption due to complexation in solution;
  - at lower pH values, corresponding to highly leached cements, carbonate complexation may be significant for some radionuclides.

12.8.1 Chloride

High background chloride concentrations could arise from waste sources or from highly saline groundwaters. The impact of chloride cannot be fully assessed without also taking into account the cation associated with chloride. In most cases, this will be sodium.

In one study, sorption onto NRVB in both non-saline and hypersaline (1.5 moldm⁻³) solutions was investigated [361]. Sorption of Tc(IV), I, U and Pu was as strong or stronger in the non-saline solution whereas Np sorption was weaker.

In the ONDRAF/NIRAS panel discussion sessions [339], the possible impact of high chloride concentrations was evaluated and the following conclusions were drawn.

- High impact: Cs, Sr, and Ra mainly due to Na⁺ competition. For Cs, Sr and Ra the sorption is much lower as a result of the higher ionic strength which is responsible for the competition.
- Medium impact: Tc(IV) as there is evidence for formation of chloride complexes; Ni (due to its speciation), Cl⁻ and I⁻ due to direct competition with Cl⁻, and CO₃²⁻. Calcite might be expected to be somewhat selective; if some form of surface process is active there could be serious competition with chloride.
- Low impact: based on preliminary calculations for U(VI) in a highly simplified system, effects were found to be low. A similar behaviour is attributed to U(IV), Pu(IV), Th, Np(IV), and Pa(V), based on similarities in speciation under alkaline conditions. It was thought Nb (but also Cl⁻) is likely to form outer complexes not inner complexes, with the sodium effect (ionic strength effect) still present but it does not bind strongly to chloride.

12.8.2 Nitrate

Nitrate has been identified [435] as having a potential effect on the sorption of radionuclides onto cements. It may also participate in redox reactions affecting radionuclide speciation. Groundwater may only have low concentrations of nitrate but some wastes (such as reprocessing residues) may provide sources of nitrate. Nitrate may affect the physical and chemical properties of cement. It is
asserted that nitrate can be incorporated into hydrated calcium aluminate minerals [436] and it is also believed that it can be incorporated into ettringite [437]. It has been suggested that the altered mineral composition, specifically the replacement of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot12\text{H}_2\text{O}$ (monosulphate) with $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca(No}_3)_2\cdot10\text{H}_2\text{O}$ may affect the sorption of anionic radioelements (e.g. iodide) [435].

12.9 Effects of non-aqueous phase liquids (NAPLs)

The possibility of increased release of radionuclides to the biosphere has been discussed as one of four key impacts resulting from the presence or formation of NAPLs in a GDF [438]. In addition, some NAPLs may spread on cementitious surfaces restricting radionuclide access to sorption sites. Sorption of caesium and plutonium onto NRVB impregnated with a light lubricating oil (Castrol Nucleol 520), a typical light NAPL, has been studied [439]. The retention of components of the oil, up to 3.5% by weight after washing, appeared to have no significant detrimental effect on the sorption of either a strongly sorbing radionuclide (plutonium) or a weakly sorbing radionuclide (caesium) to NRVB. The authors advise, however, that there is uncertainty concerning whether these results for Castrol Nucleol 520 can be extended to other light NAPLs that may be disposed of to a GDF or which may be generated over the longer term.

12.10 Effects of colloids

The generation and behaviour of colloids in a cementitious near field have been discussed in detail in a recent report for NDA RWMD [440]. Radionuclides may, in principle, sorb onto the surfaces of inorganic or organic colloids by the same processes of surface complexation and/or ion exchange by which they can sorb onto the solid surfaces of the near field such as cements or backfill materials. Although in general, sorption is regarded as beneficial to radionuclide retention in the near field, sorption to colloids may not be advantageous if the colloids are mobile and if the sorption is irreversible. The colloids would act as competition to the backfill as a sorbing medium. In general, experiments carried out to date have shown low concentrations of inorganic colloids [440] and that natural organic colloids (humic acids) are insoluble under the high-pH conditions of a cement-based near field [436]. As a consequence, relatively little work on sorption to colloids under near-field conditions has been undertaken. Colloid populations are only expected to be significant when colloidal stability is increased by charge stabilisation (i.e. low ionic strength) or by ‘steric stabilisation’ due to sorption of organic species.

Sorption of uranium, plutonium and americium onto colloids derived from NRVB and corrosion product simulants has been studied and sorption found to be very strong. In the case of NRVB colloids, the sorption of uranium as U(VI) was found to be greater by over two orders of magnitude [441] than values measured for sorption onto freshly cured NRVB [442]. The increase in the $R_d$ value is attributable to a significantly larger surface area to mass ratio available for sorption on the colloidal particles than for the solid phase. Differences in colloid composition compared to the bulk NRVB mineralogy may also have been a factor. However, the authors of reference 440 concluded that if sorption to colloids were found to show significant irreversibility and colloid particles were found to persist, then there may be a need to develop further understanding of colloid mobility and chemical stability in the near field and into the far field. However, the same processes by which radionuclides may be irreversibly sorbed to colloids are also likely to occur at the surfaces of cements and rock. In reality, given that near-field colloids are expected to have limited persistence (i.e. finite lifetimes) in the geosphere, the effects of radionuclide retardation by immobilisation with solid phases are likely to outweigh any detrimental effects of transport of radionuclide irreversibly bound to near-field colloids.
12.11 Additional potential perturbing influences

12.11.1 Temperature

The overall effects of temperature on cementitious materials have been discussed in section 7. The temperature dependence of a number of near-field processes including sorption have also been reviewed [171]. There have been few studies into the direct effect of temperature on sorption onto cements. The effect of elevated temperatures (77ºC) on the sorption of tin, uranium(VI), plutonium and americium onto fresh NRVB was found to be small [361] and no overall trend was apparent.

The secondary effect of hydrothermal ageing of the backfill modifying the mineralogy and affecting the surface area available for sorption has been discussed previously in sub-section 12.5. In recent studies looking into sorption onto hydrothermally aged NRVB samples [401, 402], it was found that these alterations have very little effect on sorption capacity of the NRVB for neptunium(IV), zirconium and tin, while there was a slight reduction for uranium(VI). Sorption of these four radionuclides onto the unaged and hydrothermally aged NRVB was found to be strong in all cases. The most likely explanation for these findings is that even after the 'ageing' treatments, C-S-H gel constitutes a large fraction of the NRVB mineralogy and it is C-S-H gel that provides the bulk of the sorption capacity [401, 402]. A small reduction in plutonium sorption capacity has been observed for cement samples cured at elevated temperatures for six months [361].

12.11.2 Radiation

As discussed in sub-section 10.6, the main effect of radiation on cementitious materials is on the porewater, although there could be interaction between radiation and any plasticisers present. Irradiation of concrete leads to radiolysis of the porewater, which affects the chemistry of the porewater and particularly the redox conditions [443]. This could therefore affect the radionuclide speciation and thus its sorption behaviour. No study looking directly at the extent of sorption as a function of radiation field was found. However, an early study [444] included looking at the effects of gamma-irradiation on a range of cement-encapsulated intermediate-level wastes. Hydrogen and / or oxygen evolution was observed, the quantities depending on the waste composition. Leaching of caesium, strontium and cobalt was studied. Leach rates after different irradiation periods were difficult to rationalise, there being no clear trends with wasteforms or with elements. In some cases, the authors explained a reduction in leach rates by incorporation into hydration product gels or a reduction in aqueous-phase diffusion caused by radiolytic gas bubbles, while an increase could have been due to mechanical cracking, or radiolytic oxidation in the case of cobalt to a more soluble complex.

12.12 Key points

- A cement-based backfill acts as a chemical barrier to migration of radionuclide and chemotoxic species by providing an excellent sorbing substrate for most radionuclides and, by maintaining a high pH, lowering the solubility of a number of key radionuclides, thus overall retarding their migration from the near field.

- There are several sorption mechanisms including surface complexation, ion exchange, physical adsorption and incorporation into the solid material. Precipitation is not normally regarded as a sorption mechanism. An understanding of sorption mechanisms is important because it underpins the treatment of sorption processes in the DSSC. Although the extent of sorption of many radionuclides is known, detailed understanding of the mechanisms is often lacking.

- Most cement minerals have a characteristically high surface area, in particular C-S-H phases. Large surface areas combined with high sorption capacity results in high surface densities of sorption sites;

- Much work has been undertaken world-wide on quantifying radionuclide sorption onto cementitious materials. There are however, relatively few data regarding the sorption of some
of the key chemotoxic species identified in recent assessments (in particular beryllium and chromium [445]) onto cements.

- A recent review looked into different stages of cement ageing, but it has however been acknowledged that experimental data for sorption onto aged cements are comparatively scarce.

- Cement ageing can be divided into four states:
  - State I: The pH (> 12.5) is controlled by the dissolution of Na₂O and K₂O; even though the duration of this state is relatively short, the very alkaline conditions typical of this state might affect the sorption of certain radionuclides such as caesium and strontium;
  - State II: The pH (~12.5) is controlled mainly by the dissolution of portlandite and is relatively constant; the predominant phases present, portlandite and C-S-H phases, are strongly sorbing;
  - State III: This state is the most complex one. The pH (falling from 12.5 to 9.8) and cement element concentrations are controlled by a sequence of dissolution and precipitation reactions of the C-S-H, AFm and AFt phases; this state ends when these phases are no longer present; the C-S-H phases present are strongly sorbing;
  - State IV: The pH (< 9) is partly buffered by calcite dissolution and by the infiltrating water; generally calcite is weakly sorbing.

Which of these states is the strongest sorbing material varies from radionuclide to radionuclide, but generally State IV is the weakest.

- The sorption properties of carbonated cements, essentially calcium carbonate, may differ significantly from uncarbonated cements, where the important sorbing mineral phases are calcium hydroxide and C-S-H gels. There are very few reports on studies examining sorption onto carbonated cements, but sorption has been shown to be lower than onto fresh cement.

- Organic degradation products can affect radionuclide sorption significantly. The chemical degradation of cellulosic materials under alkaline anaerobic conditions is believed to be the most important source of organic complexants in the near field. Sorption, especially of actinides can be much reduced by cellulosic degradation products at high concentrations. The presence of a NAPL has not been found to affect sorption significantly, although the number of NAPLs studied has been limited.

- Superplasticisers that are being considered as additives in cements contain components that may act as complexants. Some of these materials have been shown to act as strong complexants when added directly to radionuclide solutions. However, due to their strong interactions between these materials and cements, it is not yet clear whether or not the presence of superplasticisers would have a significant detrimental effect on radionuclide behaviour.

- Inorganic complexants (e.g. chloride or nitrate ions) can have two separate effects on sorption processes. Ionic strength effects can give competition for sorption sites e.g. high chloride concentrations may reduce iodide sorption and the balancing cations can affect strontium and caesium. In addition, there may be complexation of radionuclides in solution, decreasing sorption if the complex itself does not sorb.

- Radionuclides may sorb onto the surfaces of colloids by the same processes by which they sorb onto the solid surfaces of the near field, thus potentially acting as competition to the backfill. In general, experiments have shown low concentrations of colloids and thus relatively little work on sorption to colloids under near-field conditions has been undertaken. Sorption of actinides onto colloids derived from NRVB has been studied and sorption found to be very strong. However, given that near-field colloids are expected to have limited lifetimes in the geosphere, the effects of radionuclide retardation by immobilisation with solid phases are likely to outweigh any detrimental effects of transport of radionuclides irreversibly bound to near-field colloids.

- In one of the few studies into the effect of temperature on sorption onto cements, the effect on sorption onto NRVB was found to be small and no overall trend was apparent. A small reduction in plutonium sorption capacity was observed for cement samples cured at elevated
temperatures for six months. However, hydrothermal alteration of the backfill may also lead to the incorporation of sorbed radioelements into the bulk cement.

- The main effect of radiation on sorption onto cementitious materials is an indirect one and centres on the porewater, where irradiation leads to radiolysis. This affects the chemistry of the porewater and particularly the redox conditions and could therefore affect the radioelement speciation and sorption behaviour.
13 Performance of cements in sealing applications

13.1 Sealing applications utilising cement-based materials

As outlined in sub-section 2.3, cements may be used in two main sealing applications in a GDF:

- fracture sealing during excavation of the facility, if located in a higher strength, fractured rock (in addition, shotcrete vault and tunnel linings, as well as providing structural support during excavations, may be required to provide sealing of vault and tunnel walls);
- plugs for the sealing of vaults, tunnels and drifts, on completion of disposal and backfilling operations.

It is important to recognise that the scales of sealing operations vary widely from the tens of micron scale in fractured rock zones to the 5-metre scale for transverse plugs and seals for drifts and tunnels. Tunnels and vaults linings may cover areas of many thousands of square metres.

While backfills generally have requirements for high flow, a long setting time, low strength over the long term and high permeability, sealing applications require different performance characteristics, and these are dependent on the scale of the application. In particular these include:

- for fracture sealing grouts:
  - good penetrability into fractures, fluidity, limited bleed and high early strength development;
- for shotcrete linings for rock support:
  - viscosity to ensure self-supporting on application, rapid set, good surface bonding, low shrinkage and thus low surface cracking, low permeability, rapid strength development and high compressive strength; and
- for concrete drift and tunnel plugs:
  - low permeability to water flow, but permeability to gas, minimum temperature rise during curing to minimise thermal shrinkage, good bonding to the rock surface; high compressive strength.

It should be noted that the safety functions and performance requirements of sealing systems are concept specific and dependent on the local geological environment.

Portland cement-based materials have long been used in underground construction. It is anticipated that traditional civil engineering technologies applied, for example in tunnelling and mining, can in many cases be transferred to GDF applications, where the performance requirements of the cement materials are similar. Construction will need to comply with similar standards and codes of practice. However, the unique requirements of cement materials in a number of disposal concepts have demanded the development of specialised cement formulations. In particular, the requirement of disposal concepts that incorporate a bentonite buffer, for the impact of cement porewaters on the backfill to be minimised, has driven research to develop low-alkalinity cement formulations for sealing applications. This section focusses on these developments.

No significant work on cement-based sealing materials has been undertaken on the UK GDF programme to date. This position is largely due to the generic nature of research at the current stage of the programme, prior to the selection of a suitable site. Therefore, this section focusses on work undertaken on international programmes. Each application is discussed in turn.
13.2 Fracture sealing grouts

Sealing of rock by means of grouting is a key means of restricting the leakage of groundwater in fractured hard (‘crystalline’) rocks, but it is a system that is not normally employed in mudrocks. Much of the work in this area has been carried out on the Swedish and Finnish programmes.

The inflow rate of groundwater should be ‘as low as reasonably achievable’ to limit hydrogeological and hydrogeochemical disturbances (e.g. intrusion of superficial waters or up-coning of deep saline groundwater). For the ONKALO construction in Finland, this inflow rate is defined as ≤ 140 dm$^{-3}$ min$^{-1}$, or 1-2 dm$^{-3}$ min$^{-1}$ per 100 m of tunnel length [33]. To achieve this, about 70% of the fractures in the first 1000 m of the access tunnel for ONKALO were grouted with traditional high-pH OPC-based grout [27]. This high grouting frequency compares with about 25% of fractures for the second 1000 m of tunnel; the corresponding grout volumes were 422 and 35 m$^3$, respectively. As the ONKALO construction proceeds deeper, the plan is to replace the ordinary high-pH injection grout with lower alkalinity grout formulation(s) [33].

An understanding of the fractures is fundamental for effective grouting, and different geological scenarios lead to decisions to use different grout and grouting methods [32]. The success of grouting is determined by how well the fractures are filled with grout, in other words on how the grout spreads in the rock mass and how well the grout fills the fractures.

Grouting is commonly carried out by drilling boreholes that project out of the planned contour of the tunnel, hence a ‘fan’ of boreholes, as shown in Figure 71. The figure illustrates pre-grouting, which means that grouting is carried out ahead of the face. Grouting can also be carried out in boreholes in the excavated opening and is then called ‘post-grouting’. In general, pre-grouting is easier than post grouting, owing to the effect of the excavation on the flow of groundwater and grout, backflow of grout and necessary limitation of grouting pressure to avoid rock fall [32].

![Figure 71 Illustration of a part of a grouting fan in a tunnel; the boreholes that intersect conductive fractures contribute to the sealing effect (from Emmelin et al. [32])](image)

SKB works closely with Posiva on its grouting programme and plans for grouting its GDF concept for spent fuel at Forsmark are summarised in Emmelin et al. [32]. SKB has initiated a series of research and development projects concerned with rock characterisation for grouting, grouting materials, grouting predictions and grouting design. Projects have been conducted since 1993 and new projects are still under way. The goal of SKB’s grouting research and development has been expressed as follows:
“…to provide competence, grout and equipment to handle all inflow situations, taking into account the special demands made by the final repository…” [32]. Indeed, SKB notes that “it must carefully consider the processes to be used during grouting technology development, as well as processes related to design and execution of grouting. Furthermore, at the time of application, SKB must demonstrate the feasibility of the grouting technology and processes to be implemented” [32].

SKB’s requirements were outlined in sub-section 2.3.2 and are re-iterated here as follows [32]. The in-flow requirements for the KBS-3H design post grouting are:

- deposition hole spot inflow: 0.1 L min\(^{-1}\)
- deposition tunnel 10 L min\(^{-1}\) per 300 m of tunnel; spot inflow: 1 L min\(^{-1}\);
- shaft and access ramp 10 L min\(^{-1}\) per 100 m of tunnel
- other underground facility parts 10 L min\(^{-1}\) per 100 m of tunnel.

The specifications for fracture sealing grouts are:

- Only grout that gives a leachate with a pH ≤ 11 may be used.
- Superplasticisers and other additives may be used.
- There are no pre-set limits to the amount of materials that may be used, but in choosing between different approaches, the one giving the lowest material use is preferred.
- Long-term durability (durability longer than 5–10 years) is not an issue. Grouting boreholes outside the tunnel periphery may be used.
- Grouting or other boreholes must not intersect deposition holes.

SKB and Posiva have divided their grout research programme into two types, one for larger fractures, i.e. hydraulic aperture ≥ 100 µm, and one for smaller fractures, i.e. hydraulic aperture <100 µm [446]. For the smaller apertures, the focus has been on colloidal silica grouts where the penetration ability of cement-based grout is not sufficient (due to the larger particle size of cement paste). SKB has concentrated on testing and studying colloidal silica (silica sol) and its usability for grouting. Posiva has also initiated a pilot study to obtain more experience on the behaviour of colloidal silica.

Posiva have undertaken extensive development work on low-pH grouts for sealing large fractures [447-449]. Required and desired properties are given in Table 30. The principal requirement for this application, in addition to the low pH, is the penetrability (into cracks) and this was tested using a penetrability meter to determine the size of aperture through which the grout will flow. This involved pressurizing the grout through different sieve sizes to determine the minimum aperture size, \(b_{\text{min}}\), below which no grout will flow, and the critical aperture size \(b_{\text{crit}}\), above which the grout will flow indefinitely. Other desirable properties related largely to the grouting process include fluidity, measured using the Marsh cone, bleed, workability time and shear strength at 6 hours (used to assess the extent of setting and hardening).

In an initial wide-ranging study, four candidate cementing systems were investigated [101];

i) OPC plus silica fume
ii) OPC plus BFS
iii) Super sulphate cement (SSC)
iv) Low alkali cement (LAC)

PFA was to have been included in the study but was ruled out having identified potential problems in the delivery and the variability of the material.

At the end of the initial study two candidate systems were carried forward to pilot testing, one based on a silica fume/OPC ratio of 0.69 (with small amounts of CAC and gypsum to control setting, and another based on a BFS/OPC ratio of 10 (also including silica fume with a silica fume/slag ratio of 0.5). However in leaching tests and in evaluation of long term safety, it was found that sulphides in the slag dissolved in the leachates and increased the total alkalinity [447]. Furthermore, pilot tests in Finland reported that fluidity of the slag mixes was poor, but increasing the water content to improve flow resulted in inadequate development of strength [448].
Development of the slag mixes was therefore discontinued, leaving only the silica fume/OPC formulation.

### Table 30  Required and desired properties for low-alkali grout for fracture injection in GDFs (note that the requirements varied for different trials) [33]

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirement</th>
<th>Measuring method</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Development stage</strong></td>
<td><strong>Field trials in Finland</strong></td>
<td><strong>Pilot tests ONALKO</strong></td>
</tr>
<tr>
<td>pH</td>
<td>≤ 11</td>
<td>≤ 11</td>
</tr>
<tr>
<td>Penetration-ability $b_{\text{min}}$</td>
<td>≤ 80 µm at 60 min</td>
<td>≤ 80 µm at 60 min</td>
</tr>
<tr>
<td>Penetration-ability $b_{\text{crit}}$</td>
<td>≤ 120 µm at 60 min</td>
<td>≤ 120 µm at 60 min</td>
</tr>
<tr>
<td>Viscosity</td>
<td>50 mPa s</td>
<td>Not used</td>
</tr>
<tr>
<td>Yield value</td>
<td>≤ 5 Pa</td>
<td>Not used</td>
</tr>
<tr>
<td>Fluidity</td>
<td>Not used</td>
<td>Not numerically set</td>
</tr>
<tr>
<td>Bleed</td>
<td>≤ 10%</td>
<td>≤ 10%</td>
</tr>
<tr>
<td>Workability time</td>
<td>≥ 60 min</td>
<td>≥ 60 min</td>
</tr>
<tr>
<td>Shear strength</td>
<td>≥ 0.5 MPa at 6 h</td>
<td>More than about 2kPa at 6 h. Not numerically set</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>≥ 4 MPa;</td>
<td>≥ 8 MPa; 7 MPa also acceptable if other properties excellent. Not set numerically</td>
</tr>
</tbody>
</table>

In subsequent tests to assess the effectiveness of using superplasticisers to enhance fluidity and reduce water content, only the silica fume/OPC formulation was investigated [98]. Seventeen formulations were tested and small additions of gypsum and/or CAC were used in some mixes to offset the retarding effect of the superplasticiser. Nevertheless the compressive strength at 28 days was determined primarily by the w/s ratio as shown in Figure 72. For those mixes with no gypsum or CAC added to modify the set, the shear strength at 6 hours was also determined by the w/s ratio (Figure 72). The effect of adding CAC increased the shear strength (all other factors being the same) and gypsum reduced the shear strength.

No bleed was reported for any of the mixes when tested using a superplasticiser and when the grout was deemed sufficiently fluid, the penetrability criteria were met in all but one case. Seventeen mixes were tested of which five were deemed suitable, each comprising OPC, CAC, silica fume and a superplasticising admixture.

The mix selected for the final stage of pilot testing in Finland [448] comprised silica fume/OPC in the ratio 0.69, 2% superplasticisers by weight of cement (OPC plus silica fume) and a w/c ratio of 1.61. This had Marsh flow cone values of 51-54s measured over three batches [note that at this stage the target value was 40s (very good) with values in the range 40-50s deemed promising], no bleed, and a shear strength at 9 hours of about 0.5 kPa. A conventional OPC grout was used for comparison and, compared with this, the low-pH grout was considered ‘not totally satisfying’ in relation to fluidity, penetration ability and strength development. It was concluded that the grout finally tested formed a basis for further development and that improvements may be achieved if part of the silica fume could be replaced with some other pH-lowering component.
Further development of a low-pH mix was undertaken within the LPHTEK project (a Finnish project concerning the optimising of technical properties of low-pH cement grout) which involved further pilot tests [450]. A different superplasticiser was used and its dosage varied together with the w/s ratio. At the high dosage of superplasticiser needed to achieve adequate fluidity (the lowest Marsh flow cone value was 44s) the early shear strength at 6 h could not be achieved. The requirement for the trials was relaxed to achieve a shear strength of $\geq 2$ kPa at 8 h and the programme concluded that further development and trials were necessary. This programme has highlighted the difficulty in meeting the requirements for both high fluidity (requiring either a high w/s ratio or high dose of superplasticisers) and a sufficiently high early strength (which is lower when the w/s ratio or superplasticisers dose is high).

Holt [33] reviewed the potential performance of low-pH grouts for Posiva and concluded that low-pH grout is not expected to have worse durability compared with traditional injection grout. Combining high amounts of silica fume with the cement to produce low-pH grout results in a material having lower permeability, and thus greater resistance to leaching and chemical attack. However, she noted that further laboratory testing is needed to quantitatively verify her findings and to provide input to long-term modelling.

The goal of combining microcement and high amounts of silica fume is to produce a grout with a high water/solids (cement plus silica fume) ratio, low water separation and high penetration [33]. Even though using silica fume results in a higher water demand in the grout, the use of a superplasticiser allows for improved viscosity while maintaining a higher w/s ratio. Silica fume manufacturers have shown that it is possible to successfully develop and use injection grouts with a w/s ratio of 6.0 using silica fume and microcement combinations. The higher w/s ratio grouts containing silica fume also have significantly improved penetration compared to microcement grout mixtures. The most likely explanation for improved penetration of grouts containing silica fume is that the modified grout is much more stable, resulting in minimal bleeding and sedimentation, and thus, no blocking. Since water is not expelled during the injection, the solids do not settle and deposit in cracks or pores close to the borehole, so that a homogenous grout flows into the rock [33]. Silica fume grouts also provide a very good bond to granite [451]. The main concerns with using high silica fume grout are [33]: an overall ‘sticky’ feeling of the mix; the possibilities of silica fume agglomeration; and retardation or late setting times.

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13 A mixture that is too sticky results in viscosity and grouting penetrability problems.
The ingredients finally chosen for the ONKALO low-pH injection grout are as follows [33].

- **Cement**: Ultrafin 16 - sulphate resistant, low alkaline injection microcement, manufactured by Cementa AB in Sweden. Specific surface area = 1,600 m²kg⁻¹; C₃A content = 2%; alkali content = \( \sim 0.5\% \).

- **Pozzolan**: GroutAid – silica fume-based additive for grouting, produced by Elkem ASA Materials in Norway. Minimum SiO₂ content of 86 %, solids content of 50 %, specific surface area = 15,000 m²kg⁻¹; 90% of particles < 1 µm diameter; pH of 4.5 to 6.5; no accelerator additive.

- **Chemical admixture**: ‘Mighty 150’ - naphthalene sulphonate based superplasticiser produced by Degussa (now BASF Construction Chemicals).

Grouting tests were carried out at ONKALO in 2007 ([27] see Figure 73). The first test was performed in ONKALO access tunnel with low-pH cement grout, and a second was carried out in Personnel Shaft 1. The second test was divided into three stages and a low-pH cement grout was used. The third test was a pilot test with colloidal silica. In these tests, it was observed that if the injection time is not sufficiently long at the design pressure, then the smallest fractures remain ungrouted and some holes that intersect water bearing fractures are incorrectly interpreted as tight holes and are only partly filled with grout. Detailed results are presented by Sievänen [449].

![Figure 73 The sites of the low-pH grouting tests in ONKALO in 2007 [27]](image)

The durability of concrete containing silica fume has been widely studied in the past 25 years [33]. However, it must be kept in mind that typically silica fume has been used in mixtures with a low w/s ratio and having very high compressive strengths, which is not true for low-pH injection grout. One of the first constructions with silica fume was in 1952 in Norway where various concrete samples were placed in a tunnel with water with average pH 5-6 and mean sulphate content of 2.5 g dm⁻³. After 30 years of exposure, only the concretes made with either sulphate-resistant cement or incorporating 15% silica fume were in a satisfactory condition [452]. Many test concretes with w/s ratios of 0.18 to 0.42 and containing up to 50% silica fume were used in 1981 in Norway, and these are continuing to be monitored. The concretes had shown no signs of deterioration after 20 years of service [453]. These early examples are encouraging when considering longevity of the low-pH grout made from sulphate-resistant cement and silica fume.

One aspect that is potentially worse in the low-pH grout mixture compared to the standard grout is shrinkage [33]. This is because the total drying shrinkage will likely be higher for the low-pH
mixture compared to the standard reference grout due to the higher w/s ratio and higher total water content, increased superplasticiser dosage and longer setting time. Yet drying shrinkage will only be a concern at exposed surfaces, which are in contact with the surrounding environment having a lower humidity. The availability of groundwater will maintain the grout inside sealed fissures; the grout will not be subjected to water depletion and thus drying.

Al-Manaseer et al. [454] noted that the hydraulic conductivity of the high strength silica fume grout was two to three orders of magnitude lower than typically observed for intact granite (10^{-12} \text{ m s}^{-1}). They also noted that longevity models assume a permeability of 10^{-12} \text{ m s}^{-1} and predict cement grouts to function hydraulically for hundreds of thousands of years. Therefore, Al-Manaseer et al. concluded that the models for high strength silica fume grouts will tend to underestimate the material longevity.

In general, cement-based materials containing silica fume show enhanced chemical resistance compared to Portland cement with the same w/s ratio due to the lower permeability and higher C-S-H content. Decreasing the permeability is the most important factor for improving the resistance to any type of chemical attack, for this aspect influences the depth of attack, amount of exposed material, rate of attacking medium replenishment and rate of leaching [455].

Two dimensional simulations of the chemical interactions between cement grout and tunnel backfilling was carried out by Luna et al. [456], using conceptual and numerical models. The numerical models used the code PHAST, composed of a transport code H3T3D and the geochemical code PHREEQC [389]. The simulation was carried out for 4000 years to evaluate the interaction with backfill material. Their model used hydraulic conductivity, porosity and diffusion coefficients representative of shotcrete and low-pH grout. The results found that the shotcrete layer would produce total dissolution of gypsum after 640 years, while for grout it occurred after 600 years. The deposition tunnel showed no effects on the geochemical evolution of the system other than an increase in pH in the vicinity of the shotcrete grout. No performance alterations of the backfill material were expected. However, it should be noted that this modelling did not include a realistic simulation of solid-solution behaviour of C-S-H gels.

### 13.3 Shotcrete for vault and tunnel linings

As noted previously, work on the application of shotcrete for tunnel and vault linings in GDFs has been undertaken on programmes concerned with SF/HLW disposal, in the context of developing low-pH formulations. Much of this work has been undertaken through the ESDRED project [457]. The development of suitable low-pH cement formulations from commercially available cements with high percentages of mineral additions, has provided a considerable challenge; each application considered has been unique [458]. Neither the compatibility between the low-pH cement and the chemical admixtures, the hydration processes nor the strength evolution with time were known at the outset, thus an extensive characterisation process has had to be performed.

Several low-pH concrete formulations were developed under the ESDRED Project [457] and eleven (seven based on CAC and four on OPC) were chosen for the shotcrete design process. The selection was based on their pore fluid pH at 90 days and their setting time. The pH of leachates reached 11.4 or less after 30 days curing time. Shotcreting trials for checking and optimising the low-pH concrete formulations developed were carried out in Leon (Spain). Shotcreting tests were carried out, pumping the concrete along a pipeline with elevations, over short and long distances, and spraying both manually and with a spraying robot, over panel and into a steel reinforced concrete tube resembling a gallery at Äspö.

The shotcrete for rock support requires a high strength. A 60% OPC/40% silica fume formulation was used to achieve low pH with a w/c ratio reduced to about 0.45 and the solids content (OPC plus silica fume) increased to 350 kg m^{-3}. This resulted in an increase in both the compressive strength and the elastic modulus. Trials at Älvkarleby yielded 28-day compressive strengths in excess of 80 MPa with the elastic modulus exceeding 30 GPa. Samples from the Äspö Hard Rock Laboratory, which had a higher w/c = 0.5, yielded respective values of 54.6 MPa and 28 GPa.
Results for the 60% OPC/40% silica fume formulation at different w/c ratios for different applications are shown in Figure 74\textsuperscript{14}. The results are compared with the relationship between strength and elastic modulus for concrete provided by EN-1992-1-1 [130]. It is clear that the use of the formulation with a high proportion of silica fume has a significant effect on this relationship, most probably as a result of the strength enhancement achieved using silica fume.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure74.png}
\caption{The relationship between compressive strength and elastic modulus for low-pH shotcrete and self compacting concrete with 40\% silica fume}
\end{figure}

\section*{13.4 Vault and tunnel sealing plugs}

Plugs are required in GDFs in a number of places. In concepts for HLW/SF disposal, the plugs in the deposition galleries have a mechanical function, to transfer the pressure of the swelling bentonite to the rock. In some designs they must have also a hydraulic seal function (especially the interruption of any engineered disturbed zone).

A number of large-scale experiments and development programmes on tunnel seals have been undertaken since the 1990s and are reviewed briefly in the following sub-sections.

\subsection*{13.4.1 Canadian Tunnel Sealing Experiment}

The full-scale Tunnel Sealing Experiment (TSX), carried out in Canada between 1998 and 2004, was designed to characterise the sealing and structural potential of well-constructed, full-scale bulkheads for use in GDFs [459].

The TSX consisted of two bulkheads in a 3.5m high, 4.4m wide and 46m long horizontal excavation, as shown in Figure 75. One bulkhead was composed of approximately 9000 highly compacted, bentonite-sand blocks, while the other was constructed using a low-heat high-performance concrete (LHHPC) developed by Atomic Energy of Canada Limited (AECL). (Owing to its composition, the LHHPC was also a low-pH concrete.) The central 12 m long pressure chamber between the bulkheads was filled with sand and saturated with water. The swelling of the

\textsuperscript{14}The self-compacting concrete designed for use in tunnel plugs is discussed in section 13.4.4.
clay bulkhead was confined by sand in the TSX pressure chamber on one side and by a structural steel restraint on the other. The sand-filled test chamber was pressurised in a stepwise manner to 4 MPa, over the first 3 years of the experiment, by means of a static-water head. A circulation pump and heaters were added for a thermal phase that reached approximately 65 °C at the centre of the inner faces of the bulkheads. Seepage data, together with solute transport data from tracer tests, were used to quantify the sealing characteristics of the two bulkheads. At the conclusion of heating, a three-month cooling period was followed by the depressurisation of the chamber. The cement bulkhead was highly instrumented with a range of displacement transducers, pressure sensors, strain gauges, thermocouples, etc, which were monitored throughout the experiment. Samples were taken from the bulkheads during decommissioning to measure the post-test conditions in terms of density, water content, structure, chemistry and strength.

Figure 75 TSX layout and concrete bulkhead details (from Martino et al. [459])

In the LHHPC for the TSX, a substantial fraction of the Portland cement component was replaced with pozzolanic silica fume and non-pozzolanic silica flour (ground silica) in a 1:1:2 ratio. A naphthalene-based superplasticiser was used to enhance workability. The concrete typically had a 0.53 water to cementitious-materials ratio but this was increased to 0.57 to allow for easier pumping in the upper part of the bulkhead. The replacement of cement with silica products lowered the heat of hydration and also reduced the alkalinity of the cured concrete to a pH of 9.8 to 10. For the TSX, the cement, silica fume and silica flour were blended, batched and bagged for use in pre-weighed quantities at a commercial concrete plant. High-silica content sand was supplied from a local glacial deposit and was washed before use. The aggregate was a mix of crushed Lac du Bonnet pink granite and local rounded limestone. The 76 m³ concrete bulkhead was placed in a single pour in less than 8 hours. The concrete was allowed to cure for two weeks prior to flooding the chamber.

The front form of the concrete bulkhead was timber and steel construction with a geotextile inner lining to permit water to be supplied to the front face of the bulkhead for ten days after pouring. Samples taken during decommissioning suggest that this supplied water penetrated only 0.1 m into the concrete. No structural reinforcement of the concrete bulkhead was required. Grout tubes were installed at the concrete-rock interface prior to pouring to permit later grouting.

To ensure measurable responses over the timescale of the experiment, very high hydraulic gradients were generated across the bulkheads by pressurisation of the chamber (which was pressurised in a step-wise manner). The supply of water was essentially unlimited. These represented extreme hydraulic conditions that were considered unlikely in a GDF [460].

The principal measure of bulkhead performance was seepage. The seepage rate was found to increase initially each time the pressure in the chamber was increased, but subsequently decreased as the pressure was maintained. The increased seepage rate was attributed to
cracking and debonding at the concrete-rock interface due to displacement of the bulkhead under the increased load. The subsequent decrease was attributed to either the accumulation (i.e. sedimentation) of fine material in the interface or the continued hydration of incompletely hydrated regions within the bulkhead [461].

At a chamber pressure of 800 kPa, the seepage rate past the concrete bulkhead stabilised at a rate of 1.8 cm$^3$ min$^{-1}$. The seepage rate did not fully stabilise at 2 MPa, reaching a minimum of 14 cm$^3$ min$^{-1}$, before pressurising to 4 MPa in the next step. The stabilised seepage rate at 4 MPa was about 10 cm$^3$ min$^{-1}$. The seepage rate decreased during the subsequent heating phase, reaching a minimum of 2 cm$^3$ min$^{-1}$ by the end of the stage. This decrease was attributed to thermal expansion of the concrete and rock reducing the apertures of the seepage paths.

Samples were taken from the concrete mass and rock-concrete interfaces during decommissioning. The physical properties varied across the bulkhead although it appeared uniform with no visible layering of aggregate. Hydraulic tests showed that the lowest transmissivity$^{15}$ was found in the central mass of the bulkhead (~10$^{-15}$ m$^2$s$^{-1}$), while that at the perimeter was greatest (10$^{-13}$ to 10$^{-14}$ m$^2$s$^{-1}$). The transmissivities at the rock-concrete interface and internal cracks were greater (~10$^{-12}$ m$^2$s$^{-1}$). Porosity was greatest towards the downstream end (0.125), but decreased towards the centre (0.09) and the upstream end (0.065).

Although the concrete bulkhead did not reach a steady-state condition nor did it experience the full range of thermal and hydraulic conditions expected in a GDF, Martino et al. [459] consider that the conditions were sufficiently extreme that this LHHPC mix can be deemed a material worthy of further investigation of its long-term sealing and structural performance in a GDF.

13.4.2 FEBEX Project

Plugs may also be constructed from shotcrete. Shotcrete has a number of advantages, from the engineering point of view [67]:

- forms are not required;
- fast construction;
- early mechanical strength;
- excellent bonding to the rock surface;
- low permeability material;
- reduced shrinkage;
- easy to construct with tele-operated/robotised systems.

An example of this type of construction is the plug used for the FEBEX Project at the Grimsel URL illustrated in Figure 76. The plug was constructed in two phases: a first section with about 1m thickness was built in 2002, and a second section of about 2m was constructed in 2003. Both sections were constructed with layers of a thickness ranging from 5 to 67 cm. However, some shrinkage cracks were observed in the thicker layers, so the standard layer thickness was finally set to 25-30 cm [67].

$^{15}$ Transmissivity is a measure of the ability of a feature, such as a crack, an interface or a block of material, to carry flow. For example, for a uniform block of material with horizontal flow, the transmissivity is given by the product of the hydraulic conductivity in the horizontal direction (volume flowing through unit area per unit time) and the vertical thickness of the block.
13.4.3 ESDRED tunnel plug trials

Both ‘short’ (1 m) and ‘long’ (4 m) plugs constructed with low-pH cement shotcrete were constructed and tested as part of the EC ESDRED Project [457].

To construct the short plug, shotcrete spraying was done manually using a stand-alone concrete pump, over 15 m of distance and 2 m of elevation. After a hardening period, mechanical pressure was applied at the rear face of the plug to take it to failure by injecting and pressurising water into a chamber left in the back end of the drift. The plug underwent elastic deformations during the pressure increases, with recovery when pressure dropped. Despite a significant water leakage that was detected at the bottom of the plug, it was possible to increase the pressure up to 27 bar, when it was considered that the plug had ‘failed’, given a sudden increase in the rate of displacement.

The long plug test consisted of a 4 m long parallel low-pH shotcrete plug constructed at the back end of a 3.5 m diameter horizontal gallery, excavated in granite with a tunnel boring machine (TBM) at the Grimsel URL (Switzerland). The end of the gallery was sealed with 1 m of buffer constructed with blocks of highly compacted bentonite. The bentonite was provided with geotextile mats for water injection, working as an artificial hydration system to accelerate the saturation process. The plug was constructed in 7 curved layers applied during four days in total with a spraying robot and the concrete mixer and pump were installed at 80 m from the construction point. Garcia-Sineriz et al. [457] note the following improvements over previous conventional designs.

- Concrete plugs could be built with no reinforcement and with no recesses excavated in the rock for hard rock formations (granite).
- Concrete plugs could be built using a shotcreting emplacement method, which is much faster than casting concrete, can be easily automated, and could be almost continuous due to the low heat release of the low-pH concrete during hardening.
- Increase of long-term safety due to a more stable multiple barrier system (natural and engineered) due to the reduction of the alkaline plume effect associated with using low-pH cement.

13.4.4 Self-compacting concrete for deposition tunnel plugs

In the KBS-3 SF disposal concepts (see sub-section 2.3.1), plugs are required in the deposition tunnels to restrain the bentonite buffer and act as part of the deposition tunnel sealing system [462]. Although the plugs limit water movement, they are not intended to be the primary water seal in the deposition tunnels. The plugs are required to withstand a hydraulic pressure of...
4 MPa plus a 2 MPa swelling pressure from the bentonite buffer [462], and to be free of continuous cracks or gaps.

SKB has developed a ‘self-compacting’ low-pH concrete for deposition tunnel plugs [463]. Self-compacting concrete (SCC) is a concrete that is able to flow under the force of gravity alone, fills the formwork completely and achieves full compaction without additional compacting work.

SKB set the following requirements for its deposition tunnel plug concrete [463]:

- it should be pumpable;
- it should be self-compacting and keep its self-compacting properties for at least 2 hours;
- it should be possible to be produced in a normal concrete factory;
- it should have a final compressive strength of at least 50 MPa;
- it should give as low exothermic heat as possible to minimise cooling measures. The amount of binder should be kept low to minimise heat development and shrinkage;
- the components should be commercially available;
- the concrete should give a pH of less than 11 when leached; and
- the concrete is allowed to contain organic superplasticiser but the amount should be minimised; no other organic components were allowed.

The geometry of the plug design (Figure 77) requires the concrete to be self-compacting and that the fresh concrete keeps its self-compacting properties for at least two hours. The plug is designed as a reinforced convex concrete plug with a diameter of a little more than 5 m and an overall plug thickness of approximately 1.3 m. The plug may need to be reinforced due to the expected load on the structure.

Figure 77  SKB design for arch shaped concrete plugs (from Vogt et al. [463])
In large volume constructions such as plugs, an aspect that has to be considered is thermal cracking [463]. In the fresh concrete, the exothermic process of cement hydration will increase the temperature in the concrete and cause expansion of the fresh and hardening concrete. Later, the subsequent cooling will shrink the hardened concrete, resulting in tensile stresses. There will be temperature gradients within the plug which may cause internal cracking in the concrete. The temperature gradients and temperature rise must therefore be minimised and low heat cement is usually used in large volume constructions. Alternatively, the fresh concrete could be cooled before casting or be applied using cooled pipes.

The low-pH SCC formulations developed by SKB contains OPC, densified silica fume, limestone filler, a superplasticiser, high quality natural fine aggregates and average quality crushed coarse aggregate. Two mix designs have been tested, one with 200 kg of binder (cement and silica fume) per cubic meter concrete (B200) the other with 300 kg of binder (B300) [463]. In each case the binder comprised 60% OPC and 40% silica fume (i.e. the same as the low-pH shotcrete discussed in sub-section 13.3).

Both the B200 and B300 mixes achieved the required fluidity with shear stress values of about 25 Pa and 43 Pa at 10 minutes after mixing, increasing to 51 Pa and 72 Pa after 90 minutes. The plastic viscosity was initially about 35 Pa s for both mixes and did not increase significantly over 90 minutes.

In initial trials, the 28-day cube strengths were 43.4 MPa and 68 MPa, increasing to 68 MPa and 99 MPa after 91 days. In full-scale production, the strength of test specimens was marginally higher, but the strength of cores extracted from test columns 0.85m diameter x 3m high were, on average, about 15% below that of the control test specimens. This is typical for concrete construction.

The elastic modulus was also measured and results are included in Figure 74. The results are broadly consistent with those achieved for low-pH shotcrete.

Shrinkage was measured using various methods with the concrete maintained under sealed conditions to simulate the moisture state in the massive plug (i.e. autogenous shrinkage). After 4.5 months the total shrinkage was about 1000 and 1100 microstrain for B200 and B300 respectively, with about 2/3 of this occurring within the first 24 hours. EN1992-1-1 [130] gives a method for estimating autogenous shrinkage based on the 28-day compressive strength for conventional structural concrete. For the strengths achieved, values of autogenous shrinkage would be expected to be in the order of about 100 microstrain. The value achieved is about 10 times higher than estimated and confirms other findings on the effect of silica fume on autogenous shrinkage as described in sub-section 5.8.2 and illustrated in Figure 33.

Creep testing was also undertaken to support the modelling of thermal stresses which could lead to cracking. Values of creep coefficient (i.e. the ratio of the creep strain to the elastic strain) are illustrated in Figure 78. Results are compared with creep coefficients estimated using the method provided in EN1992-1-1. Based on these results it appears that the creep for the low-pH concrete is less than expected for conventional structural concrete of the same strength.
The overall conclusion of these trials was that two workable mix designs for low-pH self compacting concrete had been developed with the open time and the self-compacting properties sufficient for use in the tunnel plugs [462].

SKB has also analysed whether reinforcement of the plug is required [462]. Two-dimensional, axis-symmetric finite element analyses, assuming linear elastic material behaviour in rock and concrete where contact friction between concrete and rock is taken into consideration, have been used to study the structural response of the plug. A total of 48 main load combinations, consisting of 8 different load scenarios and 6 material combinations, were used.

It was found that the concrete plug would not remain uncracked when subjected to the loads studied but that, nevertheless, it is possible to achieve an unreinforced concrete plug that satisfies the design requirements. The minimum size of the concrete compressed zone will be 0.5 m, resulting in a water leakage through the plug lower than the requirement of 0.01 litre min⁻¹. Further, the maximum compressive stresses of interest are 33 MPa and the maximum displacement in the plug is about 3 mm, which are deemed to be satisfactory [462]. Consequently, SKB conclude that it seems possible to use low-pH concrete for the plug without using reinforcement.

Grandia et al. [464] have investigated the potential chemical interactions of low-pH tunnel plugs with other engineered barrier components. They carried out reactive transport simulations based on the geochemical degradation of the cement compounds, mainly C-S-H. The implementation of the degradation process into the geochemical model was based on a solid solution approach for C-S-H alteration. The numerical model also took into account the dependency of transport properties (e.g. molecular diffusion coefficient) with the changes in porosity due to mineral precipitation-dissolution. The simulations predicted that the effect of low-pH concrete alteration on the stability of backfill materials (bentonite) would be low. The main process governing geochemistry in the backfill-concrete boundary was the rapid loss of porosity (within about 10 years) due to ettringite precipitation. The very high molar volume of this mineral enhanced the rate of clogging. Ettringite formation was mainly driven by a high sulphate concentration in the backfill porewater, which in turn was controlled by equilibrium with gypsum. The release and diffusion of
calcium (from C-S-H replacement) and aluminium (from katoite dissolution) from the concrete, caused ettringite precipitation at the concrete-backfill boundary. The loss of porosity dramatically reduced solute diffusion and, consequently, the backfill-concrete system was calculated to remain almost unchanged up to the thousand years considered in the calculation.

13.5 Sealing boreholes

Mixes with a high proportion of silica fume were also developed for sealing 76 mm boreholes at Olkiluoto [465]. Two mixes were developed, a high flow mortar for stabilising boreholes and a low-strength concrete for plugs. Both mixes used a combination of white Portland cement and silica fume. The high flow mortar used 40% silica fume (% wt of cementitious material) with added fine ground α-quartz and fine quartz sand (up to 500 μm). The cement content was 857 kg m⁻³ with w/c = 0.285. Long term strength was not reported but the mix achieved a compressive strength in excess of 10 MPa after 24 hours.

The formulation for the plugs included 50% white OPC/50% silica fume, a cementing solids content of only 120 kg m⁻³ and w/c = 1.2. The mix also contained 200 kg m⁻³ of fine ground α-quartz and 150 kg m⁻³ of fine ground cristoballite quartz, both of which would contribute to the hydration reaction, and achieve a water/reactive powder ratio of about 0.32. 1700 kg m⁻³ of granitic aggregate (up to 4mm) was also used. The mix achieved a compressive strength of 10 MPa in 7 days.

An almost identical mix was used for borehole sealing trails at Åspö [150]. This yielded a compressive strength after 28 days of 57.1 MPa. Tests were also undertaken at different w/s to determine the effect of additional water from the rock that may mix with the concrete during placing. Increasing the w/s from 0.07 to 0.21 reduced the compressive strength from 57.1 MPa to 14.0 MPa. These results are presented in Figure 37 (sub-section 6.2.1) in terms of the w/c ratio, which increased from 0.32 to 0.96.

As part of these trials, punching shear tests were undertaking on the 28-day old concrete by simulating the potential load on a plug as shown in Figure 79. To increase the shear resistance, larger particle sized crushed granite aggregate was added corresponding to either 20% of the mass of concrete (using particles up to 10mm) or 35% by mass using particles up to 20 mm. Values of punching shear strength were 20 MPa for the control mix, 37 MPa using 20% granite and 15 MPa using 35% granite.

Figure 79 Punching apparatus for testing the shear strength of the concrete plug for borehole sealing
13.6 Key points

- Functional requirements for tunnel lining and fracture sealing grouts will be dictated in large part by the characteristics of the geological environment.

- Cements are used routinely in sealing applications in civil engineering, for example in tunnels and mining. GDFs will need to be constructed to similar standards and codes of practice as all underground structures. Transfer of current conventional cement sealing technologies to GDFs is expected where sealing requirements, determined by the local geological environment, are essentially the same as in other underground structures.

- International agencies working on HLW/SF disposal concepts that incorporate a bentonite buffer, have turned to low-pH cements as their main option for grouts, shotcrete, roadways and tunnel plugs, to mitigate the deleterious effects of conventional cement leachates on bentonite. Cement paste is replaced by at least 20% silica fume, to produce cements with a leachate of pH ≤ 11. The main emphasis so far has been on material development and testing, but conceptual and numerical models of long-term performance are starting to be published.

- Low-pH cement fracture-sealing grouts have been developed by SKB and Posiva for fractured hard rocks where fracture apertures exceed 100 µm and have been extensively tested at ONKALO and through the ESDRED Project. These grouts, by analogy with concretes developed in the 1950s, have good long-term durability due to their low permeability in comparison with conventional grouts.

- Low-pH concretes have also been developed for drift seals and plugs. These can be installed using shotcreting methods or by using ‘self-compacting’ compositions.

- Low-pH shotcrete tunnel linings and rock bolt grouts have also been developed and tested through the ESDRED Project.
Key considerations for the UK programme

The geological environment of a site for a GDF is the key determinant of the type of disposal concepts that will be selected for different UK waste types and it will play a key role in determining the specification and functional requirements for backfill, sealing and structural materials used in the facility. For example, the use of fracture grouts is envisaged primarily where the GDF is placed in a geological environment that includes fractured rock; for excavations in a lower strength sedimentary rock, the provision of tunnel and cavern support (tunnel linings and structural supports) will be essential to enable safe construction and operation of the facility. For a GDF located in an evaporite formation, cements may not be the preferred choice for backfill materials.

Owing to the diversity of the UK’s geology, access tunnels to a GDF located at depth, are likely to pass through a sequence of geological formations with differing physical and hydrogeological characteristics. Thus, the functional requirements for sealing and structural materials may vary over the length of the access tunnels and in different parts of the GDF to match the local characteristics of the rock. In addition, different pH-buffering requirements of sealing materials may be specified in disposal areas for different waste types, co-located in the same facility, depending on the backfilling and sealing strategies of the disposal concepts adopted. For example, conventional cement fracture grouts and shotcrete linings may be used in near-surface structures and ILW disposal areas of a facility whereas low-pH formulations may need to be considered in the vicinity of disposal areas containing bentonite. As a result, the development of appropriate specifications for cements in sealing applications awaits site specific information and concept selection for a UK facility.

Technical knowledge on cement-based backfills is considered to be relatively well-developed from work on the UK radioactive waste disposal programme and on overseas programmes (in particular in Switzerland). Some UK-specific factors are fairly well understood. Key points concerning the performance of cements in backfill applications were highlighted at the end of sections 5 to 12. In Table 31, the most important topics concerning backfill performance have been brought together and placed in the context of the current state of the UK programme. The table highlights those topics where further developments await site-specific information; knowledge gaps are identified and suggestions for possible future work are outlined.

The work on seals for GDF concepts undertaken to date has focussed primarily on low-pH cement materials for chemical compatibility with a bentonite buffer. It is not yet clear whether it will be either necessary or to what extent it may be either possible or appropriate to transfer these developments to the UK. Fuller specification of performance requirements of sealing materials for a UK GDF awaits the selection of a site, disposal concepts and site-specific information.

Key points concerning the performance of cements in sealing applications were highlighted at the end of sections 6 and 13 and the most important are brought together in Table 32. Potential implications for the UK GDF programme are identified and suggestions for possible future work in this area are outlined.

The review discusses in some detail aspects of the behaviour of cements and their performance in the short-, medium- and long-terms in GDF applications. Much of this behaviour is complex and it is important to recognise that different aspects of performance are coupled, sometimes strongly and sometimes in a conflicting manner. Thus the specifications for cement EBS materials will inevitably represent a compromise between differing requirements. Prioritising the key aspects of performance and the timescales over which they may be required in each application is important, therefore, for successful implementation in a GDF.
Table 31  Key topics concerning cements in backfilling applications (ILW vaults in higher strength rock or lower strength sedimentary rock)

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<th>Topic</th>
<th>Understanding</th>
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<tr>
<td>Backfilling strategy and procedures</td>
<td>While some work was undertaken on the emplacement behaviour of the NRVB as part of its development, little work has been undertaken to date concerning how the backfill would be emplaced in a GDF. Some early work has been undertaken on the backfilling strategy and the logistics of backfilling in the context on the UK cement-based ILW/LLW disposal concept in higher strength rock. The backfilling procedures are a detailed design issue that will be dependent on the disposal concept, the design of the disposal vaults and the backfilling strategy that is adopted.</td>
<td>The backfilling strategy will be dependent on the design of the GDF and the closure requirements during and at the end of operations (e.g., any requirements concerning the early closure of individual disposal vaults). The backfilling procedures and the timescales over which backfilling may take place will be dependent on the backfilling strategy adopted. Backfilling procedures may vary between different ILW vaults depending on factors such as vault size, placement distance and the arrangement of waste containers. Development and testing of the backfilling procedure(s) is likely to go hand-in-hand with refinement of the requirements for the cement-based backfill (see below).</td>
<td>Development of the backfilling strategy at the design stage once a specific site and disposal concept for ILW have been selected, with development of the backfilling procedures as the programme progresses. Demonstration of the effectiveness of backfilling under conditions that simulate those in a GDF vault.</td>
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<td>Emplacement of cement materials in backfill</td>
<td>Some work was undertaken on the emplacement behaviour of the NRVB as part of its development. This provides sufficient knowledge as a basis for refining mix design to meet evolving requirements of a cement backfill. Owing to the complexity of cement systems, there are no unique models for predicting the performance of a particular system. However, substantial empirical data has enabled critical parameters to be identified and general relationships to be established.</td>
<td>Future requirements for backfill emplacement will be disposal concept design specific. Specific requirements for fluidity, bleed, setting time, and heat of hydration of the cement backfill will be dependent on the backfilling strategy, including the required rate of backfill production, the distance to be transported, the method and rate of placement and the array of waste packages. This may lead to refinement of specifications for the cement backfill.</td>
<td>Future development of the specification for cement backfill can be envisaged depending on the design for ILW disposal vaults and the backfilling strategy adopted. Formulation development would need to be undertaken under an appropriately designed testing programme. Demonstration of the effectiveness of backfilling under conditions that simulate those in a GDF vault.</td>
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<td>Mechanical performance of backfill</td>
<td>The importance of mechanical performance varies depending on the function of the cement in the EBS system. In the case of the NRVB, for example, the specification requires only a relatively low strength material to meet the requirement for retrievability. A wide range of mechanical properties may be achieved for cementitious systems, from very low strength backfill material where retrievability is a requirement, to very high strength material where load bearing capacity and stiffness is critical. To a large degree it is possible to customise a concrete mix to meet a wide range of specification requirements. However, general civil engineering experience may be of limited value in assessing their long term mechanical performance.</td>
<td>The low compressive strength specification for the backfill in the UK ILW/LLW concept in higher strength rock is designed to meet a requirement for waste package retrievability after backfilling (and was based on an operational lifetime of 50 years before GDF closure). Depending on the host rock, concept design for ILW disposal, the backfilling strategy adopted and future decisions concerning the requirements for retrievability, the mechanical requirements for a UK backfill could change. For example, for a GDF located in a lower-strength sedimentary rock, the backfill may be required to withstand greater stresses due to rock creep. Different cement formulations (e.g. fracture grouts and waste encapsulation grouts) will be in close physical proximity to the backfill and may exhibit coupled reactions. The potential interactions between cements and the impact on their mechanical properties may need to be considered, depending on the requirements for mechanical performance post-closure.</td>
<td>Development of the backfill specification for ILW vaults as the programme progresses. Develop understanding of the long-term strength and stiffness development of the backfill. Develop understanding of the interactions between different cement types and the impact on their mechanical performance.</td>
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<td>Temperature rise due to cement hydration</td>
<td>Hydration of the cement backfill will generate heat in the ILW vaults during backfilling. Modelling of the thermal evolution of current ILW vault designs backfilled with NRVB located in a hard rock have been undertaken and shown that the maximum temperature rise in the near field due to cement hydration should not exceed 23°C within a 50-year transient. Peak temperature is reached within about 1 year after the start of backfilling; after 50 years the temperature of ILW vaults will be controlled by radiogenic heating and the ambient temperature of the host rock. The temperature rise is dependent on a large number of design parameters including the thermal conductivity of the backfill and the host rock, which are dependent on water content. Low-porosity higher strength rocks tend to have lower thermal conductivities than lower strength sedimentary rocks giving rise to higher temperature rises in the near field. A fully-saturated cement will result in a lower temperature rise than a partially saturated material. Ventilation during the operational phase will strongly influence temperature distribution in the host rock. Ventilation during the backfilling phase may draw significant heat from the facility. Modelling the thermal evolution of the near-field is well-developed using finite element codes such as ABAQUS.</td>
<td>The long-term ambient temperature of ILW vaults post-closure will depend on the location and depth of the facility. The temperature rise above ambient in the medium term will be determined by radiogenic heating which is determined by the waste inventory. Thermal evolution of the ILW near field will be dependent on the thermal properties of the host rock and the disposal concept design. Optimisation of vault design, waste layout, backfilling strategy, ventilation system design and any refinements of backfill specification / formulation development may need to take into account the thermal transient due to cement hydration.</td>
<td>Further thermal evolution modelling when site-specific data becomes available and to support optimisation studies of vault design, backfill strategy, or backfill formulation, etc. It would be desirable to integrate and manage thermal excursions as part of the overall design strategy. Experimental studies to measure heat generation from, and thermal properties of, alternative backfill formulations. Measurements of temperature rise should be incorporated into any larger-scale experiments to demonstrate backfilling procedures.</td>
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### Effects of temperature on cement materials

The general consequence of thermal excursions is to degrade cement properties (strength, permeability, etc.) giving rise to dimensional instability and cracking. However, some of these general effects may be beneficial in terms of higher creep and improved stress dissipation.

The large scale of the cement pours required for backfilling means that elevated temperatures from cement hydration reactions will persist for periods of years; heating due to radioactive decay may persist for hundreds of years. As a result, backfill curing will occur at elevated temperatures. Thermal contraction will occur on cooling, which may lead to tensile stresses and cracking.

If the temperature exceeds ~60°C, mineralogical changes may occur within the matrix, leading to significant long-term expansion with further impact on dimensional stability. The most important of these, involving the re-formation of ettringite at lower temperatures (delayed ettringite formation) may be physically disruptive. These reactions are slower than thermal contraction and thus will have an additional impact.

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<td>Effects of temperature on cement materials</td>
<td>The general consequence of thermal excursions is to degrade cement properties (strength, permeability, etc.) giving rise to dimensional instability and cracking. However, some of these general effects may be beneficial in terms of higher creep and improved stress dissipation. The large scale of the cement pours required for backfilling means that elevated temperatures from cement hydration reactions will persist for periods of years; heating due to radioactive decay may persist for hundreds of years. As a result, backfill curing will occur at elevated temperatures. Thermal contraction will occur on cooling, which may lead to tensile stresses and cracking. If the temperature exceeds ~60°C, mineralogical changes may occur within the matrix, leading to significant long-term expansion with further impact on dimensional stability. The most important of these, involving the re-formation of ettringite at lower temperatures (delayed ettringite formation) may be physically disruptive. These reactions are slower than thermal contraction and thus will have an additional impact.</td>
<td>Thermal evolution of the near field associated with backfill hydration will be dependent on the thermal properties of the host rock, the disposal concept design and the waste inventory. Some wastes may give rise to short-term exotherms associated with corrosion processes (e.g. reactive metals) leading to local thermal excursions and temperature gradients in the near field.</td>
<td>Assessment of the thermal history, with respect to proposed formulations, and of the consequences of thermal excursions in the short and long term, by a combination of modelling and focussed experiment. Develop understanding of the potential implications of elevated temperature curing on the long-term dimensional stability of the backfill up to the localised short-term high temperature limit of 80°C included in the current Disposal System Technical Specification [169]. Work is in progress on the NDA programme on the hydrothermal ageing of NRVB and of NRVB in contact with waste grouts.</td>
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<td>Mass transfer performance of cement backfills</td>
<td>The permeability and two- and three-phase flow properties of the backfill may have little effect on the flow of water and gas, and hence dissolved solutes, out of the GDF. It is likely that the flow of water and gas will be controlled by the host rock permeability. It is expected that cement backfills would crack. The contributions from cracks to the effective permeability and the two- and three-phase flow properties might dominate the contributions from the matrix. However, even if they do not provide the dominant contribution to the permeability, cracks may provide a route for gas to migrate through the backfill. The mass transfer properties of the backfill matrix are expected to evolve over time as cement components (initially portlandite and subsequently C-S-H phases) are leached out of the cement, and as secondary minerals form. There is significant uncertainty about these changes. The time scale for changes to the properties of the backfill would depend primarily on the permeability of the host rock and could be long for a host rock with very low permeability, such as a clay, shale or mudstone. If the backfill is cracked, then its diffusion properties may play an important role in ensuring that solutes migrating in water and gas flowing through the cracks access the porosity and sorption sites within the backfill matrix. This could be important in terms of leading to lower concentrations and retarding the migration of dissolved contaminants out of the GDF.</td>
<td>It is expected that the backfill would become cracked shortly after emplacement as a result of plastic settlement, early-age thermal cracking and expansion of waste packages as a result of corrosion. It is expected that the contributions from the cracks in the backfill will dominate its effective permeability and will determine the two- and three-phase flow properties. It is expected that the pattern of cracking of cementitious backfills will evolve over time and therefore the contributions to the effective permeability and the two- and three-phase flow properties will also evolve. The timescales for evolution of the backfill mass transfer properties as a result of leaching by groundwater will be dependent on the permeability of the host rock which will control water flow.</td>
<td>Develop understanding of the evolution of backfill transport properties and in particular the process of crack enlargement and healing (e.g. the effects of creep under load). Develop understanding of the effect of leaching by groundwater and secondary mineral precipitation on the mass transfer properties of the backfill.</td>
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<td>Cement-based EBS resaturation (and potential for desaturation)</td>
<td>The timescales for resaturation of the near field are strongly dependent on the host rock type. For a GDF located in a higher strength, fractured rock, estimates for resaturation times vary from the order of tens to a few hundred years; in lower strength sedimentary rocks estimated resaturation times are expected to be longer and could be of the order of thousands of years. Although high permeability backfills (such as NRVB) may be designed to have a high water content after curing, desaturation of the local backfill may occur where there is significant consumption of water by waste degradation processes, particularly if inflows from the host rock are slow. The implications of this for backfill integrity and mass transport properties are not well understood.</td>
<td>The rate of near-field resaturation will depend on the hydrogeology of the host rock. The integrity and permeability of any vault or tunnel linings and floors; and the permeability of the backfill may also play a role. For host rocks with low permeabilities, limited inflow of water could have implications for local desaturation of the backfill as a result of water consuming processes.</td>
<td>Further modelling studies of near-field resaturation once site specific information is available. Desk-based studies may be undertaken to evaluate the potential for local desaturation of the backfill. Experimental studies of the effect of backfill desaturation on backfill integrity and physical properties. Measurement of permeabilities and saturation functions for alternative backfill compositions.</td>
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**Effect of gas release from packages on cement backfill – gas release during backfilling and curing**

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<td>Gases released from waste packages (due to metal corrosion and degradation of organic materials) will affect the transport properties of the backfill through processes such as carbonation, pressurisation and the potential for cracking. Reactive metals present in some wastes will corrode in the presence of water and the rates of corrosion increase with temperature. If there is water available for reactive metal corrosion in the waste packages at the time of vault backfilling then the rates of corrosion will increase during cement hydration due to the increased temperature. This would generate increased volumes of gas during the period of cement setting and curing. This could potentially lead to pressurisation, displacement and cracking of the backfill above the waste containers and within a stack. Packages containing reactive metals will generate hydrogen gas during the early post-closure period as a result of corrosion. The rate of gas generation will depend on the availability of water and the temperature of the waste. These will depend on the resaturation time which is controlled primarily by the permeability of the host rock. The backfill may also act as a source of water prior to resaturation of the GDF with groundwater.</td>
<td>Develop understanding of the impact of gas on the properties of backfill during emplacement and curing. This includes the effects of pressurisation and gas migration on backfill transport properties and potential impact on crack development and void formation in a waste stack.</td>
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<p>| Effect of gas release from packages on cement backfill – effect of carbonation on physical properties | One contribution of the cement backfill is to remove carbon dioxide from gas and solution. Carbonation leads to changes in the physical and chemical properties of the backfill. In particular carbonation can lead to armouring of cracks – there is permeability reduction at the crack surface. This can change the accessibility of the backfill matrix to water and gas flows, affecting retardation of solute and gas transport. Bulk carbon dioxide will be generated from the degradation of organic-containing (e.g. cellulosic) wastes. | Develop understanding of the consequences of carbonation on the properties of the backfill. The authors note that work is currently ongoing on the effects of carbonation on backfill in the NDA programme. |</p>
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<td>Effect of groundwater on backfill ability to condition porewater to high pH as the backfill ages, alters and degrades.</td>
<td>Significant understanding has been developed of the effects of salinity and major groundwater components on backfill reactions and dissolution rate. Uncertainties mainly concern the evolution of the cementitious mineral phase assemblage. Ongoing international work to increase understanding, e.g. experimental studies and derivation of thermodynamic data under CEMDATA project. Thermodynamic modelling has been applied to predict evolution of backfill with continuing groundwater flow and its effect on the conditioned porewater. Improved model representations of C-S-H phases as solid solutions have been developed. However, some solid phase components such as C-S-H phases are not thermodynamically stable but are long-lived. Kinetics of their transformation to stable forms may not be accessible on laboratory timescales.</td>
<td>Type, extent and rate of reactions is very dependent on site-specific groundwater and flow rates. High $PCO_2$ groundwaters will lead to greater carbonation, and high sulphate will lead to the formation of ettringite or gypsum and potential cracking. Extent of effect on pH-buffering capacity is very dependent on UK wastes and packaging concepts.</td>
<td>Application of reactive transport modelling to scope the effects of groundwaters in support of site selection. Assess the need for further understanding when site selected and groundwater known, including the effects of groundwater flow rate and chemistry. Follow or participate in thermodynamic data developments under CEMDAT and NEA thermodynamic database project. Use of natural/industrial analogues for validation of long-term understanding and evidence of persistence of thermodynamically unstable solids.</td>
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<td>Effect of waste-form components on backfill ability to condition porewater to as the backfill ages, alters and degrades.</td>
<td>A wide range of potential reactions with waste components can lead to backfill consumption and reduce its pH-buffering performance in the long term.</td>
<td>Spreadsheet tools for evaluating backfill consumption have been developed for application to particular waste packages (all identified components) and to the vault scale (major inventory and wasteform components) with a choice of illustrative groundwater compositions.</td>
<td>Consider wider range of waste components on vault-scale calculations of backfill consumption. Update pH spreadsheet tools with more recent design and inventory information and with site-specific groundwater composition and flow at appropriate stages of the MRWS process.</td>
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<td>Effect of cements on host rock</td>
<td>The impact of cement on the rock is mediated by the groundwater, leading to changes in physicochemical properties of the rock. Potentially this may affect flow patterns around the GDF.</td>
<td>This is a site-specific issue.</td>
<td>Laboratory and underground experiments at appropriate stage.</td>
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<td>Chemical and physical heterogeneity in near field due to backfill cracking, carbonation, waste and wasteform distribution and location relative to flow.</td>
<td>Some understanding of likely cause and width of cracks. Modelling calculations of porewater mediated chemical interactions of backfill with encapsulation grouts. Potential combination of cracking with groundwater flow providing preferred pathway for radionuclide release. Limited modelling. Heterogeneity in porewater conditioning due to distribution of waste types within vaults.</td>
<td>Wide range of waste and waste-form types and relatively high flow rate (if in hard rock) make issues potentially significant.</td>
<td>Assessment of types of heterogeneity on near-field performance. Identify and develop areas where understanding of various near-field processes needs to be integrated. Consideration of scenarios for cracking patterns that may give enhanced release. Effect of carbonation of preferential pathways and lowering of pH in cracks. May be mitigated by sealing effects associated with carbonation.</td>
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<td>pH-buffering performance of cementitious backfills</td>
<td>Two main periods can be identified during backfill evolution: (i) portlandite present and accessible to porewater, where controls on the pH (and porewater chemistry) are well understood; (ii) portlandite exhausted or inaccessible, where there is significant uncertainty over the type and crystallinity of pH-buffering phases. Application of reactive transport programs has demonstrated a methodology for prediction of the spatial and temporal pH evolution in cementitious vaults, and the associated mineralogical changes. Short-term elevated temperatures may lead to an increase in the crystallinity of amorphous cementitious phases such as C-S-H due to hydrothermal alteration. Existing experimental data suggest this will significantly reduce the pH once portlandite is exhausted. It is possible that the increase in crystallinity may occur more slowly without elevated temperature</td>
<td>For current performance assessment approach, confidence is required that pH remains above pH 9. For hard rock concepts, with relatively high groundwater flow rate, portlandite exhaustion will occur earlier so that period (ii) needs to be considered on performance assessment timescales. Confidence that pH remains above pH 9 during this period is required. For clay-based concepts, only period (i) is likely to be significant. Hydrothermal alteration is potentially more significant in hard rock concepts where the period of buffering by excess portlandite is lower.</td>
<td>Extension of reactive transport modelling studies. Improved thermodynamic data and understanding from experimental programmes. Develop understanding of the evolution of C-S-H phases (crystallinity development) and more complex cementitious systems (such as C-A-S-H phases) over longer timescales than hitherto.</td>
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<td>Sorption mechanisms</td>
<td>Understanding of sorption mechanisms is important because it underpins the</td>
<td>Most of the work on sorption to backfills undertaken in the UK has used freshly-cured</td>
<td>Develop understanding of sorption mechanisms to backfill cement.</td>
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<td>treatment of sorption processes in the DSSC. Although the extent of sorption</td>
<td>NRVB using the empirical batch sorption technique to measure $R_d$ values. A limited</td>
<td>Develop understanding of the effects of cement backfill evolution on sorption.</td>
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<td>of many radionuclides with cements is known, detailed understanding of the</td>
<td>number of sorption-diffusion type studies have been undertaken with NRVB, but no</td>
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<td>mechanisms of interaction is often lacking. New spectroscopic techniques have</td>
<td>mechanistic studies to date. Some data are available for sorption of radionuclides</td>
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<td>become available that provide new insights into radionuclide behaviour and</td>
<td>to hydrothermally aged NRVB.</td>
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<td>these have been applied on overseas programmes to study sorption to cements.</td>
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<td>This is helping to improve the understanding of sorption mechanisms but further</td>
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<td>understanding is needed especially concerning the long-term fate of</td>
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<td>radionuclides. The high pH generated by cement backfills reduces the</td>
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<td>solubility of many key radionuclides (e.g. Pu(IV), Th, Am) and makes</td>
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<td>experimental studies of sorption mechanisms difficult because samples with</td>
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<td>only low concentrations of sorbed species can be prepared. However, modelling</td>
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<td>techniques are available for a range of uptake mechanisms. There are many</td>
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<td>data regarding sorption onto relatively fresh cements, but equivalent data for</td>
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<td>‘aged’ cements representing the later stages of cement evolution are often</td>
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<td>lacking. Further understanding of cement mineral phase and surface area</td>
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<td>evolution may be required, but more sorption measurements are required on</td>
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<td>‘aged’ cements that have been fully characterised.</td>
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<td>Sorption of chemotoxic species</td>
<td>Although the extent of sorption of radionuclides is generally well known, there are several important chemotoxic species whose sorption behaviour is unknown or poorly established, including beryllium and chromium. Adequate understanding of principles, but more data are required where chemical analogies cannot be used.</td>
<td>A range of chemotoxic species are present in the UK ILW/LLW inventory. Current assessment is sometimes based on drawing chemical analogies with compounds for which data is available. Key chemotoxic species identified in recent assessments include beryllium and chromium.</td>
<td>Develop understanding of the sorption of chemotoxic species to backfill cements to support chemotoxicity assessments.</td>
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<td>Influences on sorption to cements - complexants</td>
<td>Complexation by organic compounds can increase the effective solubility and decrease the extent of sorption of radionuclides to the cement backfill. The most important source of organic complexants arising from ILW is expected to be the degradation of cellulose under alkaline anaerobic conditions. These materials have been found to be strong complexants of radionuclides, in particular actinides, and high concentrations can reduce sorption to cements by an order of magnitude or more. Superplasticisers being considered as additives in cements for a number of GDF applications contain components that may act as complexants. Some of these materials have been shown to act as strong complexants when added directly to radionuclide solutions. However, due to the strong interactions that these materials have to cements, it is not yet clear whether these materials would have a significant detrimental effect on radionuclide behaviour if present in EBS materials.</td>
<td>A wide range of organic materials is present in UK wastes, some of which may have the ability to complex radionuclides or degrade to form complexants. Empirical batch sorption data are available for the sorption of a range of radionuclides to NRVB in the presence of a number of complexants, in particular cellulose degradation products. Superplasticisers are being considered as additives in a range of cement formulations for use in GDF applications both in the UK and internationally. UK studies on the potential impact of PEG superplasticisers on radionuclide behaviour have to date focussed on the impact of ADVA Cast 550/551 on radionuclide solubility.</td>
<td>Develop understanding of the effects of complexants on radionuclide sorption to cement backfill and their mechanisms of interaction. Work is in progress on the NDA programme to develop understanding of the potential impact of superplasticisers on radionuclide retardation in the near field.</td>
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### Table 32  Key topics concerning cements in sealing and structural applications

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<td><strong>Design and specification of structural elements of the EBS</strong></td>
<td>The structural elements will need to comply with conventional construction codes. These leave considerable latitude in the choice of formulations and allow for different systems of construction. For example, tunnel linings are sometime prefabricated under factory conditions and sometimes formed <em>in situ</em>. The method selected influences specification and delivery.</td>
<td>The functional specifications for structural elements of the EBS system will depend on the host geology and will form an integral part of the GDF design.</td>
<td>Development of the designs and specifications of the structural elements for the GDF as the programme progresses.</td>
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<td><strong>Mechanical performance of structural cements</strong></td>
<td>The importance of mechanical performance varies depending on the function of the cement in the EBS system. For example, a high compressive strength is required for load-bearing concretes such as shotcretes used for tunnel and vault linings. A wide range of mechanical properties may be achieved for cementitious systems, from very low strength backfill material to very high strength material where load bearing capacity and stiffness are critical. While the strength and the stiffness are related, the relationship is not universal and is affected by the amount and type of aggregate and/or sand that is used and by the cement type itself. To a large degree it is possible to customise a concrete mix to meet a wide range of specification requirements. However, general civil engineering experience may be of limited value when assessing their long term performance.</td>
<td>The chemical and physical stresses experienced by EBS cement formulations in the service conditions of the GDF environment will be both site specific (determined by the nature and properties of the host rock) and by the design of the excavations (geometry, size, etc). For cement-based ILW disposal concepts, different cement formulations (e.g. tunnel linings and waste encapsulation grouts) will be in close physical proximity to the backfill and may exhibit coupled reactions. The potential interactions between cements and the impact on their mechanical properties may need to be considered.</td>
<td>Developing understanding of the evolution of cement mechanical properties in response to physical and chemical stresses, including chemical interactions with other cement materials. This might involve the development of modelling approaches as well as test methods that accelerate the evolution of cement properties.</td>
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<td>Effect of cements on other EBS materials - bentonite.</td>
<td>Reaction of alkaline cement pore fluids with bentonite may result in changes in bentonite porosity, swelling pressure, hydraulic conductivity, and sorption capacity. Bentonite-cement interactions include complex, non-linear processes, making it difficult to extrapolate the results of laboratory experiments to the timescales of interest for the safety case. Design and use of low-calcium (low-pH) cements has been proposed to mitigate these effects. Development and testing of these materials has been undertaken on other programmes and in particular through the ESDRED project. Cement paste is replaced by at least 20% silica fume, to produce cements with a leachate of pH ≤ 11. Reactive transport models have been developed that may be used to predict the pH-evolution behaviour of low-pH cements and the evolution of mineral assemblages in bentonite in contact with cement porewaters. However, there are uncertainties associated with the data available for such modelling, such as the growth rates of mineral alteration products.</td>
<td>Disposal concept adopted for HLW/SF may include bentonite as a buffer to surround the waste packages. Some EBS materials in proximity to bentonite will be cement-based. These may include fracture grouts, tunnel linings and floors, and tunnel seals. The rate at which cement-bentonite interactions progress is likely to be dependent on the rate of groundwater flow in the host rock. Different cement formulations may be used in different parts of a GDF depending on pH-leaching requirements.</td>
<td>Develop understanding of the pH-leaching behaviour of low-pH cement formulations developed for EBS applications. Develop understanding of the evolution of mineral assemblages in bentonite in contact with cementitious materials. Participation in ongoing and future international projects and relevant natural analogue studies.</td>
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<td>Fracture sealing grouts</td>
<td>Fracture sealing grouts are widely used in the construction industry and traditional grouts may be suitable for application in those parts of a GDF where there are no GDF-specific requirements on materials performance (e.g. no pH-leaching requirement). In the context of a GDF for SF with a bentonite buffer located in a fractured hard rock, low-alkali cement grouts have been developed by SKB and Posiva for host rocks where fracture apertures exceed 100 µm and these have been extensively tested at ONKALO and through the ESDRED Project.</td>
<td>Whether or not fracture sealing grouts are required in a UK GDF will depend on the geology and hydrogeology of the site selected. Excavation damage may require stabilisation, however. The required operational lifetime for seals that are emplaced during the construction of a GDF will depend on the site. Thus the specifications for sealing materials are expected to be site specific. The pH-leaching requirements of a grout in different parts of a GDF containing co-located ILW and SF/HLW may be different and thus, differing grouts might be used in different locations (as in ONKALO).</td>
<td>Development of fracture sealing grouts as the programme progresses.</td>
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<td>Shotcrete tunnel and vault linings and rock bolt mortars</td>
<td>Shotcreting techniques for the emplacement of concrete tunnel and vault linings are widely used in the construction industry. Conventional techniques and construction materials may be suitable for application in those parts of a GDF where there are no GDF-specific requirements on materials performance (e.g. no pH-leaching requirement). For disposal concepts that incorporate a bentonite buffer, low-alkali shotcretes and rock bolt grouts have been developed and tested through the ESDRED project.</td>
<td>Performance requirements of tunnel and vault linings will be dependent on the design and geology of a UK GDF. In the case of a vault lining, the loads on the concrete will depend very specifically upon the design (geometry, size, etc) and on the geology (e.g. rock creep in the host rock). Limiting values would therefore have to be developed as part of the design process. The pH-leaching requirements of tunnel and vault linings in different parts of a GDF containing co-located ILW and SF/HLW may be different and thus, differing concretes might be used in different locations (as in ONKALO).</td>
<td>Development of shotcrete tunnel and vault linings and rock bolt mortars as the programme progresses.</td>
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<td>Sealing plugs</td>
<td>Low-alkali concretes have been developed for seals and plugs. These can be installed by shotcreting methods or by using ‘self-compacting’ compositions. A number of prototype designs of tunnel plugs constructed from different concrete formulations have been tested successfully in underground research laboratories on international programmes (e.g. TSX, FEBEX and ESDRED).</td>
<td>Performance requirements of sealing plugs will be dependent on the design and geology of a UK GDF. Different demands may be placed on sealing plugs in different parts of the facility and therefore specifications may be different.</td>
<td>Development of sealing plugs as the programme progresses.</td>
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<td>Long-term reactions of cement with fillers and aggregates</td>
<td>Many of the low-pH formulations proposed and developed for sealing and structural applications in a GDF are based on Portland cements mixed with SCMs and/or aggregates. These materials exhibit a range of reactivity with cement, ranging from rapid (hours, days) to extremely slow (perhaps decades), to inert and unreactive. The immediate consequences of using low-pH concrete formulations are largely beneficial. However, the longer term consequences of using large quantities of slowly reactive aggregates such as silica fume and fly ash are not well understood. For example, the mineralogy, and with it the physical properties and pH-buffering behaviour, may change, but the extent and direction of change are not yet known.</td>
<td>Potential formulations for cement-based seals and structural concretes in a UK GDF are likely to incorporate cement fillers and aggregates. The operational lifetimes for grouts and structural concretes emplaced in a GDF during construction are not yet known but will depend on a number of factors that will determine the full operational timescale of the GDF, including the size of the waste inventory, the handling capacity of the facilities, the rate at which wastes become available for disposal and timescales for backfilling, sealing and closure.</td>
<td>Develop understanding of the evolution of low-pH concrete formulations under UK disposal conditions to demonstrate mechanical and sealing performance over required timescales. Develop understanding of mineralogical evolution to demonstrate low alkalinity of leachates in the long term.</td>
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15 References


[40] British Standards Institution, BS EN 197-1: *Cement — Part 1: Composition, specifications and conformity criteria for common cements*.


