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A Catalogue of Natural Analogues for NWS

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Abstract

The successful implementation of plans to develop a geological disposal facility (GDF) for radioactive waste in the United Kingdom will require an assessment of the ability of a facility to meet appropriate regulatory safety criteria at all stages during its construction, operation and after closure. An associated environmental safety case (ESC) will contain a collection of claims, arguments and evidence (CAE) for which both quantitative and qualitative evidence is presented, which collectively demonstrate that long-term safety can be achieved and maintained. Analogues, whether natural, archaeological or industrial, can be helpful in demonstrating understanding of aspects of GDF performance by, for example, providing evidence that certain materials can survive for long periods. Appropriate analogues can be helpful in providing a long-term practical demonstration to support the theoretical and mathematical arguments and they may have a significant role in the overall process understanding. Natural analogue (NA) studies are examples and, in this updated version of the previous NA Catalogue (Milodowski et al. 2015), are presented in connection with the generic design of the GDF in the UK. Continuous iteration of the knowledge base is needed when moving from the generic phase to more detailed GDF designs and potential sites.

Keywords

Natural analogue, geological disposal facility, radioactive waste management, geological repository, long-term safety, safety case, geology, waste container, copper, steel, clay, bentonite, cement, concrete, host rock, high strength rock, low strength sedimentary rock, evaporite, biosphere, closure, backfill, sealing

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FOREWORD

This report is an update and for a major part a rewrite of the previous NA Catalogue by Milodowski et al. (2015). Most of the report was produced by the editors of the report. GTK experts (Jon Engström, Mira Markovaara-Koivisto, Ismo Aaltonen and Timo Ruskeeniemi) are acknowledged for their input related to climate-forcing and ice-age scenario discussion in chapter 7.

CONTENTS

1 INTRODUCTION

1.1 Background

The successful implementation of plans to develop a geological disposal facility (GDF) for radioactive waste in the United Kingdom will require an assessment of the ability of a facility to meet appropriate regulatory safety criteria at all stages during its construction, operation and after closure. An associated environmental safety case (ESC) will contain a collection of claims, arguments and evidence (CAE) for which both quantitative and qualitative evidence is presented, which collectively demonstrate that long-term safety can be achieved and maintained.

It is not possible to simulate in, or extrapolate from, laboratory and URL studies the long-term (and large-scale) processes that might affect the safety performance of a GDF. In this context, evidence from some natural systems (including archaeological and older industrial systems) can be helpful in demonstrating understanding of those aspects of GDF performance which cannot be reasonably assessed in short-term and small-scale laboratory and URL experiments and can provide evidence that, for example, certain materials can persist for the long periods relevant to the post-closure timescale for a GDF.

As noted in Reijonen & Alexander (2023a), The generally accepted definition of the term “natural analogue” (NA) is "...*an occurrence of materials or processes which resemble those expected in a proposed geological waste repository*” (Côme & Chapman 1986). This has subsequently been refined by an International Atomic Energy Agency review group (IAEA 1999) as *“Natural analogues can include both natural and human-made materials provided the processes that affect them are natural. Thus, studies of archaeological and historical artefacts, ancient buildings, anthropogenic sources of radionuclides such as nuclear weapons fallout, and examples of pathways in plants and animals can be regarded as natural analogue studies.”*. The progressive refinement of the definition reflects a maturation in the understanding and appreciation of NAs. In essence, NA studies use information from the closest possible approximations, or direct analogies, of the long-term behaviour of materials and processes found in, or caused by, a GDF to develop and test models appropriate to the safety assessment. Detailed subdivision of NAs used in this report is provided in section 1.2 below.

Analogues, whether natural, archaeological or industrial, can be helpful in demonstrating understanding of aspects of GDF performance by, for example, providing evidence that certain materials can survive for long periods. Appropriate analogues can be helpful in providing a long-term practical demonstration to support the theoretical and mathematical arguments and they may have a significant role in the overall process understanding. NA studies are examples and, in this updated version of the previous NA Catalogue (Milodowski et al. 2015), are presented in connection with the generic design of the GDF in the UK. Continuous iteration of the knowledge base is needed when moving from the generic phase to more detailed GDF designs and potential sites (see Reijonen & Alexander, 2023a, for discussion), therefore, the update presented here serves as a starting point (Figure 1-1).

NA studies are often used as one of multiple lines of reasoning that, when combined with the understanding from laboratory and URL studies, help to build confidence in process understanding as considered in the safety case (SC). In this report the definitions provided below apply. However, it must also be noted that NAs also have limitations and these have been presented elsewhere (e.g. Miller et al., 1994, 2000; Alexander et al., 2015; IAEA, 2017) and are discussed in more detail in Reijonen & Alexander (2023a). Finally, for each example presented here, limitations on the use of the derived data are also provided.

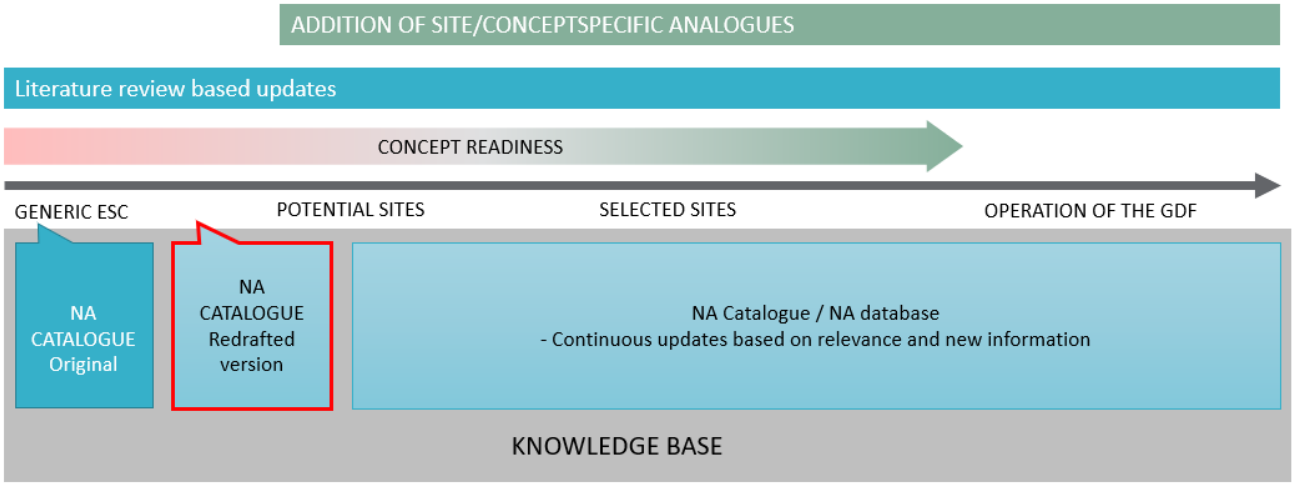

Figure 1-1. NAs form a part of the knowledge base that goes through iterations throughout the evolving GDF programme from the generic stage to operation of the GDF. Current report marked with red outline.

1.2 Definitions

In this report, the following terms are used to define the type of analogue:

- **Natural analogue**: a site where longevity of repository relevant material or host rock type has been studied for one or several safety relevant processes.
- **Regional (or self) analogue**: as noted in Alexander et al. (2015) "A self-analogue is a case where some feature of a repository site is studied to provide information on long-term repository relevant processes. For example, definition of the likely long-term behaviour of bentonites utilised in the EBS and backfill of a deep geological repository can best be carried out by examining smectite samples from candidate repository sites. Such a self-analogue has several advantages in that the site boundary conditions, including palaeohydrological evolution, are usually much better characterised than most NA sites due to the much greater site characterisation budgets involved. In addition, there is clearly enhanced confidence that the results are directly site relevant, unlike data from areas which do not share the repository site's geological history." As noted in Alexander et al. (2014), such studies are usually classified as a self or regional analogue and, here, it is felt that the term 'regional analogue' is more appropriate than 'self analogue', especially as this approach should encompass the entire geological barrier of a particular site and not just the host rock (see also Reijonen & Alexander, 2023a, chapter 2).
- **Archaeological analogue**: a study of an archaeological artefact of repository relevant materials or processes, shorter time frames than in natural analogues, but the materials (e.g., Roman concrete, see section 4.1.2) may be a closer analogy .
- **Industrial analogue:** analogue that covers an even shorter time frame, for example, relatively recent industrial examples of longevity of materials. Once again, the materials (e.g. OPC, see section 2.1.4) may be a closer analogy.

1.3 Objectives and scope of the updated NA catalogue

The main objective of the NA Catalogue is to produce examples of analogue systems that can be used to support the SC for a GDF. Its scope includes all aspects of disposal relevant to the UK programme; a range of waste types and potential GDF host rocks are considered.

For each NA example, the following information is provided:

- Item number for individual catalogue entries
- An introduction on the topical matter
- Component of relevance for the GDF
- Key IFEPs of relevance (NEA FEP list v 3.0, 2019, available at https://www.oecd-nea.org/fepdb)
- A summary description of the NA example
- A summary of limitations of the use of the NA
- Statements of relevance on the NA(s), what have we learnt?

A range of analogues have been selected to illustrate different components of a GDF system that could be used to support a generic SC and, as such, the catalogue is not an exhaustive list of all known NAs. The catalogue is supported by chapter (13) that lists potential future work to support the SC.

The updated catalogue differs from the previous catalogue as there has been a clear shift towards connecting the catalogue directly to the ESC and other NWS activities (such as the siting programme). The catalogue contents are directly used in the NWS ViSI system, which allows cross-referencing to various related content. The catalogue entries include internal cross references, links to IFEPs and references to the NWS bibliography within ViSI. The NWS keyword list and glossary have been used as a guide for the terminology.

The aim is that, while the NAs can be linked to and from other parts of the NWS documentation, the NA catalogue can also be read as a full self-standing report. As the audience for the catalogue is mainly NWS staff, the aim has been to include the studies most useful to the UK programme and indicate where further activities could be undertaken.

1.4 Catalogue organisation and structure

The catalogue is organised based on overall topics that are set around components of the GDF system as follows:

In chapter 1, the NA catalogue update is introduced

- Chapter 2 provides a review and update of NAs related to waste forms
- Chapter 3 provides a review and update of NAs related to waste containers
- Chapter 4 provides a review and update of NAs related to cementitious materials
- Chapter 5 provides a review and update of NAs related to clays
- Chapter 6 provides a review and update of NAs related to the GDF host rock
- Chapter 7 provides a review and update of NAs related to post-closure processes affecting the GDF and/or host rock
- Chapter 8 provides a review and update of NAs related to radionuclide retardation in geosphere
- Chapter 9 provides an overview of an added topic on the NAs related to other EBS materials (such as closure, sealing and borehole seal materials)
- Chapter 10 provides an overview of an added topic on the NAs related to operations (operational analogues)

- Chapter 11 provides an overview on the NAs related to whole system performance
- Chapter 12 provides an overview of an added topic on the NAs related to the biosphere
- Chapter 13 compiles the potential future studies based on the gaps identified in the review
- Chapter 14 concludes the main findings of the review/update work

References are provided individually for each section.

The contents of the catalogue are organised in a manner that allows updates in the future. The topics presented at 1st level headings then have an overview of the topic included under 2nd level headings (Table 1.4-1). In this text, more detailed design descriptions can be linked later on when new NA results are available in the future. For each topic, examples of NAs are provided and only those examples considered relevant for the current stage of NWS' GDF programme are included. Following the strategic use of NAs presented in Reijonen & Alexander (2023a), the content of this catalogue can be updated in the future based on relevance screening[1] (e.g. against selected site / design). The content is hierarchical, but metadata have also been included in the form of GDF components and FEPs (IFEPS). Other metadata can be added later as deemed necessary. For this process, please see Reijonen & Alexander (2023a) for a proposed methodology.

In this report, emphasis has been given to potential future work in Chapter 13. The aim is that any new results can readily be added to the catalogue. The contents can easily be converted in a database form, e.g. for Visi purposes, where each NA description is a database entry.

Table 1.4-1. Overall topics and NA examples forming a hierarchical system that can be updated in the future.

	Topic	NA examples
NA Catalogue update	**Waste Forms** Waste forms Criticality	Examples provided Can be updated in the future (see Chapter 13)
	Containers copper steel other materials	
	Cementitious materials	
	Clay materials	
	Geological barriers (including the host rock) HSR LSSR Evaporites	
	Post-closure processes affecting GDF Climate forcing and ice age scenarios Radiolysis Alkaline disturbance	
	Radionuclide retardation in natural systems	Overview provided Additional examples can be added in the future (see Chapter 13)
	Other EBS materials	
	Operational analogues	

[1] The screening in this case has only been carried out in a report format, in future it would clearly be more useful to do so in a digital form with the ViSI tool.

	Whole system performance	Overview provided No foreseen additions
	Biosphere	Overview provided Can be updated in the future

1.5 Connections to other NWS activities

1.5.1 Use of natural analogues in the safety case

In parallel to updating the NA catalogue, the overall strategy for utilising the NA information in the NWS GDF programme has been drawn up. The background and discussion regarding the lessons learnt on the NAs used and existence (or non-existence) of strategic thinking in this regard is presented in its own dedicated report (Reijonen & Alexander, 2023a).

1.5.2 RWM science and technology plan 2020

RWM (2020) mentions NAs as a potential part of the research and development for several topics and these are mentioned in the NA catalogue where relevant.

1.5.3 Implementation to NWS knowledgebase via ViSI

This report has been produced in collaboration with ViSI development and fully implemented in the ViSI tool. PDF versions are extracted from ViSI.

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2 WASTE FORMS

2.1 Overview on the waste forms and analogues

In general, natural analogues of various waste forms focus on vitrified waste and spent fuel (see sections 2.1.1 and 2.1.2). NWS considers a wider range of wastes for the UK GDF (see e.g. Rendell 2017 and Table 2.1-1 for compilation), including (wording from Rendell 2017):

- **HLW** – defined in the UK as waste in which the temperature may rise significantly as a result of its radioactivity, such that this factor has to be taken into account in the design of the disposal facilities. HLW arises as a by-product from the reprocessing of spent fuel at Sellafield.
- **ILW** – defined in the UK as waste with radioactivity levels exceeding the upper boundaries for LLW, but not generating sufficient heat for it to be taken into account in the design of storage or disposal facilities. ILW arises from the reprocessing of spent fuel at Sellafield, general operations and maintenance at existing and future nuclear power stations, decommissioning works, and from defence, medical, industrial and educational activities.
- **LLW** – consists largely of paper, plastics and scrap metal items that have been used in hospitals, research establishments and the nuclear industry. A small fraction of the total volume of LLW cannot be sent to the LLWR in Cumbria for disposal, due principally to higher than permissible concentrations of specific radionuclides, and will therefore need to be disposed of in the GDF.
- **Spent fuel** – currently arises in the reactors of operational power stations. Spent fuel is either reprocessed or stored pending decisions about its future disposal; spent fuel from Magnox reactors is currently reprocessed; spent fuel from AGR is either reprocessed or stored; and spent fuel from PWR is stored. Stored spent fuel, spent fuel yet to arise from the operational power stations and spent fuel from a new nuclear build programme may be declared as waste and are therefore included in the inventory for disposal for planning purposes. There is also some stored spent fuel from research reactors, and spent fuel from submarines.
- **Plutonium** – stocks of separated plutonium have been obtained from the reprocessing of spent fuel and are currently housed in safe and secure storage facilities. The Government's preferred policy for the long-term management of plutonium is for it to be re-used in the form of mixed oxide (MOX) fuel in civil nuclear reactors. Residual plutonium not re-used in new fuel manufacture may in future be declared as waste and is included in the inventory for disposal.
- **Uranium** – uranium stocks arise from fuel manufacture, enrichment processes or reprocessing of spent fuel and are stored securely, in different forms, at a number of nuclear sites. Uranium stocks are categorised as either HEU – Highly Enriched Uranium, defined as uranium with a fissile content (U-233 or U-235) of greater than 20%, or DNLEU (Depleted, Natural and Low-Enriched Uranium)– which comprises all types of uranium apart from HEU. These materials may be declared as waste and are therefore included in the inventory for disposal.

A short overview is provided on the status of the MOX and other plutonium fuels (see section 2.3). In addition, criticality is discussed separately in section 2.2.

Non-radiological hazardous substances are considered by NWS, but are not included in this report update.

Table 2.1-1. Derived Inventory waste groups (Table 2-1 in Rendell 2017).

	Waste groups	**Subdivision (if applicable)**
Low Heat Generating Waste LHGW[2]	Legacy LLW and ILW packaged in shielded containers	
	Legacy LLW and ILW packaged in unshielded containers	
	Wastes packaged in 500 litre robust shielded drums and 3 cubic metre robust shielded boxes	
	DNLEU	
	New build ILW packaged in shielded containers	
	New build ILW packaged in unshielded containers	
High Heat Generating Waste HHGW	HLW	
	Plutonium	
	HEU	
	Legacy spent fuels	Spent fuel from AGRs
		Exotic spent fuel
		Metallic spent fuel
		Spent fuel from Sizewell B PWR
	New build spent fuels	
	MOX spent fuel	

References

Rendell 2017. Geological Disposal: Technical Background to the generic Disposal System Safety Case. NDA Report no. DSSC/421/01. RWM, Harwell, UK. ISBN 978-1-84029-560-3. 77p.

2.1.1 Longevity of vitrified high-level waste

Item:

NA2.1.1

Component(s):

High Heat Generating Waste (HHGW), High Level Waste (HLW), Vitrified [Glass]

2.1.1.1 Introduction

Glass was first proposed as a matrix for high-level radioactive waste (HLW) disposal in the 1950s. The current production method for HLW generated within the UK is to dissolve the spent fuel and mix it with borosilicate

[2] Novel approaches to processing LHGW are being developed, including vitrification. Although no NAs for glass interactions with alkaline solutions of relevance to vitrified LHGW are currently available, relevant sites do exist.

glass forming minerals to form a glassy product (vitrification).. Vitrification plants are currently in operation at Sellafield (UK), Marcoule and Cap de la Hague (France), Savannah Rivers (USA) and Rokkasho (Japan). Plasma-oven vitrification of low- and intermediate-level waste (L/ILW) is also currently ongoing in Taiwan and Switzerland (Heep 2011).

Vitrification incorporates liquid HLW into the glass and the vitrified wastes are encapsulated in metal containers for storage prior to final disposal (Figure 2.1.1-1). The attraction of glass as a waste form stems from its physical and chemical durability under conditions expected in a GDF, its ease of production and the relative insensitivity of the vitrification process to waste stream composition (cf. Lutze & Ewing 1988).

Borosilicate glass (incorporating 15-25 wt. % B_2O_3) is the most common vitrified waste form because of its stability and relatively low formation temperature (about 1,100 ºC), which minimises waste losses as a result of volatilisation during manufacture. Although a relatively stable waste form, all glasses degrade with time and there is a significant body of laboratory and modelling work concerned with the durability of borosilicate glass waste forms under GDF conditions (e.g. Chinnam et al. 2018).

Figure 2.1.1-1. Section through a steel canister containing vitrified HLW (http://nuclearstreet.com/images/img/dw117.jpg)

IFEPS:

2.1.2.4 - Immobilisation matrix

2.4.1.1 - Dissolution [waste form]

NA Type:

Natural analogue

2.1.1.2 NA description

Natural glasses have been studied as analogues of vitrified HLW for more than half a century (cf. Marshall, 1961), with particular emphasis placed on defining dissolution processes, their rates and on determining the nature of solid secondary alteration products (Miller et al. 2000). They are relatively common and include volcanic glasses, meteorite impact glasses and tektites and they form when molten rocks cool so quickly that crystals cannot form in the melt.

Most natural glasses have similar bulk compositions to those of 'normal' igneous rocks, ranging from silica-poor (basaltic composition) to silica-rich (obsidian, see Figure 2.1.1-2). Previously, obsidian was investigated in more detail because it is more like the high-silica, low-alkali waste glass formulations being developed several decades ago as a waste isolation matrix. However, the basaltic glasses are more similar to the current formulations and are now generally considered to be the most appropriate analogues for the borosilicate HLW glasses (Havlova et al. 2008). Some archaeological glasses are coloured with metal oxides, including up to 5 wt% uranium in some glasses. These could provide useful information on uranium leaching and incorporation in secondary alteration products, but no such quantitative analogue studies are known to have been undertaken to date (see also Table 13.1, IDs 2.1.1-1 and 2.1.1-2).

Figure 2.1.1-2. Obsidian from the Ross of Mull, Scotland (Anderson and Radley, 1915). Note the grey-white spherical zones of devitrification within the otherwise glassy matrix in this approximately 60 million year old glass (H.A.Alexander, Bedrock Geosciences, Switzerland).

Like archaeological glasses, natural glasses lack the high B_2O_3 and radionuclide content of vitrified HLW (Miller et al. 2000). Although some natural glasses enriched in uranium have been reported, no systematic natural analogue study of these glasses has been carried out to date. The surface degradation products on marine natural glasses are often enriched in uranium, reflecting uptake of dissolved uranium from seawater (MacDougall 1977), possibly in a manner similar to that which might be expected in the uptake of radionuclides released from vitrified HLW.

Natural glasses (Figures 2.1.1-2 and 2.1.1-3) tend to be found in chemically reactive, oxidising conditions in submarine or subaerial environments where conditions are significantly different to the predominantly passive, reducing conditions in a GDF. These differences mean that it is not realistic to directly apply a degradation rate derived from a natural glass to a man-made waste-bearing glass in the GDF safety case. Nevertheless, comparison between natural degradation of basaltic glasses and degradation of borosilicate glasses induced in the laboratory qualitatively suggest that the two glass types degrade by the same mechanisms, if not at the same rates (Miller et al. 2000).

Figure 2.1.1-3. Basaltic pillow lavas from Cyprus. The outside of the pillows vitrifies as the molten lava hits seawater. The white rim around each pillow represents devitrified glassy margins in this approximately 200 million year old lava (W.R. Alexander, Bedrock Geosciences, Switzerland).

Generally, natural glasses are younger than 25 million years old, but rare exceptions have been reported – 1,100 million years old from Canada and 3,700 million years old from the moon (Husain and Schaeffer, 1973) – and their extreme longevity has been ascribed to the very dry environments in which they were found.

Examination of 425 natural glasses from North America indicated that more than half were younger than 2 million years old, but some were as old as 40 million years (Ewing 1979). Although data on the glass and groundwater compositions are not available, the average natural glass age of around two million years is significantly longer than the time periods relevant to radioactive waste disposal. As such, these data can be used to support the qualitative conclusion that complete degradation of vitrified HLW is unlikely to be a significant problem over the timescales of concern to a deep GDF in the UK.

2.1.1.3 Uncertainties and limitations

- The near-surface environments in which most natural glasses are found are of little relevance to those of a deep GDF, and are generally much more aggressive than would be expected at depth;
- The boundary conditions that have controlled the alteration of glass are often difficult to define. For example, precisely how has the groundwater chemistry changed with time over the life of the sample? This is a general observation that can be applied to many analogue systems;
- Although natural glasses with a high radionuclide content exist, none have been examined to date, so the direct analogy to vitrified HLW could be improved

2.1.1.4 Relevance – what we have learnt?

- Natural Analogue studies on basaltic glasses provide useful qualitative information on glass degradation processes which can be used in the safety case to constrain conceptual models for vitrified HLW evolution
- Natural glasses studied to date have been found in more aggressive environments than would be expected in a GDF, so the degradation rates are expected to be much higher than for vitrified HLW, but they nevertheless provide useful upper limits for HLW dissolution
- The general longevity of natural glasses provides additional confidence that rapid degradation of a carefully-designed vitrified HLW is unlikely to occur during the safety critical period of a GDF
- Uptake of dissolved uranium on natural glass surface degradation products suggests that radionuclides released from vitrified HLW could also be trapped on similar secondary degradation phases on the waste form.

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2.1.2 Longevity of spent fuel, radiolysis and fuel dissolution at Cigar Lake

Item:

NA2.1.2

Component(s):

High Heat Generating Waste (HHGW), Spent Fuel (SF)

2.1.2.1 Introduction

The fuel burned in most nuclear power plants is crystalline UO_2, although some reactor designs such as the Magnox reactors in the UK (along with Italy, Japan and North Korea) burn metallic uranium fuel. Metallic uranium does not occur in nature and consequently there are no natural analogues, so metallic uranium is not considered further. Spent fuel analogues include naturally occurring uranium minerals uraninite and, to a lesser extent, pitchblende. Crystallographically, spent fuel and uraninite are essentially identical; both are cubic, having the same structure as fluorite.

IFEPS:

2.1.2.3 - Non-metals, inorganics

2.1.2.4 - Immobilisation matrix

2.4.1.1 - Dissolution [waste form]

NA Type:

Natural analogue

2.1.2.2 NA description

As noted in section 1.2 of Milodowski et al. (2015), NA data on spent fuel corrosion rates, dissolution rates and radiolytic oxidation have been used to support numerous safety cases over the last 40 years. Radiolysis studies at Cigar Lake, Canada (Figure 2.1.2-1), were focussed on establishing whether radiolysis products could affect the oxidation and degradation of the uranium ore and whether radiolysis formed the halo of iron oxide at the ore/clay interface in the analogue EBS. Observations at Cigar Lake showed that radiolysis products were present in both groundwater and minerals. These data were used to test models of SF corrosion. If the corrosion of SF passes a certain threshold level then the possibility of the release of radionuclides increases significantly.

Radiolysis

Radiolysis studies at Cigar Lake showed that net changes were considerably overestimated by models then used in the safety case (Karlsson et al. 1994). This was considered feasible if radiolysis takes place locally and on a minor scale, such that the natural system of clay and ferrous minerals can buffer the redox potential to maintain reducing conditions to well within the stability field of UO_2.

In a later re-appraisal of the data (Smellie and Karlsson 1996), a more theoretical basis was established to understand the geometric radiation dose distributions resulting from single UO_2 grains of different sizes and establishing what fraction of the radiation reaches the surrounding aqueous phase to initiate the radiolysis reactions. The modelling results showed that only a very small fraction of the total radiation energy from a UO_2 grain, irrespective of size, is deposited in the surrounding groundwater.

These models were subsequently tested against actual observations and measurements from the Cigar Lake U orebody (Liu and Neretnieks 1996). From the outset, the Cigar Lake deposit exhibited certain disadvantages; for example, the general heterogeneous nature of the orebody itself and, on a smaller scale, the wide variation of uraninite grain sizes, their irregular distribution within the clay matrix and their tendency to occur as aggregates. Furthermore, the amount of groundwater circulating in the orebody (which really should be described as a massive clay body containing large aggregates and disseminations of uranium ore) will be extremely small and localised to discrete fractures.

Despite these drawbacks the modelling results supported the inadequacy of the then available safety case radiolysis models as applied to Cigar Lake where the calculated oxidant production rates are significantly higher. The most obvious reason for this is the uncertainty of important boundary conditions (e.g. water and grain-size distribution) at Cigar Lake due to its complexity and heterogeneity, making calculation of average dose rates highly uncertain.

However, even allowing for this disparity in the calculated oxidant production rates, which indicates that difficulties still remain to be solved, considerable advances were made in testing and developing radiolysis models used in the safety case at that time.

Fuel dissolution

The potential effect of radiolysis (however little) on the stability of the Cigar Lake uraninites as an analogue to the UO2 of spent nuclear fuel was further tested using a ReDuctive Capacity (RDC) model (details in Smellie and Karlsson 1996). In principle, a function of the concentration of radiolytic oxidants (and therefore a function of time) was used to study the dependence of the main parameters (e.g. estimated rates of oxidant generation and degree of uraninite oxidation) with time, thus deriving an overall expression for the rate of UO_2 (as a SF analogue) matrix dissolution over GDF-relevant geological timescales (Smellie and Karlsson 1996).

The modelling results showed that the amount of radiolytic oxidant produced was effectively neutralised by the reductive capacity of the UO2 crystals, resulting in slight changes in UO_2 stoichiometry. At Cigar Lake, it was suggested that the observed oxidation of the uraninites from the orebody probably occurred shortly after the ore formation phase, and the reductive capacity, and hence stability of the orebody, has essentially remained unchanged since that time.

Redox fronts

At Cigar Lake, the presence of a Fe(III)-rich halo in the clay close to the massive ore/clay interface (see Figure 1) was originally interpreted as evidence of an outward propagating redox front driven by a continuous supply of oxidants produced from radiolysis reactions within the orebody.

The amount of oxidants generated by water radiolysis in the orebody, calculated by then current models, would be certainly enough to explain the total amount of Fe(III) in the halo. This, however, was considered an unlikely explanation for two reasons (Smellie and Karlsson 1996):

- groundwater reducing conditions in the orebody would render Fe(III) effectively insoluble; quite simply there is no means of transport for ferric iron
- it has been demonstrated by theoretical calculations that Fe(III) may very well be generated by low temperature oxidation reactions resulting from late-stage ore-forming processes; in other words, the halo mainly represents fossil reactions dating back to the time of ore formation

However, radiolysis need not be ruled out entirely. One hypothesis (Smellie and Karlsson 1996) considered the possibility that oxidation of Fe(II) to Fe(III) in the clay horizon was initiated by U(VI) released through fluid interaction with the uraninites which were slightly oxidised during ore formation. This is supported by mineralogical observations and compatible with the thermodynamic evolution of the ore system. However, this redox situation should also be accompanied by co-precipitation of U (at least twice as much) in the haematite-rich clay halo. Unfortunately, there were insufficient data to conduct mass balance calculations to test this hypothesis.

It would seem, therefore, that the redox halo at Cigar Lake can be adequately explained by processes other than radiolysis, namely late-stage, low temperature hydrothermal fluids, although some small radiolysis effects should not be ruled out.

Following this work, further studies in the 1990s (e.g. Hofmann 1999) indicated that radiolysis could occur in many natural environments that did not have high radiation fields and this allowed a more detailed examination of radionuclide trapping in and around redox fronts analogous to those which could form in the EBS around a SF waste container.

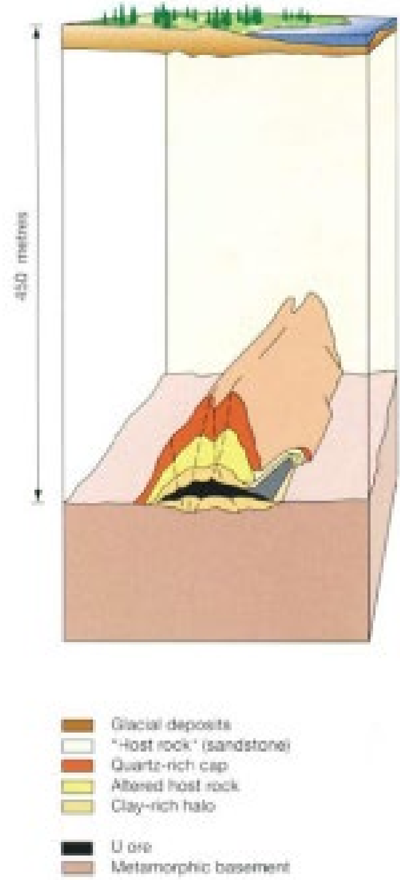

Figure 2.1.2-1. Cross-section of the Cigar Lake orebody (after Miller et al. 2000)

2.1.2.3 Uncertainties and limitations

- Although many examples of radiolysis in nature are now known, the only GDF-relevant data are from the Oklo-Bangombe (Gabon) and Cigar Lake (Canada) orebodies. However, the Oklo work has been criticised because of the very small number of samples that were analysed (section 2.2), meaning that current NA support for radiolysis models is from Cigar Lake data only
- Limitations to SF analogues are discussed in detail in Posiva (2021, section 4). For example, one gramme of SF is more than 4000 times more radioactive than is the original uranium ore so, clearly, there are limitations to the analogy. Further, SF is artificially enriched in 235U and contains nuclear reaction products whilst uraninite contains a higher proportion of other, non-radiogenic, impurities
- The thermal history of SF is also unlike that of natural uraninite. In particular, the high thermal gradient present across the fuel in the reactor may cause the spent fuel to exhibit lattice and crystallisation structures not evident in uraninite, although the high temperatures may rapidly anneal any such defects

- No further natural analogue work on SF stability has been carried out since the end of the 20th century and it is likely that improvements in analytical methods and the relevant thermodynamic databases since then could change the more than 20 year old conclusions somewhat

2.1.2.4 Relevance – what we have learnt?

- Testing the then-current SF corrosion models (which were based on short-term laboratory data) against NA data in the 1990s showed that they significantly over-estimated corrosion rates. This led to improved models which can more closely approximate the temporally more realistic natural data
- Overall, both laboratory and NA studies indicate that the kinetics of UO_2 dissolution, either as spent fuel or uraninite, is exceptionally slow under reducing conditions expected in the near field of a GDF. Although dissolution rates cannot be quantified readily from NA data, the abundance of naturally-occurring uraninite, some over 1000 million years old, can be taken as a general indication of its stability in the geological environment.
- Groundwater conditions can remain reducing if radiolysis is as low as observed at Cigar Lake; the oxidants are being consumed close to the ore and the groundwater remains reducing
- Drawing an analogy with exposed SF, a similar situation would prevent the build-up of a redox front and probably simplify the chemical processes to be considered for radionuclide release from a GDF

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2.1.3 Longevity of MOX fuel and other plutonium fuels

Item:

NA2.1.3

Component(s):

Waste, High Heat Generating Waste (HHGW), MOX fuel, Plutonium

2.1.3.1 Overview

Plutonium disposal raises particular safeguards issues because of concerns regarding the hazards of theft and incorporation into new nuclear weapons. Two options for plutonium treatment being considered are ‘burning’ in nuclear power reactors in the form of a mixed uranium-plutonium oxide (MOX) fuel and direct disposal to a repository (see also Miller et al. 2000, for discussion of a suite of plutonium GDF disposal options).

Once used, it is possible that MOX fuel will not be reprocessed but will be stored prior to geological disposal. It is likely that it will be treated in a similar manner to standard SF. Due to the different chemistries of plutonium and uranium, the behaviour of the PuO_2 component of MOX fuel may be expected to differ from the UO_2 component in the repository environment. Plutonium exists naturally in only very low concentrations of two main isotopes; as the last remaining traces of the long-lived, primordial ^{244}Pu and as shorter-lived ^{239}Pu generated by neutron capture by naturally occurring ^{238}U. Only extremely small quantities of these isotopes of plutonium can be found in uranium minerals (e.g. Katz et al. 1986, Romanchuk et al. 2020) and have been studied as NA sites such as Alligator Rivers (Fabryka-Martin & Curtis 1992), Cigar Lake (Curtis et al. 1999) and Oklo (Curtis et al. 1989). Plutonium released from nuclear weapons testing has also been studied in great detail (e.g. Penrose et al. 1990, Kersting et al. 1999). Consequently, no natural minerals with sufficiently high concentrations of plutonium exist to be suitable as analogues for MOX fuel.

Plutonium has an extremely complex chemistry and may be found in groundwaters (predominantly as anthropogenic contamination) in four oxidation states (III to VI), all of which may be present in measurable concentrations simultaneously. In anaerobic environments, plutonium is found predominantly in the III and IV oxidation states (e.g. Choppin 1999). Some III- or IV-valent (thorium or, possibly, zirconium or hafnium) elements can be considered to have similar behaviour but this analogy must be regarded with caution (see, for example, the discussion in Eisenbud et al. 1984). Under aerobic conditions, the IV, V and VI states of plutonium may all be important, the latter especially so in high carbonate concentration groundwaters. In this case, the closest analogue to the PuO_2^+ and PuO_2^{2+} species may be uranium (found predominantly as UO_2^{2+} in aerobic environments) but the analogy should also be treated with caution (cf. Clark, 2000). In groundwaters of varying redox conditions, uranium is probably the only reasonable analogue of plutonium but, especially here, the analogy should be considered as qualitative only (see Dai et al. 2002, Choppin et al. 2013).

It seems highly unlikely that minerals which could be appropriate NAs for MOX exist, so further efforts in this direction would appear to be of little value. However, whilst the complexity of the aqueous chemistry of plutonium means that the numerous historical NA studies of plutonium produced only ambiguous results, the improvements in analytical methods over the last two decades (e.g. Bishop 2020) and recent plutonium thermodynamic data updates (Lemire et al. 2020) suggest that assessment of plutonium behaviour in GDF-relevant environments may be a more profitable avenue of investigation.

IFEPS:

2.1 - Waste form

2.1.2 - Waste form characteristics and properties

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2.1.4 Longevity of cementitious waste forms

Item:

NA2.1.4

Component(s):

Range of wastes encapsulated in concrete

2.1.4.1 Introduction

As noted in RWM (2016) "Evolution processes of cements are generally well understood. Hydration, carbonation and radiolytic degradation are unlikely to have a detrimental effect on the immobilisation properties of the waste form during storage. Upon exposure to groundwater, cements are likely to undergo chemical and mineralogical changes. At this time, the mobility of encapsulated radionuclides will be affected by their sorption and solubility in the EBS." RWM (2016) further considers several processes to be of significance in understanding the long-term behaviour of cementitious waste forms, including:

- ***Hydration***: where the OPC (Ordinary Portland cement) cement slags hydrate and form a range of hydration products such as CSH (calcium silicate hydrates) within the concrete. This process has been examined at the Maqarin site in Jordan (section 4.1.3) where the cement slag is produced during natural combustion events and is then later hydrated to form a natural OPC-concrete which is some 2 million years old. Even older (up to 58 million years old) natural concretes formed along similar lines have been described at Scawt Hill in Northen Ireland (section 4.1.4), with both examples clearly indicating that CSH and related phases can last considerably longer than the current requirements for cementitious waste forms in a GDF

- ***Carbonation***: of concretes is well understood and, while it tends to be viewed as a negative process in the construction industry, it can have benefits in a GDF environment. For example, carbonation of concretes can reduce leaching rates significantly, so leading to increased longevity of the waste form (e.g. Högelund 2014). On the negative side in a GDF context, carbonation lowers the local pH of the cement, has the potential to locally increase the solubility of radionuclides in the waste form and can lower the strength of the concrete. While RWM (2016) cites examples of research into carbonation in the construction industry (Crossland 2006) as "long-term", no studies of truly long-term effects of carbonation have been reported to date. However, as noted in section 4.1.3, a preliminary study of the impact of carbonation was carried out on the 2 million year old concretes at Maqarin by Clark et al (1993) and the results indicate that this would be a suitable site for further, more focussed, studies
- ***Radiolytic degradation***: Laboratory experiments implementing accelerated dose rates have been used to infer the continued radiation stability of concrete waste forms over very long timescales (see reviews in Constable et al. 2010ab). The results suggest that gamma irradiation does not cause OPC-concretes to swell or crack to an extent that will significantly reduce the performance of the waste package. Unfortunately, these results cannot be supported by any extant NA study, but uranium-phosphate ore bodies do exist in close proximity to the natural concretes in Jordan and, if any could be shown to be particularly enriched in thorium (ca. 10%), the gamma radiation doses could be significant with time. Some 269 mt mineralisation, at an average grade of 135ppm, of exploitable uranium ore have been reported for central Jordan alone (Abzalov et al. 2015)
- ***Chloride attack, sulphate attack and leaching of cement***: these processes will occur following resaturation of the GDF following closure. They are discussed in sections 4.1.2, 4.1.3, 4.1.4 and 7.3.1. Most NA information is currently available on long-term sulphate attack and concrete leaching, but the sources discussed in section 4.1.2 could provide further information on long-term chloride attack in the future as ongoing research is finally published
- ***Release of radionuclides and toxic species from waste***: following GDF closure, it is expected that the concrete containers will be breached and the cementitious waste forms will begin to leach and release their radionuclide and toxic species loads. As the rate at which this will occur will depend on the precise form of the waste, the extent of any previous degradation of the container and waste form, it is difficult toe envisage a NA which can offer much information of direct relevance in this case. Any subsequent uptake of any released radionuclides in the EBS (e.g. grout backfill, bentonite buffer, steel supports etc.) has not been studied from the NA viewpoint to date, but certainly could be if supporting information were felt useful. For example, as reported in Alexander et al. (1992), the natural concretes in Jordan include many safety-relevant trace elements and, on leaching, they are released to the natural alkali groundwaters (Linklater et al. 1996). The interaction of these trace elements with smectite-rich clays in the vicinity of the natural concretes (e.g. at Khushaym Matruk; Pitty & Alexander 2011) would be analogous to reaction within the EBS (cf. RWM 2016). Although this process has not yet been studied, subsequent uptake in the host rock has (details in Milodowski et al. 1992, 1998) and this information is already available for comparison with the many short-term laboratory experiments (e.g. Bradbury & Baeyens 1997, 2004) on the disturbed host rock.

IFEPS:

2.3.4.5 - Alteration [waste package]

2.3.4.3 - Migration of chemical species [waste package]

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2.2 Criticality considerations based on nature (Oklo, Gabon)

Item:

NA2.2

Component(s):

High Heat Generating Waste (HHGW), Spent Fuel (SF), Plutonium, HEU

2.2.1 Introduction

For criticality safety in a GDF, the design of the waste packages is the most important preventive measure (see e.g. Hicks & Baldwin 2014). However, in case of the unlikely failure of the waste packages, criticality outside of the waste package during the long-term post-closure evolution of the GDF can be considered. It is important to stress that no known natural system represents the chemical composition of the radioactive wastes directly. Nevertheless, rare localities where the precise combination of U concentration, temperature and lack of reaction inhibitors have combined to produce natural nuclear reaction, are known in nature. For example, at Oklo, Gabon (Figure 2.2.1-1 and 2.2.1-2), a series of 16 fossil natural reactors is known to have achieved criticality (i.e., situation when the rate of neutron production and loss are equal) some ca. 2,000 million years ago. These examples of natural events have built confidence in our understanding of how critical systems might evolve.

Potential criticality was also examined at Cigar Lake, but no such evidence was found, as stated by Smellie & Karlsson (1996): *"In contrast to Oklo, nuclear criticality was never achieved at Cigar Lake even though U concentrations are higher. This has been attributed to several reasons which include a) its younger age; i.e., by the time the orebody formed, the natural* $^{235}U/^{238}U$ *ratio had decayed to too low a level to allow a critical mass to be reached, b) the presence of high amounts of poison elements (e.g., neutron-capturing nuclei such as boron and the REEs), and c) the clay barrier prevented ready access of hydrogen and water (i.e., neutron moderators). Neutrons from spontaneous fission of U, however, continuously produce radioactive isotopes such as* ^{3}H, ^{14}C, ^{36}Cl, ^{99}Tc, ^{129}I *and* ^{239}Pu. *These amounts are measurable and commonly exceed present atmospheric levels. For example, the concentration of groundwater tritium in the ore zone is higher (>100 TU) when compared to present bomb pulse tritium in near-surface groundwaters (~50 TU) from the Cigar Lake region."*

Figure 2.2.1-1. A view of the open cast mine at Oklo (Courtesy of Francois Gauthier-Lafaye)

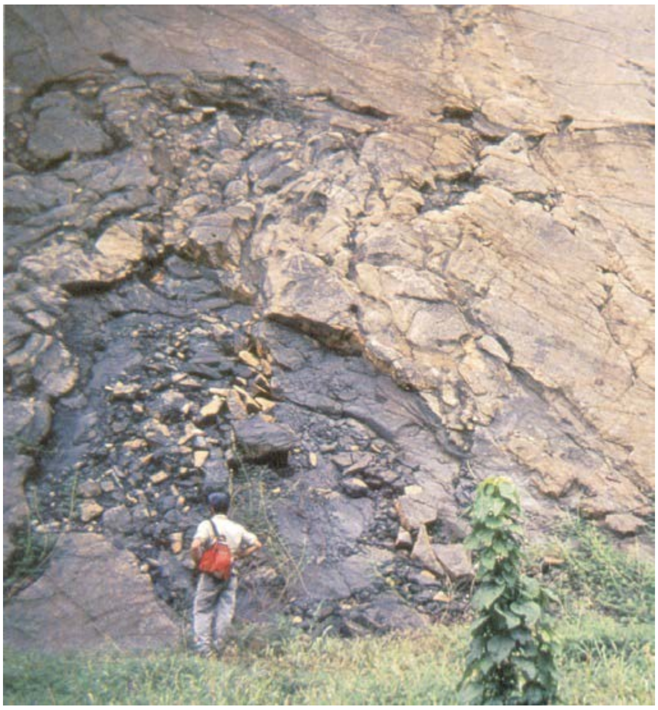

Figure 2.2.1-2. Imprint of the core of a natural reactor on the pit wall at Oklo (Miller et al. 2000).

IFEPS:

3.2.6.5 - Criticality [repository]

2.3.6.6 - Criticality [waste package]

NA Type:

Natural analogue

2.2.2 NA description

Despite Oklo's limitations as a NA for spent fuel stability or radionuclide migration, some important knowledge regarding criticality have been extracted (see e.g., Gauthier-Lafaye 1996, Oversby 1996, 2000, Smellie 2005).

Smellie (2005, 2009) reviewed the Oklo data, and some important conclusions were made regarding criticality considerations and why and how it occurred and eventually stopped:

- *"The reactor zones had the requisite physical and nuclear characteristics to form a self-sustaining chain reaction, given the abundance of ^{235}U present nearly 2 Ga ago* (which was higher than today).
- *The criticalities were self-limiting processes and there is evidence of a rapid cycling between critical and sub-critical states over periods of hours.*
- *The compact mass of the reactor zones would be conducive to minimising collapse and maximising thermal neutron utilisation in the uranium. Moreover, the surrounding sandstones, some exhibiting fracturing, would provide ample water to moderate and reflect neutrons.*
- *The inventory of fission products and the slight excess of ^{235}U in some zones support the conclusion that induced fission of ^{235}U and neutron capture by ^{238}U occurred in the area.*
- *The reactor zones during criticality, operating at 150-160 bars and 300-400°C, remained rather closed systems with respect to uranium and to most of the fission products, with the exception of alkali metals, alkaline earth elements, rare noble gases and some heavy metals such as Mo, Ag and Te.*
- *Under certain chemical conditions (i.e. possibly hydrothermal fluids of low oxidation potential due to the high content of organic matter within the reactor zones), fluid movement through uranium oxide has selectively removed and transported a fraction of plutonium during criticality.*
- *The fission process appears to have been halted (or the process at least aided) by the gradual or rapid collapse of the overlying strata resulting from the extensive and prolonged hydrothermal desilicification. This effectively reduced the porosity, closed off the source of the water (i.e. moderator) and, in some cases, disrupted the fissile ^{235}U material.*
- *It seems unlikely that such unusual geological and geochemical conditions for criticality have existed elsewhere, but the outside possibility cannot be totally excluded. However, the probablility of finding another site showing altogether different processes is even more remote. "*

These conclusions support the earlier assessments of the low likelihood for criticality to occur in the GDF (Oversby 1996, 2000). Basically, in order to achieve criticality outside the waste packages, there should be a mechanism that transports ^{235}U (oxidizing conditions would be required) and subsequently deposits ^{235}U in sufficient quantities (reducing conditions would be required for this). There is no credible mechanism that could produce these altering conditions in the GDF near field in the long-term. Similarly, for plutonium, no credible mechanisms for transport and deposition has been identified for GDFs (see also Rechard et al. 2014).

2.2.3 Uncertainties and limitations

- While the evolution of the Oklo site is reasonably well understood, the highly complex history of the area means that many detailed boundary conditions are unknown.
- In addition, only a few samples were analysed, so the process is not well understood at the site.
- As such, a fully mechanistic understanding of the process is still lacking.

2.2.4 Relevance – what we have learnt?

- Mechanisms of criticality have been studied on site, leading to a better understanding on the potential (or lack of it) of criticality during the GDF evolution to be assessed
- Although it can be shown that under the extremely rare conditions which occurred at Oklo, criticality can occur, for a GDF, no credible mechanism has been identified to result in dissolution and precipitation of U-235 or plutonium that would allow criticality outside the waste package
- There is no doubting that the Oklo reactors have caught the imagination of many people, so perhaps some message about waste disposal safety can get through. But for most (including, we suspect, the scientists involved in studying it as a natural analogue), it is much more about being in awe of an unique natural phenomenon: as the Curtin University of Technology (Australia) notes on their web site.

"Why are these Natural Fossil Reactors important? Because they are rare and fascinating objects."

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3 CONTAINERS

3.1 Overview on copper analogues

The EBS of a GDF for radioactive waste is characterised by the use of large quantities of rather simple, well-understood materials. Copper is one of the materials that may be used in a GDF to contain HLW and SF (see Figures 3.1-1 to 3.13 for examples). In addition, copper is considered for some borehole sealing concepts. For waste packaging, copper is chosen for the outer canister material because theoretical and experimental studies show that it will be resistant to corrosion in the mildly alkaline, reducing groundwater environment predicted to be persistent in the GDF environment. As a result, the copper will be expected to isolate and protect the waste for long periods of time.

There are several types of copper analogues reported in the literature:

- Anthropogenic analogues: aerobic corrosion of copper roof tiles (Morcillo et al. 2017)
- Archaeological analogues: various artefacts of copper and bronze (e.g., Bresle et al. 1983, Tylecote 1979, Johnson & Francis 1980, Crossland 2005, IAEA 2005), Kronan cannon (Hallberg et al. 1987, King 1995). Galvanic corrosion (Smart & Adams 2006)
- Natural analogues – native copper (see overview e.g., in Marcos 1989 and Posiva 2012)

Some copper corrosion processes do not have known natural analogues; these include stress-corrosion cracking (SCC), microbially influenced corrosion (MIC), radiation-induced corrosion, corrosion of welds and hydrogen effects. Of these, it is likely that microbial activity plays a role in corrosion of natural copper but this has not been studied to date (Table 13.2-1, ID 3.1-3).

In addition to usage as qualitative examples, copper NA studies have been used in safety cases to:

- Verify corrosion models (King & Kolár 1996)
- Help to develop mechanistic understanding of the corrosion processes (King 1995)
- Input data for the predicted lifetime of copper materials (Bresle et al. 1983)

Despite being the most important source of information regarding GDF-relevant timeframes of the long-term behaviour of copper, only a few studies are available on relevant geological analogues. For example, massive native copper occurrences at Keweenaw peninsula in Michigan, USA, provide good qualitative analogue data for the long-term behaviour of copper canisters, but are only now being investigated in detail to better describe the conditions at different occurrences in the area (e.g. Liebscher et al. 2021; Aaltonen et al. 2023, and Table 13.2-1, ID 3.1-1). In addition, for higher salinity systems, new samples from the Aegean Sea and existing material from the vicinity of the Dead Sea could add novel information on copper corrosion in relevant environments (Table 13.2-1, ID 3.1-2).

The amount of copper in different disposal concepts varies from ~5cm (e.g., Figure 3.1-1 and 3.1-2) to few mm (e.g. Figure 3.1-3).

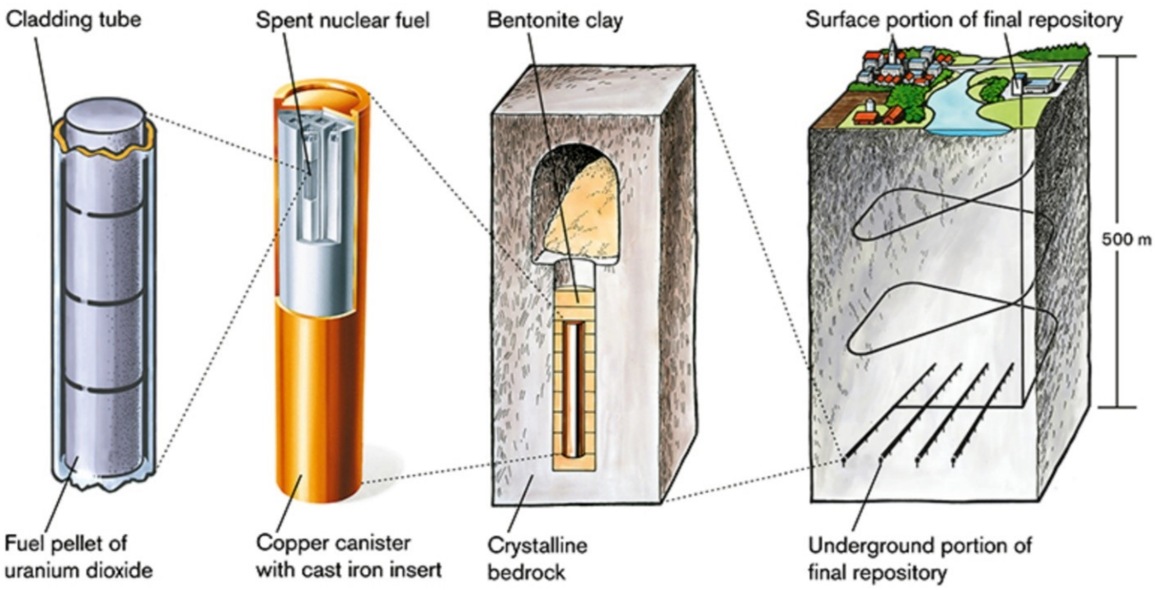

Figure 3.1-1. SKB's KBS-3V concept (SKB 2010).

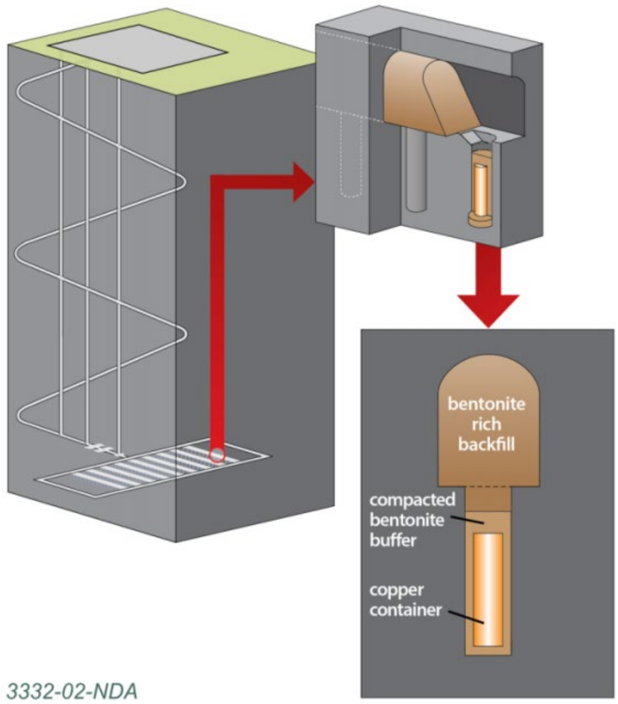

Figure 3.1-2. Schematic illustration of an example disposal concept for high heat generating waste. Disposal in higher strength rock. (RWM 2016)

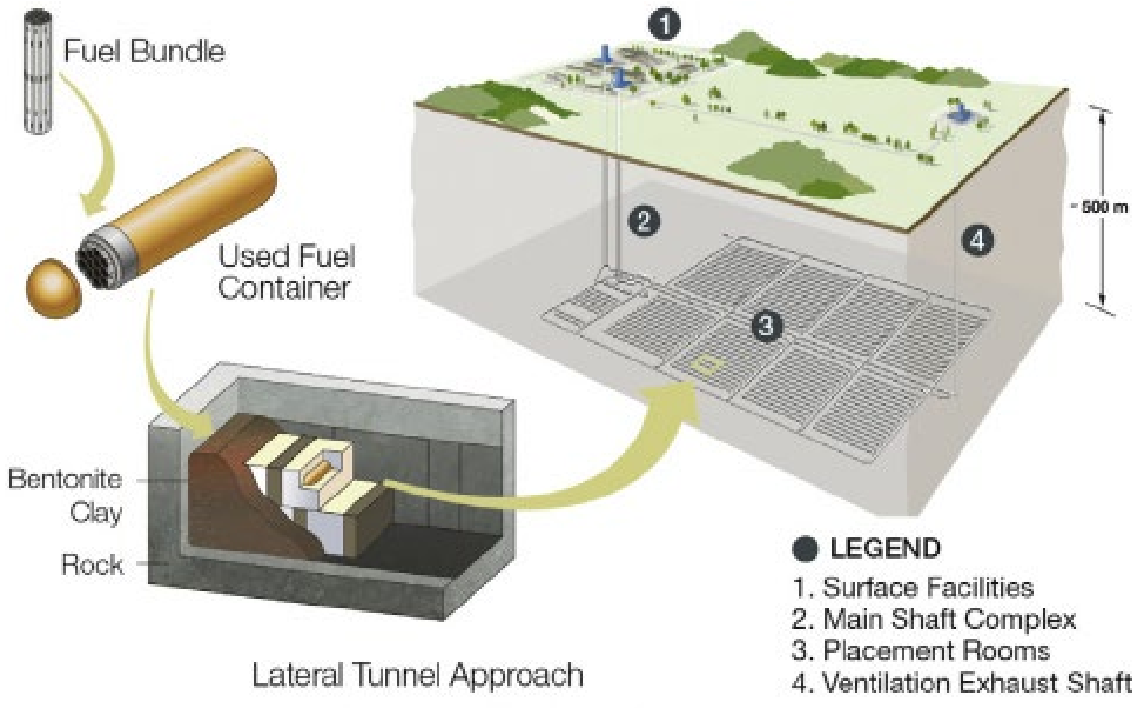

Figure 3.1-3. NWMO's Mark II concept (Boyle and Meguid 2015).

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3.1.1 Longevity of copper - Littleham Cove (UK)

Item:

NA3.1.1

Component(s):

Engineered Barrier System, Container, Copper, Other copper-based components in the repository, e.g. in bore hole seals.

3.1.1.1 Introduction

Native copper occurs in a wide variety of geological environments (Cornwall 1956, Marcos 1989, Ikehata et al. 2016) that include:

- basaltic lavas and interbedded sedimentary rocks;
- intrusive rocks, typically mafic and ultramafic;
- clastic sediments;
- oxidized copper ores
- modern swamps and lakes

A thorough overview on the native copper mineralisation types can be found in e.g. Aaltonen et al. (2022). Several repository relevant processes can be studied via NAs and these are being taken forward in the MICA project (Aaltonen et al. 2022). Here, the native copper occurrence at Littleham Cove (Littleham mudstone formation), UK is described as an example of native copper occurrences in sedimentary rock environment.

IFEPS:

3.2.4.4 - Corrosion [repository]

2.3.4.4 - Corrosion [waste package]

NA Type:

Natural analogue

3.1.1.2 NA description

Naturally occurring copper sheets are preserved in the ca. 250 to 300 million year old) Littleham Mudstone Formation, at Littleham Cove, in south Devon, England (Figure 3.1.1-1). They have been studied (Milodowski et al. 2000, 2002) to assess the long-term stability of copper enclosed in clay – such as would be found in a GDF where copper canisters are embedded in the bentonite buffer. According to Milodowski et al. (2000):

- At Littleham Cove, the copper is 99.9 % pure and occurs in discrete plates (up to 160 mm diameter and up to 4 mm thick) enclosed in a silty clay matrix. Each plate is formed of a stack of thin copper sheets, varying in thickness from <0.1 to 2 mm
- These sheets grew in situ within the mudstone, along more permeable sandstone and siltstone bedding planes. Diagenetic fabric studies show that copper was already formed prior to achieving its maximum burial compaction state, about 175 million years ago
- Since it was deposited, the copper has been altered and corroded by later sulphide and oxide mineralization but detailed studies have shown that most of this occurred soon after the copper was buried
- Following the initial corrosion, between 30 and 80 % of the original thickness of the copper remained unaltered and preserved within the clay of the Littleham Mudstone Formation, without further alteration, for over 170 million years, until uplift and erosion exposed the copper plates to the current weathering environment (Figure 3.1.1-2)

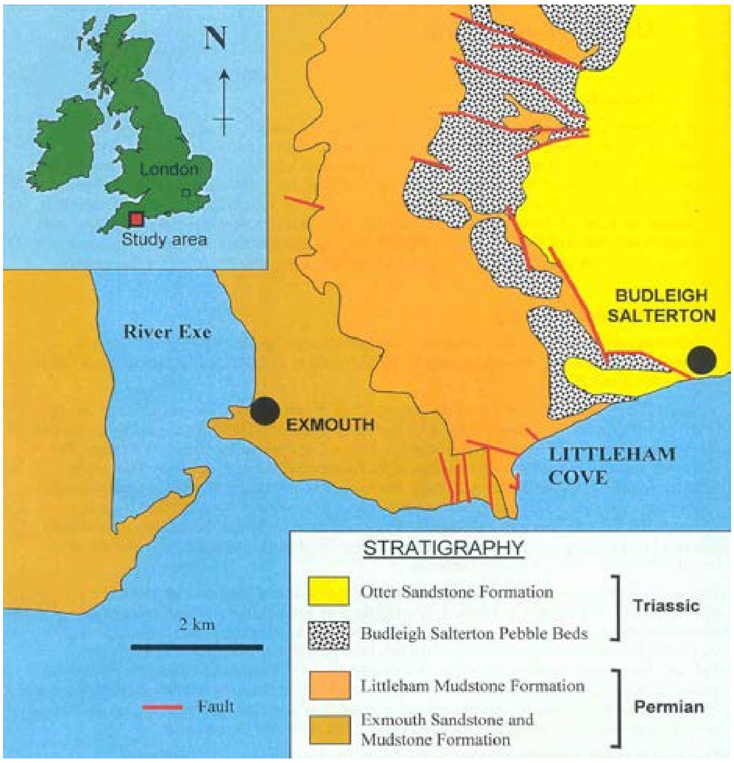

Figure 3.1.1-1. Location of the Littleham Cove Natural Analogue Site (©British Geological Survey).

Figure 3.1.1-2. Black, uranium-vanadium–rich concretions, surrounded by grey reduction halos in red mudstone, can sometimes contain well-preserved thin sheets of native copper (INSET) (©British Geological Survey).

3.1.1.3 Uncertainties and limitations

- Unlike a purpose-designed bentonite clay barrier system in a GDF, the natural clay of Littleham Mudstone Formation has a different mineral composition to bentonite, and has not been engineered to provide a good seal as would be the case in a GDF
- The natural mudstone at Littleham Cove will probably have a greater permeability (unfortunately, this

was not defined) than a carefully-engineered bentonite buffer. This means the performance of copper in an engineered bentonite barrier in an EBS should actually perform better than illustrated by this analogue

- The mineralogical assemblages present show that the porewater remained reducing following burial so that the copper and base metal sulphide and arsenide minerals were preserved, until uplift and erosion exposed the mineralisation to the present-day oxidising, near-surface weathering environment
- Groundwaters studies in rocks of a similar age elsewhere in the UK, but at greater depths, are highly saline brines. Furthermore, halite and anhydrite deposits and matrix cement minerals are known to have been formerly present in the strata overlying the Littleham Mudstone Formation and are still preserved in the deeper parts of the basin to the east. Therefore, the porewater in the Littleham Mudstone Formation is also likely to have been sulphate-rich and highly saline, possibly halite- and anhydrite saturated. Such highly saline and sulphate-rich groundwaters are expected to be more corrosive towards copper than less saline groundwaters that will be encountered in many GDF environments. The fact that the copper here has survived these more aggressive conditions gives confidence that a copper canister will survive in the (more usual) conditions
- The natural analogue study has not produced any quantitative information on corrosion rates to support safety case assessments, but the fact that the copper has survived enclosed within this clay matrix for many millions of years provides strong qualitative support to the concept of using copper canisters in a GDF

3.1.1.4 Relevance – what we have learnt?

- The Littleham Cove Natural Analogue Study demonstrates that copper metal buried in a compacted clay environment can remain stable and resist corrosion for longer than 170 million year (i.e. much longer than required in a GDF)s
- In this particular case, after early corrosion and alteration of copper during burial, the remaining copper (representing 30-80 % of the original copper mass) effectively remained inert and isolated from further corrosion within the naturally-compacted mudstone for at least 170 million years, until uplift and erosion exposed it to alteration in the present near-surface weathering environment. This time period of survival of the copper is well in excess of the timescales (up to one million years) considered in GDF safety cases;
- The preservation of copper metal in this natural environment (higher permeability mudstone to buffer, and more aggressive groundwater conditions) provides support to the prediction that copper canisters can potentially resist corrosion within a GDF environment for tens of thousands of years

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3.1.2 Longevity of copper: Hyrkkölä (Finland)

Item:

NA3.1.2

Component(s):

Engineered Barrier System, Container, Coopper

Other copper-based components in the repository, e.g. in borehole seals.

3.1.2.1 Introduction

Native copper occurs in a wide variety of geological environments (Cornwall 1956, Marcos 1989, Ikehata et al. 2016) that include:

- basaltic lavas and interbedded sedimentary rocks;
- intrusive rocks, typically mafic and ultramafic;
- clastic sediments;
- oxidized copper ores, and
- modern swamps and lakes.

A thorough overview on the native copper mineralisation types can be found in Aaltonen et al. (2022). Several repository relevant processes can be studied via NAs and these are being taken forward in the MICA project (Aaltonen et al. 2022). Here, the native copper occurrence at Hyrkkölä, Finland is described, providing NA data for corrosion in open fractures of crystalline rock, as well as insights for copper sulfidation.

IFEPS:

3.2.4.4 - Corrosion [repository]

2.3.4.4 - Corrosion [waste package]

NA Type:

Natural analogue

3.1.2.2 NA description

Native copper, copper sulphides and copper oxides occur at the Hyrkkölä site in Southern Finland (Figure 3.1.2-1) as fracture filling minerals in crystalline rocks (Marcos & Ahonen 1999). The occurrence is a 1700 -1800 million years old U-Cu mineralisation (Raisanen 1986). The site has gone through a complex history of geological processes (Marcos & Ahonen 1999), including:

1. The formation of the native copper (and uraninite), hydrothermal brecciation stage (some remobilisation of copper, recrystallisation of quartz and sulphide mineral precipitation),

2. Hydrothermal brecciation stage, during which quartz is partially recrystallized and the more brittle tourmaline and apatite grains are brecciated. Native copper may also be partially remobilised at this stage.

3. Mineralisation of younger (< 1 million years old) calcite, covellite, cuprite and uranyl compounds.

In addition to overall copper longevity estimated based on the occurrence of these > 1700 million years old native coppers, the coexistence of native copper and copper sulphides has also allowed copper sulfidation analyses for a crystalline host rock environment to be broadly assessed. Most of the native copper has remained in its native state and the sulfidation is seen only as very thin occurrences on native copper surfaces.

The current groundwater chemistry in the area is dilute, and oxidising. It has been estimated that the oxidation started about 10 to 100 thousand years ago, but native copper has persisted even in these conditions, possibly due to passivation mechanisms in the presence of smectites (Figure 3.1.2-2). In open fractures, the smaller (not defined, but all grains analysed are smaller than 1 mm) native copper occurrences have oxidised.

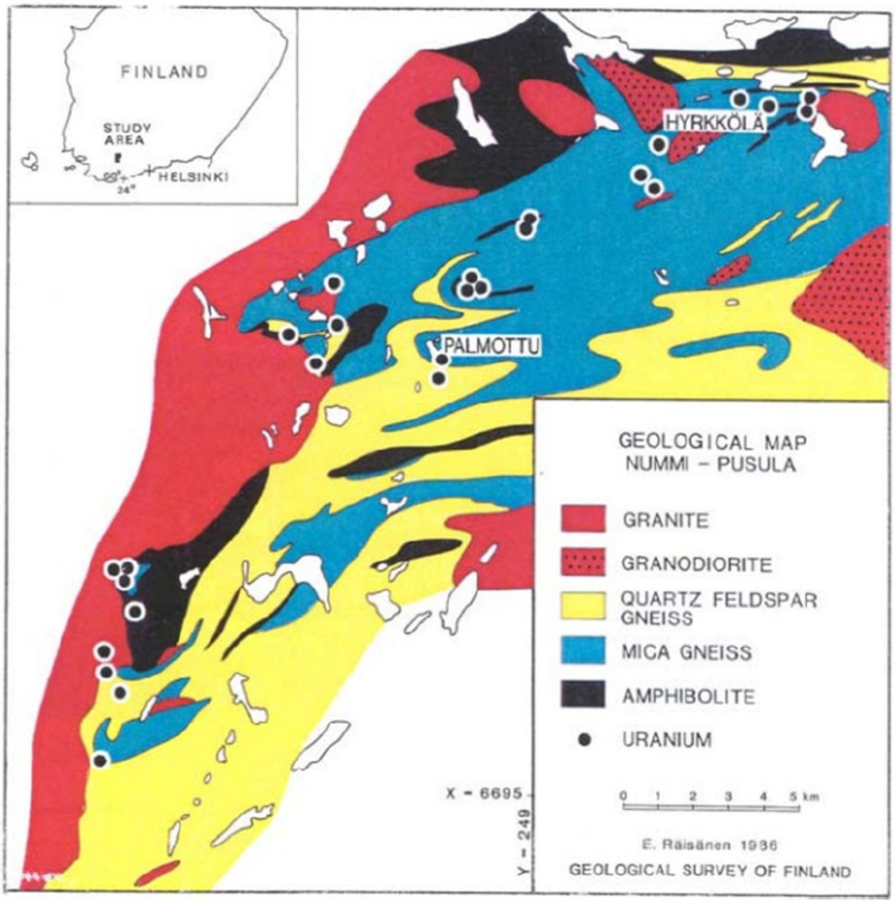

Figure 3.1.2-1. Geological map of Hyrkkölä area in Southern Finland (Marcos & Ahonen 1999).

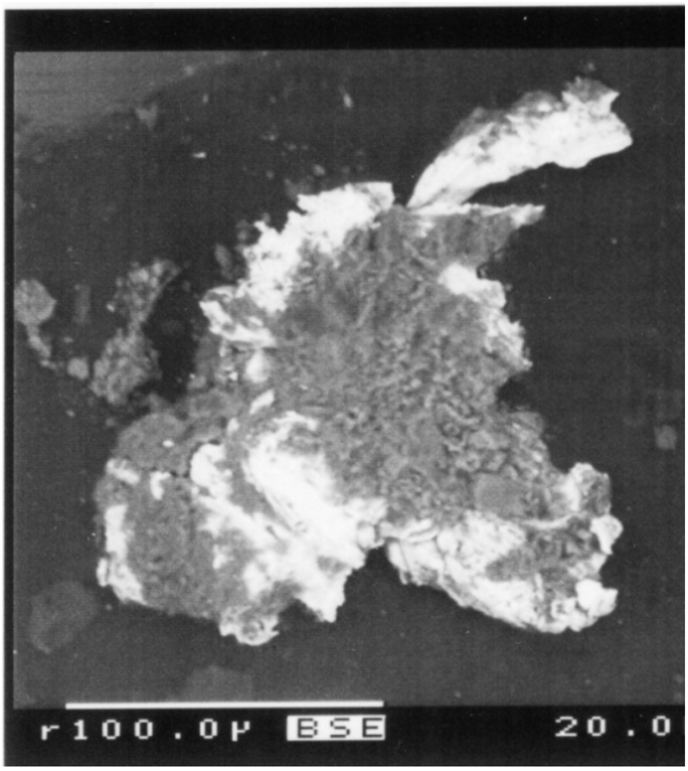

Figure 3.1.2-2. Native copper plate (white) covered with smectite (gray mass in the middle) from a groundwater conducting fracture at Hyrkkölä, SW Finland (Markovaara-Koivisto et al. 2008)

3.1.2.3 Uncertainties and limitations

- The site has a quite complex geological history and the duration of the sulfidation event is not known, so the analogue is mostly qualitative
- There are also uncertainties related to the duration of the oxidising conditions

3.1.2.4 Relevance – what we have learnt?

- Native copper has persisted in bedrock fractures for 1700 million years, and some parts of it even under oxidising conditions
- Passivation mechanisms for corrosion (due to oxidation) might be due to the presence of smectite surrounding the native copper, supporting the assumed effectiveness of bentonite as a GDF buffer material. Oxidative conditions have prevailed at for least the last 10 000 to 100 000 years
- The occurrence of smectite has been posited as an example of smectite durability in dilute groundwaters, however, this is a qualitative observation (see section 5.1.5)
- The occurrence of sulphides, even if the data cannot be used for corrosion rates, could provide useful information on the mechanistic understanding of some corrosion mechanisms, however, this has not been studied in enough detail to describe the native copper – sulfide interface (Posiva 2023).

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3.2 Overview on steel analogues

The EBS of a GDF for radioactive waste is characterised by the use of large quantities of rather simple, well-understood materials. Steel is one such material that may be used in a GDF as part of the infrastructure and to contain HLW, SF and LHGW waste matrices. Steel is a material of choice for the outer canister because theoretical and experimental studies show that it will be resistant to corrosion in the mildly alkaline, reducing groundwater environment predicted to be persistent in the GDF environment. As a result, the steel container will be expected to isolate and protect the waste for long periods of time. The main perturbations associated with the massive steel canister are canister failure through corrosion, hydrogen gas production due to anaerobic corrosion and redox changes around the canister following canister failure (Nagra 1994, Alexander and McKinley 1999).

The most important input from natural analogues for a safety case is to build confidence in the canister lifetime predictions. In addition, the study of analogues can also be used to:

- Help develop a mechanistic understanding of the canister corrosion processes (e.g. Neff et al. 2010)
- Provide input data for lifetime prediction models, such as long-term anaerobic corrosion rates for iron and steel (e.g. Crossland, 2006)
- Verify corrosion and canister lifetime models (e.g. Neff et al. 2010)

Although steel is a likely canister material (carbon steel, stainless steel) along with iron (e.g. as an insert in copper canisters), natural and archaeological analogues of steel are extremely rare, so most work to date has focussed on iron, the major component of steel. Arguably, this is not a great issue as the differences in corrosion behaviour between steel and the various archaeological and natural forms of iron (e.g. native iron, cast iron, wrought iron etc.) are well enough understood (e.g. Jones, 1996) to make little difference in interpreting the data. Certainly, it has not prevented the inclusion of iron corrosion data in several published safety cases (e.g. Nagra 1994, JNC 2000, 2005). Nevertheless, comparison of natural and archaeological analogues of steel corrosion with the mass of information on iron corrosion would clearly increase confidence in the application of the data in the safety case and at least one novel archaeological (Figures 3.2-1 and 3.2-2) and one novel natural analogue have recently been identified in the UK (see Table 13.2-1, IDs 3.2-1 and 3.2-2 respectively).

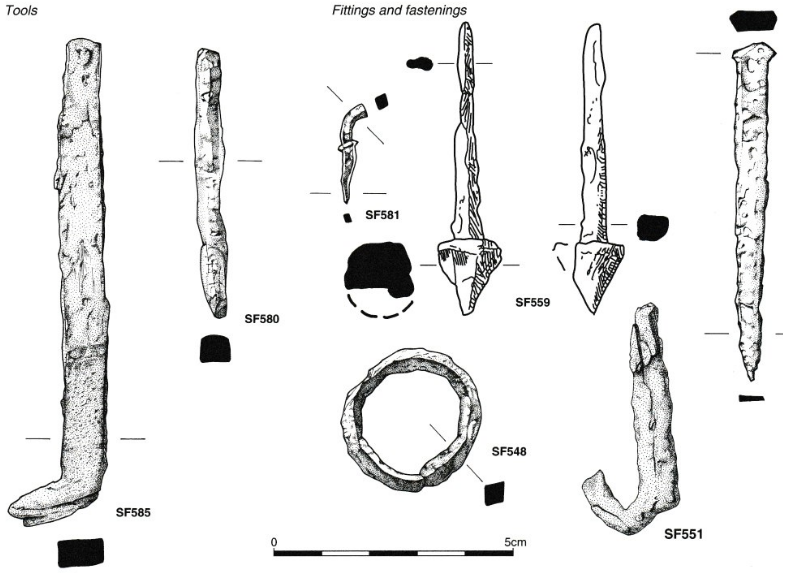

Figure 3.2-1. Examples of possibly the oldest steel yet identified, from the Broxmouth hillfort in Scotland (Armit & McKenzie 2013)

There are several types of iron analogues reported in the literature:

- Archaeological analogues: various iron artefacts (e.g. Johnson & Francis 1980, Honda et al. 2003, IAEA 2005, Neff et al. 2005, Saheb et al. 2011)
- Natural analogues – native iron, although rare (see the discussion in Miller et al. 2000), several examples have been studied (e.g. Ulff-Möller 1990, Hellmuth 1991ab, Vira 1996)

There are numerous steel corrosion processes (e.g. uniform corrosion, pitting, crevice corrosion, filiform corrosion, galvanic corrosion, environmental cracking, fretting corrosion etc.) and most have not been examined in any detail in published natural analogue studies. However, in most current designs, it is assumed that uniform corrosion will be the main process with local (pitting) corrosion also playing a role (cf. Guo et al. 2020) and these have been addressed previously.

Iron analogue data can be used to:

- Validate corrosion models (Neff et al. 2010)
- Help to develop mechanistic understanding of the corrosion processes (Neff et al. 2010)
- Provide input data for the predicted lifetime of steel materials in a GDF (e.g. Crossland 2006)

.

As such, the two examples considered in detail here (Inchtuthil and a comparison of laboratory and analogue data) are archaeological analogues, reflecting, at least in part, the scarcity of natural analogues of iron corrosion - but the recently discovered steel archaeological and natural analogues (Figure 3.2-2 and Table 13.2-1, IDs 3.2-1 and 3.2-2, respectively) may be about to change that position.

Figure 3.2-2. An unidentified steel artefact from the Broxmouth hillfort. Approximately 2 cm long, it is made from high carbon steel which has been heat-treated and quenched. A etched, B unetched (Armit & McKenzie 2013).

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3.2.1 **Longevity of steel - Inchtuthill (UK)**

Item:

NA3.2.1

Component(s):

Engineered Barrier System, Container, Carbon Steel, (Stainless Steel, Cast Iron)

3.2.1.1 Introduction

As noted in section 3.2, iron and steel may be used as canister materials in a GDF for radioactive waste for the containment of HLW, SF and L/ILW. Metals based on iron form an integral part of some proposed GDF systems, particularly in the construction of canisters. In some concepts these canisters will be enclosed within an additional canister of a different metal, such as copper. In other cases, the steel canisters may be sealed by and enclosed in compacted clay (bentonite) backfill or encased in a cement.

Natural and archaeological analogue along with laboratory and URL experimental studies have been used to understand the process and rate of corrosion of iron under the warm, mildly alkaline and reducing chemical environment that will most likely persist in a GDF.

IFEPS:

2.3.4.2 - Evolution of redox conditions [waste package]

2.3.4.4 - Corrosion [waste package]

2.3.4.5 - Alteration [waste package]

2.3.5.2 - Microbially/biologically mediated processes [waste package]

2.3.6.2 - Radiolysis [waste package]

3.2.4.2 - Evolution of redox conditions [repository]

NA Type:

Archaeological analogue

3.2.1.2 NA description

An apparently unremarkable area of pasture situated on the banks of the River Tay near Dunkeld in Perthshire, Scotland (Figure 3.2.1-1), marks the site of the most northerly legionary fortress in the Roman Empire. It was briefly occupied from A.D. 83 to 86 and then abandoned in an orderly manner (Angus et al. 1962). The only visible evidence at the site today is a relatively well-preserved ditch that formed part of the Fort's defensive perimeter. During the 1960 season of excavations at the site (active 1952- 65; Pitts & St Joseph 1985), a remarkable hoard of around one million iron nails was uncovered within the grounds of the fabrica (the Fort's workshop). Some nails came out of the ground in a near-pristine state (Mappeli et al. 2009). During the abandonment of the fort, in a (successful) attempt to put the nails out of the reach of the local tribes (Figure 3.2.1-2), the nails had been buried in a 3.66 m deep pit dug into fluvio-glacial deposits and covered by a 1.83 m layer of gravel.

As noted by Pitts & St Joseph (1985), when the hoard was first uncovered the outer layer of nails was described as having corroded to an impermeable crust, particularly those at the top. Inside the crust many nails only had a thin patina of corrosion product (scale) whilst some at the core were virtually untouched by rust (Figure 3.2.1-3). Some clusters of nails were reported to have developed a pitted style of corrosion. The nails themselves comprise low-carbon steel and appear to have been made with sophisticated metalworking skills. The internal structure of the nails is finely layered, with the layering a result of variations in carbon content and the presence of thin non-metallic inclusions containing silicate (fayalite) saturated in iron oxide (wustite). It is thought that the layered structure is because the smiths formed the nails through 'friction welding' of many thin layers (e.g. by folding of thin sheets). The non-metallic inclusions are the remnants of low-melting point slag deliberately applied to assist in this process. The nails have different shapes, sizes and hardness depending on their intended use. The degree of corrosion does not systematically reflect differences in composition.

The reaction of the outer nails with groundwater has contributed to the preservation of the central nails in two ways:

- Reaction products (i.e. rust) formed a crust that was nearly impenetrable, greatly restricting the movement of water through the hoard;
- Corrosion of the outer region of the hoard of nails lowered the redox state of the groundwater such that by the time it reached the central nails, the water was chemically reducing and no longer able to induce corrosion.

A further degree of protection of the central nails was also provided by the presence of the thin coating of scale on some surfaces of the nails themselves; surfaces coated by this scale were noted to be less corroded than surfaces without coatings (Angus et al. 1962).

Figure 3.2.1-1. The site of the Inchtuthil legionary fortress today (NDA)

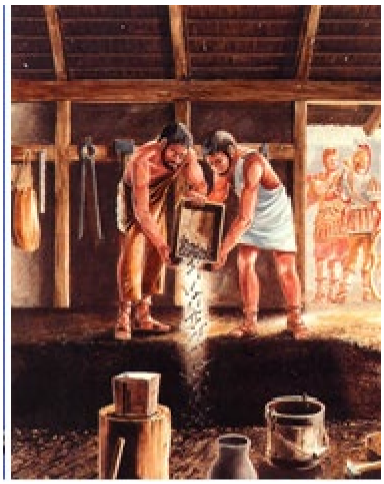

Figure 3.2.1-2. 2,000 year old Roman nails which were disposed in a pit as the Romans abandoned Inchtuthil, Scotland, the most northerly Legionnaire Fortress in the Roman Empire. Image courtesy Nagra.

Figure 3.2.1-3. An example of a remarkably preserved nail from the Roman hoard at Inchtuthil, Scotland (NDA).

3.2.1.3 Uncertainties and limitations

- The nails are of a slightly different compositions and have different internal structures to the iron-based metals likely to be used in a GDF
- The nail burial environment is different to that of a GDF – it is shallow, exposed to surface waters (more reactive), at lower temperatures and in relatively high permeability sediments
- The nails were discovered during an archaeological dig. Consequently, there has been no systematic study of the corrosion profile with distance across the hoard
- Similarly there is no information on the chemistry of the groundwater, soils or sediments

Whilst this study has provided basic information on iron corrosion in a shallow unsaturated soil environment, the application of the quantitative data to actual GDF conditions would be challenging.

3.2.1.4 Relevance – what we have learnt?

- The Inchtuthil nails show that low-carbon steel can be resistant to corrosion for thousands of years

- The corrosion resistance of low-carbon steel in part results from the inherent tendency for corrosion products (e.g. rust) to remain attached or nearby, forming protective coatings and crusts
- The preservation of the Roman nails under much more oxidising conditions than are likely to exist in a GDF, provides confidence in predictions that iron-based structures in a GDF will survive for thousands of years (cf. Posiva 2012)
- Iron corrosion data has been used in several published safety cases (e.g. Nagra 1994, JNC 2000, 2005)

Acknowledgements

Thanks to the Marischal College Museum, Aberdeen, for access and permission to photograph their Inchtuthil nails (one of which is shown above). Thanks also to the Delvine Estate for permission to access and photograph the Inchtuthil site.

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3.2.2 Longevity of iron and steel - direct comparison of archaeological (and natural) analogue and laboratory corrosion data

Item:

NA3.2.2

Component(s):

Steel Engineered Barrier System, Container, Carbon Steel, (Stainless Steel, Cast Iron)

3.2.2.1 Overview

As noted in section 3.2, iron and steel may be used in a GDF for radioactive waste. Metals based on iron form an integral part of some proposed GDF systems, particularly in the construction of canisters for the containment of HLW, SF and L/ILW. In some concepts these canisters will be enclosed within an additional canister of a different metal, such as copper. In other cases, the canisters may be sealed by and enclosed in compacted bentonite backfill or encased in concrete These sealing and backfill materials will slowly become saturated by water from the adjacent rocks after closure of the GDF.

Natural and archaeological analogue and experimental studies have been used to understand the process and rate of corrosion of steel under the warm, mildly alkaline and reducing chemical environment that will persist in a GDF.

IFEPS:

2.3.4.2 - Evolution of redox conditions [waste package]

2.3.4.4 - Corrosion [waste package]

2.3.4.5 - Alteration [waste package]

2.3.5.2 - Microbially/biologically mediated processes [waste package]

2.3.6.2 - Radiolysis [waste package]

3.2.4.2 - Evolution of redox conditions [repository]

NA Type:

Archaeological analogue

3.2.2.2 NA description

In the NA Strategy report (Reijonen & Alexander, 2023a), the point is made that NA data can often put short-term laboratory data produced under GDF-irrelevant conditions in proper GDF context. Unfortunately, this has rarely happened but, in the field of iron corrosion, several clear examples exist.

To build confidence in the long-term performance of the steel canister (or, in some designs, the iron insert in a copper canister; e.g. Posiva 2012), many studies of archaeological analogues have been produced (e.g. Nagra 1994, IAEA 2005, Yoshikawa et al. 2009). Within the French national programme Neff et al. (2006, 2010), Monnier et al. (2008) and Féron et al. (2009) examined archaeological iron artefacts and used the results to predict very long-term corrosion rates and the mechanisms by which corrosion layers passivate further corrosion. This is typical of the standard approach taken but, as a check on the long-term performance of steel canisters, both Nagra (Switzerland) and JNC (Japan) carried out natural and archaeological analogue studies of iron artefacts from a range of environments and compared those data directly with well-controlled, but short-term, laboratory corrosion data.

Even though most material studied came from aerobic to sub-aerobic environments and would, therefore, be expected to corrode to a much greater extent than in the anaerobic setting of a GDF, a maximum corrosion depth of 10 mm in 1000 years was calculated by Nagra (Figure 3.2.2-1), so increasing confidence in the results from the short-term experimental data and the safety case Base Case assumption of 29 mm (NWGCT 1984).

For JNC, a maximum corrosion depth of 15 mm in 1000 years was calculated in the H12 safety case (JNC 2000). The maximum corrosion depth was decreased to < 10 mm in the subsequent H17 safety case (JNC 2005), even though this included archaeological analogue data from aerobic environments (see the samples outlined in red dots in Figure 2). Comparison of these aerobic archaeological analogue data with well-controlled laboratory data for anaerobic conditions (Figure 3.2.2-2) indicated that even this lowered corrosion rate could be regarded as conservative.

These data, and more recent information from the medium-term FEBEX URL experiment, are shown in Table 3.2.2-1. The inclusion of the FEBEX data is interesting insofar that the second part of the experiment ran for some 18 years before dismantling and analysis. Despite this significantly longer timescale, Hadi et al. (2019) noted that only diffusion of Fe^{2+} into the bentonite was observed and that "The results indicate the occurrence of newly formed octahedral Fe^{2+} either as Fe^{2+} sorbed on the clay or as structural Fe^{2+} inside the clay (following electron transfer from sorbed Fe^{2+}). No other indications of clay transformation or newly formed clay phases were found."

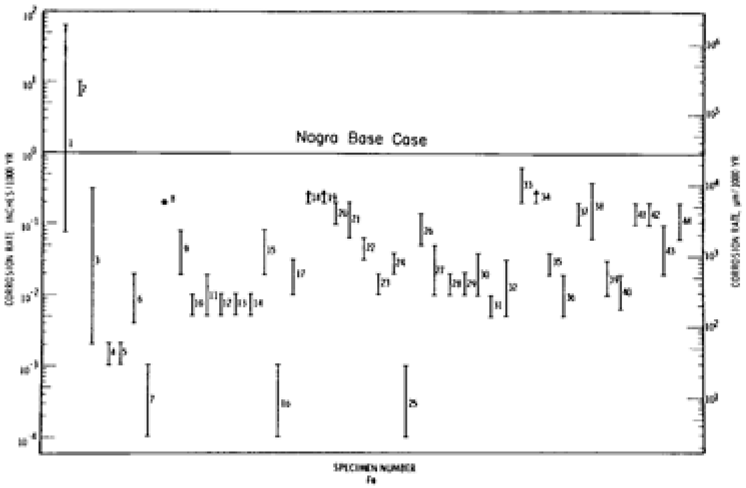

Figure 3.2.2-1. Iron corrosion rate data from natural and archaeological analogue studies (from Miller et al 1994). The corrosion rates for the archaeological artefacts range from 0.1 to 10 mm per year (note that samples 1 and 2 are from oxidising marine conditions and that details of the other 42 samples can be found in Johnson & Francis 1980). The Nagra base case corrosion rate for steel canisters from Nagra's Projekt Gewähr (NWGCT 1984) is also shown for comparison.

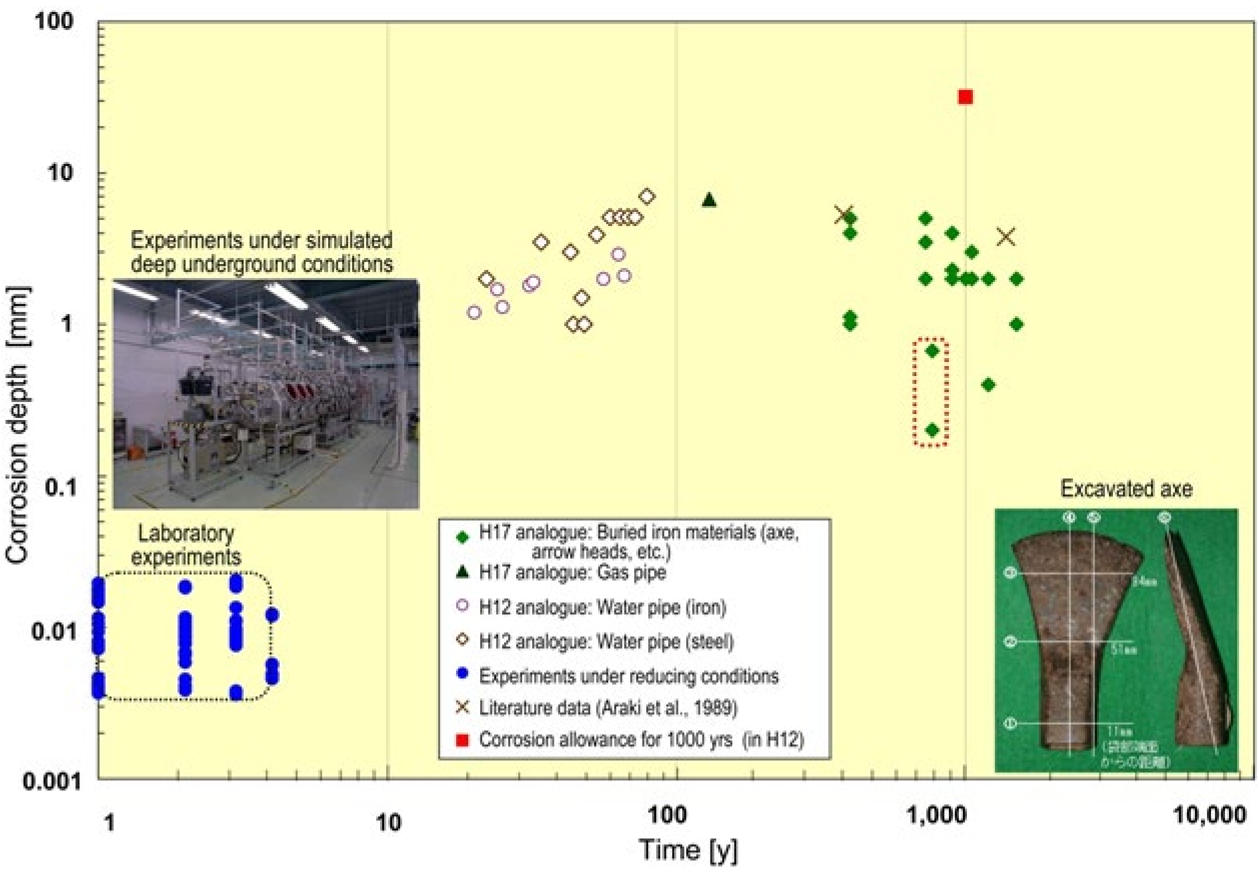

Figure 3.2.2-2. Integration of iron/steel corrosion data from laboratory experiments and several archaeological analogue sources (sample details in JNC, 2005). Note that the H17 analogues surrounded by the red dots are believed to have come from an aerobic environment (JNC 2005).

Table 3.2.2-1. Comparison of steel corrosion depths based on laboratory data cited in the H12 (JNC 2000), Kristallin-1 (Nagra 1994) and H17 (JNC 2005) safety cases (and more recent information from the FEBEX URL experiment) with a range of archaeological analogue data for steel/iron artefacts (after Posiva 2012).

Form of data	**Corrosion depth (per 1000 years)**	**Reference**	**Comments**
Short-term laboratory experiments	31.8 mm	JNC (2000)	Uniform corrosion of carbon steel. Safety case Base Case value
Short-term laboratory experiments	29 mm	NWGCT (1984)	Conservative corrosion rate, including an allowance for pitting. Safety case Base Case value
Short-term laboratory experiment	1.21 - 3.38 mm	Smart et al. (2017)	Corrosion of carbon steel in a range of bentonites (varying mineralogy, density and form)
Short-term (accelerated) laboratory experiment	0.01 mm	Neeft (2018)	Corrosion of irradiated stainless steel under alkaline, cementitious repository, conditions

Form of data	Corrosion depth (per 1000 years)	Reference	Comments
Short-term (5 years) FEBEX URL experiment	0.1 mm	Madina (2004)	Generalised corrosion of a carbon steel coupon in the bentonite (recovered following dismantling of Heater 1)
Medium-term (18 years) FEBEX URL experiment	6-11 mm	Wersin & Kober (2017)	Generalised corrosion of a carbon steel heater (Heater 2) and liner surfaces
Natural analogue	0.09×10^{-3} mm	Hellmuth (1991ab)	Weathering of native iron in basalt (Disko Island)
Archaeological analogue	10 mm	Range of studies cited in Nagra (1994)	Uniform corrosion of iron and steel
Archaeological analogue	<15 mm	Range of studies cited in JNC (2000)	Uniform corrosion of iron and steel
Archaeological analogue	0.1 - 10	David (2001)	Literature review of corrosion of archaeological samples
Archaeological analogue	<10 mm	Range of studies cited in JNC (2005)	Uniform corrosion of iron and steel

In the UK national programme, Crossland (2005, 2006) provided a useful comparative review of the corrosion of iron including laboratory, archaeological and natural analogue data. Whilst acknowledging the relatively small dataset, it was noted that:

- The rate of corrosion is very different for laboratory studies where the iron surfaces are not confined (i.e. in free water), where it is constant, while, in soils, the confined surfaces indicate that the iron corrosion kinetics follow a parabolic different rate equation (time span ranging from 0.5 to 1700 years) (see Table 13.2-1, ID 3.2.2-1)
- Estimated corrosion rates were:
  - Less than 10 mm per 1000 years for oxidising conditions in soils
  - Less than 0.1 mm per 1000 years for anoxic conditions in soils

These compare well with the cited laboratory data for comparable conditions (i.e. with confined corroding surfaces)

- Limited data on the corrosion of iron meteorites in soil would appear to support extrapolation of laboratory data to the longer timescales of relevance to a GDF (see Crossland 2006, Figure 8)
- Iron corrosion in soil results in the formation of concretions with corrosion products forming in the soil porosity and this suggests that the different parabolic kinetic rates are due to the confinement by the surrounding soil (which is arguably more relevant to the GDF environment where the canister is confined by the bentonite buffer). Crossland (2006) pointed out that the NA data support the extrapolation of the short-term laboratory data for the safety case insofar that these over-estimate long-term corrosion in the GDF and is, therefore conservative. These conclusions are supported by the inclusion in Table

3.2.2-1 of more recent short-term laboratory (e.g. Smart et al. 2017; Neeft, 2018) and URL (e.g. Madina 2004) data and medium-term URL data (Wersin & Kober 2017).

3.2.2.3 Uncertainties and limitations

- **Potential sampling bias of archaeological materials**: As noted in Miller et al. (2000) *"Archeological materials are potentially prone to bias if focussed on artefacts obtained from museum collections, because museums will (naturally) tend to house the best-preserved artefacts. Corrosion rates based solely on archaeological material could, thus, be non-conservative. This sample bias problem is likely to be less important if artefacts are collected in situ, rather than from a museum, for then it would be possible to see artefacts in all possible degradation states for that environment. Analogue studies based on archaeological artefacts must be considered carefully to determine if this type of bias has occurred."*
- The problem of biased sampling due to rapid corrosion of metals excavated from aggressive environments was investigated by Tylecote (1979). Although the problem of sample bias towards better preserved samples may have occurred in the Johnson and Francis (1980) study (see comments in Miller et al., 2000), the results of (copper) corrosion studies carried out by Tylecote (1979) produced rates which were remarkably similar to those of Johnson and Francis (1980)
- **Potential process bias of archaeological materials:** Crossland (2005, 2006) pointed out that iron artefacts corroding in soils is not necessarily representative of GDF conditions, but that extrapolating the short-term laboratory data to GDF-relevant timescales is justified in this case as the calculated long-term corrosion rates are conservative in the sense that the corrosion rates display parabolic kinetics, as compared to the constant kinetics in free water. However, this conclusion ignores the fact that, in a GDF (as noted above) a steel canister is likely to be contained in a concrete or bentonite backfill. Although steel canister corrosion rates in bentonite have been measured in the laboratory (e.g. Smart et al., 2017), the short timescales (20 months in this case) provide little information on system kinetics
- The very low laboratory corrosion rates reported by Neeft (2018) are very encouraging for cementitious repository designs. To support the use of these rates in the ESC, future NA corrosion rate studies should focus on similar environments where possible
- As the laboratory and URL experiments have been carried out under differing experimental conditions, the reported short-term corrosion rates vary significantly. The use of similar experimental protocols in future would greatly ease the comparison of data and ultimate interpretation

3.2.2.4 Relevance – what we have learnt?

- As in section 3.2.1, the preservation of a range of archaeological artefacts under much more oxidising conditions than are likely to exist in a GDF, provides confidence in predicting that iron-based structures in a GDF will survive for thousands of years
- Direct comparison of laboratory, URL and natural and archaeological analogue data increases confidence in such an integrated approach to producing safety case relevant data as the comparison illustrates the reasonable agreement in the produced corrosion rates
- Direct comparison of laboratory and natural and archaeological analogue corrosion rate data with the safety case Base Case corrosion rate clearly illustrates the conservatism of the safety case approach (see also the comments in Crossland, 2006)

- In the Japanese national programme, archaeological materials are often utilised in stakeholder communications as these have been found to be of more interest and easier to understand (than the laboratory experiments) for non-technical audiences

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3.3 Overview on other materials for containers and analogues

In addition to copper and steel discussed in sections 3.1 and 3.2, respectively, other materials have been considered to be used in waste containers for HLW and spent fuel: titanium, stainless steel, nickel-alloy and ceramic materials.

Titanium (a highly corrosion-resistant material) has been considered as an alternative to copper and carbon steel or cast iron in several national programmes (RWM 2016). No detailed NA studies have been reported so far.

For HLW and SF, there may be potential to employ stainless steel to provide a durable waste container using grades with suitable corrosion resistance with a cementitious backfill (RWM 2016). Stainless steel NAs have not been reported, but see section 3.2.2.

Nickel can be alloyed with other elements to achieve very high corrosion resistance, providing a more corrosion-resistant alternative to stainless steel. Highly resistant grades have been considered for the manufacture of

HLW/SF containers in a permanently aerobic (and therefore corrosive) disposal system (RWM 2016). No NAs have been reported for nickel-alloy materials so far[3].

Advantages for the use of ceramics containers are their high chemical stability. However, fabrication and mechanical behaviour present substantial challenges (RWM 2016). Limited information is available for ceramic materials NAs. Miller et al. 2000 report crystalline sphene as an analogue for the glass-ceramics immobilisation matrix (the natural mineral was used as a basis for the technical development).

In case one these options would be taken under more detailed consideration, the topic needs to be revisited. In theory, for all materials mentioned above, NAs could be found.

For LILW waste containers made of stainless steel, carbon steel and cast iron, as well as concrete, see sections 3.2 (and subsections) for steel and chapter 4 for concrete in this report.

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[3] Study of iron-nickel meteorites has been suggested as these can have well-constrained ages and may be indicative of weathering over sufficiently long timescales. However, as noted in Miller et al., (2000) when discussing the relevance of iron meteorites for steel corrosion studies "Metallic iron is sometimes found in certain types of meteorites but is generally alloyed with other metals which, together with the extreme conditions they have endured, means that no conclusive results can be drawn from their investigation. As a result, it is not recommended that iron meteorites are considered in future analogue studies". And a similar conclusion is made here with respect to iron-nickel meteorites.

4 CEMENTITIOUS MATERIALS

4.1 Overview on cementitious materials and analogues

Concretes are complex mixtures of compounds that continuously, albeit slowly, evolve:

- Modern concretes are largely based on Portland cement (dominantly calcium silicate hydrates (CSH), calcium aluminate hydrates (CAH) calcium hydroxide (portlandite) ± hydrous calcium alumino-sulphates). Older cements are typically calcium hydroxide (hydrated lime) based, with or without a pozzolan (non-crystalline silica-bearing material, e.g. volcanic ash)
- Cements harden through hydration reactions that generate CSH compounds of varied composition
- These CSH compounds initially form as gels that bind the intermixed aggregates (sand and gravel) to form concrete
- CSH gels are unstable in the long-term and are expected to transform into more crystalline forms which may impact chemical buffering properties of the GDF environment
- The rates of the expected transformations are typically too slow to measure in a laboratory
- The transformations are also very difficult to predict and model
- Ultimately it is the properties of the gels and their evolved crystalline forms that determine the physical and chemical properties of the cement and concrete

Consequently, studies of archaeological and industrial building cementitious materials (hundreds to thousands and tens to hundreds of years old respectively) are essential to understanding the evolution of GDF cementitious materials, in particular the CSH gels, over the periods of time that are relevant to the use of these materials in GDFs

The actual quantities of cementitious material to be used in some repositories are huge; for example, the near-field of the current Swiss GDF design for low- and intermediate-level wastes (L/ILW) will contain several million tonnes of cementitious materials, which will be approximately 90 % of the total mass of all materials emplaced in the GDF. This quantity of cementitious material is comparable to that used in other major infrastructure projects, e.g. the Channel Tunnel.

Much of the cementitious material in repositories will need to function for thousands to hundreds of thousands of years and, although laboratory studies of concrete durability are useful, the very slow rates of transformation or degradation mean that long-term supporting data are also required.

Cementitious materials analogues

Although a relatively old review, McKinley & Alexander (1992) noted that there were few good natural and archaeological analogues of cementitious systems and recent literature searches carried out by the authors supports this even today. Some new material (on low-pH concretes) is presented in section 4.1.2 and, otherwise, the main focus of recent work has been in the area of CCS (carbon capture and sequestration – see Pearce, 2006, for example). Otherwise, most information on OPC concrete longevity has been produced in the Maqarin (Jordan) Natural Analogue Project (see section 4.1.3 for details).

The natural cementitious materials at Maqarin are part of a widespread terrain which stretches from Turkey in the north, through Syria, Jordan and Israel to Saudi Arabia in the south. These cementitious materials were formed by the combustion of organic-rich limestones, a process which continues today (Kamei et al. 2005). The oldest reported cementitious materials in this area are some 2 Ma old and, although usually heavily fractured into blocks, reaction is very much restricted to the outer edge of the blocks. This is possibly because the natural material is of low porosity and permeability (generally, the cements act as an aquiclude in Jordan and Syria) and the secondary reaction products naturally seal any flowing porosity (see discussion below). Reaction only occurs following fracturing and exposure of fresh surfaces (usually following earthquakes).

The presence of unreacted natural cementitious materials from the Scawt Hill and Carneal Plug sites in Northern Ireland are discussed in section 4.1.4. These phases were produced during the thermal metamorphism of the host limestone and are estimated to be some 58 million years old. As with the cementitious materials in Jordan, these natural cements in Northern Ireland remained unchanged until accessed by groundwaters in the last 10,000 to 20,000 years.

For low-pH cementitious materials, Malinowski & Garfinkel (1991) described the use of a lime-based concrete in the floors of a Neolithic (ca. 7000 BC) construction in Galilee. The type of material used here indicates that Neolithic man had technology for the burning and calcining of limestone. Prior to this discovery, it was thought that the first inorganic cements were made from gypsum ($CaSO_4 \cdot 2H_2O$). It is generally agreed that Egyptians used gypsum in the construction of the Great Pyramid of Cheops built between 2613 and 2494 BC (Lea 1970). Thomassin & Rassineux (1992) reviewed some of the literature on Gallo-Roman cement-based materials and noted that one of the most impressive examples is the Roman mortar used in Hadrian's Wall (section 4.1.1) which has helped to ensure the Wall's preservation for the last 2000 years in this notoriously wet part of northern England. The ROMANCONS group have been studying Roman low-pH concretes for several decades and their (ongoing) work on the incredible preservation of Roman concretes is discussed in section 4.1.2. For further information of archaeological analogues of low-pH concretes, see Posiva (2021).

Finally, some mention is made of relevant industrial analogues in the chapter 10, with a potential study of iron corrosion in concrete discussed briefly.

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4.1.1 Longevity of cementitious materials: case study - Hadrian's Wall (UK)

Item:

NA4.1.1

Component(s):

Cementitious materials

4.1.1.1 Introduction

See section 4.1

IFEPS:

2.3.4.5 - Alteration [waste package]

3.2.3.1 - Material volume changes [repository]

2.3.4.3 - Migration of chemical species [waste package]

3.2.4.3 - Migration of chemical species [repository]

3.2.4.5 - Alteration [repository]

NA Type:

Archaeological analogue

4.1.1.2 NA description

There are many examples of extant Roman cements and concretes across the UK (Harris 2002, Crossland 2006), one of the most famous being Hadrian's Wall in northern England (Figure 4.1.1-1). Study of the cement mortar from Hadrian's Wall indicated that the particular materials used led to the production of secondary phases which have made the mortar particularly waterproof. It is thought that this reduced permeability has helped it survive the ravages of the climate at this far northern outpost of the Roman Empire for so long.

Examples of ancient man-made cements are found all across the former Roman Empire (see Alexander 2018, for details) and, although the precise cement chemistry varies a little because of the local materials used, they are similar in showing incredible durability regardless of the local climatic conditions.

Examination of Roman concrete still surviving in Hadrian's Wall (Figure 4.1.1-1) has provided valuable information about the stability of concrete for time periods of hundreds to thousands of years.

Figure 4.1.1-1. View of Hadrian's Wall, northern England (NDA).

Samples were taken from the heart of the Wall at a site near Sycamore Gap (Figure 4.1.1-2) where the remains of the original Roman concrete survive from a period of reconstruction around 200 AD under Emperor Septimus Severus. Several researchers (e.g. Rayment & Pettifer 1987) have since analysed these samples using a wide range of techniques and found:

- The concrete nearest the edges of the wall has been converted to carbonate minerals such as calcite
- Concrete near the centre of the wall contains a high proportion of CSH compounds

- The CSH compounds identified are calcium alumino-silicate hydrates with calcium / silicon molar ratios of 0.34-1.25
- Evidence for some reaction between the cement and the aggregate used to produce the concrete, so changing the original porosity

The presence of CSH compounds was a surprise because the cement is lime-based, with no deliberately added pozzolan, and therefore should not have developed large amounts of CSH. Further research, however, suggested that the cement was made from locally sourced limestone that contains a significant quantity of silicate that could have fortuitously produced calcium silicates (as found in Portland cement) during the manufacture of the cement.

Figure 4.1.1-2. Remains of milecastle 39 near Sycamore Gap (NDA).

4.1.1.3 Uncertainties and limitations

- Early studies of archaeological mortars focussed on the similarities with modern-day (Portland) cements because they were carried out before the current interest in low-pH cements (see Neall & Johnson, 2006, for details). This makes some of the information difficult to extrapolate to low-pH cements
- The compositions of the CSH compounds found at Hadrian’s Wall are subtly different to modern concrete, which typically have higher calcium/silicon ratios (1.2-2.0)
- The cement is exposed to the atmosphere and not surrounded by large amounts of rock and associated fluids, as in a deep GDF. Although the mechanisms (carbonation, CSH survival) are largely the same, the rate of carbonation will clearly be much higher, so this may be considered as an accelerated ageing test (relative to a GDF)
- Archaeological concretes contain little or no natural radionuclides. So they provide little information

on radionuclide containment in the GDF
- Concrete degradation can occur via other mechanisms such as attack by sulphate, chloride and magnesium that have not been observed or studied in this example
- The ages of many of the structures studied are impressive and are of direct relevance to near-surface repositories for very low- and low-level wastes. The timescales are nevertheless somewhat short for a deep GDF
- Many of the most impressive archaeological sites are now under some form of protection (e.g. Hadrian's Wall is now an UNESCO World Heritage Site), so further sampling is restricted and would require non-destructive testing

4.1.1.4 Relevance – what have we learnt?

- The compounds identified in the Hadrian's Wall concrete are similar enough to those found in modern-day (Portland) cements, partly because of the fortuitous characteristics of the source material, which allow this particular concrete to be considered a good archaeological analogue
- CSH compounds, despite their theoretical instability, have been shown to survive essentially intact for nearly 2,000 years
- Carbonation (conversion to carbonates such as calcite) is the main mechanism for the alteration of cement exposed not just to the atmosphere, but also to many groundwaters around a GDF (Alexander et al. 2015)
- To date, carbonation of concrete has been largely ignored in safety case calculations, but it could further protect the concrete in a GDF against groundwater leaching and loss of the CSH minerals
- Regardless of the limitations noted above, the clear message is that cementitious materials can survive for thousands of years, often in conditions which are much more severe (Northumbrian climate) than would be expected in a deep GDF
- Although the actual building methods used are of little relevance to modern construction techniques, the writings of Marcus Vitruvius Pollio around 27 BC (Vitruvius 27 BC) make it clear that quality control during cement production and the building work was of the greatest priority. Arguably, this has helped ensure the remarkable longevity of many archaeological types of cement and concretes from the Roman Empire and sends a clear message to current GDF operators

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4.1.2 Longevity of cementitious materials: ROMANCONS (Italy)

Item:

NA 4.1.2

Component(s):

Cementitious materials

4.1.2.1 Introduction

See section 4.1.1.

IFEPS:

2.3.4.5 - Alteration [waste package]

3.2.3.1 - Material volume changes [repository]

2.3.4.3 - Migration of chemical species [waste package]

3.2.4.3 - Migration of chemical species [repository]

3.2.4.5 - Alteration [repository]

NA Type:

Archaeological analogue

4.1.2.2 NA description

The ROMANCONS (Roman Maritime Concrete Study) group consists of an international consortium of universities and CTG Italcementi Group and their aims include:

- analysis of the concrete matrix to determine size, material, and proportions of micro and macro-aggregate
- identification of the sources of pozzolana, tuff, and other aggregate used in the concrete structures studied
- comparison of the relative compressive strength and density of various concrete mixes

Low-pH concrete is essentially the same as the pozzolanic concretes developed by the Romans in the 3rd century BC. The Romans used the pozzolan concretes in positions where it was important to prevent the penetration of water and, due to its resistance to seawater, it was used extensively for marine structures. The first recorded use of Roman pozzolanic concrete to build a harbour is that of the Port of Cosa, Italy in 200 BC, the pier of which "…is still usable at the end of the second millennium for its intended purpose if the need exists." (Bremner 1993).

The ROMANCONS group have collected samples from a range of sites around the Mediterranean (Figure 4.1.2-1) and the degree of preservation of the bulk concrete has been found to be remarkably high (Figure 4.1.2-2). They also note the likelihood of natural low-pH concretes (potential sites noted in the Table 13.3-1, ID 4.1.2-1).

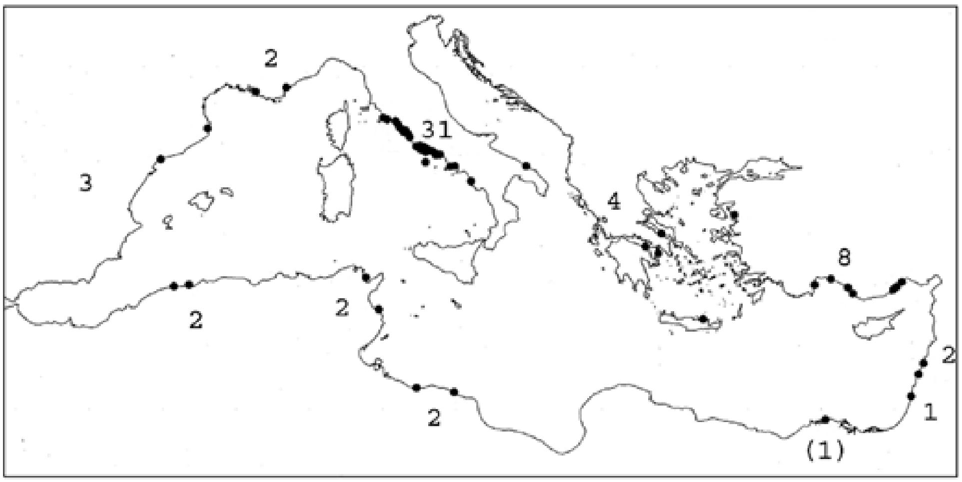

Figure 4.1.2-1. Map of the Mediterranean with the location and number of Roman maritime sites studied by the ROMACON group (Brandon et al. 2005). The sites range in age from the 2nd century BC to the Byzantine era (395 – 1453AD).

More recent work by the ROMANCONS group has focussed on long-term reactions between the cement and seawater. Vola et al. (2011) note little reaction with the aggregate, but that the cementitious matrix includes amorphous gel-like, silica-rich C-A-S-H, with subordinated "sparry" calcite cement due to the slow reaction of hydrated lime in seawater. Further analyses to investigate microstructural variability, related to different stages of dissolution and precipitation, is "ongoing" (Vola et al. 2011), so it is currently difficult to assess if seawater immersion for two millennia has had a deleterious effect on the Roman low-pH concretes.

Finally, it is worth noting that Roman low-pH concretes had very long setting times when compared with modern OPC, with some constructions reported to be still heat emitting after two years (e.g. Brandon et al. 2005). As such, they are significantly less vulnerable to fracturing to the extent that it is possible to construct low-pH concretes which have a design life of 1 thousand years and more (e.g. Mehta & Langley 2000).

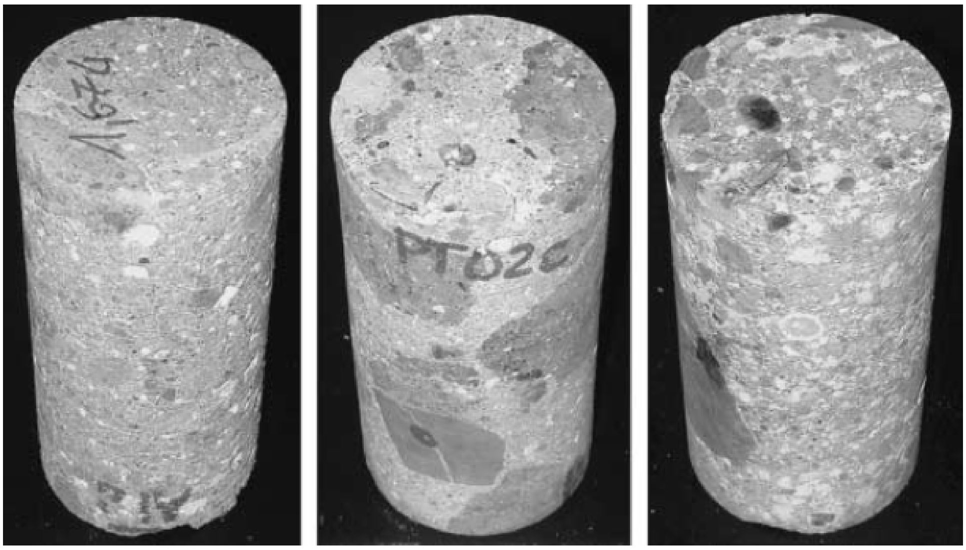

Figure 4.1.2-2 Typical low-ph concrete core samples recovered from sites at Portus and Anzio in western Italy (Oleson et al. 2004).

4.1.2.3 Uncertainties and limitations

- When compared to modern low-pH cements, the physical, mechanical and mineralogical properties of the ROMANCONS samples are not identical to modern low-pH cements (cf. Oleson et al. 2004 and Man and Martino 2009)
    - The Young's modulus and compressive strengths are generally quite low, although some samples have Young's modulus values approaching those of typical modern materials – unfortunately, Oleson et al. (2004) could see no reason why this is the case for those samples
    - Mortar to aggregate ratios and are generally a little high (Oleson et al. 2004) compared to modern ratios which are nearer 1 (cf. Man and Martino 2009)
    - Likewise, the porosity is high, but this at least means the low Young's modulus, low strength, low unit weight and high porosity are internally consistent[4]
- Comparison with the original properties of the ROMANCONS concrete is not possible and while any leaching or reaction of these cements with seawater is difficult to ascertain from the extant reports, it is likely that the different methods of handling the Roman concretes when compared to modern low-pH concretes obviously plays a role in the differences. For example, although the Roman cements were compacted, this was done by hand and so does not compare to modern compaction techniques. Evidence also suggests that the cements were poured into wooden forms which were water-filled (Oleson et al. 2004)
- As the described studies were conducted from an archaeological viewpoint, many parameters of relevance to GDF design have either not been examined or, at least, not yet reported

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[4] Note that some GDF designs include high porosity mortar to store the significant amount of gas generated from corrosion and breakdown of organic matter contained in the waste.

- The microstructural variability, related to different stages of dissolution and precipitation, which was reported as "ongoing" in Vola et al. (2011) still does not appear to have been reported

4.1.2.4 Relevance – what have we learnt?

- Samples have been collected from a range of sites around the Mediterranean and the degree of preservation of the bulk concrete has been found to be remarkably high
- The above noted differences in material handling could be tested in two simple ways:
    - make modern low-pH concretes using the Roman handling methods as laid down in Vitruvius (27 BC)
    - make Roman concretes using today's handling methods (e.g. those used in Chandler et al. 2002).

and then compare the physical and mechanical properties (see Table 13.3-1, ID 4.1.2-2).

This would allow a rapid assessment of any handling-related differences which could be subtracted from the properties described here. Gotti et al. (2008) produced a one-off sample of Roman concretes following the Roman approach and, perhaps not surprisingly, produced concrete remarkably similar to the Romans.

- Although only a qualitative observation, the ROMANCONS authors point out the incredible condition of the concretes examined so far and admire their obvious durability in such an aggressive environment.
- The Romans exercised effective quality control during cement manufacture (Vitruvius 27 BC) and this will undoubtedly have helped the preservation of most Roman cements. Davey (1974) noted "It is remarkable that these observations made by Vitruvius…..almost 2000 years ago, compare so well with those in modern specification or code of practice" suggesting that the Roman pozzolanic concretes are indeed an appropriate analogy for modern low-pH concretes which may be utilised in a GDF.

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4.1.3 Longevity of cementitious materials: case study – Maqarin (Jordan)

Item:

NA4.1.3

Component(s):

Cementitious materials

4.1.3.1 Introduction

See section 4.1.

IFEPS:

cement degradation, leaching (not in IFEP list)

2.3.4.5 - Alteration [waste package]

3.2.3.1 - Material volume changes [repository]

NA Type:

Natural analogue

4.1.3.2 NA description

The Maqarin study area is located in the Yarmouk River valley on the Syrian-Jordanian border, 16 km north of the provincial town of Irbid (Figure 4.1.3-1). This site was studied in detail for over 16 years, from 1989 to 2005, as an analogue for a cementitious GDF environment.

Discontinuous lenses of natural concretes were studied at Maqarin, but they are widespread in a zone from southern Turkey, across Syria, Jordan and Israel to northern Saudi Arabia. They have been formed by high-temperature, low-pressure heating of organic-rich, muddy-limestones and chalks (the Bituminous Marl Formation), which contain up to 25 wt % organic carbon (Khoury et al. 1992). The heating of the rock was caused by the spontaneous in situ combustion of the organic matter (Figure 4.1.3-2).

The combustion produced zones with complex calcium silicate and calcium aluminate-ferrite mineral assemblages which are very close analogues of modern OPC (Ordinary Portland Cement).

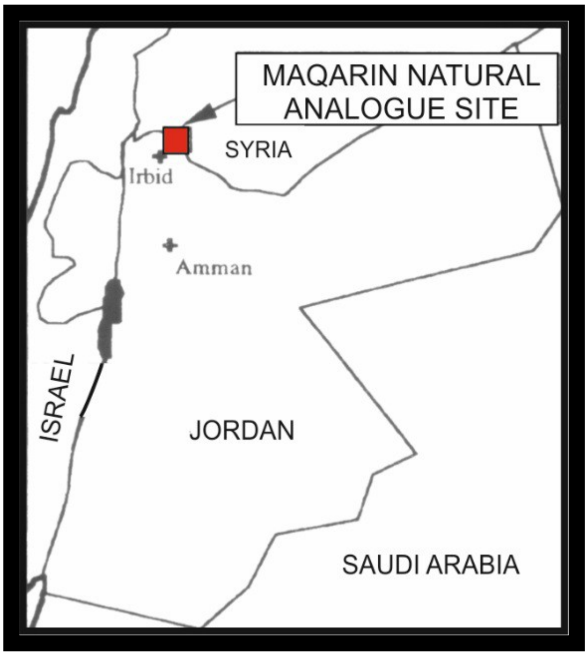

Figure 4.1.3-1. Map of Jordan showing the position of the Maqarin site (Alexander 1992).

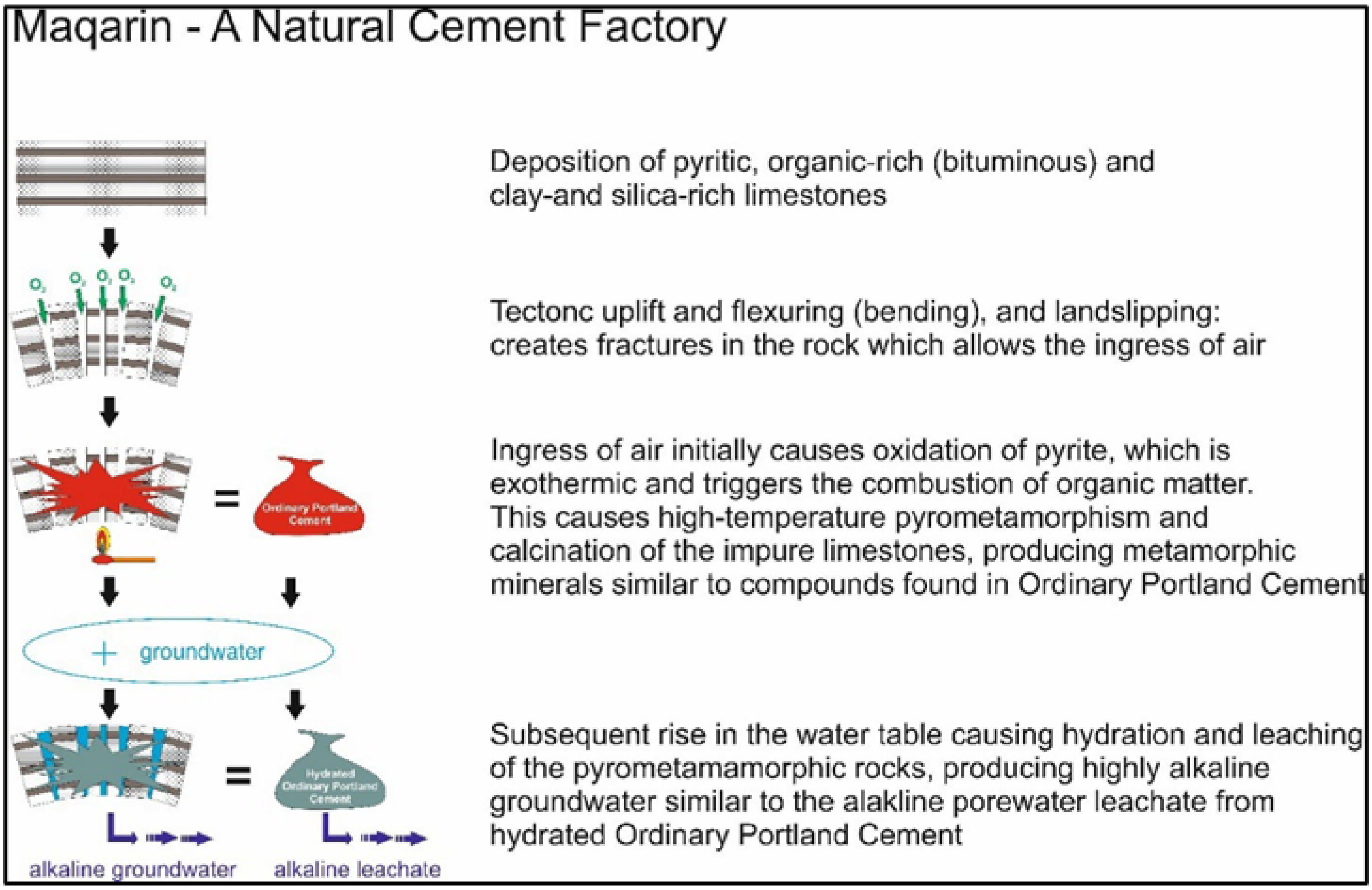

Figure 4.1.3-2. Schematic representation of the production of the natural concretes at Maqarin (Alexander et al. 2005).

Subsequent groundwater percolation through the natural OPC has resulted in the production of natural concretes. When these concretes are later fractured by the ongoing tectonism in the Maqarin area, the concrete is hydrated and leached by groundwaters. The hydration products include a wide variety of hydrated CSH minerals and gels, which closely resemble phases found in hydrated OPC. In this respect Maqarin is a unique, natural site in that not only are natural concretes formed, these concretes are then leached, producing natural highly alkaline groundwaters (up to pH 12.9) that are similar in composition to the high-pH porewaters that are expected to leach from OPC-concrete in a GDF (Atkinson 1985, Linklater 1998).

Longevity of the natural concretes

The Maqarin concretes are usually heavily fractured into blocks (Figure 4.1.3-3), but reactions are mostly restricted to the outer edges of the blocks. This is possibly because the natural concrete is of low porosity, permeability and the secondary reaction products (see Milodowski et al. 2001 for details) naturally seal the fractures (dating of the system suggests they seal in a few years; Alexander & Smellie, 1998). Generally, the natural concretes act as an aquiclude in Jordan and Syria. Reaction of the concrete in the Maqarin area, usually following local, gravitational-induced earthquakes only occur following fracturing and exposure of fresh surfaces.

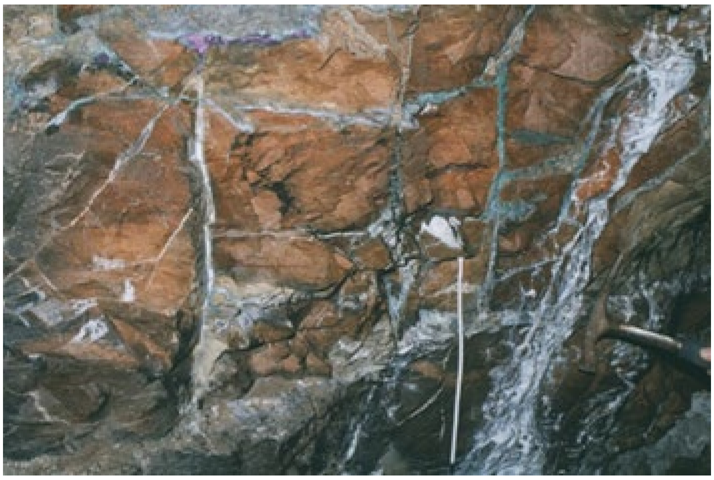

Figure 4.1.3-3. Sealed fractures in the natural concretes at the Maqarin site, Jordan (for scale, see hammer in bottom right corner) (Pitty & Alexander 2011).

4.1.3.3 Uncertainties and limitations

- Although the natural concretes discussed here are found over a very large area of the Middle East, the Maqarin site is unique in having an active groundwater system which allows study of the self-sealing of the natural concrete once it is perturbed (tectonically, in this case). Clearly, greater confidence could be placed in the results if the processes could be studied at additional sites (see Table 13.3-1, ID 4.1.3-1).
- The main focus of the project was not concrete longevity (rather it was concrete leachate-host rock interaction, see Pitty & Alexander, 2011, for details), so only limited dating of the secondary reaction mineralisation has been undertaken because of the difficulty of being able to separate pure mineral phases for radiometric analysis. 230Th/234U dating of secondary fracture minerals has shown that they are in the order of 80,000 to 100,000 years old.
- As above, the focus on concrete leaching means that there is currently no information on long-term concrete stability under high stress environments, but this could be assessed with suitable samples (Table 13.3-1, ID 4.1.3-2).

4.1.3.4 Relevance

- The natural concretes at Maqarin are some 2 million years old and clearly indicate that OPC-concretes can be stable for GDF-relevant timespans
- Although the natural concretes fracture in earthquakes, when groundwaters then react with the fractured concrete, it rapidly self-seals, with the secondary reaction phases rapidly resealing the damage zones
- The secondary reaction phases are generally the same as those produced when concrete is leached in laboratory (e.g. Bateman et al. 1995) and URL (e.g. Mäder et al. 2006) experiments and predicted in modelling studies (e.g. Savage 2005), clearly indicating the relevance of the analogy
- The secondary reaction phases (including supposedly metastable amorphous phases and gels) appear to be stable for tens to hundreds of thousands of years (Pitty & Alexander 2011), provided they remain isolated from further groundwater reaction
- If reaction phases react with groundwaters, they generally produce tertiary phases such as carbonate, ettringite, thaumasite and gypsum (Clark et al. 1993, Smellie 1998) which further seal any remaining groundwater pathways
- The Maqarin natural analogue study significantly extends our knowledge of the persistence of concretes in the natural environment beyond the timescale of archaeological analogues, and supports safety case arguments for the potential long-term stability of concretes (be they seals, tunnels liners, waste containers, waste forms etc.) in the GDF environment

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4.1.4 Longevity of cementitious materials: Case study – Scawt Hill and Carneal Plugs (Ireland)

Item:

NA 4.1.4

Component(s):

Cementitious materials

4.1.4.1 Introduction

See section 4.1

IFEPS:

2.3.4.5 - Alteration [waste package]

3.2.3.1 - Material volume changes [repository]

NA Type:

Natural analogue

4.1.4.2 NA description

The Antrim Lava Group of Northern Ireland is between 23 and 66 million years old and is intruded by at least thirty volcanic intrusions. These form prominent landmarks in places, rising above the surface of the Antrim Plateau (Mitchell 2004). In outline, these minor intrusions are roughly circular or elongated in a NNW-SSE direction. They vary from 50 m to 1 km in diameter and are composed mainly of alkaline-olivine-rich dolerite. Four of these plugs intrude chert-bearing limestones of the Ulster White Limestone Formation. Within the thermal aureole of these intrusions, high-temperature (ca. 1,100 °C), low- pressure (< 700 m cover rocks) metamorphism of the host limestones and nodular cherts has resulted in the formation of a complex calcsilicate mineral assemblage that includes minerals such as larnite. These larnite nodules have been hydrated through reaction with groundwater, resulting in the formation of natural concretes analogous to OPC (Ordinary Portland Cement) concretes which will be used in a GDF. As such, Scawt Hill and Carneal Plug have been studied as NAs for concrete longevity (Milodowski et al. 1989).

Scawt Hill in County Antrim is a very conspicuous feature at the edge of the east-facing Antrim basalt escarpment (Figure 4.1.4-1, top). It is formed by a moderately large volcanic intrusion that intrudes both the limestones and older lavas. Carneal Plug is much smaller, some 100-120 m in diameter, located to the south of Larne. The eastern margin of the intrusion is sheared, and this shearing also affects a large altered piece of the host limestone which is included within the intrusion (Figure 4.1.4-1, bottom).

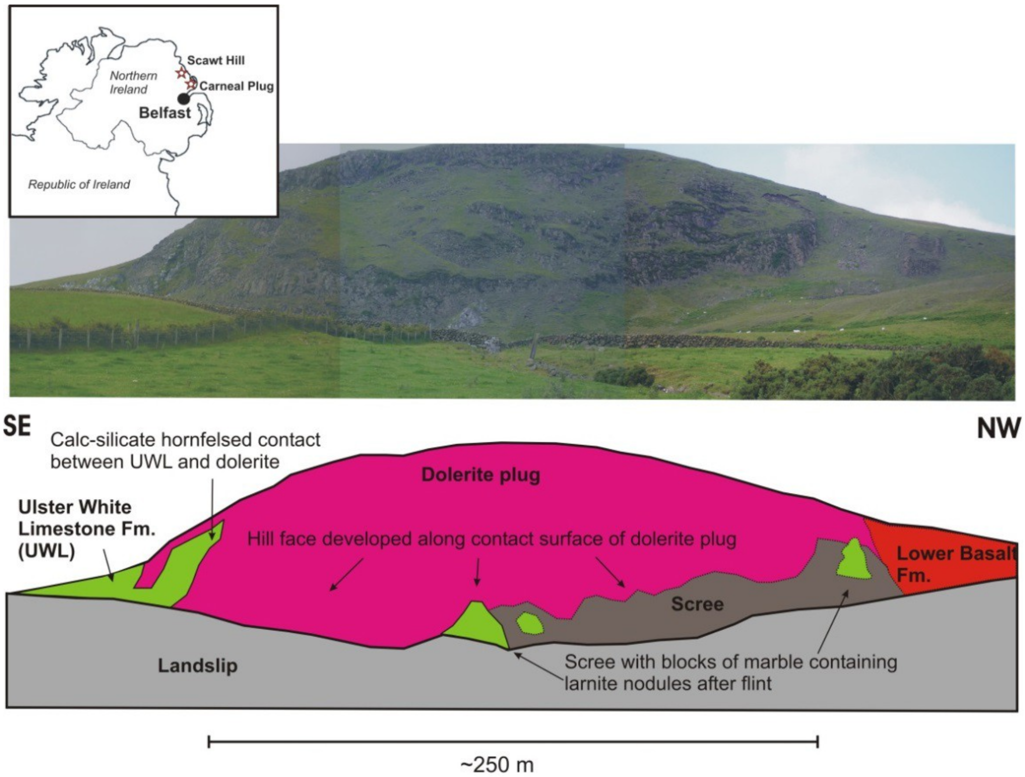

Figure 4.1.4-1. Location of the natural analogue study sites and a simplified geological cross-section of Scawt Hill (from Milodowski et al. 2011).

Mineralogy of the larnite nodules and their hydration products

The larnite nodules largely retain the morphology of the original nodular chert, but with some brecciation related to the volume change brought about by the mineralogical reaction during the thermal metamorphism. The chert is completely replaced by calcsilicate rock containing crystalline minerals (e.g. tobermorite) and amorphous CSH gels, analogous to some phases found in OPC concrete.

Figure 4.1.4-2. Hydrous gel-like phase formed by hydration and alteration of a larnite nodule, which was revealed in a freshly broken block of rock from Scawt Hill (Milodowski et al. 2011).

Hydration of the larnite nodules has produced reaction rims containing crystalline and amorphous CSH phases and other minerals analogous to those found in OPC concrete. These phases may, in turn, be replaced by calcium carbonates at a later date by reaction with bicarbonate in groundwaters, in a reaction similar to that expected to occur in a GDF (cf. section 4.1.3; Höglund 2014). Dating the hydration and carbonation events is difficult, but the evidence was interpreted by Milodowski et al. (1989) to infer an age for the formation of the CSH phases during the retrograde hydration, probably shortly after intrusion (i.e. ca. 58 million years ago). The much later carbonation of the CSH minerals in the larnite nodules is most likely to have occurred when the nodules were exposed to the atmosphere as a result of major land-slipping shortly after the retreat of ice cover at the end of the last glacial maximum (24,000 to 20,000 years ago), when the ice support to the steep slopes of the Larne Plateau was lost (Mitchell 2004, Milodowski et al. 2009, 2011)

4.1.4.3 Uncertainties and limitations

- The natural analogue study has not dated the CSH gels directly, rather the age is based on geological, geomorphological and petrographical considerations
- Similarly, the age of the carbonation event is inferred from geological and geomorphological information
- The boundary conditions of this natural analogue system are poorly-constrained. In particular, the timing and composition of past groundwaters interacting with the CSH and carbonation phases are unknown
- Cement degradation can occur via other mechanisms such as attack by sulphate, chloride and magnesium (cf. Hewlett 1998) that have not been observed here

4.1.4.4 Relevance

- CSH compounds, despite their theoretical instability, have been shown to survive essentially intact, possibly for tens of millions of years, without evolving to more crystalline forms. This natural analogue study extends knowledge of the persistence of CSH phases in a GDF-relevant environment beyond the timescale of archaeological cements (e.g. section 4.1.1) and even the Maqarin natural concrete (section 4.1.3)

- This analogue study supports arguments for the potential long-term persistence of CSH phases in the natural environment, and therefore for their potential to provide buffering capacity to maintain a high-pH in a GDF over the long-term.
- Carbonation of the OPC concrete phases is as expected in a GDF and their clear longevity (20,000 to 24,000 years) increases confidence in models of OPC concrete reaction which assume they will remain stable in a GDF environment for very long time periods

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4.1.5 The influence of cementitious materials, limited survival of microbes in cementitious environments - Maqarin (Jordan)

Item:

NA4.1.5

Component(s):

Engineered barrier system, Wasteform, Cement [cementitious], Container, Concrete, Backfill, Plugs and seals

Cementitious materials, microbes

4.1.5.1 Introduction

Microbial life can exist and adapt to extreme geochemical environments. Within a GDF environment, it is important to understand how microbes may impact the geochemistry, in particular in relation to their influence on the corrosion of metals, cements, waste materials and radionuclide mobility. Natural high pH groundwater systems, such as found in Oman or at Magarin in Jordan, provide an opportunity to study established microbial communities in GDF-relevant environments.

Microbial degradation of cements and concretes is commonly observed under aerobic conditions and could occur during the early phase of a GDF, thus possibly impacting the performance of the GDF in the short-term. This needs to be considered when carrying out the safety case.

Microbial degradation is achieved by microbes oxidising sulphur, sulphide and thiosulphate, resulting in the production of sulphuric acid, which attacks the concrete matrix by dissolving the constituent minerals (such as calcium silicate hydrate (CSH) gel and Ca(OH)2). Direct anaerobic corrosion of concrete has not been reported to date, although organic acids produced by microbial action on organic materials may be important. Biofilms can also grow on concrete surfaces but this may be because the microbes are utilising the organic plasticisers often used to make the material more workable.

IFEPS:

2.3.5 - Biological processes [waste package]

2.3.5.1 - Microbial growth and decline [waste package]

2.3.5.2 - Microbially/biologically mediated processes [waste package]

3.2.5.1 - Microbial growth and decline [repository]

3.2.5.2 - Microbially/biologically mediated processes [repository]

4.1.9 - Biological characteristics and properties

5.1.14 - Ecological/biological/microbial systems

NA Type:

Natural analogue

4.1.5.2 NA description

The Maqarin study site (Figure 4.1.5-1) is located in northern Jordan in an area with clay- and organic-rich limestones, where alkaline groundwaters are associated with leaching of the natural concretes in the area (see section 4.1.3).

Analysis of the groundwaters from Maqarin show them to be of two high-pH types: i) Ca-(Na, K)-OH, which would be expected to form in a cementitious GDF following the first stages of groundwater/concrete interaction and ii) Ca-K-(Na)-OH-SO_4, which represents a more evolved $Ca(OH)_2$-rich porewater following leaching of soluble K/NaOH phases. The pH in these natural groundwaters ranges between 12.3 and 12.9.

Microbial populations were found in the alkaline waters although these were low (10^3 to 10^5 cells mL^{-1}; West et al. 1992, Coombs et al. 1998). However, a wide range of species were detected that were shown to be metabolically active, albeit at a low level (Pedersen et al. 1998, 2004). Interestingly, simple modelling calculations indicated that the availability of nutrient and energy supplies is the key control on microbial growth and activity, and not the high pH (West et al. 1995).

Figure 4.1.5-1. A view over the Maqarin site, northern Jordan. Note the steep valley sides of the River Yarmouk in the right foreground. Unit B is basalt, lying on top of unit C, limestone, which lies on top of the natural concrete-hosting horizon (somewhere between the 'C' and the road in this image) (Pitty & Alexander 2011).

4.1.5.3 Uncertainties and limitations

- Key nutrients and energy sources for microbial metabolism are carbon, nitrogen, sulphur and iron. With the exception of sulphate, the concentration of these chemical species in the Maqarin groundwaters is very low. This contrasts with a GDF where nutrients from the breakdown of organic materials (e.g. cellulose) in L/ILW may be more readily available (cf. section 4.1.6)
- Another important difference between the post-closure environment of a cementitious GDF and

Maqarin, is that the Maqarin groundwaters are aerobic, whereas the environment in the GDF is expected to evolve and become anaerobic shortly after closure. Maqarin does not provide information on microbial activity under such anaerobic conditions. Therefore, the detection of the microbes in the Maqarin spring waters does not imply that they will prove viable and active in the anaerobic cement pore waters of a GDF over long time periods (but see section 4.1.6)

- The conditions within/around a GDF may well differ from the conditions within the analogue site and therefore the microbial populations within a GDF may differ considerably from those that have been studied here

4.1.5.4 Relevance

- The mineralogy and chemistry of the natural concretes at Maqarin are a very close analogue for the OPC-concretes used in a GDF (see section 4.1.3). This is in contrast to the Oman alkaline natural analogue site (section 4.1.6), where the alkaline groundwaters are analogous to low-pH concrete leachates
- The pH of the Maqarin alkaline groundwaters range between pH 12.3 and pH 12.9, with most being buffered by portlandite at 12.5. This is very similar to the pH conditions that are expected to persist for tens of thousands of years in a cementitious GDF where the alkalinity of porewater leaching from OPC-concretes will be around pH 12.5-13.3, and will also be buffered by portlandite dissolution. Furthermore, the highest pH groundwaters (pH12.9) at Maqarin also have elevated potassium concentrations, which although lower than the potassium concentration of a young cement porefluid from a typical OPC-concrete, also provides some degree of analogue comparison for the early stages of pH evolution in the GDF environment (see also section 4.1.3)
- The microbiological study at the Maqarin site shows that low, but diverse and viable populations of microbes can survive under the highly alkaline pH conditions that are anticipated to be developed in the cementitious GDF environment. The pH tolerance of microbial life at Maqarin appears to be higher than observed in laboratory experiments. Consequently, a highly alkaline pH may not guarantee microbial sterility in a GDF (see also section 4.1.6)
- Simple modelling calculations suggest that the very restricted availability of nutrient and energy supplies may be the key control limiting microbial growth and activity in the Maqarin groundwaters, rather than the high pH (see also section 4.1.6)
- The aerobic conditions observed at Maqarin suggests this system may be more analogous to the operational phase of a cementitious GDF (see Table 13.9-1, ID 10-1)

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4.1.6 The influence of cementitious materials, limited survival of microbes in cementitious environments – Oman

Item:

NA 4.1.6

Component(s):

Engineered barrier system, Wasteform, Cement [cementitious], Container, Concrete, Backfill,Plugs and seals, Cementitious materials, microbes

4.1.6.1 Introduction

Microbial life can exist and adapt to extreme geochemical environments. Within a GDF environment, it is important to understand how microbes may impact on the geochemistry, in particular in relation to their influence on the corrosion of metals, cements, waste materials and radionuclide mobility. Natural high pH groundwater systems, such as found in Oman or at Magarin in Jordan, provide an opportunity to study established microbial communities in GDF-relevant these environments.

Microbial degradation of cements and concretes is commonly observed under aerobic conditions and could occur during the early phase of a GDF, thus possibly impacting the performance of the GDF in the short-term. This needs to be considered when carrying out the safety case.

Microbial degradation is achieved by microbes oxidising sulphur, sulphide and thiosulphate, resulting in the production of sulphuric acid, which attacks the concrete matrix by dissolving the constituent minerals (such as calcium silicate hydrate (CSH) gel and Ca(OH)2). Direct anaerobic corrosion of concrete has not been reported to date is not known, although organic acids produced by microbial action on organic materials may be important. Biofilms can also grow on concrete surfaces but this may be because the microbes are utilising the organic plasticisers often used to make the material more workable.

IFEPS:

2.3.5 - Biological processes [waste package]

2.3.5.1 - Microbial growth and decline [waste package]

2.3.5.2 - Microbially/biologically mediated processes [waste package]

3.2.5.1 - Microbial growth and decline [repository]

3.2.5.2 - Microbially/biologically mediated processes [repository]

4.1.9 - Biological characteristics and properties

5.1.14 - Ecological/biological/microbial systems

NA Type:

Natural analogue

4.1.6.2 NA description

The Oman study site is located in the Semail Ophiolite Nappe of northern Oman. These rocks (about 15 km thick) comprise oceanic crustal and upper mantle rocks which have been tectonically thrust up to form a mountainous terrain. Penetration of meteoric waters during and since uplift has resulted in serpentinisation, a process in which ultramafic (high-Mg, high-Fe) minerals are hydrated to serpentine minerals with a release of iron which forms iron oxides. These complex reactions result in the circulating water becoming strongly alkaline and anaerobic, with the result that alkaline springs, containing hydrogen gas, flow from the lower areas of the mountains (Figure 4.1.6-1).

Analysis of the water from some of the springs show them to be Na-Cl-Ca-OH solutions with pH between 10 and 11.4, which makes them excellent analogues of the leachates from low-pH concretes (see discussion in Alexander et al. 2013).

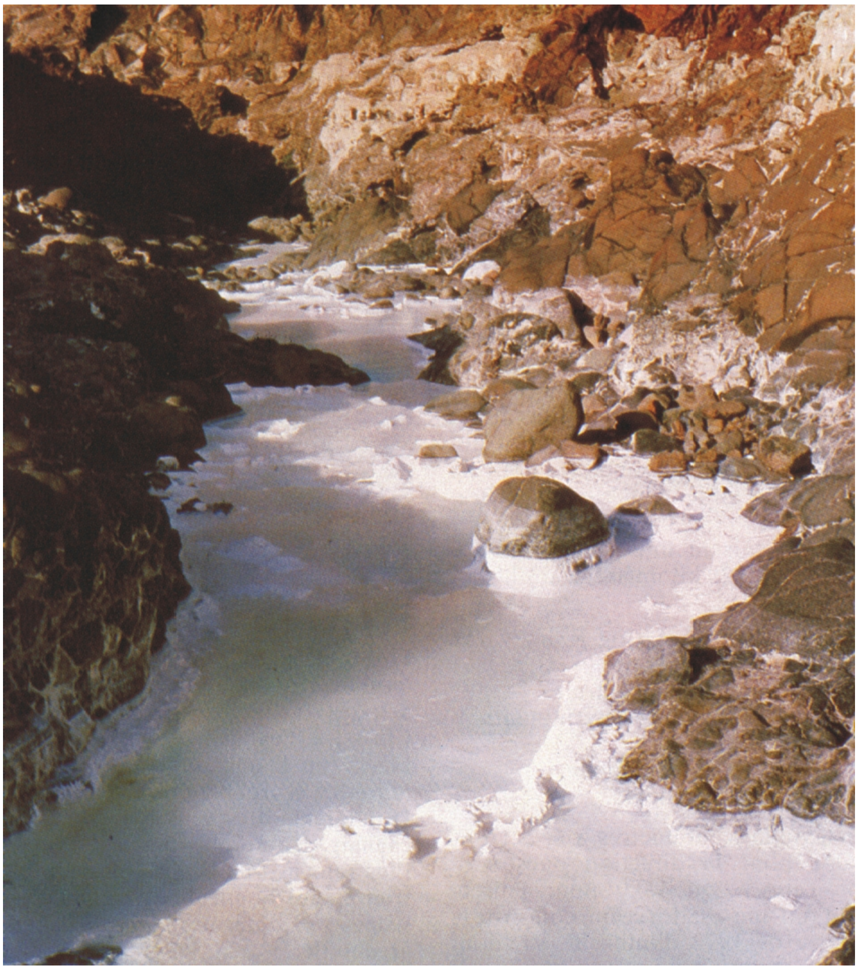

Figure 4.1.6-1. Typical view of the alkaline springs in Oman. The white precipitate is carbonate, produced when the Ca(OH)2 in the alkali groundwaters react with atmospheric carbon dioxide. Miller et al. (2000).

Microbial populations were found in the alkaline waters, although these were low (101 to 103 cells/mL-1; Bath et al. 1987). However, a wide range of species were detected that had adapted to the environment. Interestingly, as at Maqarin in Jordan (section 4.1.5) biological activity was controlled not by the alkaline pH but by the availability of carbon and phosphorus, which are required as nutrients.

4.1.6.3 Uncertainties and limitations

- The fact that microbial growth appears to be limited by the lack of nutrients means it is difficult to directly relate the results to a GDF environment where this is unlikely to be the case.
- The study was carried out some 35 years ago and analytical methods have improved considerably since then, so the results should be treated as a preliminary indication until new samples from the site can be re-analysed (see Table 13.3-1, ID 4.1.6-1)

4.1.6.4 Relevance - what have we learnt?

- The Oman study shows that low but diverse populations of microbes can survive and remain viable in a natural alkaline system with a pH up to 11.45. Laboratory studies have suggested that the limit of bacterial activity is around pH 11 but the Oman and Maqarin (section 4.1.5) natural analogues shows that alkaline pH levels will not guarantee microbial sterility.
- The pH levels of the groundwater system at Oman are within the range expected for leachates from low-pH concretes and so are an appropriate analogue for GDF designs which include such low-pH concretes
- Some of the microbial groups, including iron- and sulphate-metabolising bacteria found in the Oman alkaline groundwaters are capable of causing iron corrosion and degradation of cementitious materials. In an anaerobic GDF environment these could potentially influence the degradation of any low-pH concretes
- The data from these anaerobic alkali groundwaters provide a good comparison with the data from the aerobic alkali groundwaters in Maqarin (section 3.1.5)

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5 CLAY MATERIALS

5.1 Overview of clay barrier materials and relevant analogues

The EBS of a GDF for radioactive waste is characterised by the use of large quantities of rather simple, well-understood materials. For example, many HLW/SF and some L/ILW GDF designs specify the use of compacted bentonite clay as a backfill or buffer around waste packages or canisters (Figure 5.1-1). NWS defines clay-based materials such as bentonite to be used as buffer and backfill materials (RWM 2016). The term 'bentonite' is used here to refer to smectite-rich material (regardless of origin) with favourable chemical, hydraulic and mechanical properties.

The functions of the bentonite as a part of the EBS are:

- To protect the waste canisters from reaction with groundwater to ensure that they remain intact for as long as possible. The bentonite performs this function because the smectite clay in the bentonite swells when hydrated, producing a material with an extremely low hydraulic conductivity
- To slow the migration of any radionuclides released from the waste (because of low hydraulic conductivity of the bentonite), so much so that the vast majority of radionuclides released by the waste will decay completely within the bentonite
- Massive pH buffering capacity, so ensuring low solubility of radionuclides released from the waste
- Colloid filtration because of the microporous nature of the compacted bentonite after re-saturation
- High retardation of radionuclides in the backfill because of the good radionuclide retardation properties of the bentonite
- The very low porosity (and nutrients) will limit microbial activity, including microbially-mediated canister corrosion

Bentonite deposits are found around the world and can be studied as NAs for bentonite-based EBS materials for all the aspects mentioned above. Despite the fact that there are so many bentonite deposits around the world (see e.g., Brown et al. 2021 for overview on the mineral reserves) are being investigated for production purposes, only very few are described in the scientific literature in such detail that the data could be used directly within the NA knowledgebase. Some deposits of bentonites (and other clays) have been investigated from the NA point of view (see examples in this section and, for example, Miller et al. 2000 and Reijonen & Alexander 2015 for overviews).

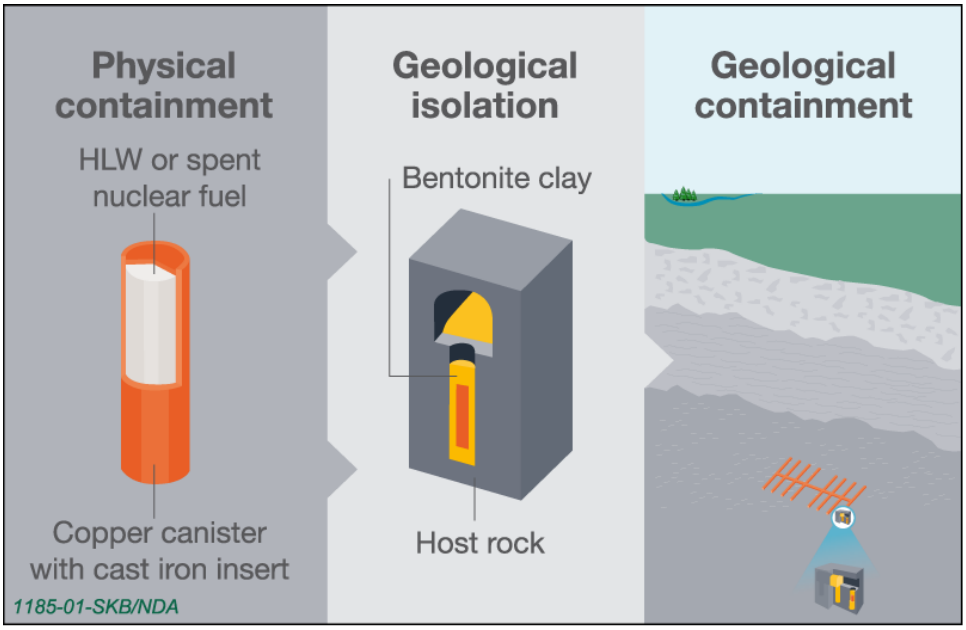

Figure 5.1-1. The multiple barriers present in the illustrative concept (adapted for disposal of UK HLW and spent fuel) in a higher strength host rock showcasing and example of the bentonite use as a buffer material.

References

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5.1.1 Longevity of clay materials, hydraulic barrier function – Dunarobba Forest (Italy)

Item:

NA5.1.1

Component(s):

Engineered Barrier System, Buffer, Bentonite [clay] (also bentonite used in other EBS components)

5.1.1.1 Introduction

Natural bentonites and clays are known for their sealing properties and their overall ability to confine liquids and gases (e.g. oil, natural gas and groundwater) within the rock. From the natural analogue point of view, most of the existing NA examples are from clay occurrences, but not from bentonite clays. The overall hydraulic barrier function of clays is demonstrated at Cigar Lake (Canada), where the orebody is surrounded by a 10 to 50 m thick illite/kaolinite clay halo, locally isolating it from the overlying sandstone host rocks. This clay halo has provided an effective, long-term seal for the orebody for most of its existence (approximately 1300 Ma), which demonstrates the long-term stability of the clay under the local hydrogeochemical conditions (see Smellie & Karlson 1996 for details). Another example is the exceptional preservation of emperor Xin Zhui's (178 to 145 BC) cadaver (Figure 5.1.1-1 and 5.1.1-2) in a tomb sealed with kaolinite clay (see Lee 1986), the clay appears to have been the main contributor to keeping the tomb air tight for over 2000 years. Regardless of these two excellent examples of clay's isolation properties, the most GDF-relevant time frame is provided by the study on the Dunarobba forest (Italy), see below.

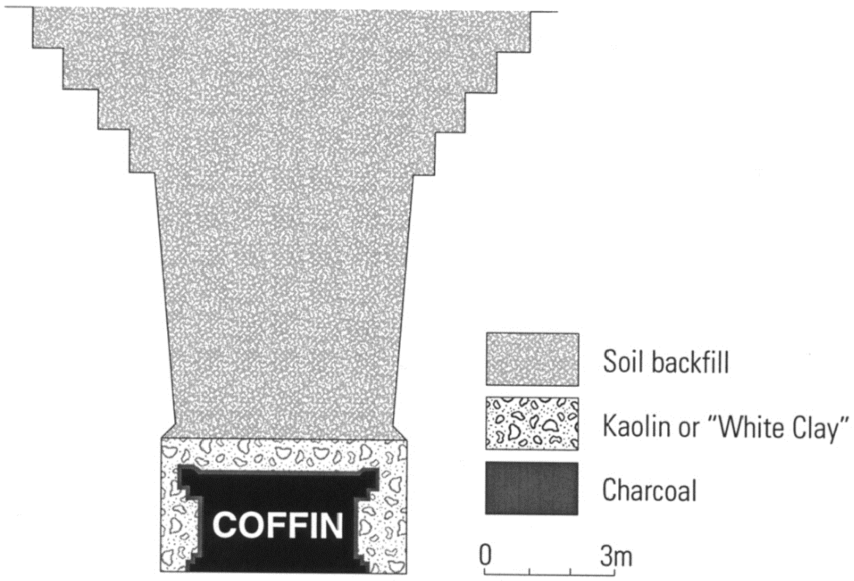

Figure 5.1.1-1. Cross-section of the Xin Zhui tomb (after Lee 1986)

Figure 5.1.1-2. The extremely well-preserved cadaver of Xin Zhui (Courtesy Hunan Provincial Museum).

IFEPS:

3.3.1.3 - Diffusion [repository]

3.2.4.3 - Migration of chemical species [repository]

3.3.1 - Water-mediated migration [repository]

NA Type:

Natural analogue

5.1.1.2 NA description

During the 1970s, in the Dunarobba and Cava Topetti quarries in Umbro, Italy (Figure 5.1.1-3), Sequoia-like (*Taxodioxylon gypsaceum*) tree roots and lower trunks were found in their original, upright position by the quarrymen as they dug out the clay surrounding them (Figure 5.1.1-4). The trees originally grew in the swampy margins of a coastal lake and the soils and clays in which they stand are approximately 2.5 million years old. Most amazingly, they are not petrified; rather they still consist of wood (Ambrosetti et al. 1995a,b for more details).

Slow and continuous sedimentation of clays and sands from the lake and nearby coast allied to a high subsidence rate caused trunks to be buried alive, so guaranteeing their remarkable degree of preservation. Not realising the significance of their find, the quarrymen cut-up and burned many of the trees before they were protected by the Italian government. Despite attempts to shelter the trees from the elements, they have started to degrade because of natural weathering processes, which the clays protected them against for so many millennia.

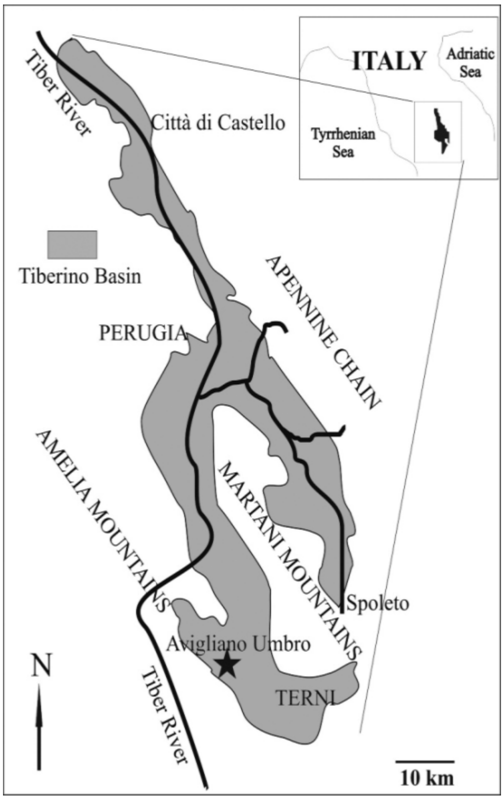

Figure 5.1.1-3. Location map of the Dunarobba Fossil Forest (Avigliano Umbro), Terni, Umbria, central Italy (from Baldanza et al. 2009).

Figure 5.1.1-4. Sequoia-like (Taxodioxylon gypsaceum) tree roots, Dunarobba Forest (from Baldanza et al. 2009).

5.1.1.3 Uncertainties and limitations

- Preservation of the wood has been attributed to the very low hydraulic conductivity of the clay surrounding the trees, with groundwater preferentially flowing through the more permeable sandy lenses that lie within the clays;
- The clay effectively stopped oxygenated waters from interacting with the wood, greatly limiting aerobic decomposition processes. Unfortunately, very little detailed mineralogical, geochemical or hydrological information of relevance to understanding the barrier behaviour of the clays has been published, so it is difficult to utilise the analogue directly in support of a safety case;
- As such, the Dunarobba Forest is generally used only as a qualitative illustration of the extremely effective isolation which can be achieved by clays such as the compacted bentonite buffer. This example has been used in the past in Switzerland for stakeholder communication (Wallenberg site).

5.1.1.4 Relevance – what have we learnt?

- Unlike the engineered bentonite clay buffer in current GDF designs, the natural clays surrounding the trees at the Dunarobba Forest were not specifically designed to protect them for millennia – but did so nevertheless, and very effectively too;
- Organic and cellulose wastes will comprise a significant part of the UK waste stream and this natural analogue suggests that, if anaerobic conditions can be maintained around the waste, decomposition of the organics, and thus gas generation (which could damage the EBS via over-pressurisation), could be minimised in the GDF near- field.

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5.1.2 Longevity of clay materials, thermal alteration – Introduction

Item:

NA5.1.2

Component(s):

Engineered Barrier System, Buffer, Bentonite [clay], lower strength sedimentary rock (clay)

5.1.2.1 Introduction

Spent fuel and HLW will emit heat in the GDF (Figure 5.1.2-1); warming the EBS to around 100°C in some design concepts (some even higher). As heating might change the mechanical and chemical properties of clay materials surrounding the waste packages, and potentially the surrounding rocks, it is important to design a deep GDF where long-term warming is considered. This is especially the case for clay-rich materials (e.g., bentonite backfill and mudrocks) where warming might affect their inherent low-permeability and hence their ability to impede groundwater flow and retard possible radionuclide migration.

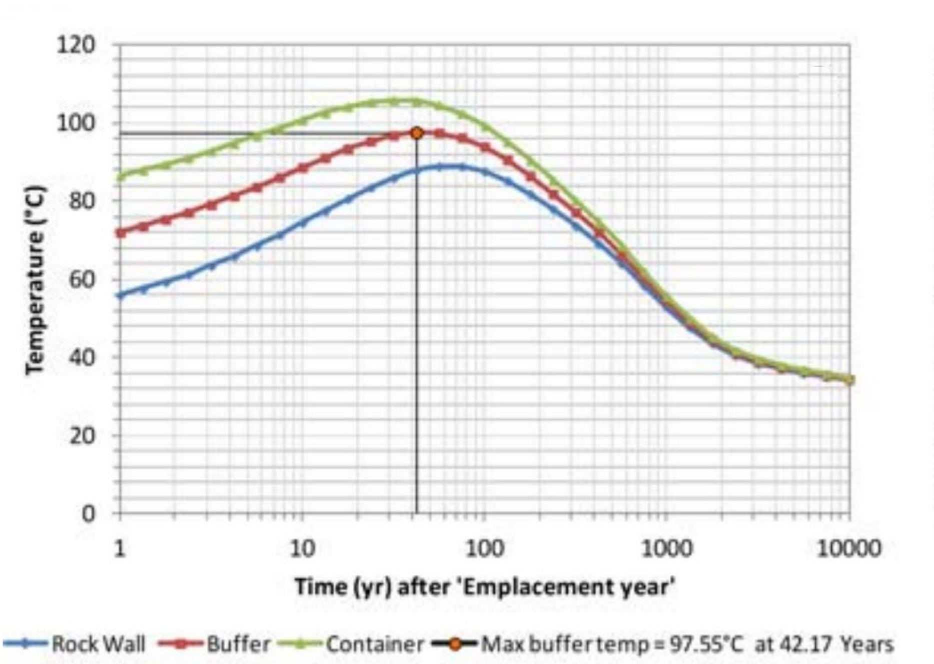

Figure 5.1.2-1. Example of thermal pulse arising from GDF based on dimensioning modelling by Mayers et al. 2015. The graphs show the evolution of the Container temperature (green), the Buffer temperature (red), and temperature of the rock adjacent to the buffer (blue) (Mayers et al. 2015).

At the moment, there is general consensus that temperatures below 100°C are acceptable in the repository. However, there is interest to also assess the effects of higher temperatures on the performance of the clay barriers (both buffer materials and clay host rocks), for example, EURAD-HITEC is an EU project dedicated to advance understanding of bentonite behaviour at temperatures higher than 100°C (Villar et al. 2021)[5]. The thermal phase after GDF closure may persist for a few thousand years (see Figure 1 for example). However, the effects of temperature increase and associated thermal gradients within backfill materials and surrounding rocks may have longer-lasting impacts than the thermal phase itself.

To understand how materials used in a GDF and the surrounding rocks will behave with long-term warming we need to study natural analogues that have undergone similar warming over tens, hundreds or thousands of years.

Several examples of clays and mudstones intruded by igneous rocks have been studied as analogues for the potential thermal impact on engineered clay barriers in a GDF (see e.g. reviews by Laine & Karttunen 2010, Wilson et al. 2011, Leupin et al. 2015). The intrusion of molten rocks at about 800-1,200 °C into clay-rich sedimentary rocks causes a locally high thermal gradient, parts of which could be analogous to those adjacent to heat-emitting radioactive waste. Palaeo-temperature reconstructions, together with observations of mineralogical and fluid chemical changes, can be used to indicate the zones relevant to possible GDF

[5] More recently, a group of organisations have launched the HotBENT project in Nagra's Grimsel URL (please see https://www.grimsel.com/gts-projects/hotbent-high-temperature-effects-on-bentonite-buffers/hotbent-introduction for details).

temperatures. Samples can be taken from these zones and tested to assess if there have been changes in the clay properties.

IFEPS:

3.2.4.5 - Alteration [repository]

1.2.7 - Hydrothermal activity

NA Type:

Natural analogue (several mentioned in the introduction)

5.1.2.2 NA description

No directly repository relevant NAs to date. See Table 13.4-1, IDs 5.1.2-1 to 5.1.2-3.

5.1.2.3 Uncertainties

The following overall uncertainties are related to thermal alteration analogues studied to date:

- The thermal and fluid evolution history of the natural analogues may be complex and poorly-constrained, involving multiple intrusions and hydrothermal events whereas, for application to GDF evolution models, the events need to be simple to facilitate conceptual or numerical modelling, ideally having just a single heating event;
- The peak temperature reached by the natural analogues may be much higher than would be expected in a GDF. High-temperature alteration is readily preserved in these rocks, whereas the temperature zone of most interest (<150 °C) is harder to define. Improved methods to determine palaeo-temperatures would aid this (see Table 13.4-1 for 'thermal alteration');
- Small igneous intrusions only cause heating for a few years, whereas warming in the GDF will last much longer;
- Large igneous intrusions are associated with longer heating events and larger zones of heating, which facilitates sampling of material suitable for mechanical testing. However, they can be structurally more complex and thus construction of an accurate thermal model can be more difficult;
- There are a greater number of examples of heated illite-rich rocks (representative of potential host rock types) than of the smectite-rich rocks representative of bentonite. Identification and investigation of additional examples of the latter would improve understanding of thermal effects on bentonite buffer/backfill materials (see Table 13.4-1 for 'thermal alteration').

5.1.2.4 Relevance – what have we learnt?

At general process understanding level, the following lessons have been learnt from natural thermally altered clays and clay rocks:

1. Heated clays are less plastic and more prone to brittle fractures and consequently results in higher permeability in comparison with the original clay;

2. Heating increases strength and over-consolidation of the clay;

3. Heating reduces the swelling capacity of the clay due to illitisation of smectite in these analogue environments (illitisation may be due to hydrothermal processes that might not be relevant to a GDF environment).

New NA work should focus on more GDF relevant conditions (relatively low T and short-term heat pulse), see examples in Table 13.4-1, IDs 5.1.2-1 to A5.1.2-3.

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5.1.3 Longevity of clay materials, deformation of bentonites – Kato Moni (Cyprus)

Item:

NA5.1.3

Component(s):

Engineered Barrier System, Buffer, Bentonite [clay] (also bentonite used in other EBS components)

5.1.3.1 Introduction

Bentonite clay in the GDF needs to maintain specified thickness in the long-term to provide the desired buffer functions to the system. This thickness could be lost if the waste container would sink, tilt or deform due to host rock movements or by the weight of the other components. Deformation of the bentonite buffer has been discussed in safety cases, specifically in relation to designs where the expected loads are higher (in the order of 0.3 to 0.4 MPa, see discussion in Alexander et al. 2017) than in the case of SF/HLW containers (in the order of 0.1 to 0.2 MPa, Börgesson & Hernelind 2006). Advances have been made in this field lately in the EU project BEACON, which is the latest effort to capture the mechanical evolution of the bentonite materials; see http://www.beacon-h2020.eu/ for details.

Natural analogues of bentonite deformation have not been studied to any great degree (see discussions in NAWG 1996 and Miller et al. 2000). An early review was produced by Keto 1999 on field observations of bentonite deformation, but only a qualitative assessment was made. However, there are several settings where deformation can and has been studied, for example plasticity aspects (see Alexander et al. 2017) and self-sealing of bentonite in case of shear movements (Reijonen & Alexander 2023b); see example of the latter, faulted bentonite, in Figure 5.1.3-1.

Figure 5.1.3-1. Faulted bentonite (with a throw of some 15 cm along the vertical fault line) in the Tsukinuno mine in Japan (H. Reijonen, GTK, Finland).

IFEPS:

1.2.3 - Deformation (elastic, plastic, or brittle)

3.2.3 - Mechanical processes [repository]

3.2.3.2 - Creep

NA Type:

Natural analogue

5.1.3.2 NA description

The Kato Moni site in Cyprus is a bentonite quarry, where bentonite occurs both subaerially and underlying the limestone overburden (Figures 5.1.3-2 and 5.1.3-3). The bentonite at Kato Moni was chosen for study as its geotechnical properties are similar to industrial bentonites (especially Ca-bentonites; see Table 5.1.3-1 for overview). Effects of the loads generated by the limestone lying on top of the bentonite have been investigated by drilling three boreholes at the site (KM1, KM2 and KM3; Alexander et al. 2017). Bentonite in KM1 and KM2 is overlain by 8.5m and 13.5m limestone cover while KM3 was drilled directly into exposed bentonite in a small valley bottom. Based on geomorphological estimates, as the Troodos Massif has been uplifted some 2000 m in ca. 2 million years, the Kato Moni site has probably been exposed for around 0.5 million years. The average erosion rates of the limestone overburden could be in the order of 50 m in 1 million years, suggesting local overburden loss at Kato Moni of some 25 m in that time. For bentonite surrounding HLW containers loads in the order of 0.1 to 0.2 MPa have been reported (Börgesson & Hernelind 2006). For cementitious waste packages the load can be higher (in the order of 0.3 to 0.4 MPa). Kato Moni limestone loads, even today, imply higher loads and longer timescales than those expected in a GDF.

The bentonite in all three boreholes display similar properties to the industrial bentonites which will be utilised in a GDF, but displays micro-fracturing and micro-scale shear planes throughout the samples analysed. The shear planes observed are multi-directional in nature and are thought to be formed due to compressive stress (loading from the overlying limestone), rather than gravitational slipping in to the neighbouring valleys. Of note is that, based on geotechnical measurements, these natural bentonites are considered prone to shearing (see Alexander et al. 2017, for details). It is known that sufficiently high swelling pressure in the buffer can counteract this tendency and this is acknowledged in SF GDF designs (e.g. Börgesson & Hernelind 2006). The Kato Moni study results support such designs, but Alexander et al. 2017 note that, for cementitious repositories, for which designs have not yet been fixed, shear movement of bentonite remains a process of interest. In addition to shear, some interesting textural observations of micro pellet textures have been made on the KM3 samples. It seems, based on only a few samples, that the shearing observed forms anastomosing networks in the pelletal bentonite, potentially suggesting that this structure spreads the shear within the material, which might be of interest for bentonite design (engineered internal structure instead of homogenous structure - see Table 13.4-1, ID 5.1.3-1). The sheared material is interpreted to be continuous, open fractures seen in samples are secondary, indicating that some self-healing may have occurred, but the methods used were not selected to study this process.

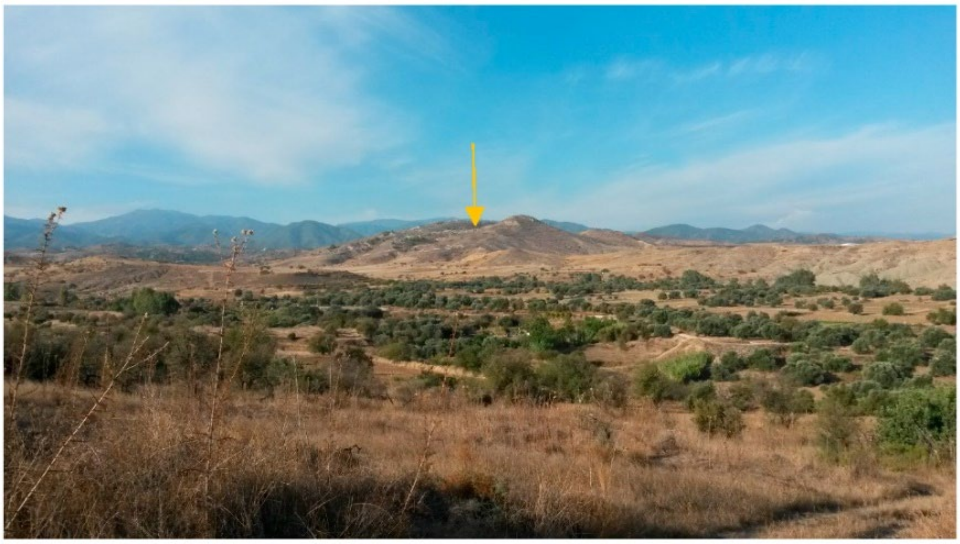

Figure 5.1.3-2. View of the Kato Moni site (NW Cyprus) looking from the SSW, with the yellow arrow indicating the study area. The overlying limestones of Figure 3 are represented here by the two topographic highs on either side of the arrow, with the weaker bentonite forming the valley walls which slope down to the Peristerona River valley in the foreground (Alexander et al. 2017).

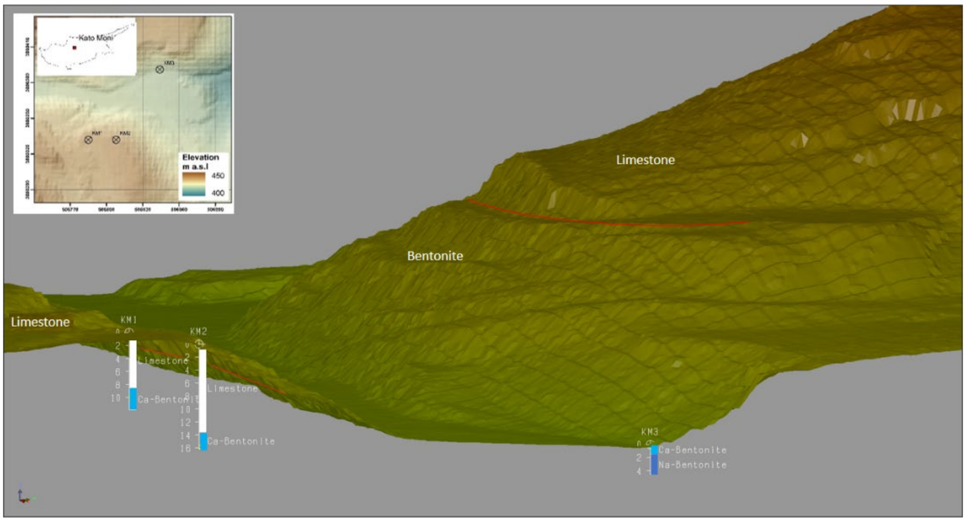

Figure 5.1.3-3. 3D model of the Kato Moni (Cyprus) quarry topography (view looking to the NW). Boreholes KM1-KM3 (depths shown in meters) with KM1 and KM2 drilled through limestone (white) into the bentonite (blue) beneath and KM3 drilled straight into bentonite (blue colours). Red line shows the bentonite - limestone boundary at the northern and southern hill slopes (modified from Reijonen et al. 2017).

Table 5.1.3-1. Comparison of physical parameters for the Kato Moni natural bentonite and MX-80 industrial bentonite and mixtures of bentonite and quartz. From Alexander et al. (2017).

Bentonite	Kato Moni KM3a	MX-80	MX-80 (mixture)	GEKO/QI (mixture)	MX-80 (mixture)	GEKO/QI (mixture)
% clay	26–33	100	50	30	30	10
Density (at water saturation) kg/m^3	1340–1700	2000	2100	2200	1950	2200
Swelling pressure (MPa in distilled water)	0.15–0.34	7.3	2.0	0.9	0.2	0.1

5.1.3.3 Uncertainties and limitations

- Timescales and loads are not precisely known; however, the loads at Kato Moni are greater and timescales longer than those expected for GDFs
- The Kato Moni analogue only focusses on the situation where there is observed loading (compression). At sites where shearing could have occurred, there are currently no micro-scale descriptions of self-sealing or self-healing, although potential exists (see Table 13.4-1, ID 5.1.3-2)
- The drillcores only sampled the material immediately below the limestone, so it would be advisable to obtain more data from deeper in the bentonite deposit to see whether deformation patterns are a feature at depth (more laterally confined due to topography)
- Overall, no other sites have been studied in detail for deformation processes in natural bentonites (see also Table 13.4-1, ID 5.1.3-3).

5.1.3.4 Relevance – what have we learnt?

- Both natural and industrial bentonites are intrinsically susceptible to shear (response of a rock to deformation). It seems that it is possible to design around the susceptibility in specific repository designs, however, high enough bentonite swelling pressure is required (and high enough degree of saturation)
- The data from Kato Moni are currently unique, but it is planned to look at other aspects of bentonite deformation within the IBL project at the Tsukinuno bentonite mine in Japan (see Table 13.4-1, ID 5.1.3-2)
- Bentonite micropellet structures observed at Kato Moni could provide new insights on bentonite buffer design (Table 13.4-1, ID 5.1.3-1)

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5.1.4 Longevity of clay materials, cation exchange – Kuroishi bentonite deposit (Japan)

Item:

NA5.1.4

Component(s):

Engineered Barrier System, Buffer, Bentonite [clay] (also bentonite used in other EBS components)

5.1.4.1 Introduction

Cation exchange phenomena are well known in clays. However, there is an ongoing discussion on how much and how fast the bentonite exchangeable cation composition (ECC) will change during saturation of the GDF and, subsequently, how much it will change due to potential changes in the surrounding groundwater system in the future (e.g., from meteoric water infiltration or saline groundwater upconing). Cation exchange is of importance to the safety case as it can lead to changes of the properties of the initially emplaced bentonites (e.g., originally Na-bentonite can be transformed towards Ca-form). The properties of Ca and Na bentonites differ, especially in relation to their geotechnical properties (e.g., shear strength, swelling properties, dispersion behaviour).

The most important cations that take part in the exchange process are Na, K, Ca, and Mg, but other cations are also observed (Fe, H, NH_4 etc.). Bentonites are well known for their sorption properties, and this is reflected in the cation uptake. Cation exchange can occur at different rates depending on the density of the material, this has been observed both experimentally (e.g., Muurinen & Lehikoinen 1999) and in nature (e.g., Pietracaprina et al. 1987).

Cation exchange processes can be studied in natural bentonite deposits, although the literature available is limited to the in-situ conditions prevailing in different bentonite localities. The results indicate that bentonites show large variation in their ECC, and often the changes in the composition are observed at the interfaces (bentonite – adjacent rock). What is missing from most studies is the timing of these changes. Some indications of cation exchange processes have been observed in the CNAP project (see NA7.3.2 and Alexander & Milodowski 2014). In addition, at Tsukinuno, Japan, cation exchange due to interaction of bentonite deposits with meteoric/groundwater water is known to have occurred, but no detailed studies have been undertaken so far (see Reijonen & Alexander 2023b and Table 13.4-1, ID 5.4.1-1, for 'cation exchange').

IFEPS:

3.3.1.3 - Diffusion [repository]

3.2.4.3 - Migration of chemical species [repository]

3.3.1 - Water-mediated migration [repository]

Note: there is no explicit FEP for cation exchange in IFEP list

NA Type:

Natural analogue

5.1.4.2 NA description

At Kuroishi, Japan, cation composition has been measured in a bentonite deposit outcropping at the surface (Figure 5.1.4-1). Ohe et al. (1998), measured exchangeable cations as a function of depth from the surface to ~40m deep. In the profile, a clear exchange of original Na to Mg and Ca can be observed (Figure 5.1.4-2). The geological history of the site is well known and has allowed estimates to be made on the duration of the cation exchange (4 cm / 1000 years). The upheaval of the area is estimated to have been completed ~1.5 million years ago, providing an estimate on the initiation of the interaction of the deposit with meteoric waters. The overall geological evolution is based on a set of analyses listed in Table 5.1.4-1.

Table 5.1.4-1. Overview of the main geological events at Kuroishi site and methods used in the analyses (Ohe et al. 1998).

Events	Age	Methods
Sedimentation of the original tuff	12~14 Ma	fission track dating of the zircon in the bentonite
	11.6 ~13.8 Ma	K-Ar dating of the surrounding ryolite
Hydrothermal alteration	1.8 ~5.8 Ma	K-Ar dating
	4.7~7.9 Ma	fission track dating of the apatite in the bentonite

Events	Age	Methods
Thermal history of the alteration - duration	1.35 and 2.92 Ma 122 Ma	Electron Spin Resonance Thermal Lumininescence
Temperature	52 ~83°C	isotopic analyses of the D and ^{18}O in the bentonite
Upheaval of the basal rocks	1.5 Ma	Muraoka and Hase 1990.

The authors have also made some simple analytical calculations, with variable boundary conditions for reacting waters, resulting in exchange rates of 0.17 - 25 cm / 1000 years that are in accordance with the geomorphological estimates.

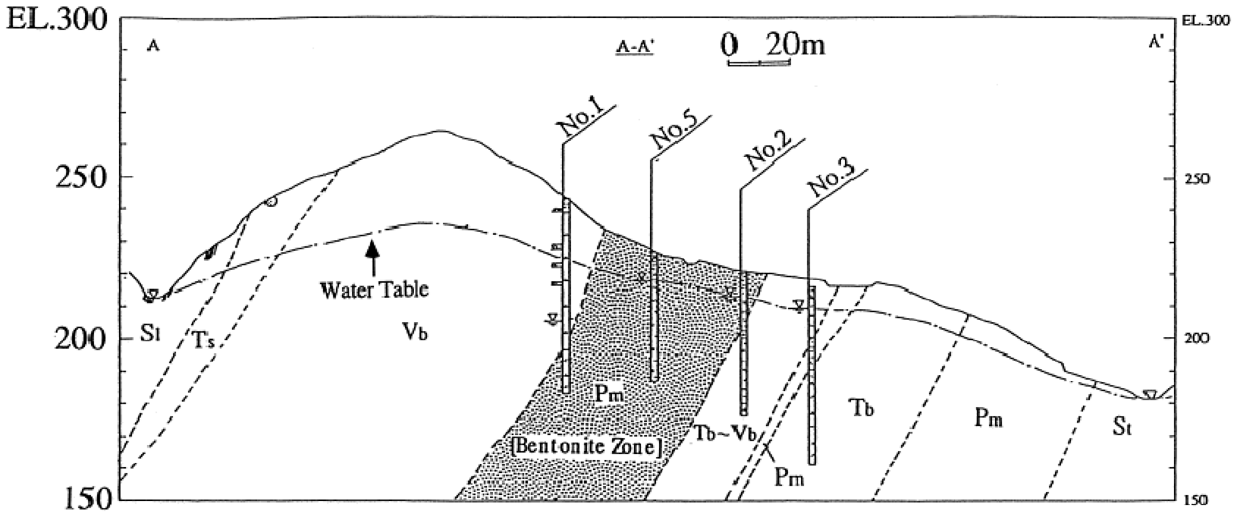

Figure 5.1.4-1. Cross section of the Kuroishi bentonite quarry in Japan. S1: siltstone, Ts: tufaceous sand, Vb: volcanic breccia, Pm: pumice tuff, Tb: tuff breccia, St: sandy tuff. Samples mainly from drill hole No. 5 were used in the study by Ohe et al. (1998).

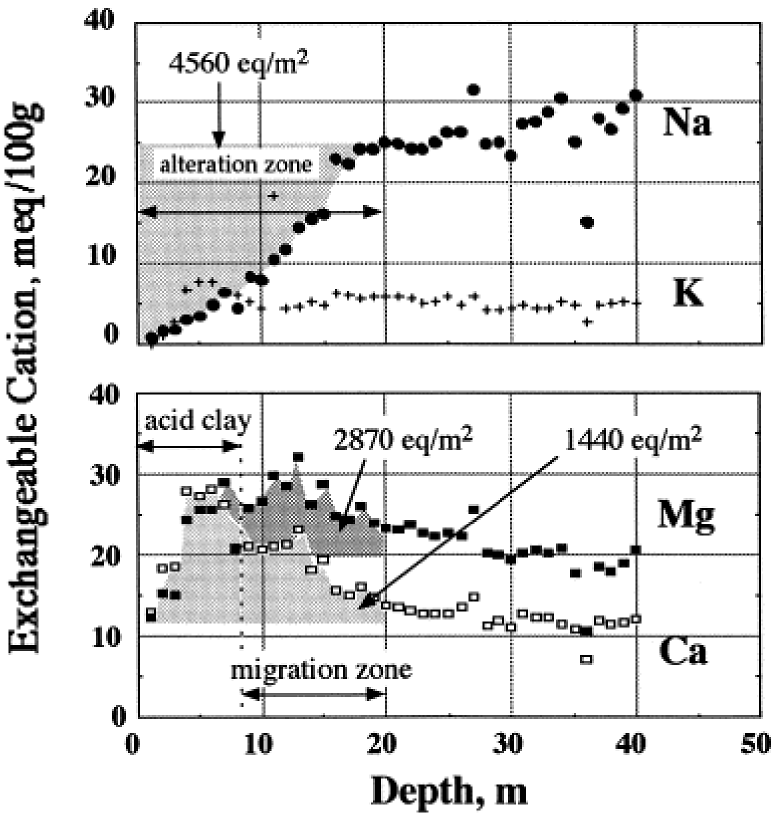

Figure 5.1.4-2. Exchangeable cation compositions as a function of depth at the Kuroishi bentonite deposit in Japan (Ohe et al. 1998).

5.1.4.3 Uncertainties and limitations

- Limitations in the study are related to water chemistry - it is known that the water interacting is meteoric, so the relevance to a GDF is weaker.
- The very top-most part (acid clay) has been affected by the weathering process, which is not expected in underground GDF.
- Water flux at the site may not be in the same range as expected in the GDF, and, as such, the rates calculated here cannot be directly applied to the GDF environment.
- Further investigations would be advisable in settings where the groundwater chemistry and availability vary and is more GDF relevant (see Table 13.4-1, ID 5.1.4-1)
- There is no information available on the impact of the cation exchange on the physico-chemical characteristics of the bentonite (being examined in the IBL project, see Table 13.4-1ID 5.1.4-1)

5.1.4.4 Relevance – what have we learnt?

- Site shows a clear example of a cation exchange process in action in a natural bentonite setting, and showcases a process that has been ongoing over a long period of time.
- Diffusional process is observed, and the rate of the process has been estimated (0.17 - 25 cm / 1000 years), although there is no precise knowledge on the availability of the water at the site.
- For ESC this means that the initial exchangeable cation composition of the bentonite is likely to change depending on the chemistry of the saturating groundwater. The extent of the process depends on the availability of water in addition to the chemistry.

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5.1.5 Longevity of clay materials, chemical erosion – Introduction

Item:

NA5.1.5

Component(s):

Engineered Barrier System, Buffer, Bentonite [clay] (also bentonite used in other EBS components)

5.1.5.1 Introduction

Chemical erosion is a process related to bentonite clay interaction with dilute groundwater. The main concern is, if there is in the future prolonged meteoric groundwater infiltration to GDF depth, the conditions for the buffer clay could become such that bentonite would form colloids and therefore lead to erosion of the material. Whereas the process at GDF depth is very unlikely, it might be of more relevance for structures containing bentonite closer to the surface (e.g., borehole seals).

Wide-ranging reviews have been produced on potential natural analogues of bentonite longevity in dilute groundwater conditions (e.g., Puura & Kirsimäe 2010, Reijonen & Alexander 2015, Reijonen & Marcos 2016 and Smith et al. 2017). In the existing literature, both bentonite deposits and smectite occurrences in fractures (e.g., Arthur & Savage 2012) and other geological settings experiencing dilute groundwater conditions have been reported (see Reijonen & Marcos 2016 for an overview). However, very few dedicated studies have been undertaken but there is work under way (Table 13.4-1, ID 5.1.5-1)

In general, surficial bentonite deposits are exposed to high-energy weathering processes and these are of little relevance to chemical erosion of bentonite in the GDF environment. Hence, it has been suggested (Reijonen & Alexander 2015) that bentonites at depth would provide more relevant sites for bentonite stability analogues. Kuno et al. (2002) attempted to study the process in the Tsukinuno mine in Japan, but only a few samples were collected from the water seeping into tunnels and the results were found to be inconclusive (see the discussion in Posiva 2012). The initiative has been taken forward within the IBL project (see Table 13.4-1, ID 5.1.4-1). Of note is that chemical erosion is heavily influenced by the overall chemistry of the groundwater and the exchanger composition of the montmorillonite. Therefore, for process understanding, see also section 5.1.4 for cation exchange process and related NA.

IFEPS:

Chemical erosion is not included explicitly in the IFEP list.

NA Type:

Natural analogue

5.1.5.2 NA description

No detailed studies available so far (see Table 13.4-1, ID 5.1.4-1)

5.1.5.3 Uncertainties and limitations

- No detailed studies available so far but see Table 13.4-1, ID 5.1.5-1
- Within IBL project (Reijonen & Alexander 2023b) at least four environments were identified where bentonite erosion studies could be conducted at Tsukinuno site, but as noted by the authors, successful (i.e. artefact-free) sampling is extremely difficult, and time should be spent in considering appropriate approaches to the assessment of bentonite erosion in situ before any attempt is made to embark on such work in the identified environments.

5.1.5.4 Relevance – what have we learnt?

No detailed studies available so far (see Table 13.4-1, ID 5.1.5-1). Only qualitative statements can be made based on the current understanding (see e.g. Smith et al 2017).

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5.1.6 Longevity of clay materials in saline/brine conditions - introduction

Item:

NA5.1.6

Component(s):

Engineered Barrier System, Buffer, Bentonite [clay] (also bentonite used in other EBS components)

5.1.6.1 Introduction

Wide-ranging reviews have been produced on potential natural analogues of bentonite longevity in brine groundwater conditions, but many of them have been inconclusive.

- Smellie (2001) has suggested that in Wyoming, bentonites in basinal settings, where porewaters have evolved to be more saline over time, actually show no evidence of post depositional alteration due to the salinity increase. However, the presumed impermeable boundaries of the bentonites have not been studied in detail to assess the fluxes of saline groundwater and so assess how much groundwater-bentonite interaction has occurred since deposition.
- Neoformation of smectites at the small scale, but with no effects on the total smectite content, has been reported from Colorado (ca. 2 km depth with basal brine reactions at 25-30°C: Cadrin et al. 1995, see also discussion in Laine & Karttunen 2010), potentially supporting the observations from Smellie (2001).
- Reactions of smectites at high salinity and pH at Searles Lake have been reported (Savage et al. 2010), but at very low solid/liquid ratios, so not representative of GDF conditions
- Indications of potential stability of bentonites have also been proposed from Perapedhi, Cyprus, which was studied in connection to the CNAP project (Alexander & Milodowski 2014). Prolonged marine conditions have been proposed to have occurred for 90 million years with no substantial reduction in swelling pressure of the bentonite (Kremer & Alexander 2015).

Bentonites and other smectite rich formations occur in the sedimentary strata in many sedimentary basins, providing potential sites for further analysis (see e.g. Reijonen & Alexander 2015 and Table 13.4-1, ID 5.1.6-1)

In addition to the bentonite observations above, fracture filling smectites have also been considered as potential NAs to assess stability under saline conditions. Reijonen & Alexander (2015) noted that the potential for studying fracture smectites at sites where they occur at depth in increasingly saline groundwater environments could be useful (see Table 13.4-1, ID 5.1.6-2).

Related to high salinities, high potassium concentrations are a particular matter in ESCs due to the potential illitisation reactions of smectites. Based on existing literature (e.g. Miller et al. 2000 and Wersin et al. 2007), illitisation is unlikely to be of any significance for a GDF at temperatures under 150°C . The reaction is common during diagenesis, and the smectite- illite transformation is a well-known process but, for GDF-relevant conditions, it is difficult to find analogous setting with same T and P conditions. However, it is known that the illitisation process depends on the availability of K in the system, which is often limited (Robertson & Lahann 1981 and Pusch& Karnland 1988). In some sites, if the K concentrations are high, this might need to be assessed (as was the case in the Swiss programme in the 1990s – see Alexander & McKinley, 1999, for details).

High Mg conditions have also been assessed for potential mineralogical alteration (note that Mg can also change the cation composition in the bentonite interlayer). At high temperatures, formation of Mg-smectites is possible (Leupin et al. 2015) but, in general, bentonites seem to be stable under long exposures to saline conditions and high Mg concentrations of sea water (>1000 ppm, see e.g. Hardie 1996). Examples of bentonite deposits close to the coast are known (e.g. Cala de Tomate and Cortijo de Archidona, see Villar et al. 2006 and San José, see Karnland et al. 2004), but not enough data have been reported to make definitive conclusions (see discussion in Posiva, 2012). Studies in brine environments would also be useful in the future.

Expected salinities in the GDF depend highly on the site selected and further assessment can be made for more specific site conditions after site selection is completed.

For the current generic stage, it might be worthwhile to assess the potential specifically in bentonite-brine analogue studies (see Table 13.4-1, ID 5.1.6-1).

IFEPS:

3.2.4.5 - Alteration [repository]

NA Type:

Natural analogue (several potential examples)

5.1.6.2 NA description

No directly repository relevant NAs to date. See Table 13.4-1, IDs 5.1.6-1 to 5.1.6-2.

5.1.6.3 Uncertainties and limitations

Qualitative information can be used to support the process understanding but dedicated NA data is not available. See Table 13.4-1, IDs5.1.6-1 to 5.1.6-2.

5.1.6.4 Relevance – what have we learnt?

See introduction.

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5.1.7 Longevity of clay materials, saturation - introduction

Item:

NA5.1.7

Component(s):

Engineered Barrier System, Buffer, Bentonite [clay] (also bentonite used in other EBS components)

5.1.7.1 Introduction

Bentonite based components are planned, in most GDF designs, to be installed in an at least slightly undersaturated state. In some concepts initial wetting has been suggested (such as KBS-3H, see e.g. Posiva 2016). Most of the bentonite properties related to long-term performance of the system are assessed for the saturated state, i.e. after resaturation of the system by host rock groundwaters. Periods of unsaturated state are generally assumed to be relatively short during the early evolution of the GDF systems, but they could last at least thousands of years. Obviously, the saturation process depends on the water availability, but in some dry host rocks, full saturation might never be reached at all (e.g. at Yucca Mountain, USA, the plan was to locate a GDF in the unsaturated zone, see e.g. USDOE 2008).

In the unsaturated state, many chemical processes are slower due to the limited flux of reactants. Gas transport through the clay, for example, could be faster than in the saturated state, especially if there are initial boundaries in the buffer bentonite (e.g. precompressed bentonite blocks). For this reason, it is of interest in ESC if the dry condition processes need to be assessed for extended periods.

From natural bentonites, several aspects of the issue could be clarified, including:

- What are the controls of the saturation degree in natural bentonites? (Unsaturated bentonites are known)

- How long have they been unsaturated/saturated? Bentonite is a hydrophilic material, so it does not like to give once retained water away, so it is of interest why some bentonites deep underground actually have dried in the first place (or were never saturated).
- How much saturation degree affects the GDF relevant processes (specifically alteration and cation exchange due to water-rock interaction)?

For bentonites, a knowledge gap exists regarding the saturation degrees for in situ bentonite deposits. Degree of saturation is measured in many standard geotechnical examinations, but such in situ data are mostly not reported in scientific studies of bentonite deposits. Within the IBL project (Reijonen & Alexander 2023b), such data are being compiled for bentonites from the Tsukinuno mine, Japan, and from the literature, see Table 13.4-1, ID 5.1.7-1.

Despite of the paucity of data, it is evident that undersaturated bentonite exists: to date, they have been reported from, for example, Kato Moni, Cyprus (Alexander et al. 2017) and Parsata, Cyprus (Alexander & Milodowski 2014), but at relatively shallow depths (in the order of 10 m below the surface). From the deep Tsukinuno mine, there are indications of unsaturated bentonites even at repository relevant depths.

IFEPS:

3.2.2.1: Desaturation/resaturation [repository]

NA Type:

Natural analogue

5.1.7.2 NA description

No NAs studied to date, but the process is included in the IBL project (Reijonen & Alexander 2023b) (see also www.iblproject.com and Table 13.4-1, ID 5.1.7-1)

5.1.7.3 Uncertainties and limitations

See above.

5.1.7.4 Relevance – what have we learnt?

- The current saturation states of natural bentonite will not necessarily help to determine repository evolution, where water availability might differ from those natural deposits. These natural bentonite localities can, however, help to understand the effects of the undersaturated conditions to overall longevity of bentonites related to different thermal, hydraulic, chemical, mechanical or biological (THMCB) processes, which might be of relevance in cases where saturation times are very long or when desaturation might be expected (drying of the bentonite, for example due to a heat pulse from the waste)
- Under the controlled conditions of the deep Tsukinuno mine, comparison between long-term dry areas with those which have been historically/currently wet, may provide a mechanistic understanding of the processes of relevance to GDF buffer resaturation

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5.1.8 Longevity of clay materials, interaction with metals - Introduction

Item:

NA5.1.8

Component(s):

Engineered Barrier System, Buffer, Bentonite [clay] (also bentonite used in other EBS components), iron, copper

5.1.8.1 Introduction

Bentonite interaction with potential waste package materials is of interest in the safety case due to potential effects on the system performance. Mostly the processes are relevant in the near-field of the HLW/SF packages where copper or steel canisters are surrounded by bentonite.

For copper-bentonite interaction the Kronan Cannon study (Hallberg et al. 1988) is probably the only NA study of some qualitative relevance showing copper diffusion in the clay (4 cm over 300 years). However, there is no information on the actual products of the interaction process, making any mechanistic understanding impossible. NAs of copper in clay have been identified elsewhere (e.g. Smart & Adams 2006) but these are mostly archaeological artefacts buried in clay-rich sediments, not bentonite. However, perhaps the most interesting settings would be those where native copper occurs with clay. At Littleham cove (see section 3.1.1) native copper occurs in silty clay (higher porosity than buffer bentonite). Native copper does exist in clays, e.g. copper deposits called copper clays are known from the Mount Lyell, Tasmania (e.g. Solomon 1959, Corbett 2001). No detailed examination of the deposits have been made with a view of obtaining GDF-relevant information and the composition of the clay is unknown (see Table 13.4-1, ID 5.1.8-1).

For NAs of iron-bentonite interactions, existing analogues are rather limited. In Spain, at Pecho de los Cristos bentonite interaction with iron-bearing solutions has been assessed (Marcos 2004), but the bentonite at the site was too poor in smectite to be of GDF relevance. However, the new KiNa project has potential to provide further information on the topic (see below and Table 13.4-1, ID 5.1.8-2).

The KiNa (Kiruna Natural Analogue) project is an IGD-TP (Implementing Geological Disposal of radioactive waste Technology Platform) study of the long-term interaction between the corrosion products of steel canisters and the bentonite buffer. Other areas of relevance to buffer processes are also included (Table 5.1.8-1).

Table 5.1.8-1. Overview of the various work packages in the KINA project.

Activity	Team
Work Package 1. Geological Description	Nagra/Technical University of Munich/ LKAB
Work Package 2.1. Bentonite Dating	Nagra/Technical University of Munich/University of Bern
Work Package 2.2. Bentonite Characterisation	SKB/Posiva
Work Package 3. Assessment of bentonite safety relevant parameters (physico-chemical features etc.)	SKB/Posiva
Work Package 4. Bentonite Erosion	SKB
Work Package 5. Iron corrosion products/Bentonite interaction	NUMO/Hokkaido University
Work Package 6. Bentonite Microbiology	Nagra/NWMO/EPFL
Work Package 7. Reporting	Nagra/RWM/Bedrock Geosciences

The KiNa project is based in the Kiruna, Sweden, iron-ore mine of LKAB and was initiated in September 2019. Although preliminary sampling took place at that time, the Corona virus pandemic prevented further studies at the mine until September, 2021, so only preliminary results are currently available.

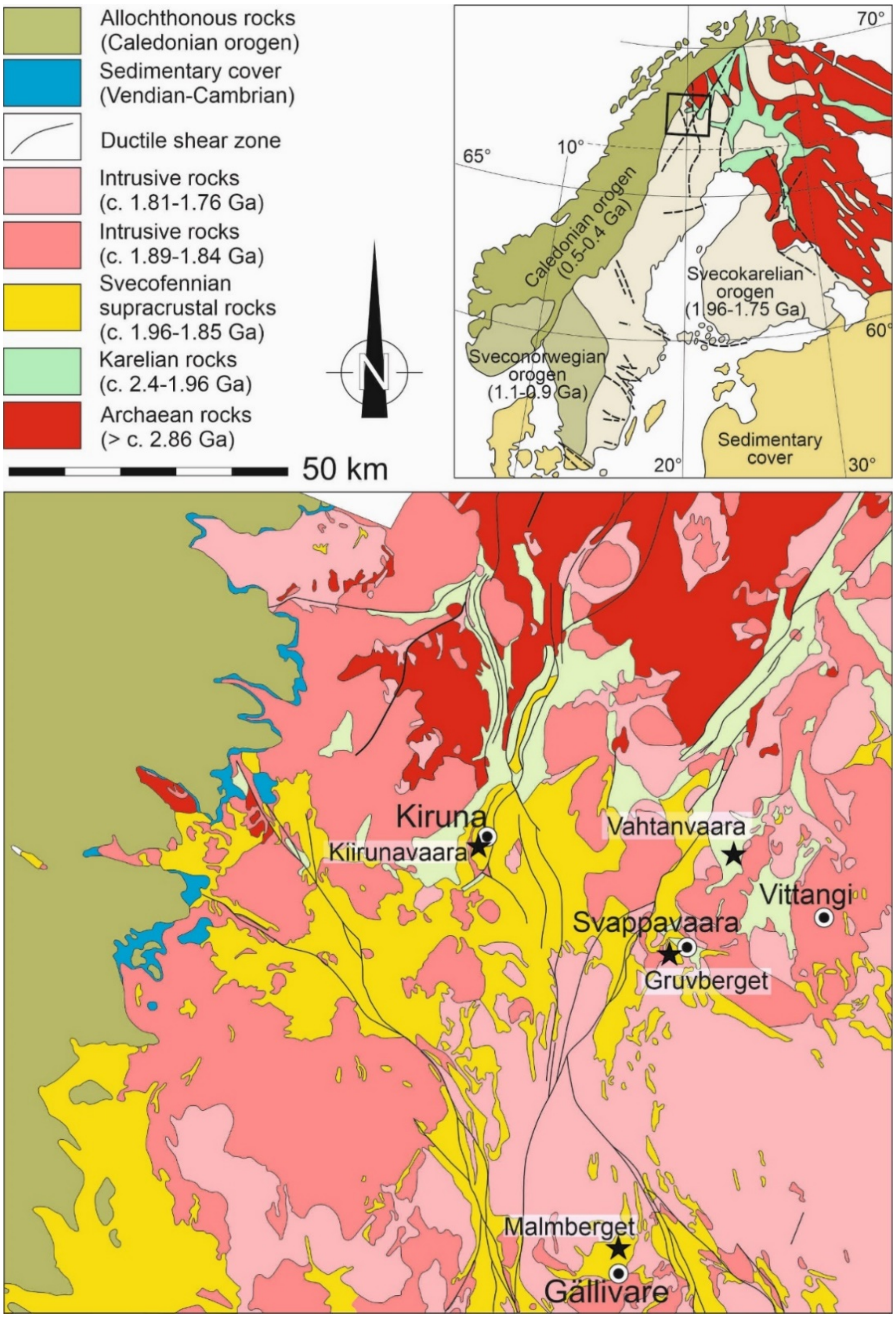

Figure 5.1.8-1. Simplified geological map of the region around Kiruna with the location of iron ore deposits with associated bentonites marked with a black star (Gilg & Andersson 2021, modified from Bergman et al. 2001).

The largest iron ore deposits in Europe are hosted in the Fennoscandian Shield in the northern Norrbotten province, Sweden. Significant clay alteration zones have been encountered in the Kiruna magnetite(-haematite)-apatite ore deposits, which are hosted in weakly to strongly metamorphosed intermediate to acid volcanic and subvolcanic rocks. The up to 50 m thick clay alteration zones occur within ores and within the country rocks along the ore contact of the southern Kiirunavaara ore body, at various levels to depths of at least 1200 m below surface (Gilg et al. 2015).

Iron ore formation occurred ca. 1900 million years ago and alteration of the ore host rocks to smectite-rich (bentonite - dominated by a dioctahedral smectite with rare illite-smectite and kaolinite) clays followed soon afterwards. No direct ages currently exist for the bentonites (this is the focus of Work Package 2.1, Table 5.1.8-1), but indirect ages indicate that the oldest material was formed around 1620 to 1740 million years ago. If these ages are confirmed, this will make the KINA bentonites the oldest ever studied to supply GDF safety assessment supporting evidence. Clearly, these ages are much greater than the timescales of interest for a GDF, but they will most certainly increase confidence in the longevity of bentonite in GDF-relevant conditions.

The ongoing Work Package 2.2 (Table 5.1.8-1) indicates smectite contents in the clays of up to 81% and swelling pressure measurements show similar swelling pressure curves to buffer and backfill bentonites (IGD-TP 2022). Work Package 3 (assessment of bentonite safety relevant parameters), Work Package 4 (bentonite erosion) and Work Package 6 (bentonite microbiology) are all at a very early stage, but preliminary information is available from Work Package 5 (iron corrosion products/bentonite interaction). Although dedicated sampling has not yet been possible, some samples from the preliminary sampling campaign proved appropriate for analysis (Figure 5.1.8-2).

Figure 5.1.8-2. Sample collected in the Kiruna mine for Work Package 5 analysis (sample 1-1). Dark material (upper half of the sample) is the ore (predominantly magnetite) and the lighter material (bottom half of the sample) the bentonite (Sato et al. 2021).

The preliminary results of Work Package 5 indicate no obvious uptake of iron in the smectite immediately adjacent to the ore-clay contact. However, in some places, the contact is characterised by the presence of an intimate mixture of smectite-biotite and these mixed phases will be investigated further to establish a formation mechanism and establish if they are of relevance to iron corrosion products-bentonite interaction.

Although the KiNa project has been temporarily disrupted by the corona virus pandemic, the preliminary results are promising and it is expected that much of relevance to both corrosion product-bentonite interaction and overall bentonite longevity will be produced by the expected end of the project in 2022.

IFEPS:

3.2.4.5 - Alteration [repository]

NA Type:

Natural analogue

5.1.8.2 NA description

No detailed studies of relevance to date, but ongoing project KiNa should provide input.

5.1.8.3 Uncertainties and limitations

As above.

5.1.8.4 Relevance – what have we learnt?

As above. See introduction.

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5.1.9 Longevity of clay materials, microbial activity

Item:

NA5.1.9

Component(s):

Engineered Barrier System, Buffer, Bentonite [clay] (also bentonite used in other EBS components)

5.1.9.1 Introduction

One of the functions of bentonite buffers is limiting microbial activity due to potential corrosive agent formation (e.g. sulfide) via microbial processes. For bentonite materials and clays, reviews on potential microbial activity has been assessed based on laboratory (Fru & Athar 2008, Stroess-Gascoyne & Hamon 2008, Černá et al. 2018) and URL experiments (e.g. Stroess-Gascoyne et al. 2007, Vikman et al. 2018). NA studies on in situ bentonites is lacking.

This lack of knowledge has been acknowledged and in two international NA projects, IBL and KINA, the topic is being addressed. In IBL, a preliminary assessment of samples from the deep Tsukinuno mine bentonites have been reported (Beaver et al. 2021; Table 13.4-1, ID 5.1.9-1), while in the KINA project, smectite samples from fractured rock are currently under investigation (see section 5.1.8 and Table 13.4-1, IDs 5.1.8-2 and 5.1.9-1).

IFEPS:

3.2.5.1 - Microbial growth and decline [repository]

3.2.5.2 - Microbially/biologically mediated processes [repository]

NA Type:

Natural analogue

5.1.9.2 NA description

No detailed studies of relevance to date, but ongoing projects IBL and KiNa should provide input.

5.1.9.3 Uncertainties and limitations

As above.

5.1.9.4 Relevance – what have we learnt?

As above. See introduction.

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6 LONG-TERM STABILITY OF HOST ROCK

6.1 Overview of the long-term stability of GDF host rocks

The host rock has several safety functions and is expected to:

- provide favourable thermal conditions for the GDF
- provide stable mechanical conditions for the EBS
- provide favourable hydrogeochemical conditions for the EBS
- provide favourable hydrogeological conditions for the EBS
- retard the transport of any harmful (i.e. radio- and chemotoxic) substances that could be released from the GDF
- isolate the GDF from the biosphere to minimise any potential doses from radionuclide releases and to buffer the GDF from changing climatic conditions
- limit the possibility of human intrusion into the GDF

The most important source of confidence in the long-term stability of the site (and hence site suitability) is the overall site understanding and the predictability of the site behaviour in the future. This is largely based on obtaining a deep enough knowledge of the site properties via the site characterisation process and this can be supported by the NA approach in a range of ways. The long-term stability of GDF host rocks can be assessed from several viewpoints:

- Climatic stability: changes in climate can impact site stability by altering the flow and chemistry of the shallow and, to a lesser extent, deep groundwaters. Assessment of such stability can be made by examining groundwaters (see the discussion in Dragoni and Sukhija, 2008, for example) and/or the mineralogy of fracture-filling minerals (see the overview in Blyth et al. 2009, for example) in HSR and both approaches are examined below. The transport properties of LSSR have been examined by investigating the porewater chemistry and matrix properties of the rock and, more recently, this has been extended to HSR too and examples from both environments will be presented here. Climate-driven processes such as permafrost and glaciations are discussed also in chapter 7.
- Tectonic stability: are either the larger-scale host formation or the smaller-scale deposition tunnels and caverns likely to be disturbed during the assessment period by tectonic activity? For example, could new or re-activated fracture systems induce changes in the host rock groundwater system (large-scale flow and chemistry; see JNC, 2000, for discussion) or damage waste vaults or packages (smaller-scale movement in a deposition tunnel; see McEwen et al. 2012, for discussion)? As tectonic stability is site specific (being dependent on the current and past regional and local tectonic regimes and the rock mechanical properties of the lithologies present at the site), it will not be discussed further here at this time, but NA evidence of relevance is presented in Alexander (2021). Glaciotectonics are discussed in chapter 7.
- Rock mechanical stability: the mechanical properties for both the intact host rock and any discontinuities (i.e. fractures) present, thermal properties and the *in situ* stress affecting the site (i.e. for the whole rock mass) should be known. When this is the case, areas of high stress can be excluded from the GDF (to avoid tunnel collapse, for example). As rock mechanical stability is site specific (being dependent on the local lithologies present and the current and past regional and local tectonic regimes), no site-related analogues have been examined, but NA evidence of relevance to some specific HSR environments is discussed in Posiva (2021) and, for LSSR, in Bossart et al. (2017)
- Vulcanogenic stability: this is an extreme case as any such risk is normally identified at an early stage in the site characterisation and the site declared unsuitable. However, this has been assessed in detail for the Yucca Mountain site in the US (see CRWMS 1996, for details)

In this chapter, these and other aspects of GDF host rock stability will be examined and examples of how NA information may be used to assess the likely long-term stability of GDF host rocks of relevance to the UK national programme will be discussed. Here, it is also apt to discuss the use of regional analogues when considering GDF host rock stability as, at this stage of the UK national programme, it is not yet possible to investigate potential host rocks of interest directly. It is nevertheless possible to conduct fundamental geoscientific research on the same rock formations in areas outwith potential future GDF sites.

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6.2 Long-term stability of higher strength rocks

An important requirement of a safety case for a GDF is to be able to demonstrate that future climatic changes will not adversely affect the flow or chemistry of the groundwater system at GDF depths over the period of time during which the waste will be a hazard. The last 2.6 million years (Quaternary Period) saw the climate in northern Europe vary between extremes of glaciations and conditions warmer than today. During periods of glaciation, for example, of concern is the potential for dilute, oxidising groundwaters (driven by the pressure of the glacial ice on the surface) to penetrate to GDF depth, thereby increasing the mobility of some radionuclides and possibly eroding some of the bentonite buffer (cf. Reijonen & Alexander 2015). It is therefore important to demonstrate that the penetration of dilute, oxidising water to potential GDF depths is highly unlikely. Here, two approaches to assessing such stability are presented: in the first (Olkiluoto, Finland), focus is on the host rock stability as indicated from the ground- and porewaters and, in the second (Äspö/Laxemar, Sweden and Sellafield, UK), focus is on indications of stability provided by secondary fracture filling minerals. Both approaches are highly complimentary and, indeed, both have been implemented at all sites, but with differing emphasis (cf., Posiva 2022, Andersson et al. 2013 and Bath et al. 2006, respectively). Finally, as an example of a complex system where definition of solute transport (and therefore host rock stability) is far from simple, an example of the use of yet another set of indicators (deposition and remobilisation of an orebody) is provided from the Tsukiyoshi orebody in Mizunami, Japan.

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6.2.1 Long-term stability of higher strength rocks: Olkiluoto

Item:

NA6.2.1

Component(s):

HSR

6.2.1.1 Introduction

Posiva's GDF site on Olkiluoto Island in SW Finland (Figure 6.2.1-1) is currently the most thoroughly characterised host rock in the world. Olkiluoto has been selected as the disposal site for Finland's SF and the GDF, which is currently under construction, is located at a depth of 400 to 450 m in the bedrock of the Fennoscandian Shield (Posiva 2023). A comprehensive site characterisation programme has been ongoing at the site for more than three decades: in addition to detailed surface exploration, a total of 58 deep boreholes (shallow sampling points no included) have been drilled and, since 2004, additional data have been collected in the ONKALO URL.

The Olkiluoto site has been glaciated and experienced glacial meltwater intrusion into the bedrock (see Boulten et al. 1993 for a discussion of the mechanisms involved). Following glacial retreat, the area was then inundated (Figure 6.2.1-2) by the fresh Ancylus Lake. Olkiluoto remained submerged in the subsequent saline Littorina Sea and the denser, brackish seawater of the Littorina Sea percolated into the bedrock by gravity, resulting in a density turnover. A similar process (Littorina Sea water infiltration after glacial meltwater intrusion) has occurred at several sites across the Baltic Sea basin (cf. Pitkänen et al. 1998, Laaksoharju et al. 2008, Alexander et al. 2022).

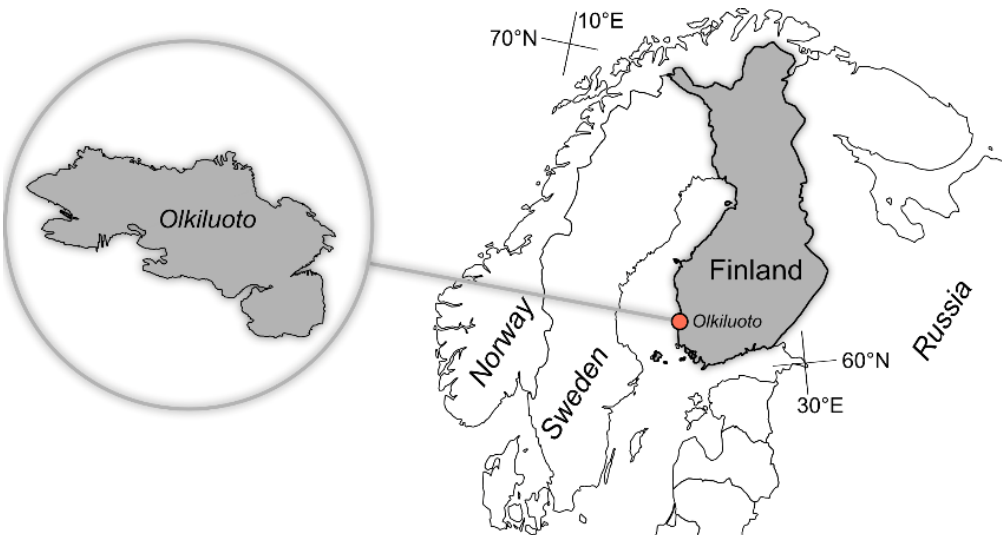

Figure 6.2.1-1. Location of Posiva's Olkiluoto GDF site, SW Finland (Posiva 2023).

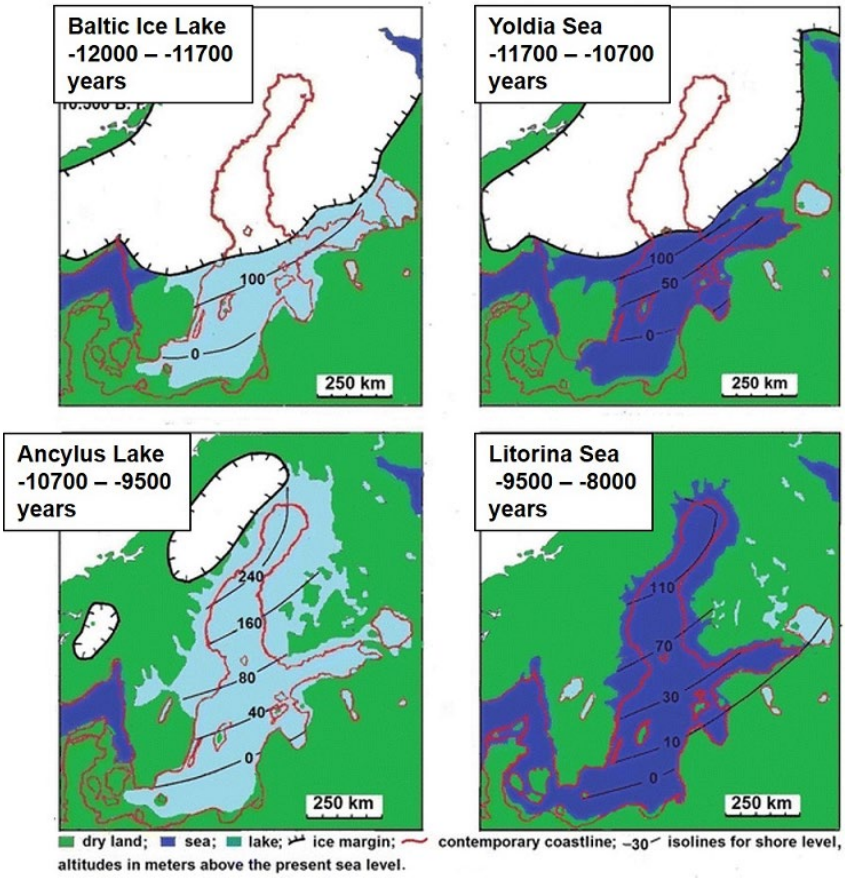

Figure 6.2.1-2. A schematic overview of the main stages leading to the development of the current Baltic Sea (Ojaveer 2017). Ages shown are before present.

IFEPS:

4.1.2 - Large-scale discontinuities

4.1.6 - Hydraulic characteristics and properties

4.1.8 - Geochemical characteristics and properties

4.2.4 - Chemical processes [geosphere]

NA Type:

Natural analogue

6.2.1.2 NA description

The exact depth of glacial meltwater infiltration varies and lies between 100 and 500 m at several sites across Finland (Alexander et al. 2022). At the Olkiluoto site, there are no indications of oxidation at GDF depth in the anoxic host rock (Posiva 2022). The groundwater composition from the bedrock surface to 1000 m deep is characterised by a significant range in salinity (Figure 6.2.1-3):

- fresh groundwater with low total dissolved solids (TDS less than about 1000 mgL^{-1}) is found only in the uppermost tens of metres at the site
- brackish groundwater (TDS up to 10,000 mgL^{-1}) dominates at depths between 30 m and about 450 m
- saline groundwaters (TDS > 10,000 mgL^{-1}) dominate at depths >450 m.

The current salinity of groundwater at the GDF depth (400 to 450 m) is around 10,000 mgL^{-1}. Studies of dissolved methane (Pitkänen et al. 2022) indicate that, below about 300 m depth, the deep stable groundwater system has not been disturbed by glacial and post-glacial transients. In addition, neither oxidising glacial meltwater nor marine water appear to have mixed in this deeper system (Pitkänen & Partamies, 2007). Aalto et al. (2022) also note that major sub-horizontal hydrogeological zones exist in the shallow bedrock of Olkiluoto and these may have been able to limit deep infiltration from the surface (see also discussion in Alexander et al. 2022).

Studies of rock matrix porewaters at Olkiluoto (e.g. Eichinger et al. 2018; Eichinger 2021), where matrix samples were collected at distances away from water-conducting fractures and analysed for a range of natural tracers, indicated that transport in the rock matrix is diffusive (Dp for Cl of 5–6 x 10-11 $m^{-2}s^{-1}$). The δ18O isotope ratios indicate long residence times for matrix porewaters, confirming the above data and suggesting that the host rock is, in any case, unlikely to be altered significantly by the ingress of any oxidising groundwaters in the future.

Early modelling studies (e.g. Luukkonen 2006) of potential host rock buffering of any intruded groundwater oxidants suggested it was highly unlikely that aerobic groundwaters could penetrate to GDF depths. More recently, this has been supported by in situ experiments (Lamminmäki et al. 2021) in the ONKALO facility which demonstrated the relevance of fracture pyrites and organic matter in the consumption of dissolved oxygen and their significant buffering capacity to prevent intrusion of aerobic groundwaters to GDF depths.

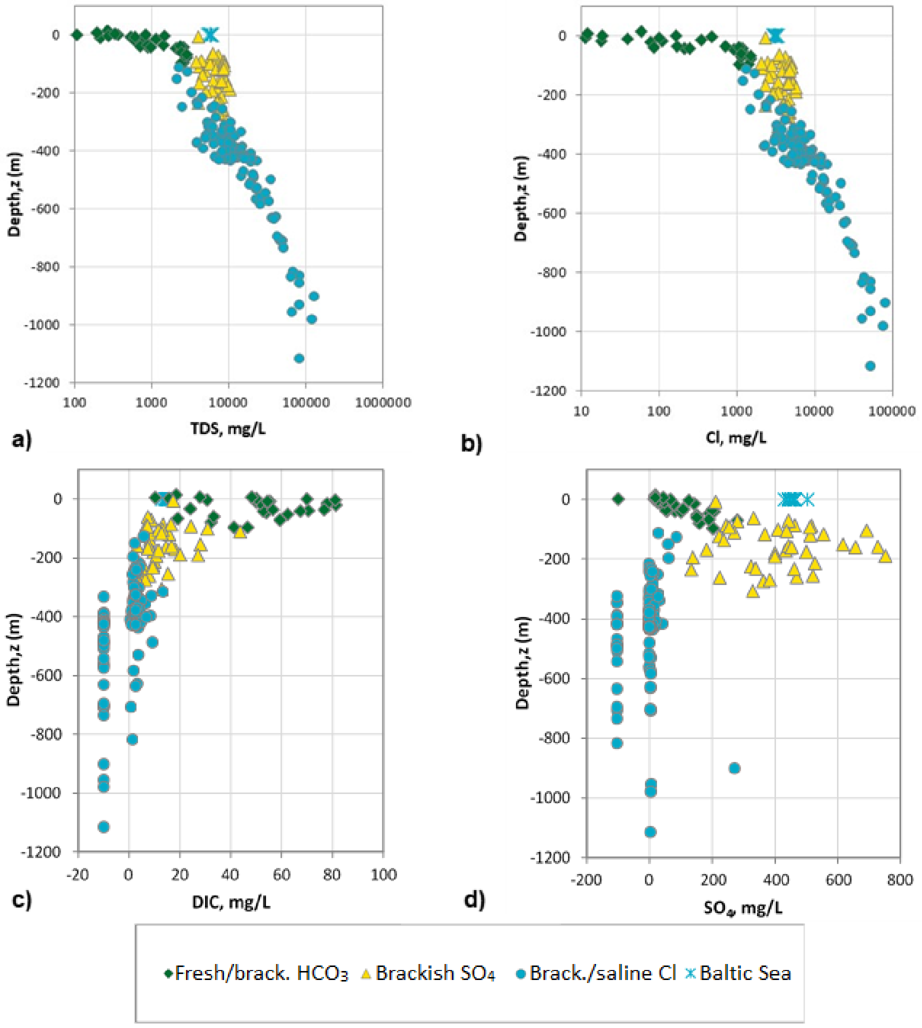

Figure 6.2.1-3. a) TDS, b) Cl, c) DIC and d) SO_4 concentrations of Olkiluoto baseline[6] groundwater samples as a function of depth. Negative values in c) and d) indicate results below detection limit. Note, a logarithmic scale is used for TDS and Cl, whereas a linear scale is used for DIC and SO_4. Posiva (2022).

6.2.1.3 Uncertainties and limitations

- The salinity-depth pattern observed at Olkiluoto is not replicated exactly at other sites around Finland which have been examined by Posiva. Nevertheless, the hydrogeochemical conceptual model for Olkiluoto can explain most of the features observed elsewhere

[6] Posiva define baseline conditions as those that represent natural groundwater compositions at Olkiluoto before hydrogeological changes caused by construction of the ONKALO facility and site characterization field investigations (see discussion in Posiva, 2022, for further details).

- Although anion exclusion, which is assumed to decrease available matrix porosity and diffusivity for anionic species, has been identified in certain lithologies at the site (see Aalto et al., 2022; Alexander et al., 2022 for details), the full effects of this mechanism on the site hydrogeochemical conceptual model are still under consideration

6.2.1.4 Relevance, what have we learnt?

- Despite the significant climatic changes (including repeated glaciations) at the Olkiluoto site over the last 100,000 years, the deep groundwater (and porewater) system appears to be highly stable. It is likely that it has remained unperturbed for several million years
- Further, specific aspects of the site hydrogeology, structure, hydrogeochemistry and mineralogy have buffered the impact of the intrusion of young, aerobic groundwaters
- The current site understanding is that aerobic groundwaters are highly unlikely to penetrate to GDF depths, even under future glacial conditions. This observation is supported by comparison with other HSR sites across Fennoscandia
- Olkiluoto is not an unique site worldwide (see the discussions in Posiva 2023 and Alexander et al. 2022), so similarly stable deep conditions with significant host rock buffering capacity for aerobic groundwaters are also to be expected at sites of interest in the UK programme (see also section 6.2.3 and 13.5).

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6.2.2 Long-term stability of higher strength rocks: Äspö and Laxemar, SE Sweden

Item:

NA6.2.2

Component(s):

HSR

6.2.2.1 Introduction

IFEPS:

4.1.2 - Large-scale discontinuities

4.1.6 - Hydraulic characteristics and properties

4.1.8 - Geochemical characteristics and properties

4.2.4 - Chemical processes [geosphere]

NA Type:

Natural analogue

6.2.2.2 NA description

Geological background

Äspö and Laxemar are situated on the Baltic coast of southeast Sweden and SKB has constructed an URL on the low-lying island of Äspö, where it is carrying out a programme of investigations to develop and test methodologies for the disposal of SF. SKB have also carried out regional studies in relation to GDF-related investigations for the nearby Laxemar and Forsmark sites.

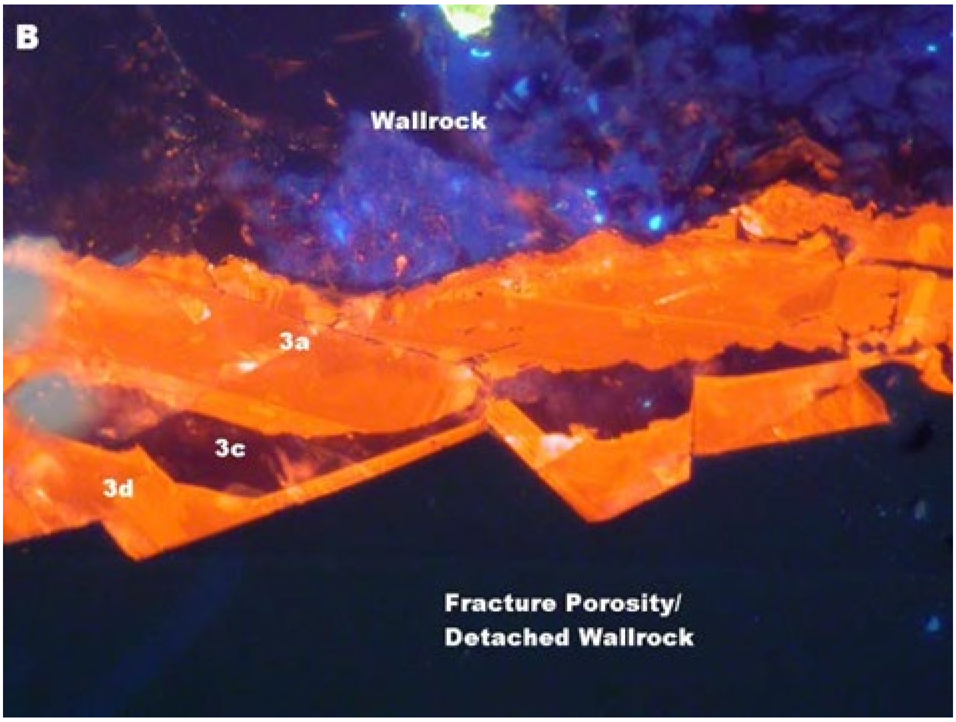

Figure 6.2.2-1. Cathodoluminescence microscopy image of zoned luminescent (3a and 3d) and non-luminescent (3c) late-stage calcite coating a fracture surface from the Laxemar site (Milodowski et al., 1998, 2005).

Detailed geochemical, mineralogical, stable isotope and uranium-series disequilibrium studies of fracture filling minerals at the sites (Figure 6.2.2-1) have identified a long history of fracturing, groundwater movement and associated mineralisation events (see Tullborg, 2004; Drake & Tullborg, 2009; Drake et al., 2012). Most of these are geologically old features, but the most recent mineralisation is associated with relatively young groundwater circulation over the last 2-3 million years.

The majority of the fractures in the Laxemar-Simpevarp-Äspö area were formed before 500 million years ago and have subsequently been reactivated. Calcite mineralisation associated with these fracture events is characterised by hydrothermal stable isotope signatures. From around 500 million years ago, the region was covered with a thick sequence of marine and freshwater sediments and this cover remained for at least 400 Ma although, from around 300 million years ago, it was successively reduced by erosion, until finally being removed around 2-3 million years ago (Milodowski et al., 2005).

Subsequent low temperature fracture mineralisation was dominated by calcite (with some pyrite) at depth and, close to the surface, by goethite related to the percolation of oxidising meteoric groundwater causing weathering of the host rock.

Groundwater scenarios

Since the Äspö-Laxemar area is situated on the low-lying Baltic Sea coast, the post-glacial evolution of the area has been strongly influenced by a complex interplay between global sea-level changes, freshwater run-off from the surrounding terrain and the rise and fall of the land surface after glaciation. Consequently, the sites have experienced several different episodes during which either fresh or brackish water environments developed between glaciations (see Figure 6.2.2-2) and which have had a large influence on the present groundwater chemistry. Although a very complex picture, these changes in the groundwater conditions can be followed using the information trapped in the fracture filling minerals.

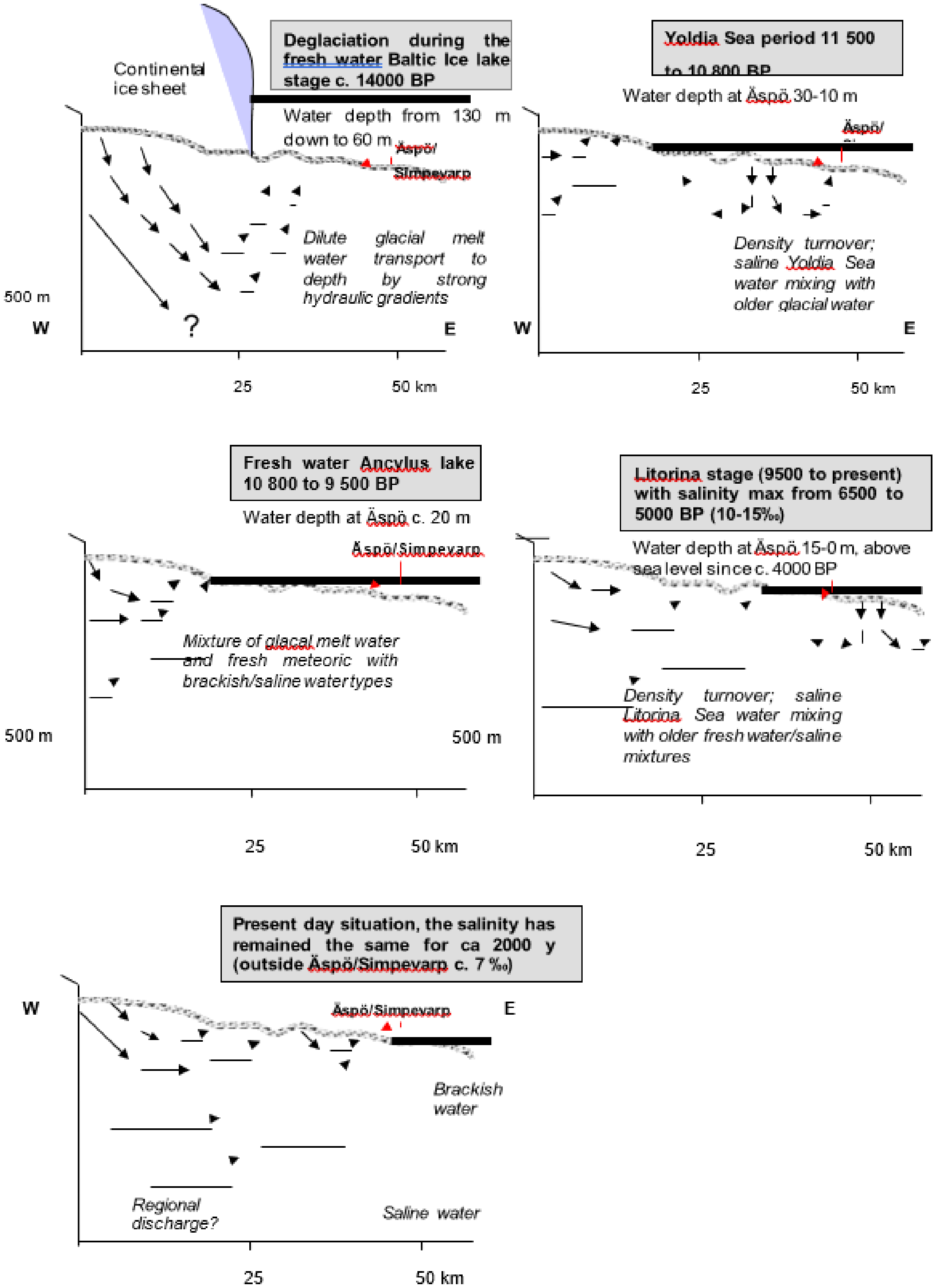

Figure 6.2.2-2. Conceptual postglacial scenario model for the Äspö/Simpevarp area. The figures show possible flow lines, density-driven turnover events, and non-saline, brackish and saline water interfaces. Different stages are: a) Deglaciation, b) Yoldia Sea stage, c) Ancylus Lake stage d) Littorina Sea stage, and e) present day Baltic Sea stage. (from Milodowski et al. 2005).

6.2.2.3 Uncertainties and limitations

- Multiple reactivation of existing fractures is very common in the Äspö-Laxemar area and the current water-conducting fractures and their associated mineralisation usually have a very long and complex history
- Since the water-conducting fractures in the area have been reactivated and several generations of calcites are commonly found together in the same vein, the characterization and differentiation of each generation of calcite is critical to any palaeohydrogeological investigations using calcite
- The amount of late-stage calcite mineralisation is small, and the latest generations of calcite are often present only as thin veneers or overgrowths developed on older calcite mineralisation, thereby making sampling of the latest calcite for analysis difficult
- The area has been subject to several episodes of glaciation and it is difficult to attribute the fracture mineralisation to a specific event or episode
- The fracture minerals do not represent a complete record of the precipitation history because:
    - the amounts of minerals produced can be very small
    - unsaturated chemical conditions and/or lack of flow may result in periods of non-deposition
    - periods of mineral dissolution may have destroyed traces of previous groundwater regimes

6.2.2.4 Relevance

- Past groundwaters have left precipitates from which the different groundwater regimes can be traced right up to the current groundwaters present at the sites
- Late-stage calcite mineralisation can be correlated with current groundwater flow paths in the rock
- Useful information on the long-term stability of the Äspö-Laxemar sites has been obtained from studying the geochemistry of late-stage calcite minerals, detailed mapping of the distribution of redox-sensitive minerals (such as pyrite, secondary iron oxides and iron oxyhydroxides such as goethite) and uranium-series disequilibrium of fracture-coatings
- The morphology of the latest calcite minerals found in the fractures reflects the salinity of the groundwater from which it precipitated (Dideriksen et al. 2007)
- Low temperature calcites precipitated from brackish and marine water are only found down to a depth of around 500 m, whereas calcites with isotopic evidence of meteoric/cold climate recharge signatures can be traced to greater depth, possibly as deep as 1000 m. These “cold” calcites have been interpreted to be precipitated from glacial groundwaters

Nevertheless, the distribution of secondary iron oxides and the preservation of redox-sensitive minerals such as pyrite show that there is no evidence for oxidation below approximately 100 m depth at the sites (Figure 6.2.2-3). Uranium series disequilibrium studies show that this has been the case for at least the past 1 million years.

- The calcite at depth contains reduced iron (Fe^{2+}) and manganese (Mn^{2+}), demonstrating that conditions have remained anaerobic during groundwater circulation at depth at all times.
- Whilst geochemical evidence and mineralogical observations indicate that glacial groundwaters have

potentially reached depths up to 1000 m over the past 1 million years, this study demonstrates that reducing conditions have been adequately maintained at these depths as a result of water-rock interactions consuming the oxygen introduced by recharging groundwater (as might occur beneath an ice sheet). In other areas, the actual depth range will depend upon site-specific characteristics, but similar results have been reported for many sites worldwide (see, for example section 6.2.1).

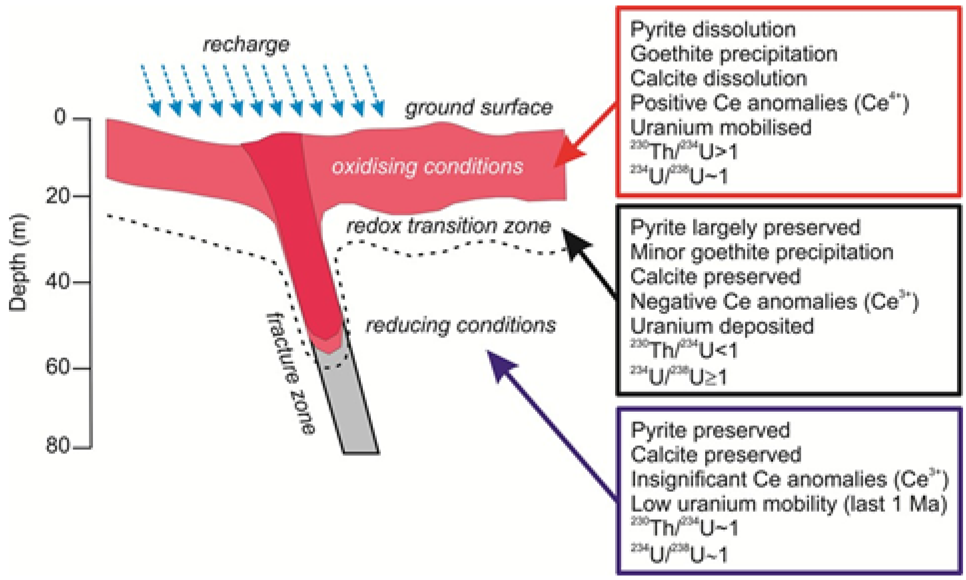

Figure 6.2.2-3. Schematic model of the near-surface redox front in the Laxemar area, Sweden. The different fields represent the depth intervals where geochemical analyses and uranium series disequilibria in fracture coatings indicate Quaternary oxidizing conditions, reducing conditions, or a transition zone between these (modified after Drake et al. 2009).

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6.2.3 Long-term stability of higher strength rocks: the Sellafield regional analogue

Item:

NA6.2.3

Component(s):

HSR

6.2.3.1 Introduction

The present-day climate in the UK is not representative of that which existed for much of the previous 2.5 million years and it could be argued that present day groundwater conditions are not an adequate basis for assessing long-term GDF safety. Observations of the impacts of past climate changes in the UK (see, for example, Table 6.2.3-1) may therefore provide valuable information on how the current groundwater system might respond to future climate changes. Of particular concern is the potential for oxidising groundwater to penetrate to GDF depth during periods of glaciation, thereby increasing the mobility of some radionuclides.

Table 6.2.3-1. Climate state in the United Kingdom over the past 900,000 years (from Milodowski et al. 2005).

FLANDRIAN	10-0 ka BP	Temperate
DEVENSIAN	11-10 ka BP	Periglacial
	14-11 ka BP	Boreal/Temperate
	25-14 ka BP	Glacial
	50-25 ka BP	Periglacial
	60-50 ka BP	Temperate/Boreal
	70-60 ka BP	Glacial
	110-70 ka BP	Periglacial/Boreal
IPSWICHIAN	130-70 ka BP	Temperate/warm
WOLSTONIAN	270-130	Glacial/temperate/periglacial
HOXNIAN	319-400	Temperate/warm
ANGLIAN	400-460	Glacial

CROMERIAN	460-880	Temperate/glacial/temperate

IFEPS:

4.1.2 - Large-scale discontinuities

4.1.6 - Hydraulic characteristics and properties

4.1.8 - Geochemical characteristics and properties

4.2.4 - Chemical processes [geosphere]

NA Type:

Regional analogue

6.2.3.2 NA description

The Sellafield area

Sellafield is located in West Cumbria, in north-west England. It has a coastal groundwater system of shallow freshwater, deep saline water and brine and experienced several episodes of glaciation and periglaciation during the last 2.5 million years (Figure 6.2.3-1). For a time, the Sellafield area was the focus of several detailed palaeohydrogeology studies, initially as part of the UK Nirex Ltd GDF site characterisation programme (e.g. Nirex 1997) and afterwards in the EU-funded EQUIP (Bath et al., 2000) and PADAMOT (Degnan et al. 2005) projects. As such, the large body of available data and associated interpretations make it a valuable regional analogue for potential GDF sites in the West Cumbria area.

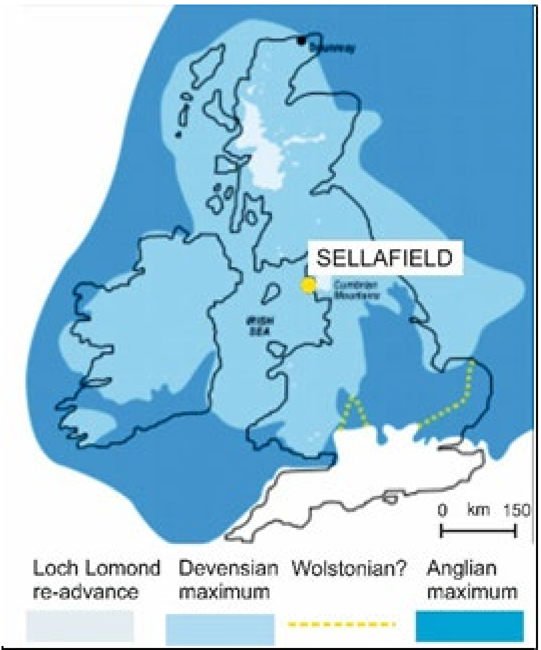


Figure 6.2.3-1. Location of Sellafield. West Cumbria, in relation to the extent of glaciations in the British Isles over the last 2.5 million years (from Milodowski et al. 2005).

Detailed petrological analysis of fracture mineralisation in 23 deep boreholes drilled at Sellafield identified a complex sequence of mineralisation events referred to as ME1-ME9. Much of the mineralisation is geologically-old (occurring from around 550 to 65 million years ago) but the distribution of the youngest (ME9) calcite mineralisation correlates closely with measured modern groundwater flow. Calcite is an ideal target because crystals grow at low temperature within the depth range and timescale of interest to a GDF site characterisation and can record information on past groundwater conditions in various ways, including:

- Crystal morphology generally changes systematically with groundwater salinity
- Growth zones in the crystal preserve a physical and chemical record of groundwater composition
- Crystals dissolve in certain groundwater conditions, creating corrosion surfaces
- Trace elements reflect the oxidation state of groundwater
- Stable isotopes of oxygen and carbon are sensitive to groundwater temperature and sources of dissolved carbon
- Fluid inclusions (small pockets of groundwater trapped in growing crystals) reveal the chemical composition and temperature of past groundwater

In addition, detailed investigation of groundwater geochemistry including 36-chlorine studies (Metcalfe et al., 2007) were used to shed light on the origin and timing of past groundwater movement.

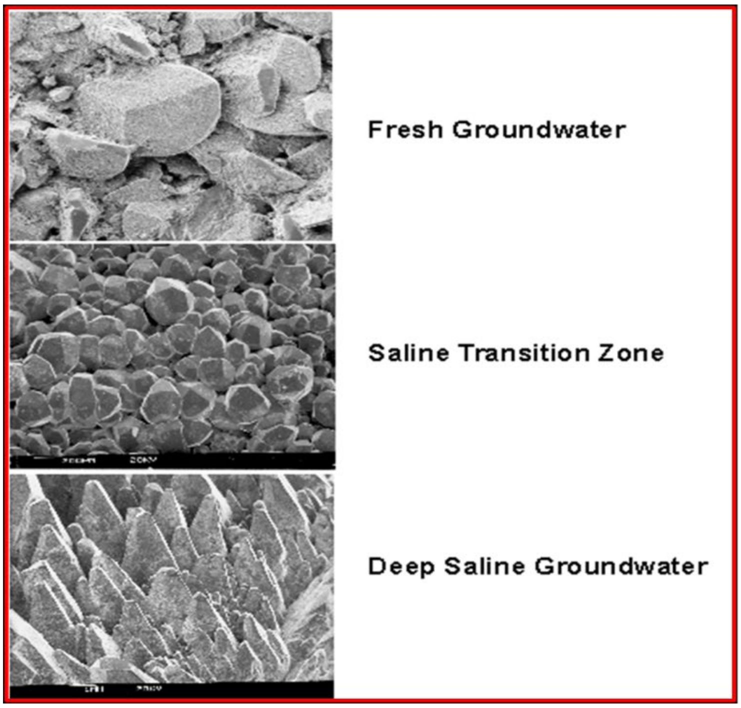
Palaeohydrogeological studies at Sellafield

Palaeohydrogeology studies focussed mainly on the youngest (ME9) calcite mineralisation, which is closely associated with the present-day groundwater system and is well developed in fractures across the area, to a depth of at least 1.5 km.

The distribution of ME9 calcite was found to correlate with groundwater flow. Its crystal morphology changes systematically with the variation in groundwater salinity: characterised by “nailhead” crystals in freshwater zones but becoming more “dog-tooth-shaped” with increasing salinity (Figure 6.2.3-2).

Petrographical and microchemical analyses of these late calcite crystals reveals that they are strongly growth zoned, reflecting variations in Fe and Mn in the groundwater. The variation in cathodoluminescence and chemical zoning characteristics (Figure 6.2.3-3) also correlates closely with the position of the modern-day freshwater and saline groundwater zones, with calcites at the freshwater-saline water interface displaying overgrowth of freshwater-type calcite on cores of saline-type calcite.

Fluid inclusion data and strontium isotope ratios of this late calcite are also consistent with low- temperature (<80°C) precipitation from relatively recent groundwaters.



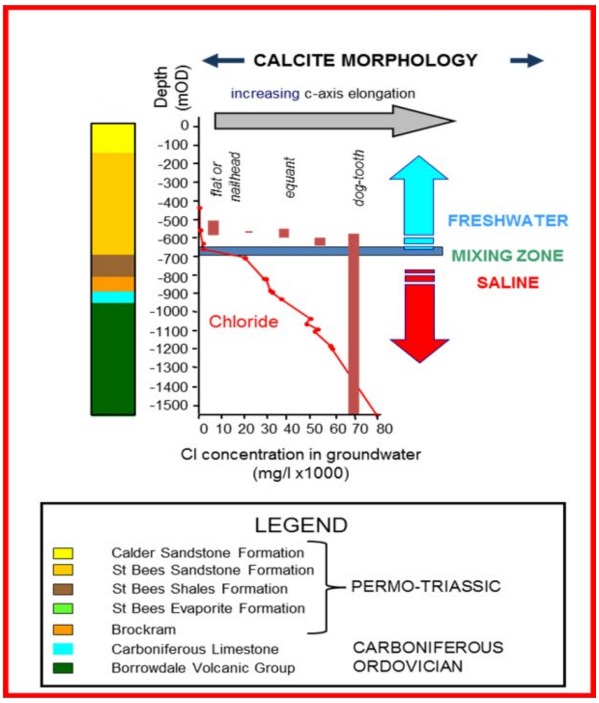


Figure 6.2.3-2. Left: SEM images showing systematic variation in calcite morphology reflecting depth variations in salinity of the present-day groundwater. Right: Distribution of calcite morphology types from Sellafield BH 10A (Milodowski et al. 2015).

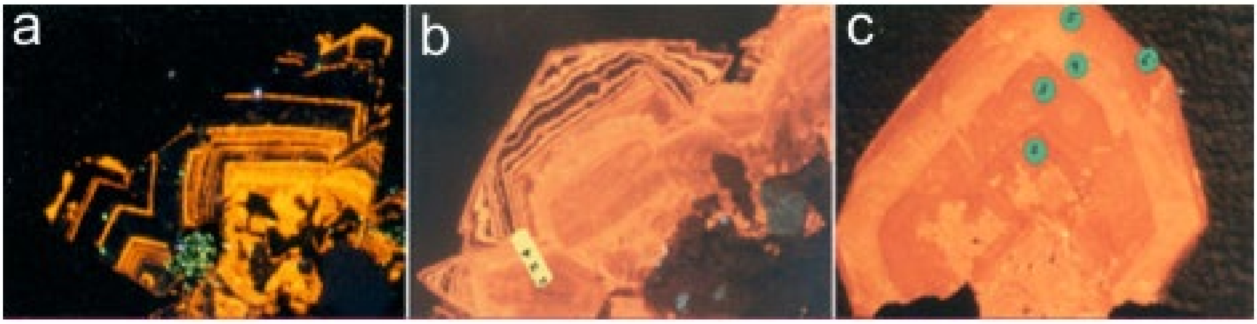


Figure 6.2.3-3. Cathodoluminescence (CL) images showing: (a) freshwater zone (Sellafield BH PRZ2, 243 m); (b) morphological transition zone just above the saline transition zone (Sellafield BH 10A, 558 m); (c) saline transition zone (Sellafield BH RCF1, 885 m). Milodowski et al. (2005).

Stable C and O isotope analyses show considerable variation between growth zones and indicate that the calcites precipitated from groundwaters containing a significant component of glacially-recharged water.

Rare-earth element geochemical patterns of the calcite precipitated in the modern groundwater flow system show a marked negative cerium anomaly only within the freshwater zone, indicating oxidizing conditions (i.e. cerium has behaved as Ce^{4+}). However, at depth in the saline zone, cerium in the calcite is reduced (i.e. Ce^{3+}) and behaves as the other trivalent REEs. This, together with the presence of Fe^{2+} and Mn^{2+} incorporated into the calcite in this depth zone, clearly show that the groundwater has remained reducing during mineralisation, regardless of the input of any glacial-recharge water.

6.2.3.3 Uncertainties and limitations

- Future climate evolution may not follow the patterns and impacts of the past and climate change could significantly modify the natural patterns of climate variation in the future and the magnitude of their impact on the geosphere
- Although the late (ME9) calcite mineralisation can be clearly demonstrated to have formed during the last 2.5 million years and can be correlated to the modern groundwater flow system, precise dating of individual growth zones in the calcite crystals was not possible. This means that the impact of specific glaciation events could not be differentiated

6.2.3.4 Relevance – what have we learnt?

- For the UK, present-day climate is not representative of much of the last 2.5 million years, in terms of either temperature or rainfall. As such, it is important to study past climate variability and its effects on an area such as Sellafield to inform predictions of potential future changes and their impact on the West Cumbria area
- Palaeohydrogeology studies such as this can provide direct evidence of the effects of climate variability on the groundwater in the past and play an important role in constraining site-specific models of future groundwater evolution in response to climate change
- The Sellafield area is an excellent regional analogue for the potential future GDF sites currently under discussion in West Cumbria and, as such, provides an invaluable dataset and conceptual model for future site characterisation studies in the area
- The location and geometry of groundwater flow pathways in the area has evolved continuously as older fracture minerals dissolved and younger (<2.5 million years old in this case) minerals grew. These processes continue today and appear to propagate from east to west, following the regional meteoric groundwater flow-gradient. As noted above, this regional analogue information will be of great value in any future site characterisation studies in West Cumbria
- The latest calcite mineralisation preserves evidence showing that the depth of the fresh–saline groundwater boundary has fluctuated over the last 60 million years or so, with a net increase in depth of this interface of several 10's of metres in central and eastern parts of the Sellafield area. However, fresh water has not penetrated the rock to a significantly greater depth than at the present day
- The range in groundwater salinity values across the Sellafield area as a whole has remained broadly stable during the last 2.5 milion years but, in parts of the site, present-day salinity is significantly lower than it has been previously
- Redox conditions have fluctuated most in the freshwater zone; the magnitude and frequency of redox perturbations diminishes with depth. Observations from the calcite crystals indicate that moderately anaerobic conditions have been the norm at GDF-relevant depths, beneath the shallow freshwater zone

Studies in the Sellafield area have shown that glacially-recharged groundwater can penetrate to GDF depths, but that groundwater remained anaerobic because the rock mass itself is capable of removing the oxygen from the young, fresh water very efficiently at shallow depth. Similar patterns of the rock protecting the deep groundwaters has been observed at numerous coastal sites around the world, including Aspö/Laxemar and Forsmark (Sweden), Olkiluoto (Finland) and Horonobe (Japan)[7]. This builds confidence that is it at least plausible that conditions will remain similarly reducing at depth at other sites during future episodes of climate change.

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[7] See Dragoni & Sukhija (2008), Edmunds & Shand (2008) and Alexander et al. (2022) for detailed discussions of a wide range of other sites showing similar protection mechanisms.

6.2.4 Long-term stability of higher strength rocks: the Tsukiyoshi orebody, Mizunami, Japan

6.2.4.1 Introduction

Item:

NA6.2.4

Component(s):

HSR

The very old Cigar Lake uranium orebody is often presented as evidence that a GDF should be able to isolate waste for millions of years if necessary (see section 2.1.2). Akin to the tectonic setting of the UK, Cigar Lake lies in a stable intraplate setting and even the main fractures at the site are several hundred million years old. In comparison, an example for host rock stability in an active tectonic environment can be found in Japan. Here, in the centre of the country, a group of uranium orebodies occur which have persisted despite many periods of disturbance. Situated near the small town of Mizunami (Figure 6.2.4-1), the ore bodies have been explored, but never exploited. One in particular, the Tsukiyoshi ore body was investigated by means of the Tono exploratory mine (now closed) and, through this, by a dedicated NA (TAP: Tono Analogue Project) study by JAEA (see JNC 2000, for details).

IFEPS:

4.1.2 - Large-scale discontinuities

4.1.6 - Hydraulic characteristics and properties

4.1.8 - Geochemical characteristics and properties

4.2.4 - Chemical processes [geosphere]

4.3.1 - Water-mediated migration [geosphere]

4.3.1.3 - Diffusion [geosphere]

4.3.1.5 - Dissolution, precipitation, and crystallisation [geosphere]

4.3.1.6 - Speciation and solubility [geosphere]

NA Type:

Natural analogue

6.2.4.2 NA description

This 20 million year old uranium ore body has been examined in detail by JAEA to gain an understanding of how the uranium has remained in place, despite the many changes the area has undergone since the initial uranium deposition.

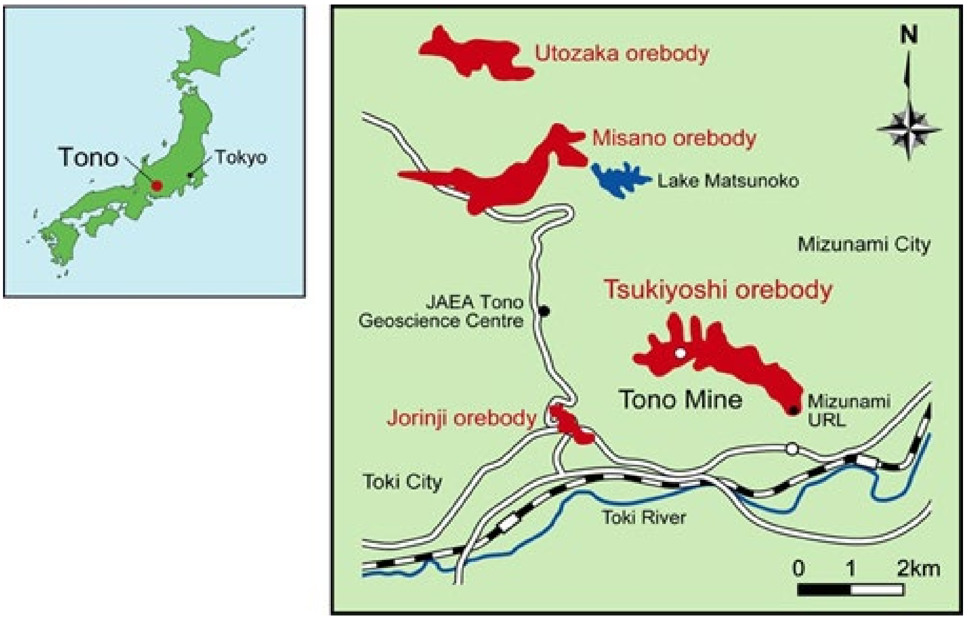

Figure 6.2.4-1. Location map of the Tsukiyoshi uranium orebody in central Japan (image courtesy JAEA).

The area has been inundated by the sea several times (Figure 6.2.4-2), has been cut through by large fractures and has been uplifted due to regional mountain-building and, finally, has been deeply eroded to produce the rugged scenery of the area today (Sasao et al. 2006). Despite this, the Tsukiyoshi uranium orebody (and several others nearby) has survived intact for up to 20 million years, showing that deep geological disposal can be expected to work even in areas which are not perfectly stable as long as the host rock offers appropriate hydrological and hydrogeochemical protection to the waste (Alexander et al. 2006).

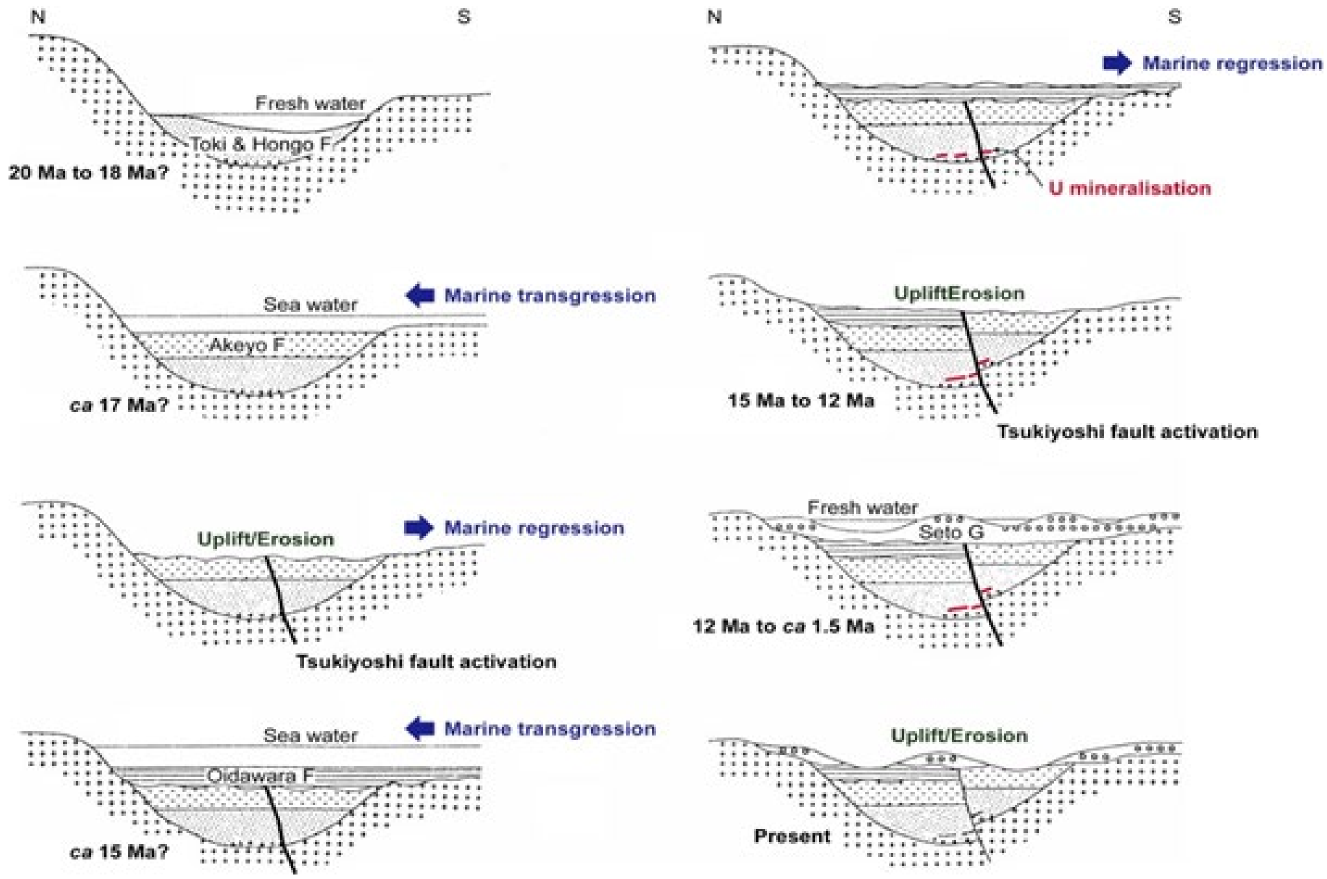

Figure 6.2.4-2. The area around the Tsukiyoshi uranium orebody has undergone many perturbations over the last 20 million years (image courtesy JAEA).

Detailed examination of the orebody shows that the uranium has been trapped on the surface and in the pores and fractures of a wide range of minerals in the host rock (see Figure 6.2.4-3). An important part of this trapping mechanism is that the rock and groundwaters contain little or no oxygen, which maintains anaerobic conditions in the orebody and limits the mobility of uranium. In detail, a range of geochemical processes contribute to the low oxygen levels in the orebody (Figure 6.2.4-4). Many of these uranium minerals are also found in potential GDF host rocks worldwide and this increases confidence in the ability of the rock around a GDF to minimise the movement of uranium (and other redox-sensitive radionuclides) which might be released from the EBS.

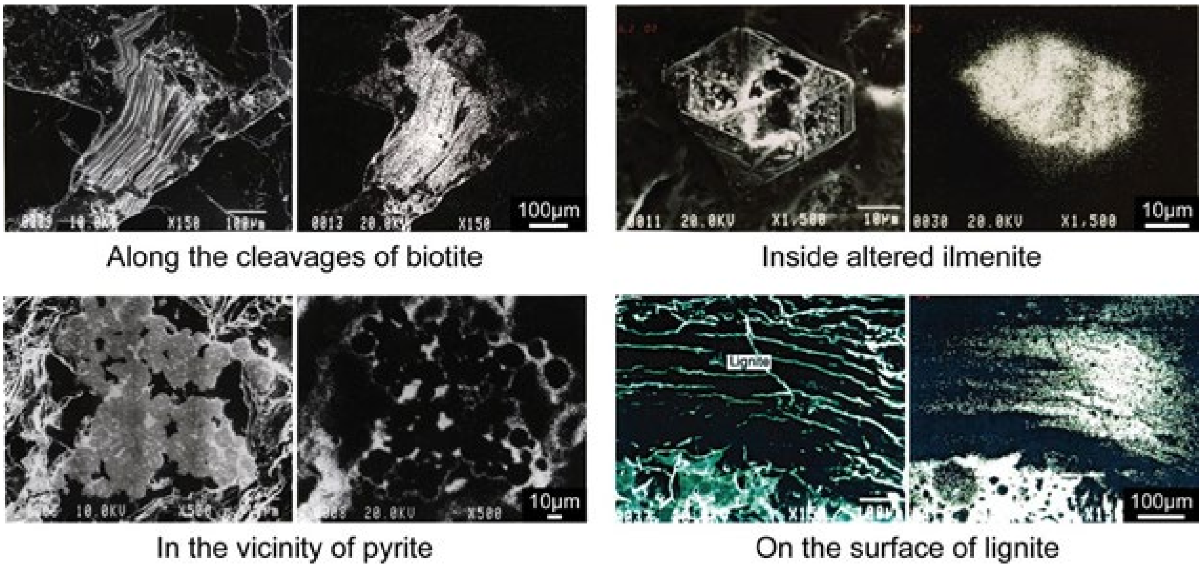

Figure 6.2.4-3. A range of microscope images showing uranium retardation in and on many of the minerals in the host rock in the Tsukiyoshi orebody. The image on the left of each pair shows the mineral and the bright areas in the image on the right shows the uranium distribution (image courtesy JAEA).

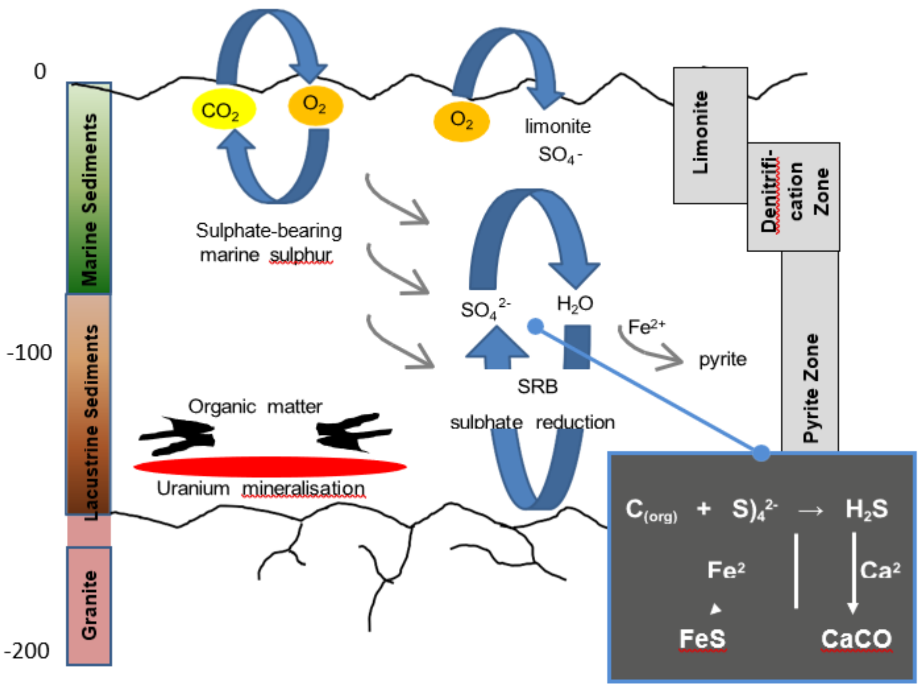

Figure 6.2.4-4. A range of geochemical processes contribute to the low oxygen levels in the orebody (modified from Mizuno & Iwatsuki 2005).

6.2.4.3 Uncertainties and limitations

- The Tono analogue study suffers from the general limitation that applies to all natural uranium orebody studies, i.e. the primary mineral assemblage does not mimic exactly the solid phase compositions to be found in spent fuel, vitrified waste or cementitious waste
- While the evolution of the site is reasonably well understood, the highly complex history of the area means that many detailed boundary conditions are unknown – for example, what was the original form of the uranium in the orebody? If it was different to what is now observed, did that influence the long-term stability of the orebody?

6.2.4.4 Relevance – what have we learnt?

- Despite an incredibly complex history of repeated, regional and local perturbations at the Tsukiyoshi site, the Tsukiyoshi and neighbouring ore bodies are still present after 20 million years, clearly showing that the fundamental hydrological and hydrogeochemical stability of a host rock can survive significant physical and chemical perturbations and so guarantee the longevity and performance of a GDF (see also sections 6.2.1 and 6.2.3)
- The low oxygen levels in the rock and groundwater are important for trapping the uranium at the site. These low levels are partly because of the presence of the high concentrations of organic material at the site (something unlikely in most GDF host rocks), but significant amounts of other reducing minerals (such as pyrite) are also present, so strengthening the connection with potential GDF sites
- Several specific uranium trapping processes have been identified at the site and the long-term, large-scale NA data support the mechanisms elucidated in short-term, small-scale, laboratory experiments, so increasing confidence in their use in GDF safety cases

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6.3 Long-term stability of lower strength sedimentary rocks

As noted in section 6.2, an important requirement of a safety case for a GDF is to be able to demonstrate that future climatic changes will not adversely affect the groundwater system at GDF depths over the period of time during which the waste will be a hazard. This remains the case for LSSR, even when solute transport is predominantly diffusive.

6.3.1 Site stability of lower strength sedimentary rocks: Opalinus Clay

6.3.1.1 Introduction

Item:

NA6.3.1

Component(s):

LSSR

The Opalinus Clay is one of several potential GDF host rocks in the Swiss national programme and, in addition to an extensive (and currently ongoing; Nagra 2021) site characterisation programme, regional analogue studies were carried out on the long-term host rock stability in the Mont Terri URL (Figure 6.3.1-1). SC relevant studies continue in the URL (see www.mont-terri.ch for details) and an overview of the work on the host rock stability as established from 25 years of porewater studies has recently been published (Wersin et al. 2020).

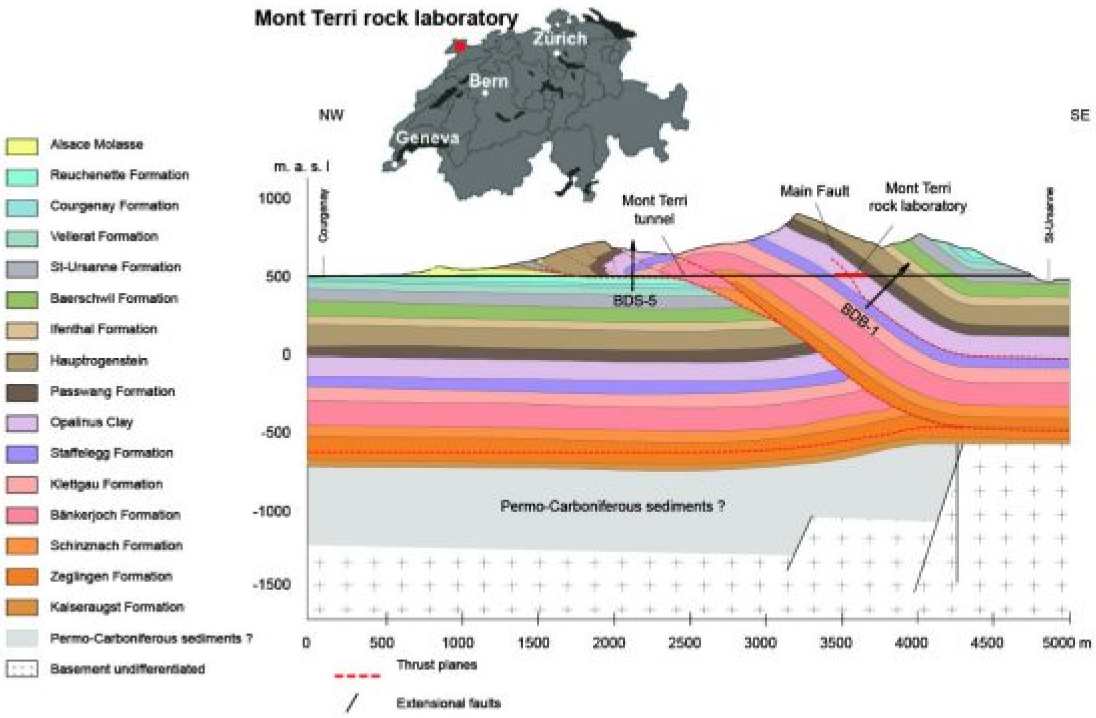

Figure 6.3.1-1. Geologic profile through the Mont Terri anticline, Switzerland. The location of the Mont Terri URL (situated almost entirely in the Opalinus Clay) and deep drillholes BDS-5 and BDB-1 are noted (from https://www.mont-terri.ch/en/geology%20/geological-structures.html)

IFEPS:
4.1.6 - Hydraulic characteristics and properties

4.1.8 - Geochemical characteristics and properties

4.2.3 - Mechanical processes [geosphere]

4.2.4 - Chemical processes [geosphere]

4.3.1.3 - Diffusion [geosphere]

NA Type:

Natural analogue, Regional analogue

6.3.1.2 NA description

Studies of natural tracer distribution across the Opalinus Clay from a variety of experimental approaches[8] as a function of distance from the Opalinus Clay contact with the overlying Passwang Formation aquifer and the underlying Staffelegg Formation aquifer in the Mont Terri anticline (Figure 6.3.1-1) have shown that the tracers display smooth, regular profiles with depth. Some profiles are more symmetrical than the others (see Figure 6.3.1-2), and the asymmetric shape of the chloride profile has been explained by the distinct erosion history of the two adjacent aquifer units. Based on regional studies, it is assumed (Mazurek et al. 2011) that the upper aquifer was activated first (at 6.5 million years ago), followed by the lower (at 0.5 million years ago) and this produced excellent (diffusive transport) model fits to the data (NEA 2009). The laboratory-derived diffusion coefficients also apply at the site scale (providing an excellent example of upscaling, cf. Mazurek et al. 2006).

[8] These include in situ URL experiments to a range of laboratory methods as diverse as vacuum distillation and diffusive exchange; see Wersin et al. 2020, for details.

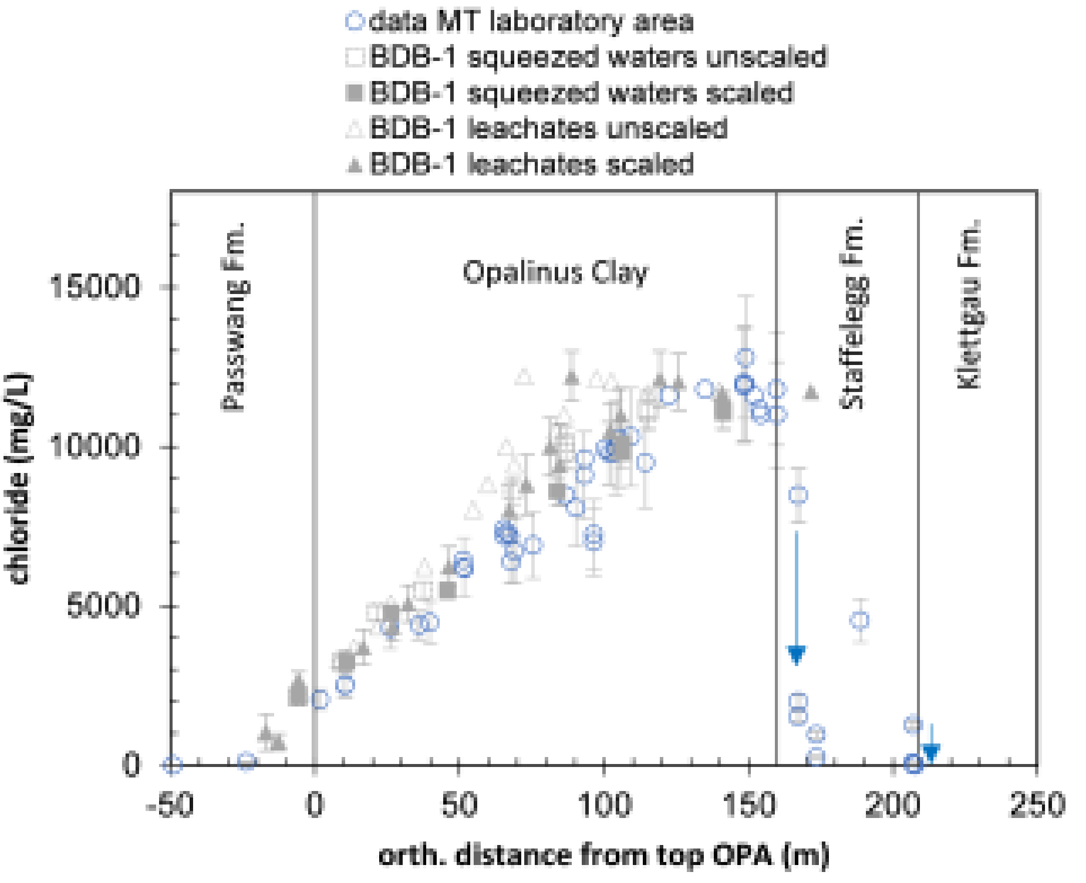

Figure 6.3.1-2. Chloride concentration profile across the Opalinus Clay. A comparison of data from the Mont Terri URL (data MT laboratory area) and those from borehole BDB-1 which was drilled normal to the Opalinus Clay bedding (Wersin et al. 2020).

Similarly, Figure 6.3.1-3 shows δ2H and δ18O profiles as a function of distance across the Passwang Formation/Opalinus Clay/Staffelegg Formation.

As with the chloride data, these profiles suggest diffusive solute transport across the Opalinus Clay and between the Opalinus Clay and the surrounding aquifers, but show a steeper decrease towards the underlying Staffelegg Formation aquifer(Figure 6.3.1-1). Nevertheless, the same erosional scenario explains the asymmetry of the Cl profile and the symmetry of the He profile (due to different De values)..

It is worth noting that studies of the Opalinus Clay from other environments (e.g. from short drillcores in the Mont Russelin motorway tunnel some 5 km from the Mont Terri URL), have produced a similar picture of diffusive solute transport in the host rock (Mazurek et al. 2009). This particular example is of interest as the site displays a highly complex tectonic history and the Opalinus Clay here is strongly affected by faulting and fracturing. Finally, a 1.5 km deep borehole which penetrated the Opalinus Clay Formation some 10 km NE of Nagra's original Benken GDF site exploration borehole was studied by Nagra (Wersin et al. 2013). This further confirmed the diffusive nature of solute transport in the Opalinus Clay.

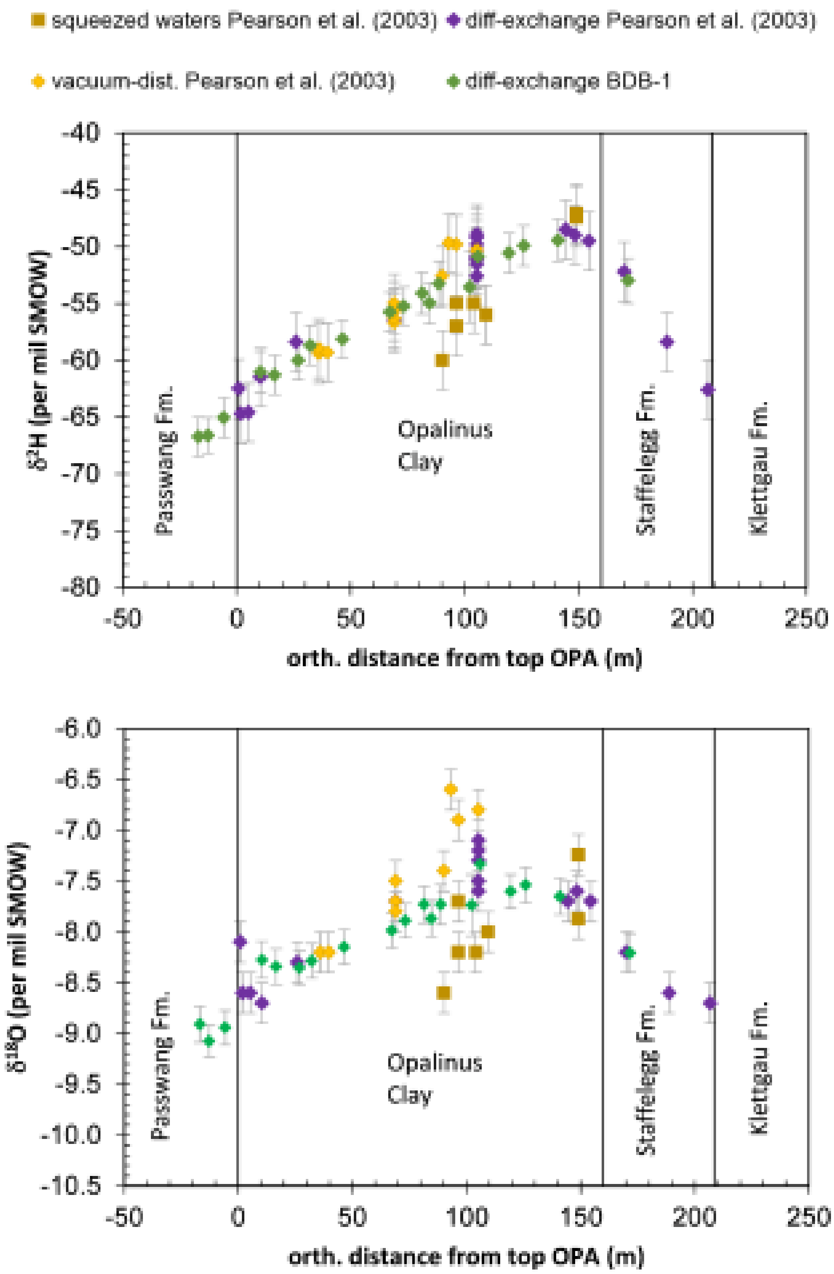

Figure 6.3.1-3. Profiles for δ2H (top) and δ18O (bottom) obtained from a range of core samples (see Wersin et al. 2020 for details).

6.3.1.3 Uncertainties and limitations

- Analytical uncertainties were initially significant, but a re-assessment of the uncertainties in the various sampling and analytical methods utilised (see Wersin et al. 2020 for details) has reduced these to a minimum, so increasing confidence in the data

- As the Mont Terri site is some 150 km away from the potential GDF site and is situated in a significantly different tectonic regime, the relevance of the example has been questioned
- Quantification of tracer profiles requires a good understanding of the site palaeohydrogeology, something which is typically the case for potential GDF host formations, but not always for generic natural analogue sites

6.3.1.4 Relevance – what have we learnt?

- Despite being in a tectonically active area of Switzerland, solute transport in the Opalinus Clay remains diffusive, indicating that the long-term barrier qualities of the clay host rock remain intact
- Despite the differences in the two sites, this led to no perceptible weakening of the message of GDF host rock stability and was deemed acceptable by technical audiences
- Studies at other, tectonically more complex sites (such as the Mont Russelin motorway tunnel), also show diffusive solute transport in the Opalinus Clay, so adding support to both the URL-focussed studies and the overall regional analogue approach
- The study has provided an excellent example of upscaling as the laboratory-derived diffusion coefficients (conducted on samples some 10 cm long) have been shown to also apply at the site scale of over 200 m, so increasing confidence in appropriately produced laboratory data
- The results have also increased confidence in the approach where widely differing experimental methods have been utilised to produce comparable results
- In the case of GDF site-scale studies like these, consideration of several tracers in parallel adds confidence in the interpretation

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6.3.2 Site stability of lower strength sedimentary rocks: Couche-Silteuse

6.3.2.1 Introduction

Item:

NA6.3.2

Component(s):

LSSR

The argillaceous sediments at the Couche Silteuse at Marcoule, France (Figure 6.3.2-1) are 100 million year old marine silty-shales. The geological conditions are slightly more complicated than at Mont Terri (section 6.3.1) with a significant erosion event happening 5.85−5.3 million years ago producing deep canyons which refilled under marine conditions ~3 million years ago before final emergence.

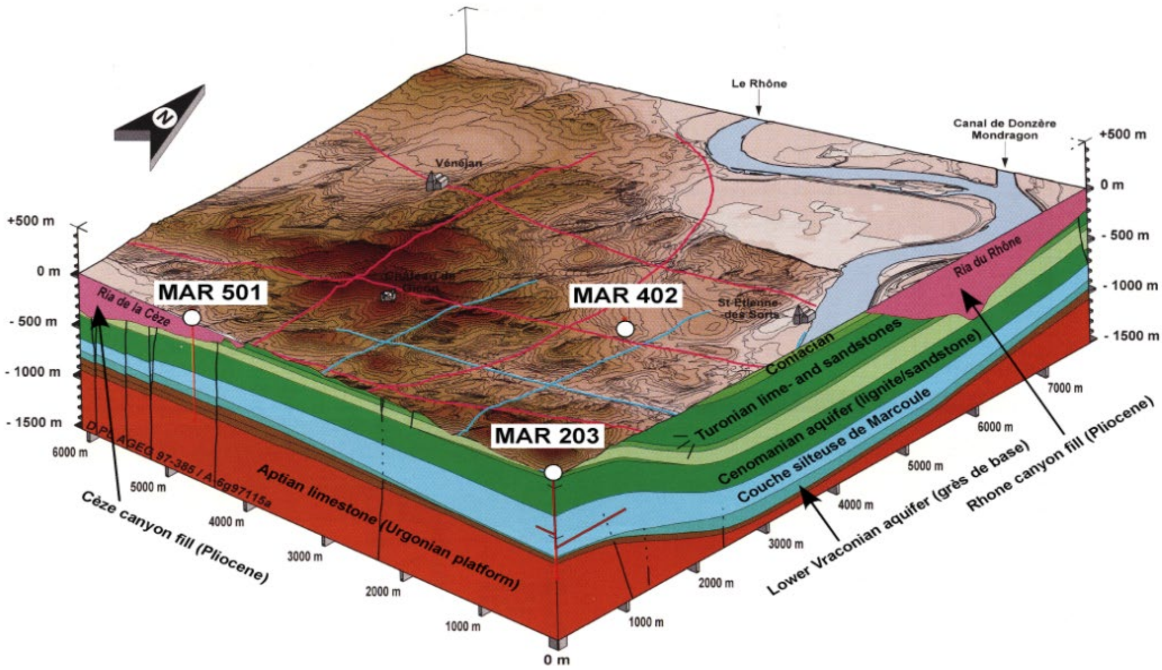

Figure 6.3.2-1. Block diagram of the Couche Silteuse area with the three boreholes marked (MAR). The canyon fill is marked in pink in the figure (at the NE & SW corners of the block). After Mouroux & Brulhet (1999).

IFEPS:

4.1.6 - Hydraulic characteristics and properties

4.1.8 - Geochemical characteristics and properties

4.2.4 - Chemical processes [geosphere]

4.3.1.3 - Diffusion [geosphere]

NA Type:

Natural analogue

6.3.2.2 NA description

As in the Opalinus Clay, the natural tracer profiles in the porewaters (Figure 6.3.2-2) were modelled[9], but note that the Cl concentrations, although generally exhibiting smooth diffusive transport profiles, contrast significantly between boreholes. The highest Cl concentrations are at depth in borehole MAR 203 and are near to the full marine value (currently 20,500 –21,500 mgL^{-1} in the Mediterranean). The task for the modellers was to show that the same model and the same palaeohydrogeological scenario could explain all three profiles.

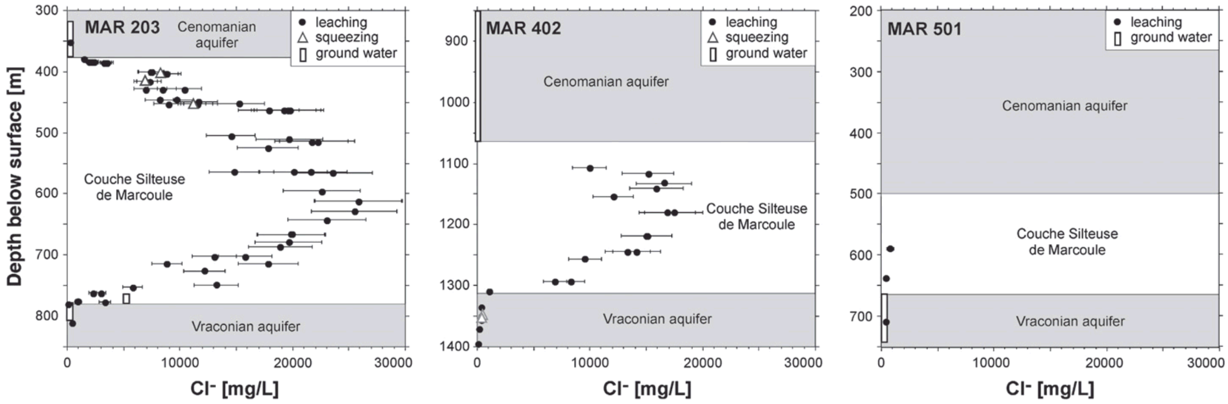

Figure 6.3.2-2. Distribution of Cl$^-$ in pore- and groundwaters in the Couche Silteuse de Marcoule in boreholes MAR203, MAR402 and MAR501. As in the Opalinus Clay, the grey areas indicate aquifers above and below the white of the Couche Silteuse de Marcoule. From Mazurek et al. (2009).

The modelling results are shown in Figure 6.3.2-3 and Mazurek et al. (2009) claim that they indicate that diffusion times of 3 million years are consistent with the data obtained for boreholes MAR 203 and 501 and agreeing with the estimated time of final emergence of the site (based on pan-Mediterannean considerations). However, this thesis needs to be better tested with more data from borehole MAR 501. Currently, the diffusion time of 1.5 million years obtained for borehole MAR 402 indicates delayed activation of the aquifers, but this is plausible due to the greater depth of the formation here (Figure 6.3.2-2) and an increased distance from the infilled canyons (Figure 6.3.2-1). So, as in the Opalinus Clay, the natural tracer profiles in the Couche Silteuse de Marcoule clays can be explained by diffusional transport properties alone, despite the complex geological history of the site.

[9] According to Mazurek et al. (2009), only diffusive transport was considered.

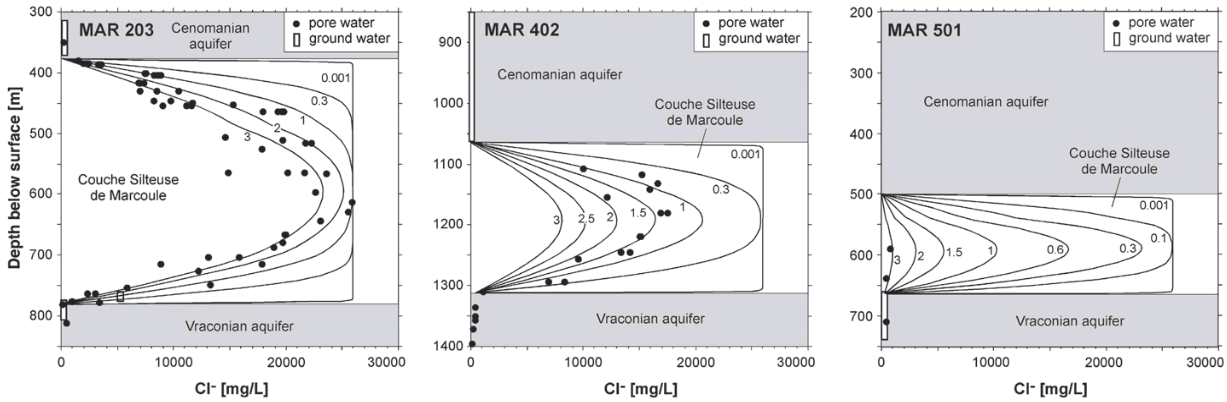

Figure 6.3.2-3. Base-case model (runs G203 A5, G402 A5, G501 A5 are shown) for the out-diffusion of Cl^- in the Couche Silteuse de Marcoule considering an initial concentration of 25,900 mgL^{-1} (the maximum observed Cl- concentration in the Couche Silteuse – see Figure 6.3.2-2). Values adjacent to model curves indicate evolution times in million years since activation of the aquifers. From Mazurek et al. (2009).

6.3.2.3 Uncertainties and limitations

- Interpretation is difficult as this is a complex site: the thickness of the Couche Silteuse at Gard varies greatly due to local differences in subsidence of fault-bounded blocks of the sequence in this area, just to the west of the Rhône valley. In three boreholes that are <5 km apart, the thickness of the Couche Silteuse is 404, 246 and 163 m
- The initial salinity of pore waters in the Couche Silteuse when the present profiles began to evolve is somewhat uncertain because various hypotheses are possible for the palaeohydrogeology of the aquifers at that site since the last marine incursion occurred (ca. 5.5 million years ago)
- Appropriate initial and boundary conditions for the model of σ37Cl in the Couche Silteuse cannot be defined. Although not presented here, modelling porewaterisotopic fractionation has not been able to achieve a reasonable match with the observed σ37Cl data unless heterogeneous initial σ37Cl distribution is assumed. However, to date, it has proved impossible to establish any independent support for this inference, which points to an inadequate understanding of the geological evolution of the site that would have affected this isotopic tracer (cf. comment in section 6.3.1.3 on the differences in the degree of characterization of a potential GDF host rock and a generic NA site)
- While the modeling results for boreholes MAR 203 and 501 are consistent with the overall site understanding, they could be better tested with additional data from borehole MAR 402

6.3.2.4 Relevance – what have we learnt?

- As in the Opalinus Clay, there is strong support for diffusive solute transport in the Couche Silteuse from modelling of the three profiles with different thicknesses. Modelling the Cl- concentration profiles shows that the marked variations of salinity, from saline to brackish, between the three profiles are entirely consistent with diffusion with the same boundary conditions and the same (or very similar) time periods (i.e. >3 to 1.5 million years ago) since activation of the aquifers
- As in the Opalinus Clay at Mont Terri, a complex geological history has not significantly disturbed solute transport processes in the Couche Silteuse and it remains diffusive, indicating that the long-term barrier qualities of the clay host rock remain intact

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6.3.3 Site stability of lower strength sedimentary rocks: regional analogues of the Mercia Mudstone Group

6.3.3.1 Introduction

Item:

NA6.3.3

Component(s):

LSSR, Regional analogues

The Mercia Mudstone Group is mid- to upper-Triassic in age (ca. 247 to 201 million years old; Ogg et al. 2016) and is of current interest in the UK programme as a potential GDF host rock and it can be found across the UK in some 10 depositional basins (Figure 6.3.3-1). While it is currently not possible to examine the Mercia Mudstone at potential GDF sites directly, regional analogues are accessible and, here, those in Basins 10 (Carlisle), 6 (East Midlands Shelf) 2 (Somerset/Avon/South Wales) and 3 (Worcester/Knowle) will be examined.

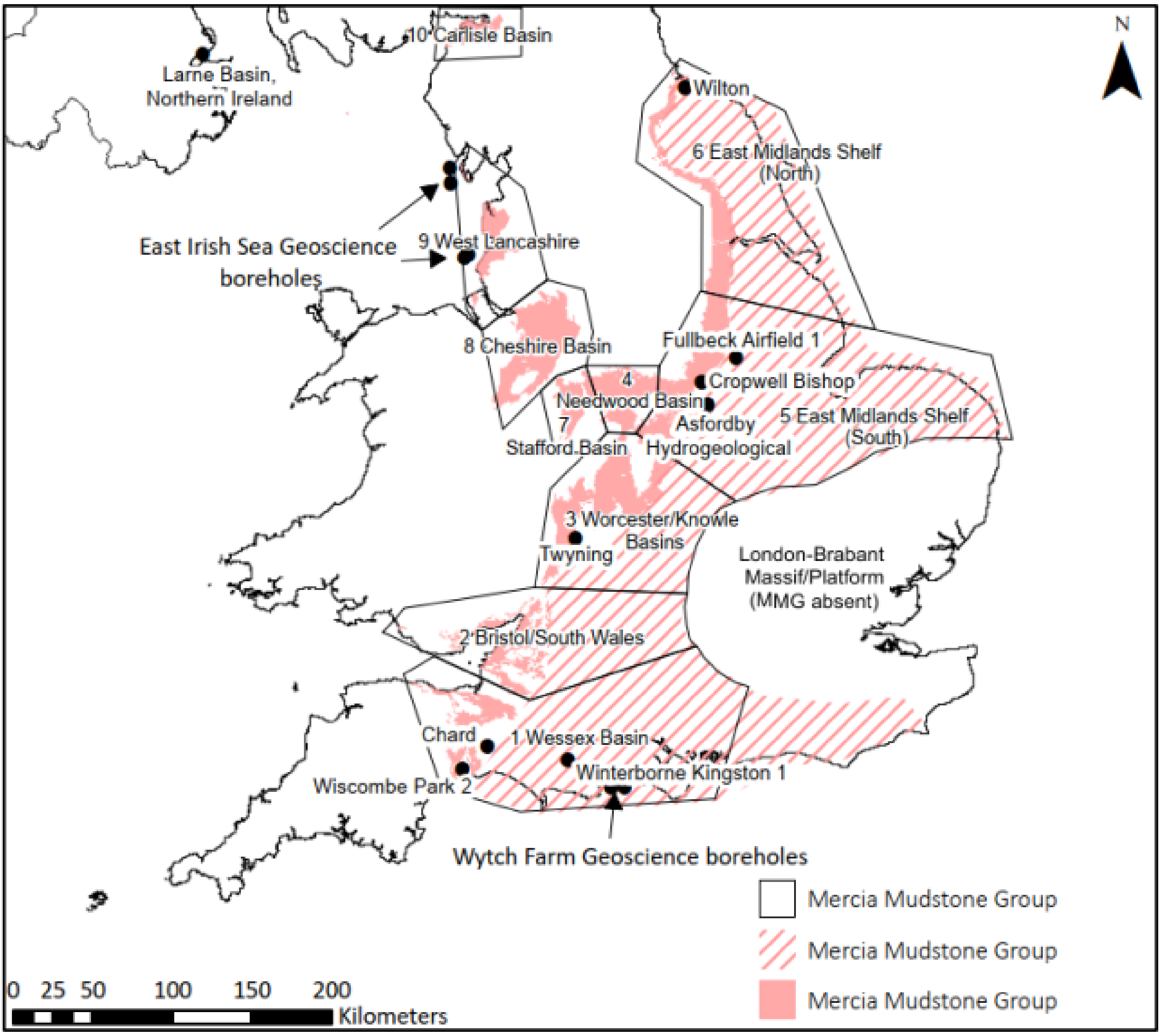

Figure 6.3.3-1. Mercia Mudstone outcrop (solid colour), subcrop (diagonal hatching), regions and locations where the Mercia Mudstone Group at depth has been investigated (black dots and associated text). Rose et al. (2022) after Howard et al. (2008).

Currently, Basin 10 (and the East Irish Sea Geoscience boreholes of Basin 9) is clearly of greater interest due to the proximity of the 3 volunteer communities in Cumbria and Basin 6 (East Midlands Shelf) similarly so due to the presence of the volunteer community in Lincolnshire. Basins 2 and 3 are of interest as they are within reasonable travel distance of NWS' office (and many of their contractors' offices). Apart from the logistics of working at sites in these basins, Rose et al. (2022) noted that:

"The Mercia Mudstone Group is subdivided into five formations. The vertical and horizontal variation in mineralogy through the Mercia Mudstone Group, and between different basins, is predominantly caused by the presence of halite members in the Sidmouth Mudstone Formation and the presence of siltstone and sandstone beds, members and formations (e.g. Arden Sandstone Formation). Relative similarity in mineralogy of the mudstone component of the formations between regions indicates that these intervals could be parameterised similarly or potentially modelled as combined homogenous units, however, due to variations in the presence of halite, siltstone and sandstone between regions, the site-specific sequence should be considered before combining units."

Whilst keeping the last sentence in mind, it is still possible to carry out regional analogue studies of the type noted in Reijonen & Alexander (2023a, chapters 3 and 4) which can support the UK national programme until site-specific work can be initiated[10] and some examples will be discussed here.

IFEPS:
4.1.6 - Hydraulic characteristics and properties

4.1.8 - Geochemical characteristics and properties

4.2.4 - Chemical processes [geosphere]

4.3.1 - Water-mediated migration [geosphere]

4.3.1.3 - Diffusion [geosphere]

NA Type:

Regional analogue

6.3.3.2 NA description

Despite (at the time of writing) the existence of 4 volunteer communities in the UK national programme, it is unlikely that any site-specific investigations will be possible for some time yet. As such, the regional analogue approach would appear to offer the most appropriate method of obtaining potential GDF host rock information, so allowing progress on a range of technical fronts in the interim. It should, however, be emphasised that the heterogeneous nature of the Mercia Mudstone (e.g. Jeans 2006 and Figure 6.3.3-2) implies that it is not advisable to simply study any Mercia Mudstone site, rather the work should focus primarily on finding sites which are most relevant to the GDF host rock in the current areas of interest.

Although full SC-relevant data are limited, Rose et al. (2022) produced a thorough assessment of geotechnical data availability on the Mercia Mudstone and, whilst noting some limitations on potential data usage for geotechnical purposes (section 6.3.3.3), they also report the availability of mineralogical data for several sites. Of relevance here, Howard et al. (2008) provided detailed information on UK localities for the various geological Formations which constitute the Mercia Mudstone Group, including:

- Formation type area
- Formation type section
- Primary (and other) reference section
- Extant (in 2008) exposures/sections

[10] As noted in Reijonen & Alexander (2023a), regional analogue studies have continued in some national programmes after site-specific studies have been initiated, for example when the number of boreholes on-site have been limited (e.g. Nagra's studies on the Palfris Formation and Opalinus Clay host rocks – see section 6.3.1) or when EBS-specific studies have been implemented (e.g. Posiva and NWMO's studies on smectite stability in the GDF host rock).

- Formation geographical extent
- Core availability
  - e.g. Fulbeck F/B1 Borehole (SK85SE/25[11]) [SK 8889 5053[12]], Fulbeck, Lincolnshire[13]: from 111.52 to 117.52 m depth (Berridge et al., 1999). Curated core held at the National Geosciences Records centre, BGS, Keyworth, UK
- Mine information. This tends to be rare, but generally more relevant (see comments in section 6.3.3.3)
  - e.g. Staithes No.20 Borehole (NZ71NE/14) [NZ 76034 18000], Boulby mine site, North Yorkshire: from 391.36 to 397.00 m depth (Woods, 1973). Curated core held at the National Geosciences Records centre, BGS, Keyworth, UK
  - e.g. Blue Anchor Formation. A good section was accessible in the British Gypsum Bantycock opencast mine [SK 8123 4949] near Newark, Nottinghamshire in 2005. An occurrence in the Carlisle Basin (Basin 10, Figure 6.3.4-1) has been documented by Ivimey-Cook et al. (1995)

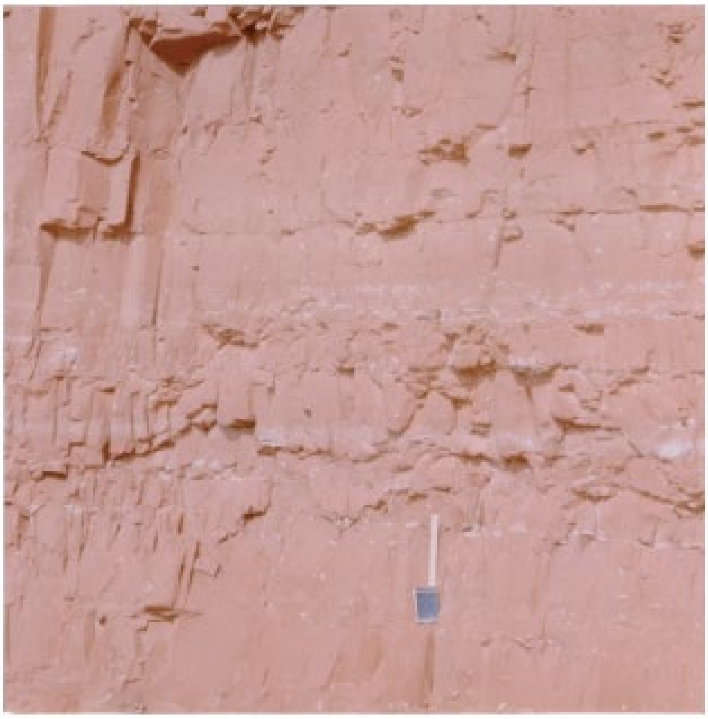

Figure 6.3.3-2. Massive unbedded and poorly bedded mudstone from the Sidmouth Mudstone Formation of the Mercia Mudstone Group, Salcombe Hill Cliff, south Devon (scale 30 cm). The clay mineralogy of this lithology is highly variable, ranging from simple mica-chlorite assemblages to those rich in authigenic minerals (smectite, smectite-chlorite, corrensite, sepiolite, palygorskite). Jeans (2006).

[11] Borehole identification number in Howard et al. (2008).
[12] Grid reference in Howard et al. (2008).
[13] Fulbeck is some 80 km southwest of the Theddlethorpe volunteer site in Lincolnshire.

Although, as noted above, information on GDF-relevant sites in the Mercia Mudstone Group is limited, more general information on geotechnical properties is available (e.g. Hobbs et al. 2002) as are mineralogical data (e.g. Bloodworth & Prior 1993, Kemp 1999), although geochemical data appear to be rarer (e.g. Taylor 1983, Leslie 1989).

6.3.3.3 Uncertainties and limitations

- The use of data (and/or future samples) from quarries and shallow boreholes must be treated with caution as certain processes which occur near-surface are irrelevant to GDF depths. For example, within the regional analogue studies on the Opalinus Clay in Switzerland, Mazurek et al (1996) reported on retardation properties of the host rock and concluded that matrix diffusion was active to some 0.08 m into the host rock behind fractures and that fracture-related redox fronts retarded contaminant migration. However, the samples were collected from a quarry and the samples had experienced significant weathering, so restricting the matrix porosity for diffusional processes meaning the measured diffusion depths were conservative (in the SC sense) compared to the situation at GDF depth. Similarly, the observed redox front-related retardation is not observed at GDF depth (as no redox fronts propagate to such depths in the Opalinus Clay), so the data were non-conservative in the SC sense. Although the study provided some hands-on experience of working with the host rock, the so-produced data were of little SC value
- For the Mercia Mudstone Group itself, Rose et al. (2022) noted that the geotechnical data published in the literature come predominantly from shallow (<250 m deep) boreholes and so their GDF-relevance must be debateable. Further, they noted that the current borehole data are restricted geographically to "….the Yorkshire-Lincolnshire area, Keyworth and Nottinghamshire area, Wilton near Teesside and from the Larne Basin in Northern Ireland.", areas which are not directly relevant to the current national programme
- It would appear that, even when existing boreholes have sampled the Mercia Mudstone at GDF-relevant depths (e.g. Howard et al. 2008, chapter 4, Rose et al. 2022, Tables B1 and B2), the cores are unfit for re-sampling and re-analysis as none are known to have been stored under appropriate conditions to prevent desiccation (and subsequent collapse) and atmospheric contamination (see discussion in Kunimaru et al. 2010, Ewy 2015, for example)
- Another significant body of information on the Mercia Mudstone Group comes from surface (to near surface) engineering investigations (e.g. Hobbs et al. 2002; HS2, 2017) and this information unfortunately is also of little relevance to a GDF SC

6.3.3.4 Relevance – what have we learnt?

- Regardless of the limitations noted above, as reported in Reijonen & Alexander (2023a) and elsewhere (e.g. Yamada & Ota 2016), the regional analogue approach can provide data of direct relevance to a GDF SC when the studies are conducted on sites/samples which are GDF-relevant
- In the current situation in the UK GDF programme, it is recommended that a considered approach is implemented. Proposed potential future work is discussed in section 13.5 (Table 13.5-1, IDs 6.3.3-1 to 6.3.3-7).

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6.4 Long-term stability of evaporite rocks

As noted in section 6.2, an important requirement of a safety case for a GDF is to be able to demonstrate that future climatic changes will not adversely affect the groundwater system at GDF depths over the period of time during which the waste will be a hazard. This remains the case for LSSR, even when solute transport is predominantly diffusive.

6.4.1 Evaporite rocks - overview

Evaporite deposits form by the evaporation of enclosed seas or lakes to leave behind an accumulation of salt. They tend to be located in sedimentary basins and, hence, can be interstratified with clays and other sediments (as is the case in the Mercia Mudstone Group in the UK – see section 6.3.3). Thick bedded evaporites may remain in the original horizontal layers (as in the case of the WIPP GDF in New Mexico, USA; Figure 6.4.1-1), but they may become unstable (in terms of density and plasticity) and rise upwards to form salt domes (as in the Morsleben and Gorleben sites in the German national programme) (see Figure 6.4.1-2).

Figure 6.4-1. The WIPP GDF in New Mexico, USA, has been operational for over two decades. Image courtesy Nuclear Waste Partnership LLC (Carlsbad, USA).

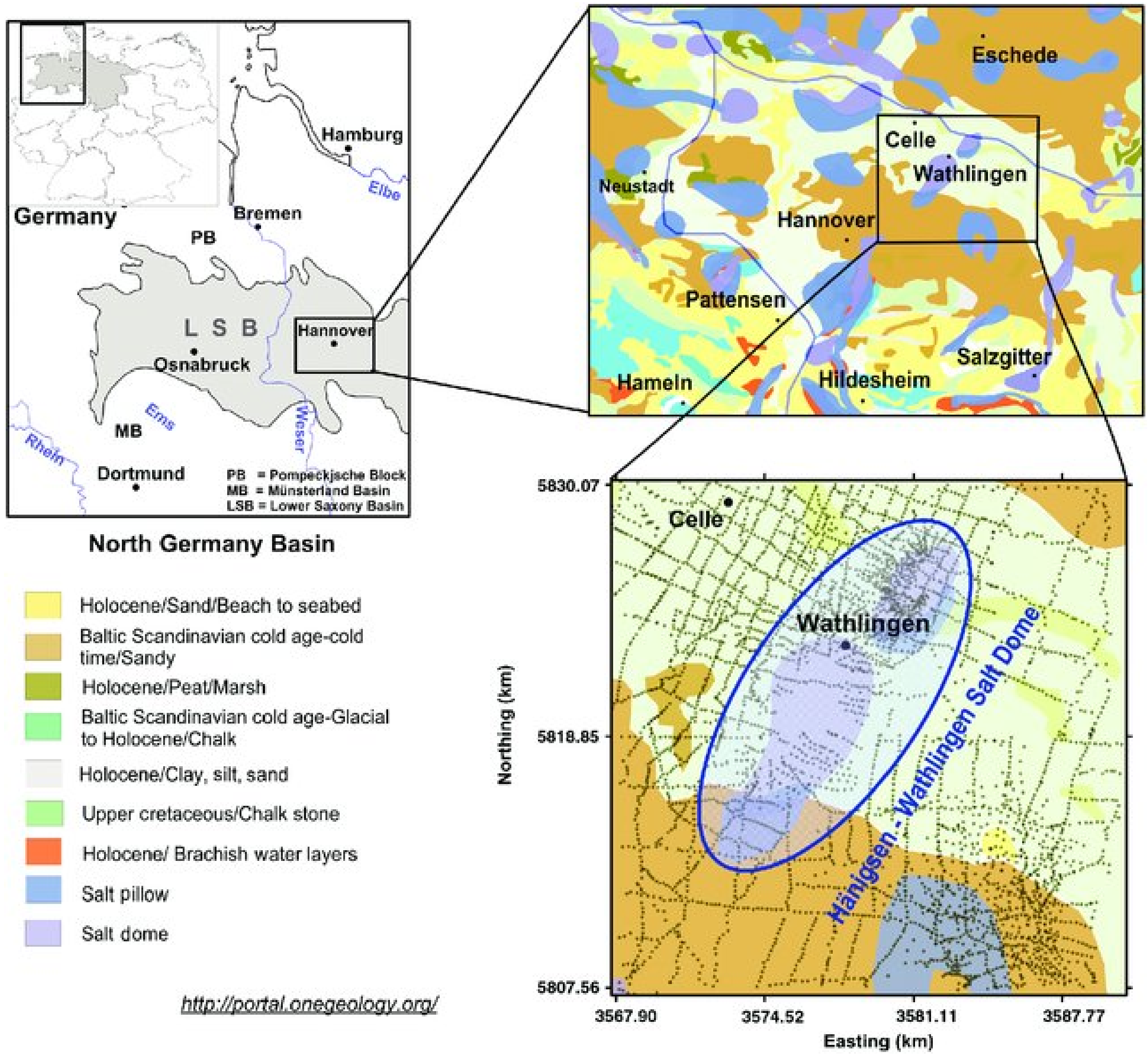

Figure 6.4.1-2. Geology map of Lower Saxony Block (top right) showing the numerous salt domes, salt pillows and other salt structures over and around the Wathlingen-Hänigsen salt dome. Observation stations shown with black dots (·) bottom right. Prakash Dubey et al. (2014).

Regardless of the precise form, both types provide some of the most suitable environments for a GDF because migration within salt of any radionuclides released from the near-field will mostly be diffusive. In addition, due to their plastic behaviour, evaporites are essentially self-sealing.

Consequently, safety cases have been developed for a GDF in evaporites in both the German (e.g. Brasser et al. 2008) and US (e.g. Patterson 2013) national programmes. In these cases, the GDF host rock is of utmost importance, because the 'normal' evolution of the GDF is expected to lead to complete confinement of the radioactive waste in the host rock for millions to 10s of millions of years. This is because the salt, which behaves plastically over geological timescales, will slowly close in around the waste and any EBS. As such, long-term NA observations indicating that the evaporite is stable and maintains a high integrity over geological time frames are crucial for the SC (see also discussion in Noseck & Miller 2013)[14].

The only significant alternative scenario considered is that of brine intrusion. Soon after GDF closure, as heat from the waste increases the evaporite temperature, the reduction of voids in the GDF (by the natural inward collapse of the salt) and brine intrusion (from outside the salt body or from migrating brine bubbles in the salt) are the dominating processes in the system. In this scenario, back pressure of fluids prolongs the process of void reduction. Access of brine to the emplacement area may lead to container corrosion, which can play an important role, and mobilisation of radionuclides from the waste is assumed to begin after container failure. After the emplacement boreholes and/or drifts have been completely filled with brine, radionuclide transport will occur as further compaction of the brine-filled voids expels the brine. After release from the salt host rock, radionuclide migration and dispersion play a role. Highest radionuclide releases are usually predicted to occur soon after GDF closure when the flow rate of the brine out of the evaporite is assumed to be at its highest.

6.4.2 Evaporite rock and natural analogues - introduction

Item:

NA6.4.2

Component(s):

LSSR

Evaporites

6.4.2.1 Introduction

See overview in section 6.4.1 above.

IFEPS:

1.2.1.1 - Salt dissolution

1.2.3 - Deformation

1.4.6 - Mining

3.2.3.2 - Creep

4.2.4 - Chemical processes [geosphere]

NA Type:

Natural analogue, Regional analogue

6.4.2.2 NA description

As a detailed SC for a GDF in evaporites has yet to be carried out in the UK programme, it seems more apt to list here (Table 6.4.2-1) those NA studies which have been carried out to date. It is clear from Table 6.4.2-1 that a

[14] Other approaches, such as assessing long-term stability of borehole seals in evaporites by modelling only (Jacobs 2013) have, however, been reported.

lack of a site- and design-specific SC in any national programme has led to a biased output, with tunnel convergance/sealing studies dominating to date. Without speculating further on the cause of this bias, these examples serve to indicate that evaporite-relevant NA studies already exist and that the scope for more focussed efforts in future is clearly there (see also comments in section 6.4.2.3 and 13.5).

Table 6.4.2-1. a non-exhaustive list of international evaporite-relevant NA studies

Process	Description of NA study	Reference
Safety case support	Various reports have looked at the requirements for NA data on evaporites to support the SC. To date, all are focussed on the German national programme. Most conclude that the data currently available offer only qualitative support.	Krone et al. (2008) Noseck (2000) Noseck & Miller (2013)
Transport processes		
Diffusive transport in evaporite	Investigated evaporites which have been intruded by crystalline rock. In all the cases examined, the migration of uranium and thorium from the igneous rock to the salt is minimal after tens to hundreds of millions of years.	Wollenberg et al. (1984)
Waste analogues		
Long-term behaviour of TRU (trans-uranic)waste	Studied anthropogenic analogues of a range of man-made materials stored for long periods in WIPP as an analogy of the long-term behaviour of TRU waste.	Martell et al. (1998)
Evaporite isolation properties		
Long-term isolation properties of evaporites	Review of NA data which support the assumptions that salt diapirs can isolate wastes for geological timescales. Results indicate the presence of very old (250 million years) brine pockets and gas bubbles showing no contact with environments outwith the evaporite.	Brasser et al. (2008)
Subrosion (post-depositional dissolution of salt) process understanding	Examined tunnels and shafts in the Goreleben salt dome for evidence of subrosion via the	Bornemann & Fischbeck (1986)

Process	Description of NA study	Reference
	presence of secondary features (e.g. caprock development)	
Tunnel/borehole convergance/sealing		
Tunnel convergence (model testing)	Examined behaviour of compacted rock salt used to backfill openings to assess how well the current convergence models describe the processes involved and if alternatives could be utilised. While actual NA data were not used *per se*, information from observations in the tunnels was used to assess the models.	Navarro (2013)
Tunnel convergence (self healing)	Self-healing of the EdZ (excavation disturbed zone) examined by assessing *in situ* long-term creep.	Brenner (1999) Rothfuchs et al. (2008)
Tunnel seals/plugs (crushed rock salt backfill)	Information from anthropogenic analogues of crushed rock salt on the medium-term behaviour of tunnel backfill (see Figure 6.4.2-1). Have shown a significant void reduction (e.g. a decrease in the rock permeability of more than two orders of magnitude in 85 years) as predicted by current models of salt behaviour, so increasing confidence in the 'normal' GDF evolution scenario.	Brenner et al. (1999)
Tunnel seals/plugs (range of material)	Information from anthropogenic analogues of seals for waste cells in toxic waste disposal facilities[15] in salt and potash could be utilised.	Noseck et al. (2015)
Tunnel seals/plugs (crushed rock salt)	Due to the importance of crushed rock salt in the GDF design, it was	Wolf & Noseck (2015)

[15] Note that, in Germany, these are facilities for the permanent disposal of highly toxic wastes, so the regulations for disposal are comparable to radioactive wastes, making the analogy highly apt.

Process	Description of NA study	Reference
	essential to find appropriate NA support for the laboratory data that, to date, has been the basis of the safety case.	
Borehole seals/plugs (bentonite)	Longevity of bentonite in evaporites: naturally occurring saliferous clays from Germany (Figure 6.4.2-2), which have been exposed to saturated brines over geological timescales, have been examined as NA of bentonites in evaporites. The results indicate that the swelling pressures of the natural salt-saturated clays remain as high as industrial bentonites intended for use in a GDF.	Gruner et al. (2003)
Borehole seals/plugs (asphalt)	Interest has been expressed in possible mixed asphalt-sand-lime borehole seals. Although this is a difficult combination of materials to find naturally, it exists at a site in Holzen, Germany. A preliminary study indicated close similarity between the natural and technical bitumens (Figure 6.4.2-2).	Hellmuth (1989) Heckers et al. (2000) Kremer & Alexander (2015)
Other material studies		
Longevity of saltcrete[16]	Studied anthropogenic analogues of this material, examining its use in salt and potash mines in the US, Germany and Canada. Noted that saltcrete emplacement underground had been shown to be practicable and that the material was robust over the	Eyermann et al. (1995)

[16] *Saltcrete* is a mixture of cement with salts and brine, usually originating from liquid waste treatment plants as a waste immobilisation matrix. It has also been discussed as a potential tunnel support material.

Process	Description of NA study	Reference
	periods of concern for the mines (i.e. decades).	

Figure 6.4.2-1. Core through 20 year old compacted salt (from the Riedel mine, Germany), taken to assess void reduction efficiency with time. (Brenner et al. 1999).

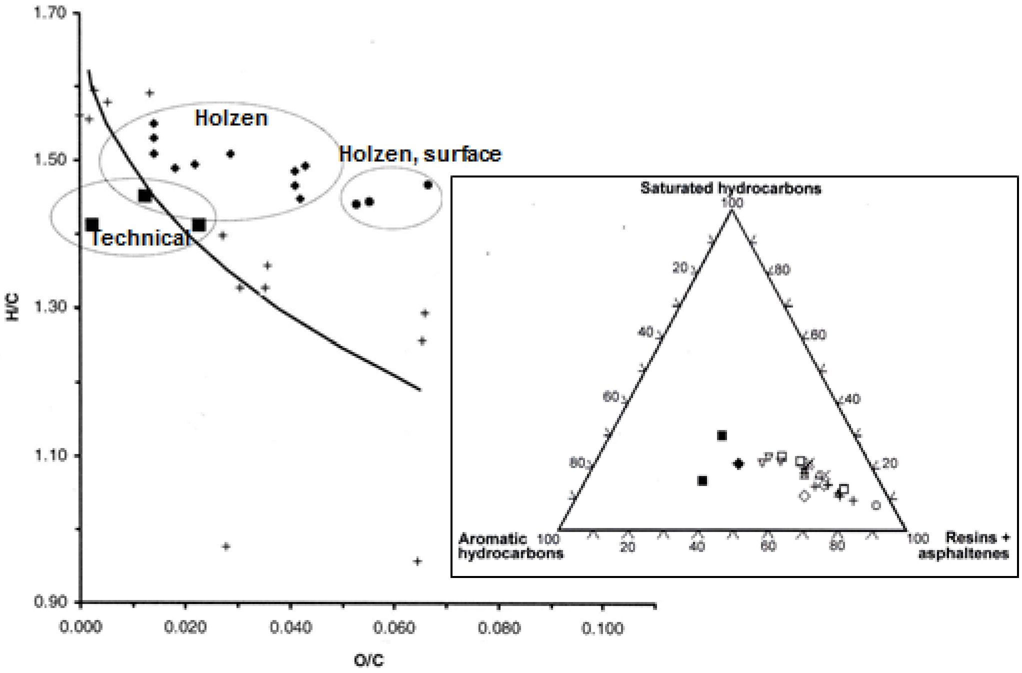

Figure 6.4.2-2. Comparison of the properties of the Holzen bitumen and typical technical bitumens (Heckers et al. 2000).

6.4.2.3 Uncertainties and limitations

- The current focus on anthropogenic analogues means that the physical behaviour of the salt host rock in the immediate post-closure period of the GDF is well understood, but not the long-term outlook
- While the boundary conditions for the anthropogenic analogues are well defined, those for older systems are often much less clear, so weakening any natural analogue arguments
- Care has to be taken with some studies insofar that they offer an insight into one process, but not another. For example, Brenner et al. (1999) can only offer information about the compaction process and not about the convergence process, so care must be taken when interpreting the output
- Currently, most relevant output is in German, which may lead to potential information gaps in the UK programme

6.4.2.4 Relevance – what we have learnt?

- Natural analogue studies on brine pockets in a wide range of salt deposits suggests a high degree of host rock stability. Examples from Germany indicate little disturbance for up to 250 million years, despite repeated periods of glaciation in this period
- This has been supported by work on gas bubbles in salt crystals which also indicate little interaction with the environment outside the salt deposits

- Currently, little attention has been paid to the oil and gas literature and it seems likely that much information of relevance could be obtained from intensively data mining this resource (cf. comment in section 13.5)
- Further, once a SC for evaporites has been established in the UK programme, it would be worthwhile examining oil and gas storage facilities to assess their potential to provide relevant NA output on, for example, stability of the evaporite host rock and stability of the overall geological setting (cf. comments in section 13.5)

References

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7 POST CLOSURE PROCESSES AFFECTING HOST ROCK AND REPOSITORY

7.1 Climate forcing and ice-age scenarios - overview

A GDF must be shown to operate satisfactorily over very long timescales, from thousands to hundreds of thousands of years (up to 1 million years in some cases). Over such timescales, climate variation can be expected. In the past, Quaternary climate changes have followed a cyclic pattern, believed to result from orbital (Milankovitch) forcing. For northern Europe, three different past climate domains can be identified which impacted environmental processes affecting the subsurface; these are temperate/boreal, permafrost and glacial. Long-term climate variation has been described as a cyclic repetition of these domains as illustrated in Figure 7.1-1.

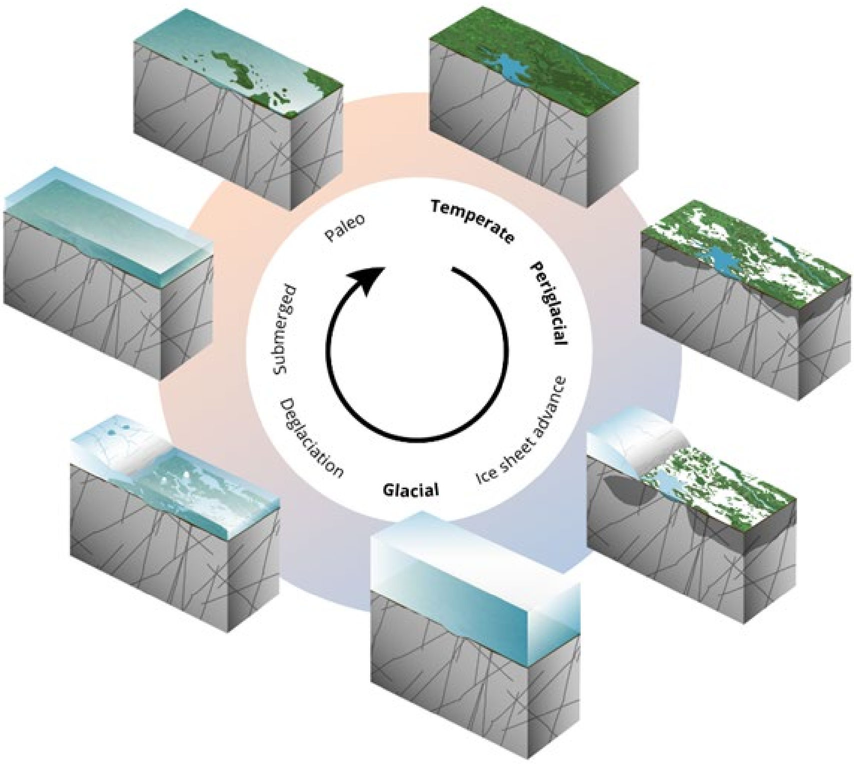

Figure 7.1-1. Climate variation shows a cyclic pattern. The extent of the climate stages varies both temporally and spatially. At any given site (around NW Europe), a climate state can prevail from hundreds to more than tens of thousands of years, depending both on global climate and geographical location (image from SKB 2019).

During the last glaciation, the northern part of the British Isles was covered at maximum by an 1500 m thick (Figure 7.1-2) ice sheet, depressing the bedrock ca. 100 m in the process (Bradley et al. 2011).

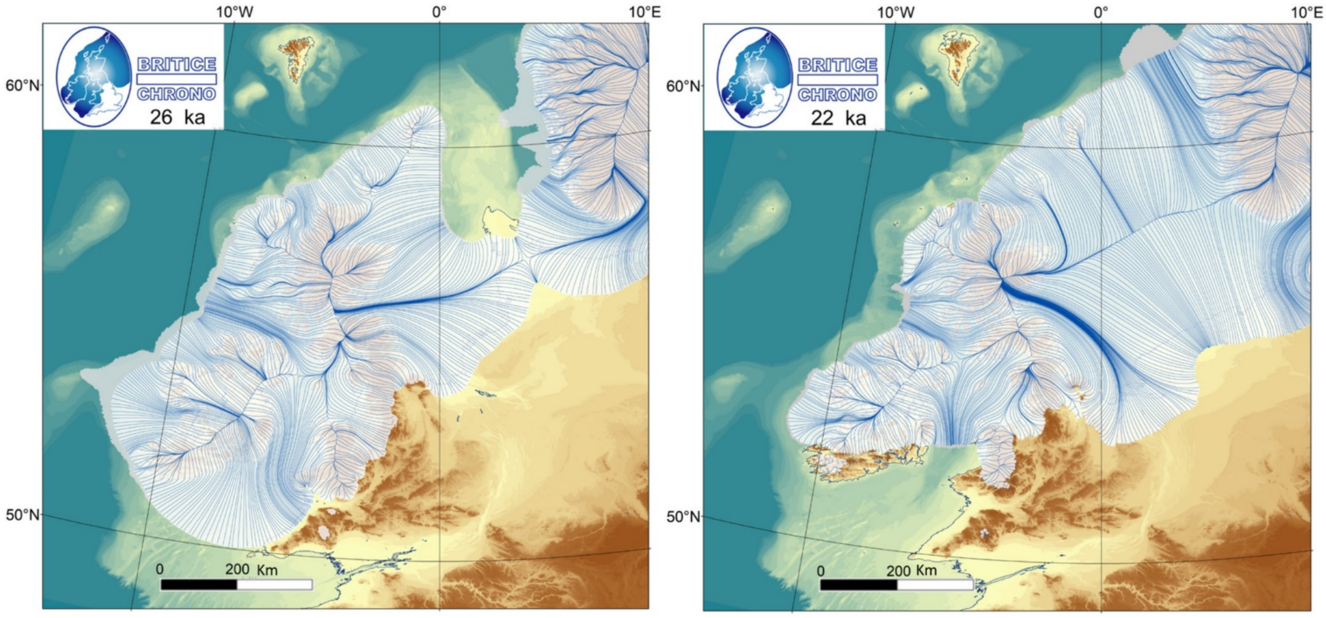

Figure 7.1-2. Ice-sheet extent and flow geometry (ice shelves in grey) at the maximum areal extent of the British–Irish Ice Sheet (left panel; 26 ka) and North Sea Ice Sheet (right panel; 22 ka). Build-up of ice over the North Sea occurred by head-on collision of British and Scandinavian ice lobes (left panel; 26 ka) resulting in an ice saddle that rapidly grew in elevation to build the major North Sea Ice Divide (1500 m thick) by 22 ka. Clark et al. (2022)

Changes from the current situation can be expected during periods of glaciation (including permafrost). Consequently, investigation of the impact of climate variation on the subsurface has focussed on glacial conditions and permafrost (see sections 7.1.1-7.1.3). However, a less studied topic is the consequences of long-term temperate climate on regions such as northern Europe. The past evolution has been dominated by the cyclic appearance of permafrost and glacial conditions, so no direct evidence exists on how the system evolves without this pattern. This is specifically of importance in relation to groundwater chemistry evolution under such conditions, since prolonged meteoric water infiltration could dilute the deep groundwaters. Some new insight could be obtained by studying unglaciated areas, but finding a suitable analogy is difficult. See also discussions in chapter 6, on long-term stability of the host rock.

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7.1.1 Climate forcing and ice age scenarios: Greenland Analogue Project (GAP)

Item:

NA 7.1.1

Component(s):

Host rock

7.1.1.1 Introduction

Over the assessment time frame for a GDF in the UK, glacial conditions are expected to occur repeatedly (RWM 2016, section 4.3). Climate-induced changes, such as the advance and retreat of ice sheets and development of permafrost (section 7.1), will influence and alter the surface and subsurface environment, including the hydrogeology, hydrogeochemistry and bedrock stress state, which may impact the long-term GDF performance. In assessments of glacial impacts on long term GDF performance, simplified models and cautious assumptions are used, e.g. in relation to the representation of ice sheet hydrology, generation of dilute meltwater and the penetration of that dilute meltwater into the underlying rock (Claesson Liljedahl et al. 2016).

A glacial scenario is included in the ESC to evaluate how a GDF will perform in the future. To assist in this process, it is valuable to compare currently glaciated and periglaciated areas with that of potential GDF sites in the UK.

IFEPS:

1.3.1 - Global climate change

1.3.4 - Periglacial effects

1.3.5 - Glacial and ice-sheet effects

1.3.7 - Hydrological/Hydrogeological response to climate change

4.2.4 - Chemical processes [geosphere]

NA Type:

Regional analogue

7.1.1.2 NA description

The Greenland Analogue Project (GAP) study area is located east of Kangerlussuaq village on the west coast of Greenland and covers approximately 12,000 km^2, of which approximately 70% is occupied by the Greenland Ice Sheet (GrIS) (Figure 7.1.1-1). To advance understanding of glaciation related hydrogeological processes, GAP research activities included both extensive field work and modelling studies (2008-2016) of the GrIS, focussed on three main project areas: 1) surface-based ice sheet studies; 2) ice drilling and direct studies of basal conditions (of the ice sheet); and 3) geosphere studies (Harper et al. 2016).

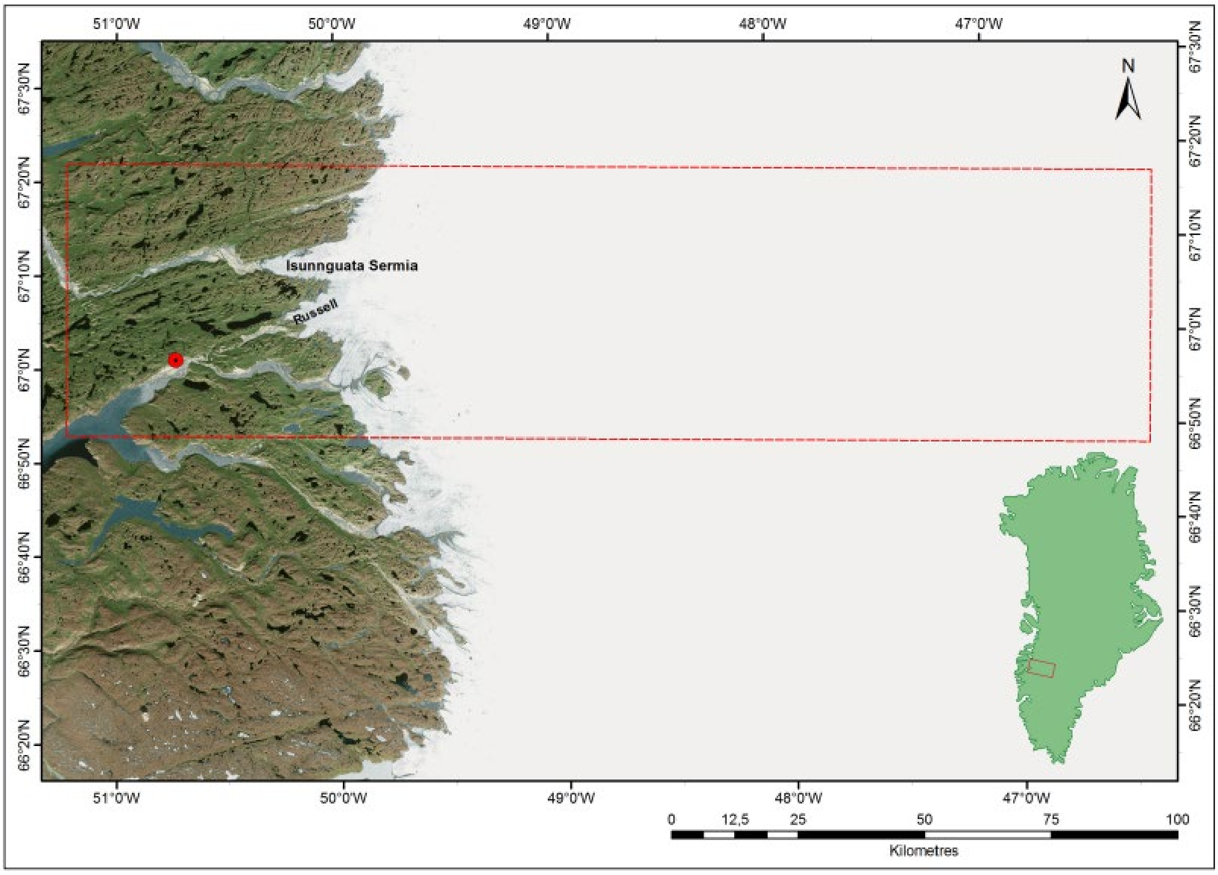

Figure 7.1.1-1. Overview map showing the GAP study area (red dashed rectangle). The key outlet glaciers, Isunnguata Sermia and Russell, are indicated. Red circle shows the location of the Kangerlussuaq village. (Claesson Liljedahl et al. 2016).

The growth and decay of ice sheets and the associated distribution of permafrost will affect the chemical composition of the groundwater and its flow pattern. Since significant changes may take place, the understanding of groundwater flow patterns and composition during glaciations is an important safety issue for long-term geological disposal (Jaquet et al. 2012).

The objective of the GAP geosphere modelling was to investigate the conditions and processes that impact the recharge of glacial melt water into the geosphere, in particular to GDF depth in a fractured rock and over safety assessment time scales. Specific focus was set on the recharge of dilute and oxygenated glacial melt waters that are of most relevance for GDFs (potential for significant change to the sub-surface conditions and integrity of the EBS (Vidstrand 2017).

The main findings (with some sampling locations) of the GAP project are summarized in Figure 7.1.1-2, showing:

- areas of permafrost observed, the maximum depth is around 400m
- type of ice-sheet base (warm-based / cold-based) and related groundwater recharge conceptual understanding
- talik (and talik lake), including groundwater recharge/discharge patterns
- selected geochemical and isotopic results (see Claesson Liljedahl et al. 2016 for details), indicating the anoxic conditions at depth

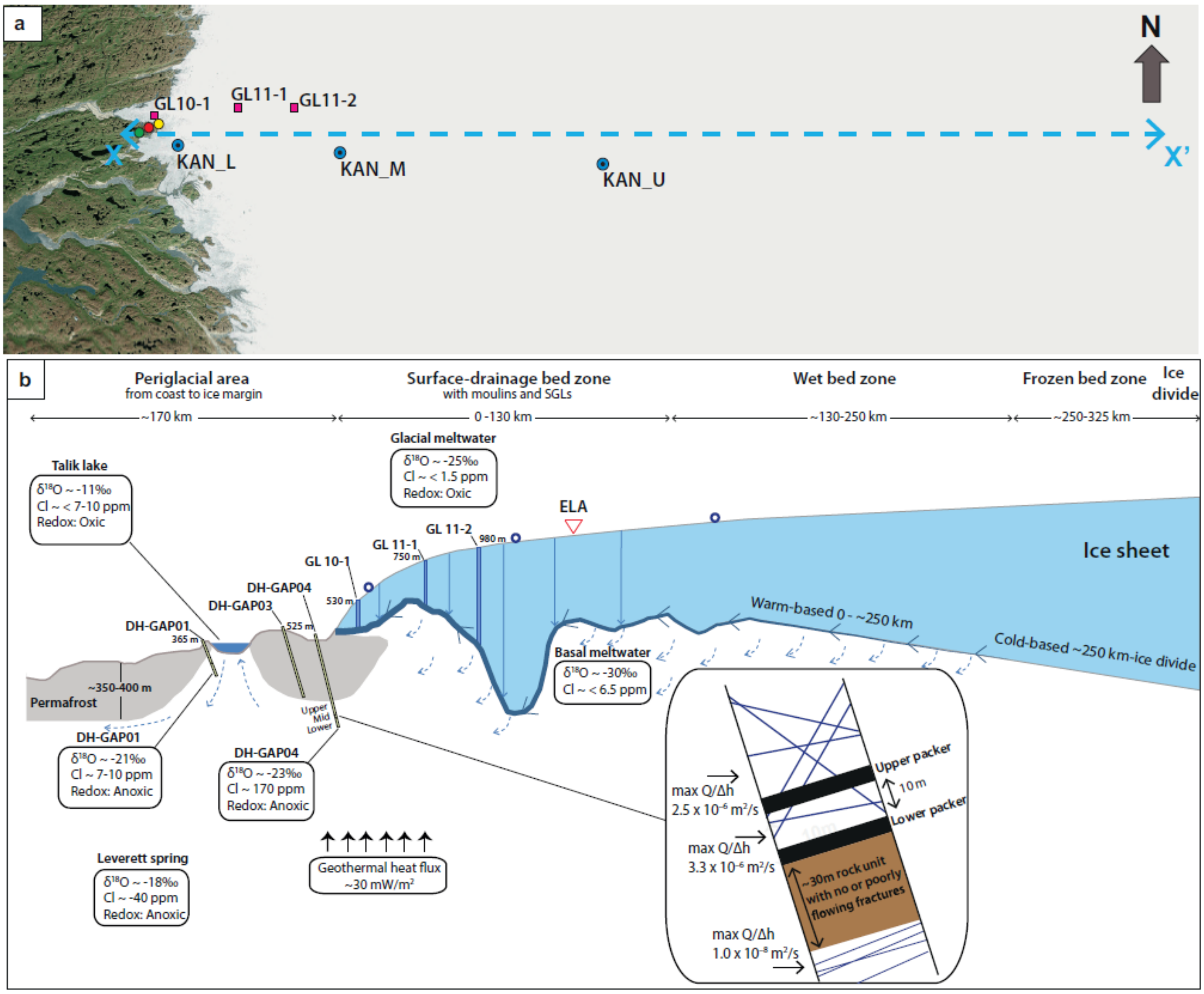

Figure 7.1.1-2. Synthesis of the main results and conceptual understanding of the hydrology within the GAP study area. GL= ice drill hole, DH = drill hole (Claesson Liljedahl et al. 2016).

7.1.1.3 Uncertainties and limitations

GAP results can and have been used to produce better modelling tools but, overall, GAP is not a direct analogue for the UK. Greenland has had ice-sheet coverage for much longer period of time than was the case in Europe during the last glacial period, so the effects on the groundwater system, permafrost etc. are a result of much longer interaction and therefore could be much less extensive in the case of UK GDF. In addition, as GAP was a novel study, there must remain uncertainty about the representativity of the results. As such, care must be taken when applying the results to other glaciated areas.

7.1.1.4 Relevance – what we have learnt?

GAP has produced novel, GDF-relevant results that have shed new light on the complex hydrological systems in the glaciated and periglacial environments (Claesson Liljedahl et al. 2016) which are likely at some point in the future in the UK. These include:

- **Basal thermal distribution and generation of water at the ice sheet bed and hydraulic boundary conditions:** Direct observations made in 23 boreholes drilled to the ice sheet bed at distances between 200 m and 30 km from the ice margin provide novel evidence that the entire outer flank of the study area has a melted bed, with liquid water present, rather than a universally or locally frozen bed (warm-based/cold-based in Figure 7.1.1-2). No evidence has been found to suggest that a complex pattern of patchy frozen/melted bed conditions exist in the ice marginal areas within the region studied. Much of the bed inward of the ice margin is covered by water, rather than mostly drained by discrete conduits with little water in between. Hydraulic measurements and analyses from the ice boreholes imply that ice overburden hydraulic pressure provides an appropriate description of the basal hydraulic pressure as an average value for the entire ice sheet over the year, which can be used as input in modelling work. As such, this evidence can be used to better constrain surface hydrogeological and groundwater recharge modelling of a glaciated GDFs.

- **Role of permafrost and taliks:** The GAP study area is located in a region of continuous permafrost, but the fact that most of the area presently glaciated was also glaciated throughout the past 10,000 years, indicates that permafrost does not exist under the major part of the large, warm-based areas of the ice. An exception is at the ice margin, where a wedge of permafrost most likely stretches in under the ice. It is not known how far (a few hundreds of metres or several kilometres) this subglacial permafrost wedge stretches (Ruskeeniemi et al. 2018). A borehole was drilled underneath a Talik lake, confirming for the first time the existence of a through talik beneath a lake in an area of continuous permafrost. Although it had been hypothesised that Talik lakes would act entirely as a discharge feature, evidence from hydraulic head measurements and the stable isotopic composition of the sampled groundwaters are consistent with seasonal recharging conditions occurring at this location.
    - Scheidegger et al. (2019) used GAP results in their numerical permafrost development modelling. The modelling has shown that maximum permafrost thickness is most sensitive to the surface temperature boundary condition applied, and that the uncertainty associated with this must be considered carefully if a site-specific assessment is to be made as part of a GDF SC. When considering the maximum permafrost thickness at potential GDF locations in the UK, fully exploring the uncertainty of the surface temperature time-series, to derive bounds of potential permafrost thicknesses were suggested (Scheidegger et al., 2019).

- **Meltwater end-member water compositions:** The results show that a glacial meltwater end-member has depleted δ18O (–30 to –25‰) and δ2H signatures (–235 to –200‰) consistent with cold climate conditions and a very low total dissolved solids content, with solute concentrations ranging from below detection to approximately 1 mM. These characteristics of a meltwater end-member can be used in future as a reference water for modelling groundwater flow and reactive solute transport in the bedrock of a GDF in a glacial area.

- **Depth of glacial recharge:** The millions of years of predominantly glacial conditions in this region, the local structural geology and fracture distribution, the presence of high hydraulic gradients and the presence of low salinity fluids at depth in the rock mass have likely facilitated the penetration of glacial meltwaters at this site to depths of at least 500 m (that may be over hundreds of thousands of years old). Together with the extensive persistence of gypsum (a highly soluble mineral) below 300 m, this suggests stable conditions with limited groundwater flow at depths below 300 m, supporting the overall stability of GDF host rock at repository depths.

- **Redox stability of the groundwater system:** as indicated by the presence of pyrite in fractures below approximately 50 m depth, past penetration into the bedrock of aerobic meltwaters has been limited to shallow depths. This is a valuable indicator of bedrock stability (cf. section 6.2), but of perhaps greater importance is that the redox buffering capacity of the bedrock at the GAP site shows no sign of depletion, despite the presence of the glacier for much longer than would likely be the case in the UK.

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7.1.2 Climate forcing and ice age scenarios: Permafrost project (Canada)

Item:

NA7.1.2

Component(s):

Host rock, external processes affecting the repository and host rock

7.1.2.1 Introduction

The potential risks of permafrost to GDFs were recognized decades ago (e.g. McEwen and De Marsilly 1991, Gasgoyne 2000). The most frequently addressed permafrost events potentially affecting the geochemical stability of a deep-seated repository include: 1) formation of increasingly saline groundwater fronts pushed down by the development of permafrost, 2) presence of unfrozen zones/pathways (taliks) supporting lateral and/or vertical flow through the permafrost and 3) accumulation of gases in pressurized low-temperature conditions leading to the formation of gas hydrates (clathrates). Each of the above have an influence on the stability of the engineered barriers or on the mobility and transport of radionuclides in the case of canister failure.

Information from Fennoscandian and NW Russian localities indicate that, during the last glacial cycle, permafrost[17] conditions may have prevailed over larger areas, over longer periods and at greater depths than previously believed. Since periods of permafrost can be expected across NW Europe (including the UK), permafrost may be an important climate scenario for long-term GDF safety and performance.

The present borders of the discontinuous and continuous permafrost are expected to migrate south during the next glacial cycle and, at the same time, the existing permafrost will gradually melt beneath the advancing glacial cover. To what extent the permafrost will disappear depends on the duration of the glacial period. After deglaciation, new permafrost will start to form again at a rate determined by the future postglacial climate.

Permafrost and its effect on the geochemical stability of a repository

In areas with continuous permafrost the ground is frozen everywhere, apart from beneath large lakes, rivers, and sea inlets or bays. In areas with discontinuous permafrost, areas of unfrozen ground separate bodies of frozen ground.

An extensive body of literature exists on permafrost, but much of the work published is related to the stability of permafrost in shallow and/or sedimentary environments with focus on geomorphological processes, construction issues, gas hydrate research and environmental aspects. Although the observations are partly relevant for deep bedrock conditions, much less is known about the effects at depth.

The temporal frames also limit the use of some of the available permafrost knowledge for NW Europe. Much of the deep permafrost, for example in Siberia, is 1-3 million years old and has been formed in a cyclic, accumulative manner. In Fennoscandia, it is expected that future permafrost will form essentially during one phase, since the subsequently forming glacial cover and following interstadial/interglacial periods will melt the permafrost before the onset of the next periglacial cycle. In northern Canada, it is suggested that much of the present permafrost, up to 700 m deep, formed after the last deglaciation within the last 6 000 years. In West Greenland, the proglacial permafrost has grown during the past 5 000 years. In the UK, future permafrost stages will follow climatic forcing first affecting the higher latitudes and triggering the next glacial period. Whether the permafrost conditions in UK will be the same as during the previous glaciation (e.g. Scheidegger et al. 2019) depends on the precise climatic conditions and the duration of the cold period before the onset of the ice sheet. Ongoing global warming complicates the climatic predictions, but the general view is that it may delay, but not prevent, the next glacial stage (Berger et al. 1993, Posiva 2020).

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[17] Permafrost is normally classified as ground with temperatures below 0°C and can be either continuous or discontinuous depending on climate and other environmental conditions.

IFEPS:

1.3.1 - Global climate change

1.3.2 - Regional and local climate change

1.3.4 - Periglacial effects

1.3.5 - Glacial and ice-sheet effects

NA Type:

Regional analogue

7.1.2.2 NA description

The objective of the international Permafrost Project (2000-2008) was to investigate the potential impact of permafrost on the long-term performance of a GDF in crystalline bedrock (Ruskeeniemi et al. 2002, 2004). An expected result of the project was the collection of in-situ information on the physical and geochemical characteristics of a permafrost environment and to increase understanding of the processes involved and their interaction with each other (e.g. possible freezing induced fracturing, flow and fractionation of water chemistry).

The site of the project, the Lupin Mine is located about 1300 km north of Edmonton, Canada, and some 80 km south of the Arctic Circle (Figure 7.1.2-1). The site is within the continuous permafrost zone and measurements conducted in the shaft of the mine indicated that permafrost persisted down to a depth of 541 m.

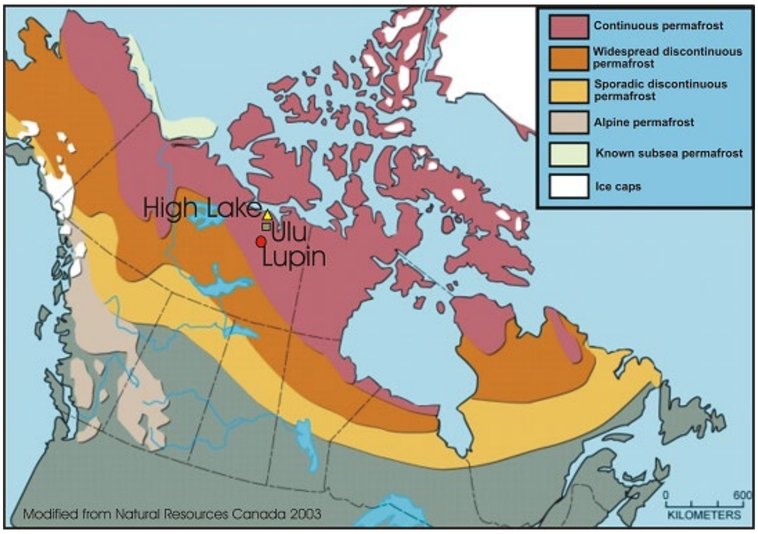

Figure 7.1.2-1. Investigation sites of the Permafrost Project (modified from the Geological Survey of Canada by Ruskeeniemi et al. 2004).

The general aims were to define:

- The occurrence and depth of permafrost
  - Existence/extension of continuous/discontinuous permafrost regimes

- Geological evidence of permafrost features (morphological, induced fracturing etc.)
- Hydraulic conditions – groundwater flow
  - Formation and importance of taliks (vertical and localized unfrozen zones, which exist under larger lakes, rivers or thick peat bogs)
  - Permafrost around major fracture zones
  - Role of the active layer (i.e. soil or bedrock, which thaws during warm summer months)
- Chemical conditions
  - Changes in groundwater chemistry
  - Salinity-increase due to out-freezing (formation of highly saline groundwater[18], cryopeg, at the base of the permafrost)
  - Distribution of cryopegs: as inclusions in the frozen rock vs. beneath it as a saline front
  - Role of small-scale (grain-boundary) salinity
  - Occurrence of chlathrates
- Mechanical impact of permafrost
  - Effects on site hydrology
  - Effects of freezing/thawing on rock and soil stability
- Biosphere conditions
  - Surface hydrology
  - Dominating ecosystem processes

7.1.2.3 Uncertainties and limitations

- Access to mine workings was necessary for studies from the surface down to sub-permafrost levels. However, despite of the wide-spread permafrost conditions at high latitudes, in the early 2000s there were only a few active mines extending through deep permafrost. At the Lupin mine, more than 20 years of extensive mining down to the 1300 m level had some negative consequences, such as, drawdown of the groundwater table and contamination of groundwaters. These problems were managed by exploiting long exploration boreholes, drilling new research boreholes, using a wide range of chemical and isotopic tools, long-term monitoring and repeated sampling to assess the site.
- The Permafrost Project well understood the limitations data collection from only one site may generate. Therefore, effort was made to work with two exploration prospects and to use reference data from literature and other sources but, for various reasons, the amount of more widely representative data remained rather limited.

7.1.2.4 Relevance – what have we learnt?

The results are discussed at length in: Ruskeeniemi et al. (2002, 2004), Zhang & Frape (2003), Korhonen et al. (2009), Onstott et al. (2009), Pfiffner et al. (2008), Stotler (2008), Stottler et al. (2009, 2010 and 2011).

Briefly, the main conclusions were:

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[18] Typically 60-300 gL^{-1}.

- Most, if not all, of the present permafrost in the Lupin mine region has formed after the last deglaciation and the Holocene Optimum (ca. 9,000 to 5,000 years ago) when the climate started to cool.
- No evidence was found of cryopegs at the base of the permafrost. Boreholes drilled at the base of permafrost at a depth of 550 and 570 m produced water with a salinity of < 9 gL^{-1}. The highest recorded salinity in the mine was 40 gL^{-1} at the 1130 m level, well below the base of the permafrost and a salinity which is not uncommon at these depths.

  To have a further look at this topic, laboratory freezing tests (Zhang & Frape 2003) were conducted for several groundwaters observed at the repository depths in Canada, Finland and Sweden. Although isotopic and chemical fractionation occurs between ice and the residual fluid, the increase in salinity remains modest and the resulting volume is very small at the realistic freezing temperatures observed in present permafrost regions at around 500 m depth. Due to increasing fluid salinity, the temperature should decline continuously with depth to support further freezing, a process which is rarely observed .

  An 161dditionnal piece of evidence against cryopegs was gained from electromagnetic geophysical measurements (Korhonen et al. 2009). A highly saline water should generate a significant electrical contrast relative to frozen bedrock, but no such anomaly was observed close to the known base of the permafrost.

  It was concluded that, at low volumetric amount of water and low porosity in the host rocks, the low salinity of shallow groundwaters prevents the development of a freeze-out front. Salts tend to fractionate between ice and the residual fluid, but the fluid is trapped at grain boundaries and in discontinuous fractures and fissures.
- The groundwaters contain a significant amount of dissolved methane. Some features in gas composition and isotopic (C, H) signatures point to the involvement of methane clathrate (Stotler et al. 2010). No direct observations of clathrates were made but, at Lupin, the environmental conditions at the base of the permafrost are within the clathrate stability field.
- In terms of hydrogeology, it is obvious that permafrost considerably slows down or even prevents the recharge of surface waters (e.g. the Lupin mine was so dry that drilling water had to be transported to lower mine levels). Long, horizontal exploration boreholes drilled in the early 1990's produce water at a flow rate of a few litres per minute at subpermafrost levels. Historical records and the project's own observations showed that the chemistry of the water has remained stable, showing no signs of dilution by shallow waters.
- In time, as a result of geothermal heatflow and the insulating effect of the water body, taliks form even through thick permafrost. Under smaller ponds and lakes, only shallow bowl-shaped taliks may form. Through-taliks may support routes for vertical water flow down to repository depths. How they eventually contribute to the hydrogeology depends on the properties of the lake bottom sediments, the underlying bedrock structures and the ambient hydraulic gradients.

  The Lupin underground mine workings extend close to the shore of Lake Contwoyto, which supports a major through talik in the area (Figure 7.1.2-2). The border of the talik was not intersected by the mine workings or exploration boreholes. No chemical or isotopic signs of recharge of meteoric water was observed in deep groundwaters.
- Hydrogeological and hydrogeochemical conditions seem to have remained stable below the permafrost for significant time periods. No evidence of meteoric waters or glacial meltwaters was detected. Neither pressurized waters nor gases were found. All groundwater dating methods indicated mixing of pre-

permafrost waters. Radiocarbon dates suggest some kind of recharge event about 25 000 years before present (Stotler 2008, Stotler et al. 2009).

- Various periglacial features we reported at the surface, mainly related to the overburden, but the removal of blocks of bedrock at the surface by the ice and subsequent displacement of these blocks due to frost heave was observed. As far as could be seen from outcrops or open pits, the mechanical breaking of shallow bedrock was no different from that observed in other glaciated landscapes and it was normally related to the pre-existing fracture network.
    - The same observation was made underground, down to the base of the permafrost at 540 m. No indications of permafrost-related breaking of bedrock was observed. The mining personnel confirmed the lack of any unusual stability problems at the permafrost levels. This was expected, because frost heave requires cyclic freezing-thawing to be effective and such temperature fluctuations do not occur deep in the bedrock.

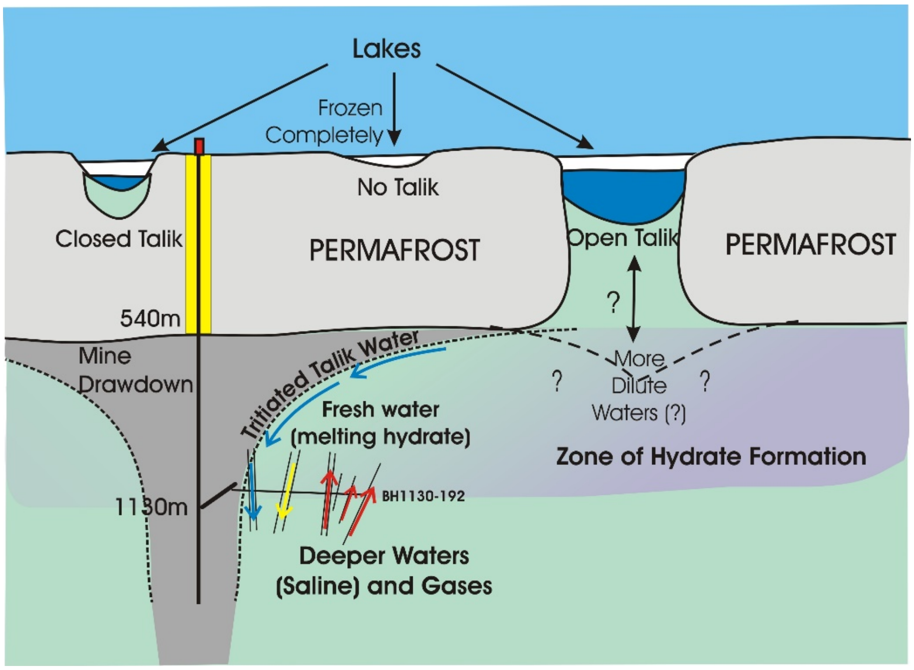

Figure 7.1.2-2. Conceptual hydrogeological model of the Lupin mine area (Stotler 2008). The mine is marked with the red box and the black line represents the mine shaft and tunnel.

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7.1.3 Glacially induced seismicity: case study – lessons learnt from Northern Finland

Item:

NA 7.1.3

Component(s):

Geosphere, host rock, HSR, unconsolidated overburden

7.1.3.1 Introduction

The ESC for deep geological disposal needs to show that GDF performance will not be degraded by seismic events. In addition to the overall seismicity of a disposal site in the UK, different stages of the potential future glacial cycle will change the stress state in the bedrock and this may cause seismic events in the pre-existing fault structures. The estimates of fault slip, induced landslides and moment magnitudes of historical earthquakes are NAs for the seismic events during and after future glaciation cycles. The interpretation of the glacially-induced seismic events can be used as input for rock mechanical modelling of the events taking place in the pre-existing fault zones near the potential GDF site to define safety distances and to compute if the amount of slip along the secondary rock fractures potentially intersecting the disposal facility is within safe displacement and velocity range (e.g. Fälth et al. 2019).

During the last glaciation, the northern part of the UK was covered by an 1800 m thick (Figure 7.1-1) ice cover, depressing the bedrock ca. 100 m (Bradley et al. 2011). During and after deglaciation, release of the lithospheric flexure induces seismic events and fault reactivation as the bedrock regains isostatic equilibrium. As such, the most important factors to study are which faults have and can be reactivated, how large are the fault displacements and how powerful were the induced earthquakes.

IFEPS:

1.2.3 - Deformation (elastic, plastic, or brittle)

1.2.4 - Seismicity

1.3.5 - Glacial and ice-sheet effects

NA Type:

Regional analogue

7.1.3.2 NA description

Post glacial fault (PGF) and landslide studies

Glacially-induced seismicity in Finland is known to be hosted by pre-existing faults which have been reactivated on several occasions (Figure 7.1.3-1). Tectonic stresses from the mid-Atlantic ridge are the main driving force for postglacial earthquakes in the studied area, but the triggering effect is related to the Fennoscandian Ice Sheet and flexure of the lithosphere which was released during the melting of the ice sheet. PGFs in Northern Fennoscandia are connected to non-stationary seismicity during and after the retreat of continental glacier (Ojala et al. 2019a). Evidence of seismic events is preserved in sedimentary structures mostly in Northern Finland, above the highest sea level after deglaciation (Figure 7.1.3-1). Reactivation of faults has occurred during and after deglaciation and small earthquakes caused by the ongoing isostatic rebound currently occur along the reactivated pre-existing faults.

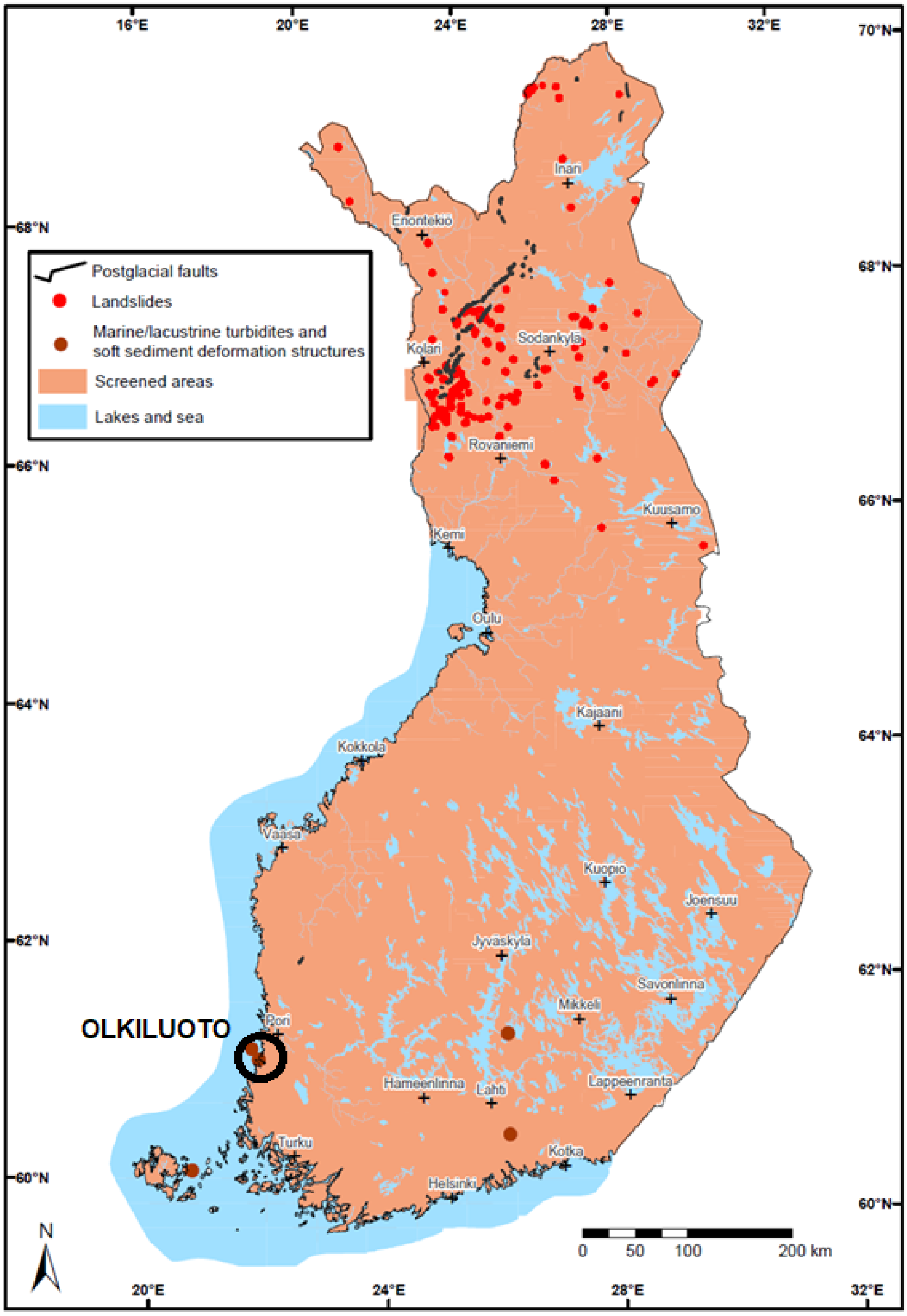

Figure 7.1.3-1. PGFs, landslides and marine/lacustrine turbidites and soft sediment deformation structures known within the areas screened from LiDAR-DEMs. (Modified from Ojala et al. 2019b). PGFs are common in northern Finland, but scarce in the south (partially due to thicker sedimentary cover). Marine and lacustrine turbidites and deformation structures are from the literature (no wide-ranging mapping has been performed). For reference, the site (Olkiluoto) of the planned Finnish GDF is marked.

Dating of seismic events can be carried out by a range of methods, including radiocarbon dating of basal peat buried by landslides, optically-stimulated luminescence of sediments deformed by the upthrown postglacial fault scarps and radiocarbon and palaeomagnetic methods for lake sediments. At the sites studied in northern

Fennoscandia, maximum moment magnitudes of the seismic events have been estimated from the height and length of the postglacial fault surface rupture features and areas of landslides located in the vicinity (Figure 7.1.3-2). These moment magnitude estimates represent earthquakes occurring at the ice margin during or after glaciation and they can significantly improve long-term seismic hazard understanding when compared to the use of historic and measured earthquake data (for example, Posiva 2012 and McEvoy et al. 2016).

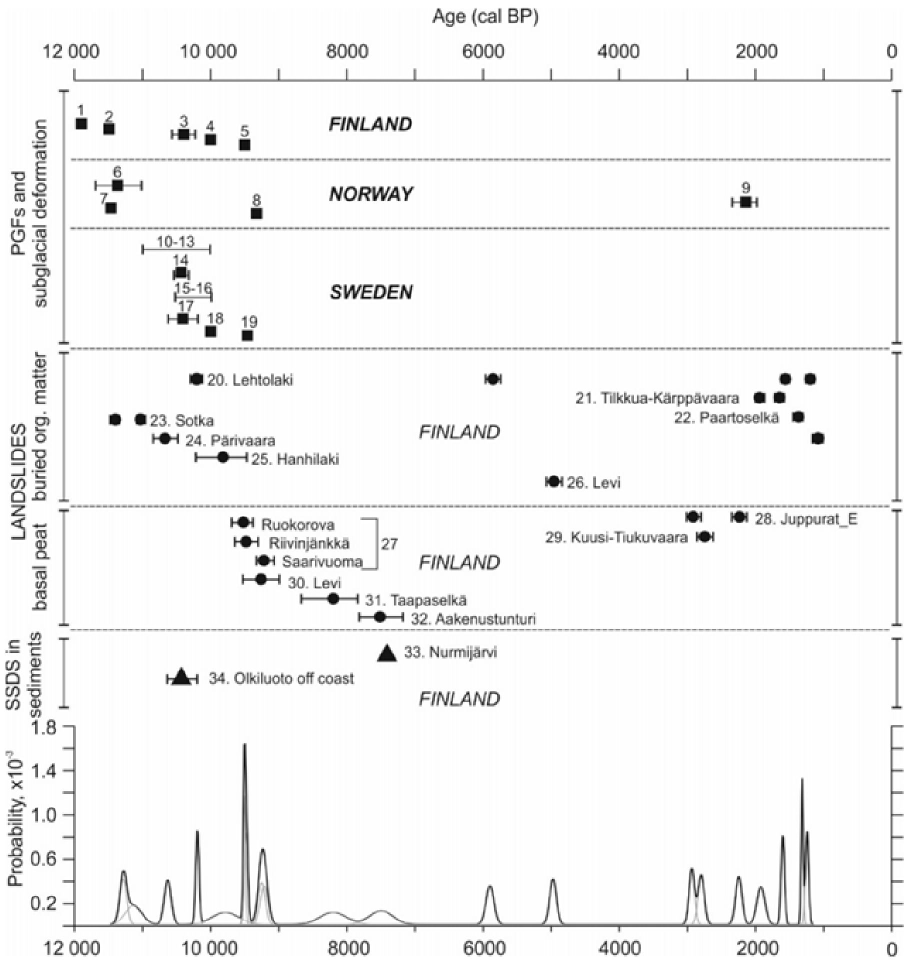

Figure 7.1.3-2. Ages of basal peat and organic material buried by landslides in Fennoscandia (Ojala et al. 2019a). Landslides, possibly caused by earthquakes, have occurred since deglaciation. SSDS Soft Sediment Deformation Structure.

Rock mechanical modelling (Fälth et al. 2019) of seismic events at the Olkiluoto GDF site (Figure 7.1.3-1) aimed at calculating the displacement along secondary fractures crossed by the GDF tunnels. The estimated fault displacements of the pre-existing faults under different stress stages mimicking forebulge (uplift of the lithosphere in front if the proceeding glacier) and deglaciation (uplift of the depressed lithosphere after the glacier retreats) stages acted as the driving force. The forebulge stage caused displacements mainly along the steeply dipping fractures and the deglaciation stage along the gently dipping fractures (e.g. Lund et al. 2009).

7.1.3.3 Uncertainties and limitations

Earthquake moment magnitude estimates are based on empirical equations based on present day earthquakes and surface rupture length, fault scarp height, volume, and area of induced landslides. However, according to

Ojala et al. (2019b), landslide area gives better estimates than volume when compared with the surface rupture lengths and height of post-glacial surface faults.

Modelled effect of the earthquakes on the pre-existing fractures under different glaciation stages depends much on the fault and fracture surface parameters, refinement of finite difference mesh and spatial variation of rock mass stiffness and they can affect the fracture surface displacement 5-25% (Fälth et al. 2019). The uncertainty of the input data and computational limits of the simulations causes uncertainties in the modelling results of where and what kind of fractures may exceed the displacement tolerance of the EBS.

7.1.3.4 Relevance – what have we learnt?

The postglacial fault and landslide studies have revealed that:

- Pre-existing faults have reactivated several times during and after deglaciation
- Surface rupture length and height of PGFs and landslide areas yield the most realistic moment magnitude estimates and they can be used as input for displacement simulation of the faults and fractures within the GDF
- A seismic event in a pre-existing fault in the vicinity of a GDF will potentially cause displacement along secondary fractures, so this should be taken into account when defining waste emplacement features during the design and operational phases

Differing reactivation has been suggested for forebulge and deglaciation stages (e.g. Lund et al. 2009). The initial studies focussed on northern Fennoscandia, but the methodology has since been successfully extended to an understanding of the likely disturbance on the Olkiluoto GDF host rock (Posiva 2023). As such, the method can be applied to any potential GDF host rock (see Table 13.6.1, ID 7.1.3-1).

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7.2 Radiolysis effects on GDF - overview

Significant radiation fields may exist within the near-field of GDFs and these may cause radiolysis of a number of materials (e.g. cellulose, bitumen and other organic materials) in the waste or in the EBS. Radiolysis is essentially splitting of the water molecule into its component parts: oxygen (an active oxidant), hydrogen (reductants), and other reactive species by the action of radiation (Figure 7.2-1). For this to occur at significant levels, groundwater must be able to come into contact with the waste in the canister.

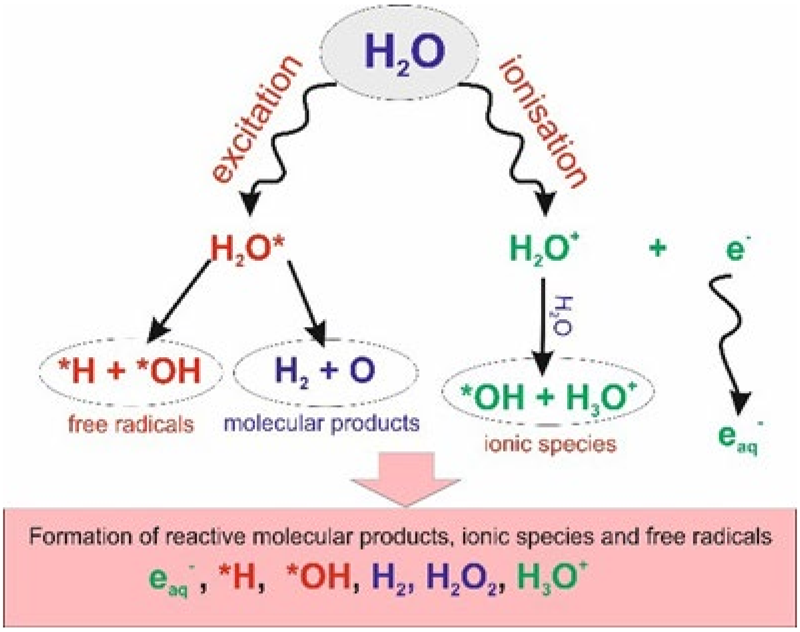

Figure 7.2-1. Schematic illustration showing the formation of reactive species by the radiolysis of water (modified after Nilson, 2008).

Most SCs assume that a net build-up of oxidants would occur in the near-field because the principal reductant, hydrogen gas, is relatively inert and would rapidly diffuse out of the EBS. The oxidants, in contrast, are more reactive and would diffuse away more slowly. This might result in the creation of a slowly moving redox front (see Figure 7.2-2) that migrates outwards from the waste into the EBS and, eventually, the host rock. The extent of redox front migration would be controlled by the balance between oxidant production within the canister by radiolysis and oxidant consumption by reductants, most likely iron-rich material in the EBS (e.g. the steel of the waste canister, accessory pyrite in the bentonite buffer) and the rock.

Steel canisters will eventually corrode, in much the same way that cars rust and eventually fall apart. However, the concern for radioactive waste management is that the oxidants and other reactive species produced by the radiolysis of water will enhance the corrosion of metal canisters and lead to their premature failure. In addition, dissolution of spent fuel will be much quicker in the oxidising zone and some of the radionuclides released from the waste could stay in solution longer; possibly long enough to diffuse through the bentonite and out into the host rock, thus increasing radionuclide migration from a GDF.

Figure 7.2-2. Small-scale redox front in a rock sample (note knife for scale). The orange-red area on the left is the oxidising zone, the grey area on the right is the reducing zone (Waber et al. 1990).

The issues of most relevance to radiolysis that could be addressed in NA studies are:

- The processes involved in the radiolysis of groundwater;
- How common is radiolysis in nature?;
- The potential for reduced iron corrosion phases (from corroding EBS elements such as the steel canister) to soak up free oxygen.

7.2.1 Oklo and Cigar Lake as radiolysis analogues

7.2.1.1 Introduction

See section 7.2.

Item:

NA7.2

Component(s):

Waste, EBS, Host rock

IFEPS:

2.3.6.2 - Radiolysis [waste package]

3.2.6.2 - Radiolysis [repository]

3.2.6 - Radiological processes [repository]

2.1.2 - Waste form characteristics and properties

2.1.2.4 - Immobilisation matrix

2.3.6 - Radiological processes [waste package]

2.4.2 - Gas-mediated release

4.2.6 - Radiological processes [geosphere]

NA Type:

Natural analogue

7.2.1.2 NA description

The first detailed NA investigation of radiolysis under GDF-relevant conditions was carried out at the Oklo natural fission reactors (see section 2.2 for details of the site). This study indicated that radiolysis did occur within the reactor zones and that a redox front had formed and had migrated out into the host rocks.

An inventory of radionuclides in the Oklo reactor zones showed that approximately 80 % of molybdenum, 35 % technetium and 25 % ruthenium were missing. It was suggested that radiolysis had converted these elements into their oxidised forms and they had migrated out of the reactor zones behind the expanding redox front. These elements were then reduced and precipitated in depositional haloes, which mark the limit of the redox front migration. Unfortunately, a lack of data on some important parts of the story (e.g. what happened to the hydrogen gas) and some differences compared to other repositories (e.g. the maximum temperature at Oklo of 600 °C is much higher than expected in a GDF; this could have increased some of the reaction rates) mean that the data cannot be used directly in a GDF SC. However, the results suggest that this process could occur in a GDF.

Radiolysis studies at Cigar Lake, Canada (see section 2.1.2 for details of the site), were focussed on establishing whether radiolysis products could affect the oxidation and degradation of the uranium ore and whether radiolysis formed the halo of iron oxide at the ore/clay interface in the analogue EBS. Observations at Cigar Lake showed that radiolysis products were present in both groundwater and minerals (Figure 7.2.1-1). These data were used to test models of spent fuel corrosion (see Smellie & Karlsson, 1996, Nilson, 2008 for details). If the corrosion of spent fuel passes a certain threshold, then the possibility of the release of radionuclides increases significantly. Preliminary tests showed corrosion was less severe than predicted by these models, which used laboratory derived corrosion rates. This led to a re-examination of the entire process in the Swedish programme and current models more closely replicate the observations at Cigar Lake. This is a good example of the use of NA data to develop and improve SC models.

Work in the 1990s indicated that radiolysis could occur in many natural environments that did not have high radiation fields and this allowed a more detailed examination of radionuclide trapping in and around redox fronts (see Hofmann, 1999, for example).

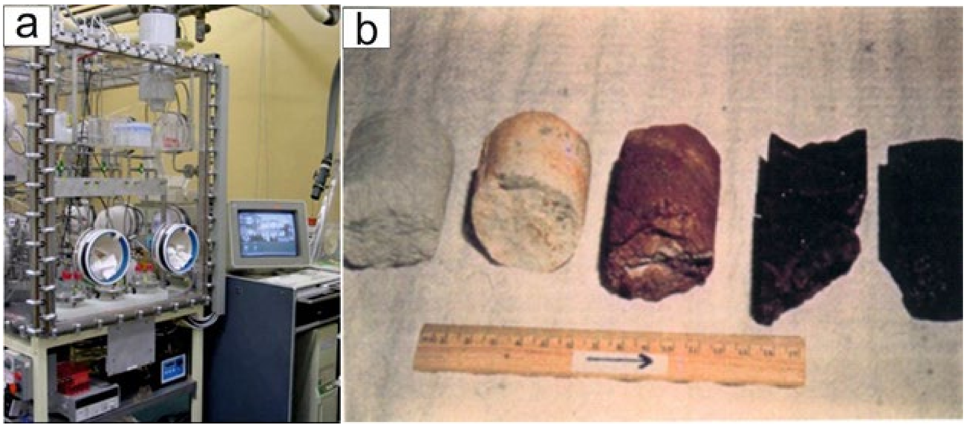

Figure 7.2.1-1. a) Spent fuel corrosion studies have been carried out in the laboratory for many years (EU-JRC). b) Core sections through the Cigar Lake ore body. On the right is the black, reducing uranium ore and, between the ore and the surrounding oxidised clay (white) is the red iron oxide halo, assumed to be the redox front (Image courtesy of John Smellie, Conterra).

7.2.1.3 Uncertainties and limitations

- Although many examples of radiolysis in nature are now known, the only GDF-relevant data are from the Oklo and Cigar Lake sites. However, the Oklo work has been criticised because of the very small number of samples that were analysed, meaning that NA support for the radiolysis models is from Cigar Lake data only;
- Qualitative data from other ore bodies (e.g. Waber et al. 1990) suggest that a fully mechanistic understanding of radiolysis in a GDF is still lacking.

7.2.1.4 Relevance

- Testing previous-generation spent fuel corrosion models (which were based on short- term laboratory data) against NA data showed that they significantly over-estimated corrosion rates. This led to improved models for use in the SC

References

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7.3 Overview of alkaline disturbance

Cements and concrete will be extensively used in some GDF concepts for low- and intermediate- level waste (L/ILW) and will also be used in some parts of a GDF for high-level waste (HLW) and spent fuel (SF). Cement and concrete may also form part of the waste itself, e.g. waste from reactor decommissioning.

- Cement and concrete will be used for structural purposes: as tunnel liners, seals and grouts, where their structural integrity (mechanical strength) and hydraulic properties (sealing against groundwater movement) of the cement are important;
- Cements and concretes may be used in containment: for backfilling excavated tunnels and galleries, as a buffer or waste matrix material, or in waste containers for L/ILW. In this case, the chemical properties of the cement are important, in particular, the highly alkaline porewaters in the cement matrix. A major role of cement is to maintain porewaters within the GDF at a high pH (~pH12) because the solubility of many radionuclides is very low in alkaline porewaters and therefore radionuclide migration will be

restricted. Alkaline porewaters leaching from the cement in a GDF will interact with the adjacent host rock and this may result in the solution of host rock minerals and / or the precipitation of new secondary alteration phases, which may change the porosity and permeability in the host rock immediately adjacent to an engineered GDF (cf. Savage 2005).

Natural concretes (ca 0.5 to 2 Ma old) and their associated alkaline groundwater plumes (with in situ pH values of up to 12.9, the highest ever measured for natural waters) that occur in northern and central Jordan are ideal NAs of the long-term evolution of a cementitious GDF for radioactive wastes.

7.3.1 The influence of cementitious materials, alkali disturbed zone - case study Magarin (Jordan)

Item:

NA7.3.1

Component(s):

Host rock (interaction with cementitious materials)

7.3.1.1 Introduction

See overview in section 7.3.

IFEPS:

3.2.4.1 - Evolution of pH conditions [repository]

3.3.1 - Water-mediated migration [repository]

3.2.4.3 - Migration of chemical species [repository]

NA Type:

Natural analogue

7.3.1.2 NA description

The Maqarin natural analogue study area is located in the Yarmouk River valley on the Syrian-Jordanian border, 16 km north of the town of Irbid (Figure 7.3.1-1).

Discontinuous lenses of naturally-occurring concrete are found within the sedimentary sequence at Maqarin and also in several other places in central Jordan (Khoury et al. 1992). They have been formed by high-temperature, low-pressure thermal metamorphism of organic rich, clay- limestones and chalks (the Bituminous Marl Formation), which contain up to 25 weight % organic carbon. The metamorphism was caused by the spontaneous in situ combustion of the organic matter (Linklater 1998).

Combustion takes place within highly fractured zones that allow oxygen ingress into the rock mass and are probably triggered by spontaneous exothermic pyrite oxidation, possibly due to tectonic activity or landslides initiating such oxidation. The pyrometamorphism produces marble “pods” with complex calcium silicate and calcium aluminate-ferrite mineral assemblages typical of man-made concretes (such as OPC: Ordinary Portland Cement; Atkinson & Hearne 1989).

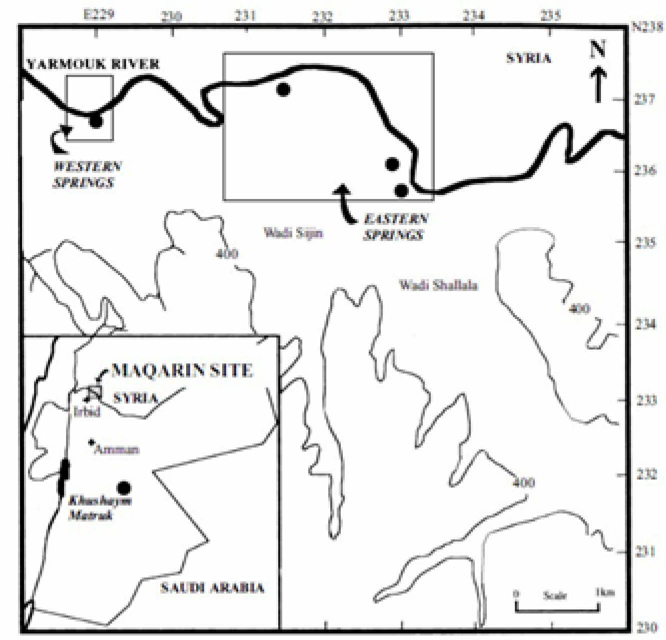

Figure 7.3.1-1. Site of the natural concretes, Maqarin in Jordan (Alexander 1992)

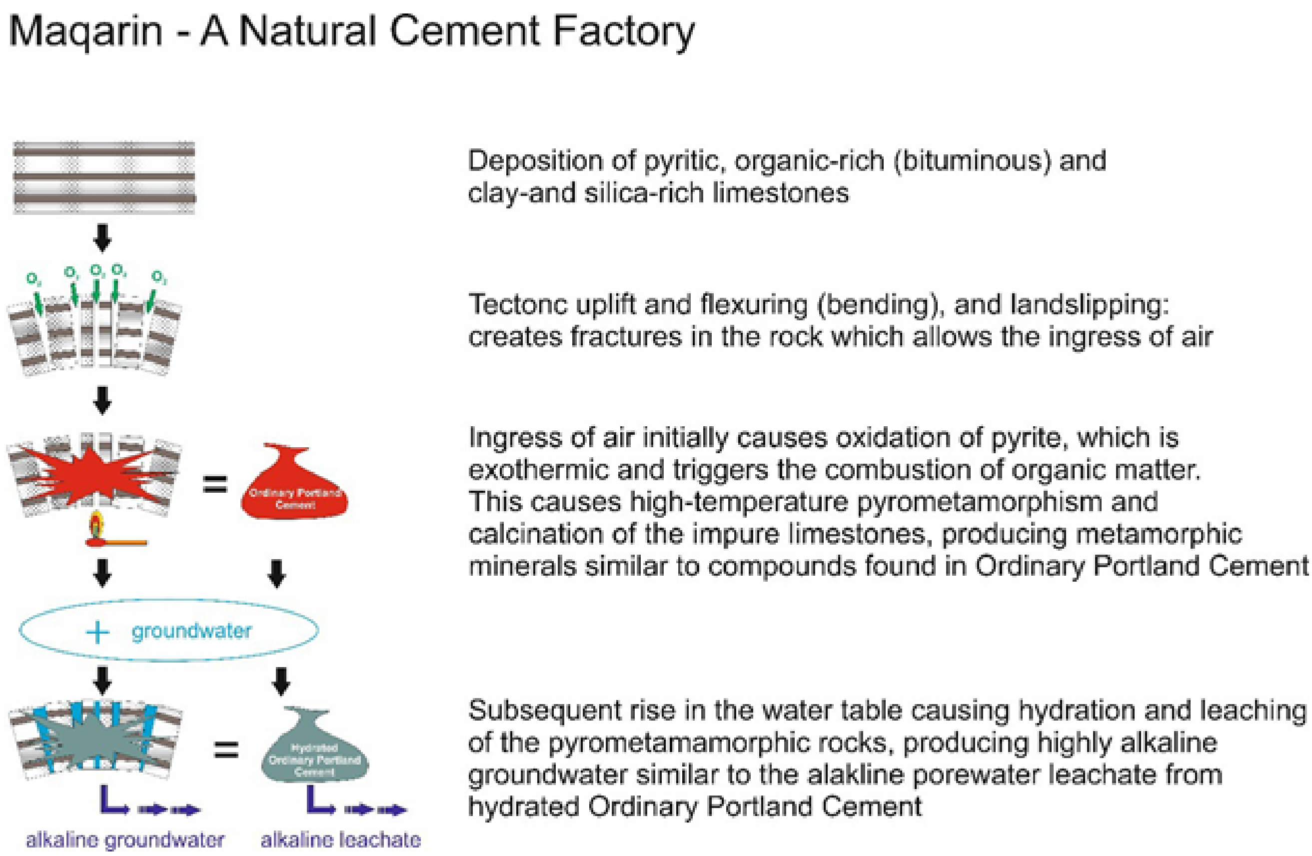

Figure 7.3.1-2. Schematic representation of the production of the natural analogue cements at Maqarin and in central Jordan (Alexander 1995).

Subsequent groundwater percolation through the initial concrete slag has resulted in the hydration, alteration and leaching of the mineral assemblage (Figure 7.3.1-2) to produce a natural concrete. The hydration products include a wide variety of cement-analogue hydrated CSH minerals and gels, which closely resemble phases found in hydrated Portland cements (see Milodowski et al. 1992, for details) (producing natural concretes). These hydrous secondary minerals now buffer the chemistry and high pH of the groundwater (Alexander & Smellie 1998). In this respect Maqarin is a unique, natural site that will most closely resemble Portland cement, where natural highly alkaline groundwaters (up to pH 12.9) occur that are similar in composition to the high-pH porewaters that are expected to leach from Portland-type cements and concretes in a GDF (see Höglund 2014, for example).

Although these natural concretes are found across a wide area from Syria through Israel and Jordan to Saudi Arabia, the Maqarin area of northern Jordan (Figure 7.3.1-3) contains the only known site of active alkaline plumes (up to pH 12.9), produced by groundwater leaching the natural concretes and, as such, this site is unique. This area was studied in detail for over 16 years, between 1989 and 2005, as an analogue for a cementitious GDF environment.

Hydrochemistry

Two hydrochemically distinct high pH groundwater systems have been identified that are associated with two separate natural concrete bodies and hydrological drainage systems and are referred to as the “Western Springs” and the “Eastern Springs”.

The Western Springs are characterised by higher pH (12.9), K, Na, Ca, OH-, SO_4^{2-} rich groundwaters, and are heavily mineralised with high concentrations of Cr, Se, Re and several other metals. This groundwater system is geologically the younger and analogous to the higher pH and K-rich porewater derived from a Portland-type cement during the early stages of cement hydration and leaching (normally referred to as Stage I leachate; Atkinson 1985)

The Eastern Springs are characterised by slightly lower pH (12.0-12.5), low-K and Na, Ca-OH- SO_4^{2-}-type groundwater buffered by portlandite ($Ca(OH)_2$) dissolution. This groundwater system is geologically older (i.e. the natural concrete source rocks have suffered leaching for a longer period of time) and is analogous to a more evolved cement porewater (referred to as Stage II leachate).

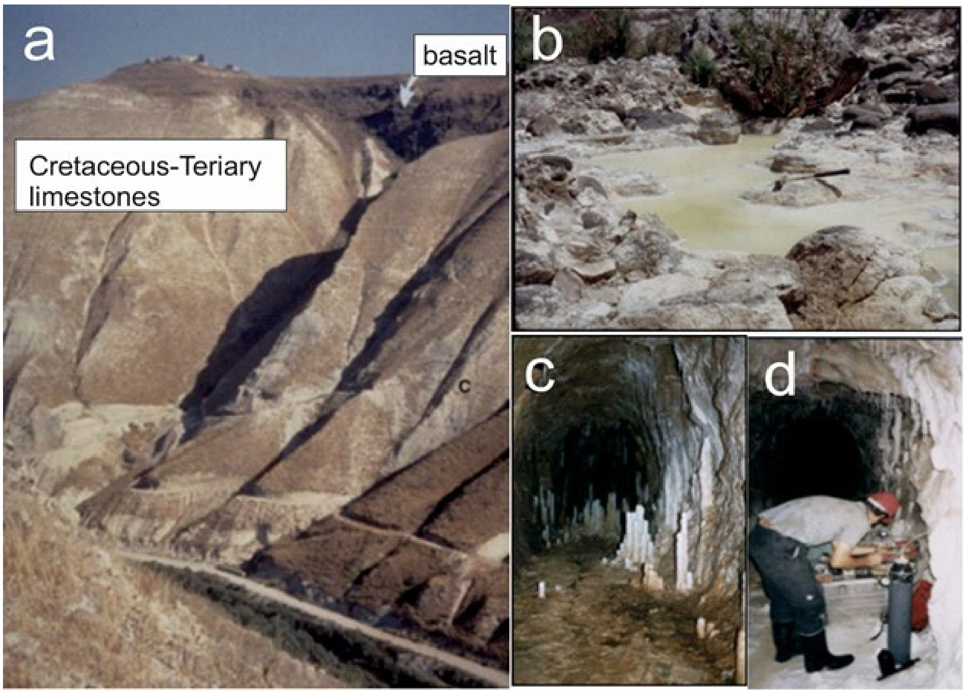

Figure 7.3.1-3. The Maqarin area, northern Jordan: (a) The Yarmouk Valley (Wadi Yarmouk) looking from Jordan towards Syria, showing basalt lava flows filling depressions in the palaeo-land surface on top of the sequence of organic rich, clay-limestones and chalks of the Bituminous Marl Formation; (b) Alkaline springs discharging through basalt colluvium in the Western Springs area, Maqarin. The bright yellow colour is due to the presence of the high concentration of chromium (as chromate); (c) Alkaline groundwater discharging through fractures in the walls of a dam site investigation adit (Adit A-6) in the Eastern Springs area, Maqarin; (d) Sampling for natural cement colloids in Adit-6. Images courtesy W.R. Alexander, Bedrock Geosciences.

The alkaline groundwaters flow away from the natural concrete source rock through the local sediments and basalts (Figure 7.3.1-3) and react with these rocks to produce secondary minerals (see Milodowski et al., 2001, for details) which are the same as would be expected when the alkaline leachates from a cementitious GDF interact with the GDF host rock (Figure 7.3.1-4). Generally, the secondary reaction products block the original groundwater flow paths, inducing changes in the host rock hydrology (see discussion in Alexander & Mazurek 1996). More recently, information from the site has been used to assess the longevity of GDF concretes (see Clark et al. 1993, Crossland 2006, Alexander et al. 2016)

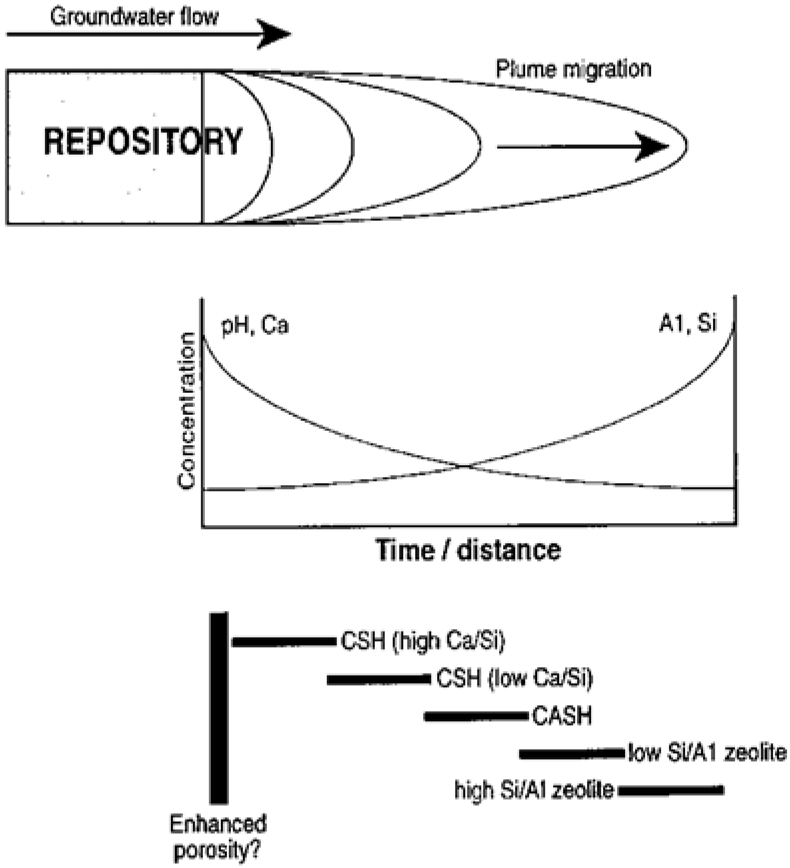

Figure 7.3.1-4. Conceptual model of the evolution of a cement leachate plume downstream from a cementitious GDF as it then reacts with the GDF host rock (from Smellie 1998)

7.3.1.3 Uncertainties and limitations

- The precise age of the production of the natural concretes at Maqarin is uncertain. Dating of CSH minerals at the site indicates the alkaline groundwater fracture-flow system has been operating for 80,000 to 100,000 years
- Although the Maqarin (and other similar natural concrete sites in central Jordan) provide very valuable insights into the chemical interactions between high pH leachate and clay minerals, the clay content of the sedimentary host rocks is low (Pitty & Alexander 2011). Therefore, it is difficult to extrapolate information on physical property changes that would be directly relevant to a GDF in a clay host rock
- The clay mineralogy at Maqarin is dominated by illite and kaolinite rather than smectite. Therefore, this limits the comparison of clay mineral alteration at Maqarin with the alteration of the smectite-rich bentonite backfill and buffer material in a GDF
- The fracture flow system at Maqarin has much higher flow gradients than would be expected in a GDF environment (although this can be taken into account, see Alexander & Mazurek 1996)

7.3.1.4 Relevance

- Detailed geomorphological reconstructions at Maqarin, together with dating of secondary fracture mineralisation associated with the high pH groundwaters, show that the natural concretes are about 0.5 to 2 Ma old, and the alkaline groundwater system has been operative for at least 80,000 to 100,000 years. These timescales are directly relevant to the SC timescales considered for a GDF
- Alkaline pore fluid conditions, generated by minerals analogous to those found in industrial concretes, are long-lived at these sites (in excess of hundreds of thousands of years)
- The Maqarin study well-illustrates the long-term cement/clay stability/degradation in the near-field, and the evolution and propagation of a high pH plume in both the GDF near-field and host rock
- Data from the Maqarin site have proved extremely valuable for testing and validating the applicability of available thermodynamic data to alkaline conditions to predict the extent of high pH water/rock interaction and radionuclide transport. In particular it has provided justification for including specific mineral phases in the models (Linklater 1998)
- Reaction between alkaline cement leachate and silicate rock produces secondary phases with high molar volumes. The observations from Maqarin (and other sites in central Jordan) suggest that the volume increase in secondary reaction products will tend to lead to sealing of flow paths and subsequent changes to the hydrological conditions of a GDF host rock
- The reaction and mineral precipitation sequences observed at Maqarin correspond closely to the observed and predicted behaviour of industrial concretes and the evolutionary sequence of mineralogical reactions associated with the propagation of an alkaline plume downstream of the GDF. Despite the simplified modelling approaches used and the inadequacies of the thermodynamic data base, the model results show a good correlation with observations on the natural system at Maqarin

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7.3.2 Influence of cementitious materials, low alkali cement bentonite interaction (CNAP) (Cyprus)

Item:

NA7.3.2

Component(s):

EBS, Wasteform, Cement [Cementitious]; Container, Concrete; Backfill, Concrete [cementitious], Mass backfill, Concrete [cementitious]

Buffer, Bentonite [clay]; Plugs and seals: Bentonite [clay]

7.3.2.1 Introduction

Bentonite is unstable in the high-pH leachates derived from concrete construction materials (e.g. tunnel liners) grouts, etc. and cementitious wastes in a GDF (e.g. Rozalen et al., 2009). This fact has led several national programmes to assess alternative construction and sealing materials such as low-pH cements (initial leachates have pH 10-11). Overall understanding based on laboratory studies (e.g. Cama et al. 2000, Huertas et al. 2005, Marty et al. 2011) indicate that below pH 10, smectite dissolution is very slow, but it increases with increasing pH. OPC (Ordinary Portland Cement)-based cements generally produce leachates with an initial pH >13. Mineralogical changes in smectites are also observed in laboratory studies arising from highly alkaline conditions pH < 12, and much less data are available for low pH conditions. Laboratory studies by Heikola et al. (2013) for example, indicate loss of smectite in batch experiments (both Na and Ca bentonites, durations 1.5 years at 25°C) where the simulated cement leachates have pH 11.3 and 12, but not in samples kept in pH 9.7. Unfortunately, very few long-term data exist for comparison with the significant body of short-term, laboratory data. Although medium-term, industrial analogues have been reported for high pH settings (e.g. Watson et al. 2013), NAs are needed to assess the longer term processes. One project has been ongoing in the Philippines assessing low-pH cement leachate/bentonite interaction (e.g. Fujii et al. 2015), but little or nothing of GDF relevance has been published to date. For low-pH cement interaction, an international project in Cyprus (CNAP, Cyprus Natural Analogue Project, e.g. Milodowski et al. 2016) has been completed, focussing on the low pH cement bentonite interaction.

IFEPS:

6.2.4.5 Alteration [repository]

NA Type:

Natural analogue

7.3.2.2 NA description

Natural groundwaters with the same pH-range as the low-pH cement leachates (Table 7.3.2-1) are found in the Troodos Ophiolite on the Island of Cyprus. Ophiolites are formed when ancient ocean crust has been 'scraped off' and thrust onto the edge of continental plates and subsequently end up exposed on land.

Low-temperature reaction of near-neutral pH groundwater with olivine and pyroxene within the ophiolite produce highly alkaline groundwaters that are a common feature of ophiolites worldwide.

Bentonites are often present within the sedimentary sequence which constitutes the upper-most layer of most ophiolites. Here the serendipitous combination of alkaline groundwater circulation and bentonite deposits provides a natural laboratory in which to study the long-term reaction of bentonite under geochemical conditions similar to that in a GDF, where low-pH cement and bentonite are used together (Alexander & Milodowski 2014).

The analogue site is located around the abandoned village of Parsata, which sits on a plateau above the Vasilikos valley, which drains the Limassol Forest. At Parsata, 90 million-year-old bentonite-rich sediments infill palaeo-depressions in the highly irregular surface of the basalt pillow lavas at the top of the ophiolite sequence. Alkaline (pH ≤11) groundwaters produced by currently active low- temperature alteration of the underlying ultrabasic rocks discharge through the fractured and permeable pillow lavas, penetrating into the base of the overlying bentonite (Figure 7.3.2-1). A series of trenches were dug, and boreholes drilled and sampled across this interface to study the interaction between the alkaline groundwater and bentonite.

Table 7.3.2-1. Major element concentrations for the groundwaters sampled in CNAP Phase II (Alexander and Milodowski, 2011) and CNAP Phase III (Alexander et al., 2011) (all concentrations mgL^{-1}). P=Parsata borehole, A=Allas Springs, E=valley E1 spring (immediately east of Allas Springs), C=Chysovrysi Springs (full details of all sites in Alexander and Milodowski, 2011; Alexander et al., 2011).

Sample	Field pH	Lab pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	OH^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}
P1-2010a	nd	11.1	48.3	0.11	96.5	1.34	5.40	nd		80.9	149	<0.200
P1-2010b	nd	11.1	50.1	0.11	97.2	1.39	7.20	nd		85.6	159	<0.200
P1-2010c	nd	11.1	48.8	0.10	95.0	1.35	9.00	nd		85.1	158	<0.200
P1-2009	11.42	10.3	36.5	0.021	116	<0.5	27.6	<10		80.9	149	<0.03

A4-1	n.d.	9.77	3.20	58.7	747	31.4	127	152		1093	87.2	0.343
A4-2	n.d.	9.90	3.43	58.4	893	40.5	161	121		1342	106	1.82
A4-3	n.d.	9.71	3.37	58.8	921	40.7	140	154		1321	106	2.40
A5	9.8	9.22	1.34	64.2	224	9.76	n/a	307		346	27.7	1.98
A3	9.84	9.29	1.32	63.9	238	10.2	50.5	203		369	30.5	2.22
A2	9.69	9.04	1.61	65.5	172	7.33	38.5	232		254	22.8	1.66
A1-1	11.9	11.3	37.2	0.101	1435	63.1	n/a	272		2177	101	<1.5
A1-3	10.01	9.31	12.2	0.554	1337	60.1	54.1	96.4		1926	114	10.3
A1-2	9.26	8.82	4.87	48.3	502	23.7	25.8	288		699	50.7	3.90
A1-4	9.78	9.27	11.2	5.73	1214	54.0	61.2	124		1748	78.5	8.33
A6	9.67	9.60	2.22	50.7	921	42.9	102	150		1383	97.0	7.31
E1-1	9.5	9.48	1.07	56.4	75.3	2.62	52.2	190		92.7	7.128	1.03
C2	9.58	8.90	1.69	67.9	4.79	<0.5	23.7	255		8.361	3.207	0.580
C1	9.41	8.85	1.80	68.3	4.68	<0.5	n/a	309		8.486	3.272	0.640
C3	9.69	9.11	1.67	92.7	5.14	0.926	44.5	311		18.2	2.484	1.86

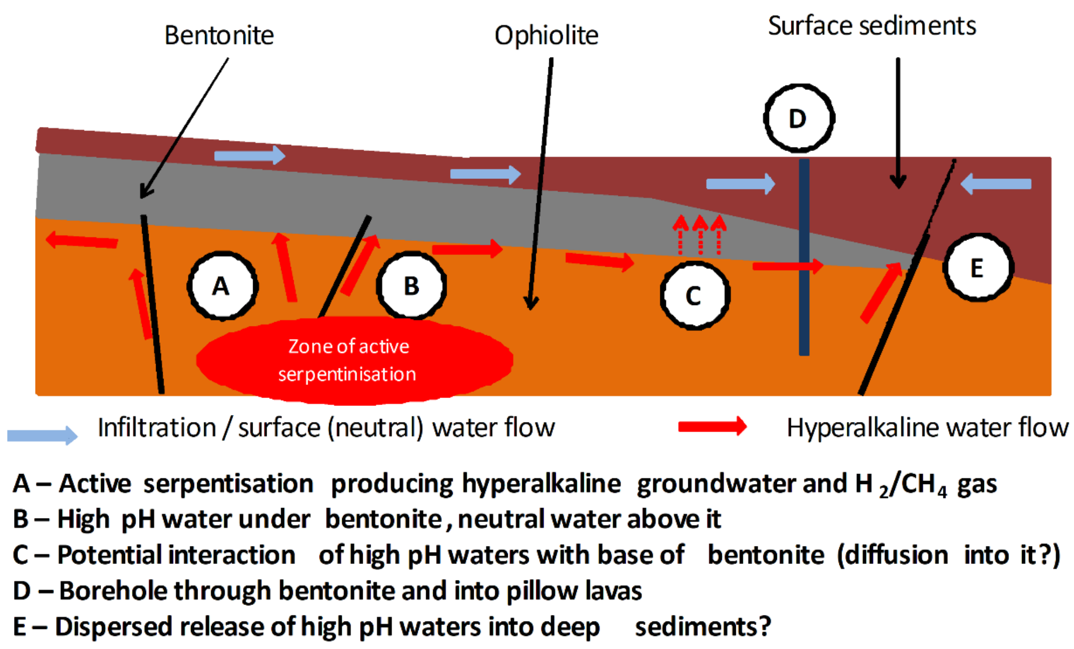

Figure 7.3.2-1. Conceptual model for alkaline groundwater - bentonite interaction at the Parsata site in southern Cyprus (Alexander & Milodowski 2011).

Field investigations in Cyprus have shown that both the base of the bentonite and sparse fracture faces in the bentonite show a very small degree of reaction, with the smectites producing palygorskite as the reaction product (see Alexander & Milodowski 2014 for details), consistent with observations from other natural alkaline systems (e.g. Singer 1991) and limited laboratory data, that indicate rapid development of palygorskite in a closed system. At Parsata, less than one percent of the smectite has altered to palygorskite over a period of some 0.5 million years. Bentonite has retained its isolating properties regardless of this (minor) reaction.

7.3.2.3 Uncertainties and limitations

- Palygorskite is identified as an alteration product of bentonite by alkaline groundwater in the Cyprus NA. This contrasts with geochemical models of cement pore fluid-bentonite interaction in the EBS which suggests that palygorskite is only stable under very high silica concentrations such as those associated with the dissolution of glass or amorphous silica. The Cyprus bentonite contains significant amounts of both amorphous (biogenic) silica and relict volcanic glass which would dissolve in the high-pH groundwater, producing the high silica activities required to stabilise palygorskite. But it should be noted that this is different to the typical bentonite formulations proposed for use in a GDF
- Nevertheless, the Parsata observations are similar to other recent mineralogical studies, which identified palygorskite- and sepiolite-like, fibrous Mg-rich silicates, as alteration products in long-term (15 years) experimental studies examining the interaction of 'young' (K-Ca-rich) and 'evolved' (Ca-rich) cement pore fluids with quartz-rich volcanic rocks from the Sellafield area of the UK (Moyce et al. 2014)
- Although, high silica contents are not to be expected in most processed bentonites, typical requirements for GDF bentonites require only >75% smectite, so high silica contents may not be out of the question. In addition, some GDF designs consider using processed bentonite mixed with silica sand or the local GDF host rock, to produce a mix with higher silica levels. Unfortunately, models of bentonite reaction do not currently include the dissolution of silica sand, amorphous materials and/or glasses
- Bentonite at Cyprus is not as smectite-rich as some potential GDF bentonites (e.g. MX-80), indicating that direct quantification for process rates is not possible in these designs
- The groundwaters which interact with the bentonite have a similar chemistry to the leachates from low alkali cements, but they are not identical and this will influence the mineralogy of the alteration phases

7.3.2.4 Relevance – what have we learnt?

- This study suggests that it will be feasible to use bentonite clay barrier materials together with low-alkali cement and concrete in a GDF, and that any long-term bentonite reaction with leachates derived from low-alkali cement in a GDF could be minimal
- The field conditions of this analogue are considered to realistically simulate those that could occur in a GDF
- The results indicate that minimal mineralogical alteration of bentonite by alkaline groundwater has occurred over a period of 0.5 million years. Only very minor alteration and replacement of smectite to fibrous palygorskite was observed, typically along micro-fractures (see e.g. Milodowski et al. 2016)
- The main effect of interaction between bentonite and alkaline groundwater has been the replacement of exchangeable Na^{+} in the bentonite by Ca^{2+} from the fluid. Consequently, this might be expected to impact on the swelling behaviour and plasticity of the bentonite
- Due to the high silica contents, bentonites at Cyprus provide potential analogue for bentonite – sand mixture (see also NA9.1 on longevity of other EBS materials)

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8 RADIONUCLIDE RETARDATION IN THE GEOSPHERE

8.1 Introduction

To understand radionuclide retardation in the geosphere, it is necessary that all relevant processes and all structures are represented in an appropriate manner. This is the case whether transport in the rock formation is predominantly controlled by diffusion or by advection in porous or fractured media. In addition to the direct processes of advection, dispersion and diffusion, a range of coupled processes, including thermal, chemical and electrical osmosis, thermal diffusion, hyperfiltration and electrophoresis, can transport groundwater/porewater and radionuclides in solution in response to gradients in temperature, pressure, solute concentration and electrical potential. Although such coupling is generally negligible (and mostly excluded from FEP lists) for most practical applications, some of these processes, including chemical osmosis and hyperfiltration, can be significant in argillaceous LSSR or altered HSR, where the overlapping diffuse double layers of clays result in the rock acting as a semi-permeable membrane.

The complete Onsager matrix of direct and coupled processes is given in Table 8.1-1. In addition, a number of chemical retardation mechanisms have been identified in natural systems, including:

- adsorption
- ion-exchange (and isotope exchange)
- precipitation (and co-precipitation)
- mineralisation

Finally, radioactive decay and ingrowth are, of course, important processes to be taken into account in evaluating radionuclide retardation as the decay process can produce daughter nuclides whose geochemical characteristics, and hence retardation properties, differ markedly from those of the parent.

Table 8.1-1. The Onsager matrix of direct (diagonal) and coupled (off-diagonal) transport processes (from Horseman et al. 1996).

	POTENTIAL GRADIENT			
FLUX	**Temperature**	**Hydraulic**	**Chemical**	**Electrical**
Heat	Thermal conduction (Fourier's Law)	Thermal filtration	Dufour effect	Peltier effect
Fluid	Thermal osmosis	Advection (Darcy's Law)	Chemical osmosis	Electrical osmosis
Solute	Thermal diffusion or Soret effect	Hyperfiltration	Diffusion (Fick's Law)	Electrophoresis
Current	Seebeck or Thompson effect	Rouss effect	Diffusion and membrane potential	Electrical conduction (Ohm's Law)

Between the examination of radionuclide retardation in the laboratory and URLs and the study of natural analogues, it is generally felt that all significant processes are now understood and are taken into account in the SC (see e.g. Alexander et al. 2003).

References

Alexander, W.R., Smith, P.A. & I.G.McKinley, I.G. 2003. Modelling radionuclide transport in the geological environment: a case study from the field of radioactive waste disposal. Ch.5 pp 109-145 in Modelling Radioactivity in the Environment (ed E.M.Scott), Elsevier, Amsterdam, The Netherlands.

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8.2 Radionuclide retardation analogues - overview

Despite the above-noted conclusion that most radionuclide transport processes were understood, in the 1970s it was felt that more realistic examination of geosphere transport processes were required as laboratory (and, to a degree, URL) studies could not address:

- the large spatial scales of relevance to a GDF which cannot be directly addressed in a laboratory—how can the migration of radionuclides through several hundred metres of host rock from a GDF to the biosphere be studied and modelled?
- the heterogeneity and structural complexity of the geological environment which will host the GDF - how can this ever be approached in a laboratory or how could models hope to address this without appropriate field-scale information?

As such, numerous studies (mainly based on uranium ore bodies) to examine radionuclide retardation were initiated, including Pocos de Caldas (Brazil), El Berrocal (Spain), Alligator River (Australia), Palmottu (Finland) and Needles Eye (UK). These and numerous other similar field investigations are addressed in detail in Miller et al. (2000, 2006), Alexander et al. (2015), Milodowski et al. (2016) and Posiva (2021). These studies will not be examined here further as their impact in SC to date has been minimal, for a range of reasons, including:

- **Irrelevant environment**: for example, the Koongarra uranium ore body (Figure 8.2-1) which was the focus of the Alligator River Analogue Project is at the surface, has suffered extensive tropical weathering and the shallower parts of the ore body are unsaturated for a significant part of the year. The environment is clearly not deep GDF relevant and similar criticism can be levelled at many of these early studies.

- **Highly disturbed site**: the South Terras mine (UK; Hooker et al. 1989) study site is "….highly disturbed and differentiating the relevant processes (physical, chemical and microbiological) that have influenced uranium and thorium migration and distribution can be problematic" (Milodowski et al. 2015).
- **Under-defined site**: while the Loch Lomond study illustrated the expected slow diffusion of radionuclides through a clay barrier analogous to the bentonite buffer (Neall et al. 2007), the lack of detailed hydrological and mineralogical information means that it has never been used directly in a SC
- **Highly complex site**: the Osamu Utsumi mine site (Brazil) was part of the Pocos de Caldas study (Chapman et al. 1992) and is also near-surface. The site turned out to be so complex that even using information from the study to test geochemical models has been problematic. Trinchero et al. (2017) stated that the occurrence of fracture-controlled redox fronts in the mine (Figure 8.2-2) offered qualitative support to their geochemical model assessment of redox front development in fractured HSR in Sweden. This would appear to be a case of model correctly mimicking reality for the wrong reason as West et al. (1991) clearly show the significant role that microbial processes play in the development of redox fronts at the site.

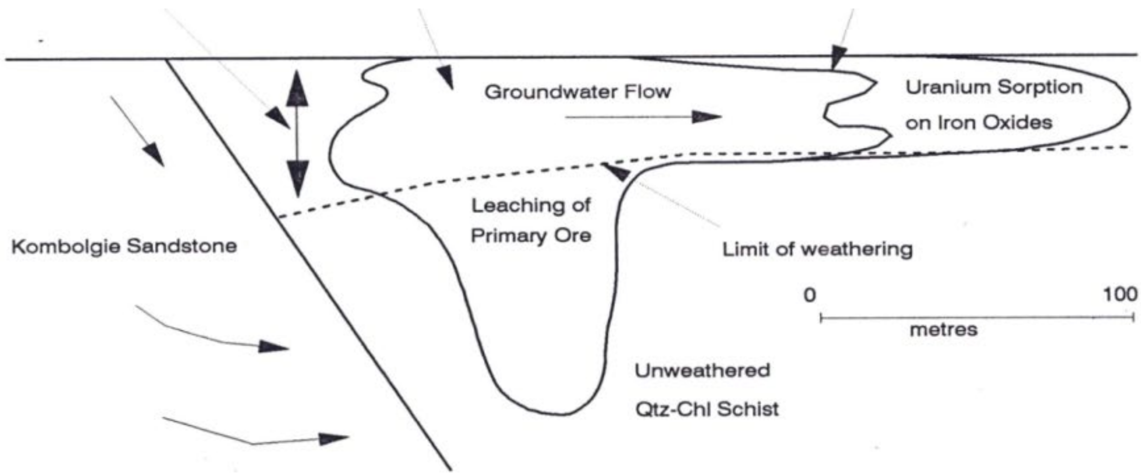

Figure 8.2-1. conceptual transport model in and around the Koongarra uranium ore body which was the focus of the Alligator River Analogue Project (Duerden et al. 1992). The shallow nature and the depth of weathering of the study site is clear from this figure.

Figure 8.2-2. A hand specimen from the Osamu Utsumi mine showing the redox front, formed by the percolation of oxygenated surface water into the rock. Unoxidised rock is blue-grey, right, oxidised rock is red-brown, left. (Miller et al. 2000)

Conclusions

For a variety of reasons (noted above), little of direct relevance to a GDF SC was produced in the early, generic radionuclide retardation NA studies. As several national programmes move towards identifying potential GDF host rocks and specific sites, any such future studies would be more appropriate examining processes of relevance on site. As an example of this approach, the potential to study natural 226-Ra as an analogue for 226-Ra released from the near-field of a spent fuel GDF will be addressed in chapter 13 (Table 13.7-1).

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8.3 Colloid transport analogues – overview

Colloids can affect the transport of radionuclides in the groundwater in several ways (Figure 8.3-1), some of which (e.g. sorption on colloids) could increase radionuclide transport through the geosphere while others (e.g. filtration of colloids after sorbing radionuclides) would decrease the overall transport through the host rock of a GDF. While it has been shown that these processes occur in surface waters and shallow groundwaters, the difficulties of defining colloid populations, sorption rates of radionuclides onto colloids, colloid transport processes, etc in deep groundwaters means that it has so far proven very difficult to quantitatively define the likely impact of colloids on radionuclide transport in a deep GDF environment.

Two reviews on the significance of colloids to a GDF SC were produced for RWMD over a decade ago, one looking at near-field colloids (Swanton et al. 2010) and the other examining colloids in the geosphere (Alexander et al. 2011). More recent reviews (e.g. Takala & Manninen 2006, Sen & Khilar 2006, Schaefer et al. 2012, Suorsa 2017, Posiva 2023) have been produced, but none match the breadth and depth of the original RWMD reviews, which include information on a wide range of NA studies (see Table 8.3-1 for examples).

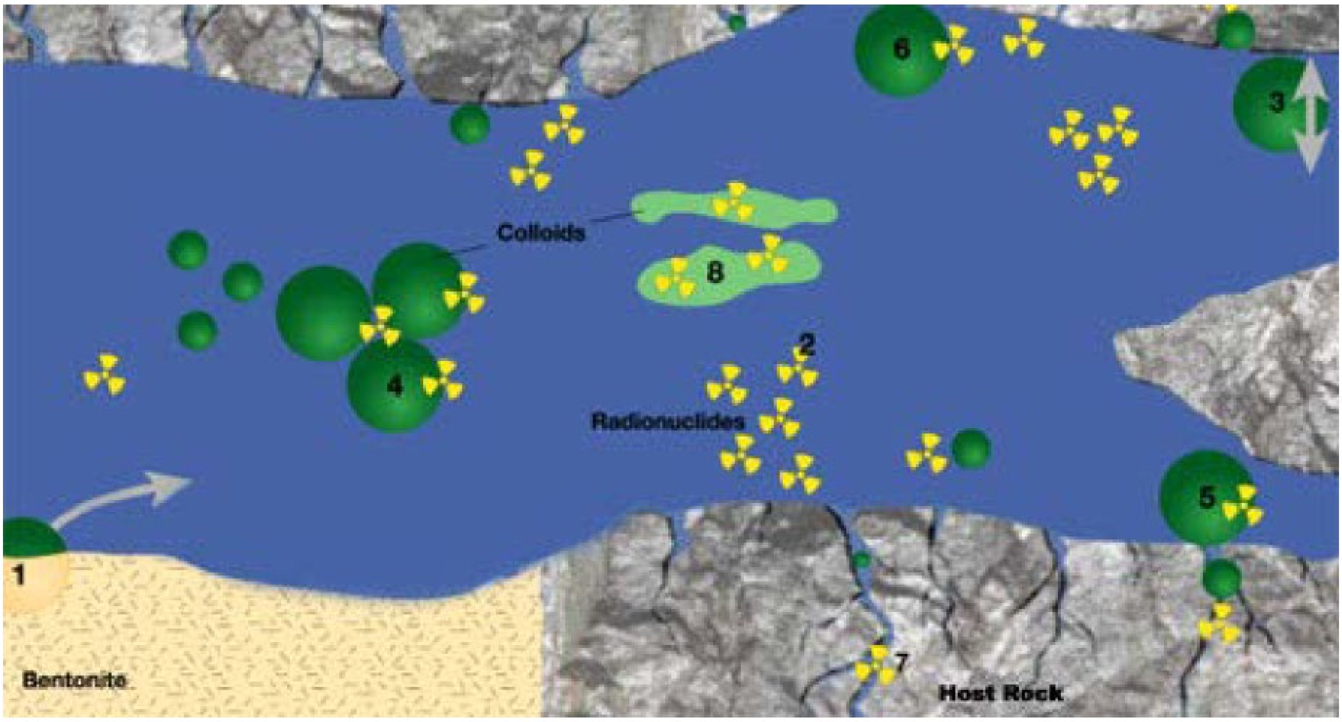

Figure 8.3-1. Potential production mechanisms of colloids (for example at the bentonite barrier/host rock interface) and subsequent transport of radionuclides in fractures in the host rock (Image courtesy of Nagra).

(1) Generation of GDF-derived colloids (in this case, from the bentonite barrier)
(2) Dissolved radionuclides (from the waste) in groundwater
(3) Sorption/de-sorption of natural and GDF-derived colloids onto/from rock surface
(4) Sorption of radionuclides onto inorganic colloids
(5) Filtration of colloids in pores and micro-fractures in the rock
(6) Colloid size prevents penetration into smaller pores in the rock
(7) Diffusion of radionuclides into the pores in the rock
(8) Sorption of radionuclides onto organic colloids or incorporation of radionuclides into organic colloids.

Table 8.3-1. Examples of groundwater colloid populations in various host rocks and groundwaters (from Alexander et al. 2011, where detailed information on the sampling and analytical techniques are reported in full).

Site	Rock type and groundwater	Flow system	Colloid number (/l)	Size and form	Sampling and analytical methods	Colloid composition	Comments
1. Canadian Shield (Whiteshell Research Area), Canada	Canadian Shield (crystalline) with deep saline (pH 6.1–7.7) or shallow Na-Ca-HCO_3 type (low ionic strength), pH 7.4–8.9 groundwaters.	Fractures	Range 0.04 to 14 Mean 0.34 ± 0.34	10−450 nm	Sequential ultrafiltration (colloid concentrations calculated from compositions)	Iron oxides, aluminosilicates (probably clays) and carbonates	URL and so flow conditions disturbed. No significant difference in populations between shallow and deep waters. No observable ionic strength effect.
2. Canadian Shield (Atikokan), Canada [i]	Canadian Shield (crystalline) with deep saline or shallow Na-Ca-HCO_3 type (low ionic strength).	Fractures	Mean 2.4 ± 0.3		Sequential ultrafiltration		Suggested that highly fractured and altered rock has greater surface area to produce colloids than at Whiteshell URL.
3. Fennoscandian Shield (Äspö), Sweden [ii]	Granitoids with basic sills and xenoliths and dykes of fine-grained granite.	Fractures and deformation zones	<0.1 [232] <0.3 [iii] $0.01 \cdot 10^{-3}$ to $1.00 \cdot 10^{3}$ [iv]	19−993 nm	PCS Ultrafiltration (SEM/EDS) LIBD	Organics, inorganic colloids (clay, calcite, ironoxo-hydroxide) and microbes	URL and so flow conditions disturbed.
4. Fennoscandian Shield (Forsmark), Sweden	Granite with muscovite/ biotite, feldspar, quartz and clays (chlorite and illite). Groundwater Na-Ca-Cl type, pH=7.53 Eh=–203 mV.	Fractures and deformation zones	0.14 to $1.8 \cdot 10^{-3}$		Sequential ultrafiltration and SEM/EDS	Clay	From borehole KFM11A, at 391 m depth.

Site	Rock type and groundwater	Flow system	Colloid number (/l)	Size and form	Sampling and analytical methods	Colloid composition	Comments
5. Fennoscandian Shield (Laxemar), Sweden [v]	Porphyritic granitoids and red/grey granites to quartz monzodiorite. Groundwater pH 8.2−8.5, Eh -277 mV.	Fractures and deformation zones	$6–12\cdot10^{-3}$ $2–5\cdot10^{-3}$		Sequential ultrafiltration, with mass calculation from the filter chemistry LIBD	Illite, calcite, iron and manganese hydroxide (colloid compositions calculated from the filtrate chemistry)	Very careful groundwater and colloid sampling.
6. Fennoscandian Shield (Olkiluoto), Finland	Migmatite granite with tonalite and granodiorite with Na-Ca-Cl groundwater, anoxic, pH~8.5.	Fractures and deformation zones	0.020−0.450 0.028−0.142 0.039−0.091	20−450 nm 50−2500 nm 2−1000 nm	Ultracentrifugal deposition, ultrafiltration and AF4 with SEM/EDS	Clays, silica, pyrite, goethite and magnesium oxide	URL so site is disturbed by tunnels. High salinity groundwater will induce colloid agglomeration.
7. Fennoscandian Shield (Palmottu), Finland [vi]	Mica gneiss and granite, groundwater is split between shallow Ca-HCO_3 to Na-HCO_3 types and deep Na-SO_4 and Na-CL types. pH 7.0−8.5 (100 m) to 9.0−9.5 (300 m), anoxic. I=30 mmol/L at depth.	Fractures and deformation zones	0.05 0.89	290 nm 217−229 nm	Ultrafiltration for PCS and EDAX	Silica gel and organics	Although uranium ore is present at the site, the only disturbance is from sampling boreholes. In the deepest, stagnant water (>400 m), no colloids were detected.
8. Grimsel Test Site, Switzerland [vii]	Granite and granodiorite, low salinity Na-Ca-HCO_3-F groundwater, sub-oxic, pH 9.6.	Fractures filled with fault gouge	Range 0.13 to 13 $4.2\cdot10^{6}$ to $3.9\cdot10^{10}$	Angular to rounded, 20−450 nm	Suite of methods used	Silica, phyllosilicates (illite/ muscovite/ biotite) and calcium silicates	Low salinity water induces colloid stability. URL and so flow conditions disturbed.

Site	Rock type and groundwater	Flow system	Colloid number (/l)	Size and form	Sampling and analytical methods	Colloid composition	Comments
						(probably plagioclase)	
9. Transitgas Tunnel, Switzerland	Granite and granodiorite, gneiss and mafic amphibolite, low salinity Na-Ca-SO_4-HCO_3 groundwater, oxic, pH 8−9.6.	Fractures (no detailed description)	$<2\cdot10^{-4}$ to $<2\cdot10^{-3}$	10−1000 nm	Cross-filtration, bulk water for SPC and colloids on membrane for XRD	Clay (including illite), silica	Collected from seeps in a tunnel, therefore drawdown disturbance.
10. Menzenschwand, Germany	Granite intruded into gneiss and metasediment, Ca-HCO_3 water, oxic, pH 6.5.	Large aperture fracture	$<4\cdot10^{-4}$	10−1000 nm	Cross-filtration, bulk water for SPC and colloids on membrane for XRD	Clay, silica	Uranium prospect, heavy pumping of water (up to 2000 L/min) therefore significant disturbance of the local groundwater system. Evidence of long-distance (1−5 km) transport of colloids.
11. Leuggern, Switzerland	Mica-granite, Na-HCO_3-Cl-SO_4 water, strongly anoxic, pH 7.8	Not described, assumed to be fractures	<20	10−1000 nm	Cross-filtration, bulk water for SPC and colloids on membrane for XRD	Silica, clay	Water pumped 1700 m to the surface, so degassed.
12. Fanay-Augères, France [viii]	Granite with Na-Ca-HCO_3-SO_4-Cl groundwater.	Fractures	$<0.1\cdot10^{-3}$	100−1000 nm		Silica and organics	Former uranium mine, so significant disturbance to the system.

Site	Rock type and groundwater	Flow system	Colloid number (/l)	Size and form	Sampling and analytical methods	Colloid composition	Comments
13. El Berrocal, Spain	Two-mica granite (with leucogranite and pegmoaplites), groundwater Na-Ca-HCO_3-Cl type to Ca-Na-HCO_3-Cl type, pH 6.2 to 7.3, oxic, I= 6−11 mmol/L.	Fractures	<0.1 10^{12} 10^{10} $10-10^{8}$	down to 1 nm down to 50 nm 208 to 342 nm [239]	Tangential flow ultrafiltration with TEM and PCS/SEM	Quartz/silica, iron oxy-hydroxides and alumina gels Albite, apatite, clays, calcite, other carbonates and Al- and Fe-oxyhydroxides. Some organics too [239]	Shallow (S1 and S7) boreholes in a former uranium mine, so heavily disturbed site [ix]. Boreholes were left open for a long time and "...geochemical stabilisation....may not have been reached at all....sampled water may represent mixtures...". Majority of U and Th in solution.
14. Sellafield, UK	Borrowdale Volcanic Group.	Fractures			Tangential flow ultrafiltration and STEM/EDAX	Fe-oxyhydroxides	Borehole 9A, drilled specifically for geochemical sampling. No detailed analysis carried out due to interference from Fe-oxyhydroxides on filters.
15. Cigar Lake, Canada [x]	Zone of altered crystalline basement, Na-Ca-HCO_3-Cl groundwater, oxic to anoxic, pH 6.1 to 7.8	Heavily damaged zone, crushed rock Fracture in basement	7.78 ± 4.14 0.03 to 2.21		Tangential flow ultrafiltration and colloids on membrane for XRD and SEM/EDX	Clays (illite, chlorite, kaolinite), amorphous Fe-Si oxides, quartz and organics	U deposit has been explored with several hundred boreholes, so significant disturbance.

Site	Rock type and groundwater	Flow system	Colloid number (/l)	Size and form	Sampling and analytical methods	Colloid composition	Comments
16. Osamu Utsumi, Brazil [xi]	Phonolite, K-Fe-SO_4, oxidising and weakly to strongly acidic groundwaters, oxic.	Fractures (with extensive redox front development near surface)	<0.5 (generally 0.1 to 0.2) by filtrate chemistry		Sequential (cascade) cross-flow ultrafiltration (filter size 450 to 1.5 nm) with ESCA, SEM, XRD	DOC (80−90 %), Fe-oxyhydroxides (2−20 %) and clay±chalcedony (<2 %)	U deposit extensively mined, therefore highly disturbed site. Groundwater flow from depth to surface, the opposite of the state before mining.
17. Morro do Ferro, Brazil	Phonolite, groundwater varies from the bottom of the hill, which resembles the water from Osamu Utsumi (above), to the ore body at the top of the hill which is similar but less mineralised and more oxidising, representing unsaturated conditions.	Fractures in heavily weathered host rock	0.01 to 0.10 by SEM 0.26 by filtrate chemistry $3.4{\cdot}10^7$	Large (0.5−1.0 µm), irreg-ular/angu-lar shaped particles, agglomerates (5−10 µM) of these particles and long (humic) chains (2−3 µM)	Sequential (cascade) cross-flow ultrafiltration (filter size 450 to 1.5 nm) with ESCA, SEM and XRD	DOC (80 %), Fe-oxyhydroxides (18 %) and clay (2 %)	Th, REE deposit has been explored with a drift and several boreholes, so some disturbance. Colloid concentration range represents the same borehole, but different samples.
18. Wellenberg, Switzerland [xii]	Tectonised marl (clay-rich limestone).	Heavily tectonised fractures		Colloids are cylinders 30–100 nm diameter and 5−15 nm long. Mean	Cross-filtration and colloids on membrane for AFM (atomic force microscopy) LIBD [206]	Clay	Pumped from depth, but borehole was supposedly hydrochemically ‘stable’.

Site	Rock type and groundwater	Flow system	Colloid number (/l)	Size and form	Sampling and analytical methods	Colloid composition	Comments
				diam. 72 nm			
19. Cigar Lake, Canada	Sandstone and ore (within clay halo), Na-Ca-HCO_3-Cl groundwater, oxic to anoxic, pH 6.1 to 7.8.	Porous matrix	Mean 0.6±0.09 to 1.52±0.29	10 nm to 20 µm, but most in 100−400 nm range	Tangential flow ultrafiltration and colloids on membrane for XRD and SEM/EDX	Clays (illite, chlorite, kaolinite), amorphous Fe-Si oxides, quartz and organics	No significant U association with the colloids found downflow of the ore body.
20. Sellafield, UK	St Bees Sandstone Formations.	Porous matrix	0.5 $8 \cdot 10^{10}$	100−200 n m	Tangential flow ultrafiltration and STEM/EDAX	Silica, coated with iron oxy-hydroxide associated with an illitic clay mineral. Significant amounts of Ca, S, Zn and As also associated with these colloids	Borehole RCF3 (NB long-term pump test ongoing, so likely to be disturbed).
21. Oklo and Bangombé natural reactors, Gabon [xiii]	Sandstone, conglomerates and clays, Na-Mg-Ca-HCO_3 groundwater, pH 6−7, slightly negative Eh.	Porous matrix	0.03 to 0.92 $2 \cdot 10^5$ to $2 \cdot 10^7$	>100 nm	Colloids on membranes for SEM/EDAX and ICP-MS, bulk water samples for SPC	Silica, clay and iron oxyhydroxides	Sampled from 4 shallow (<105 m) boreholes below the reactor zone. Bacteria and organics examined in parallel, but no attempt to link the results.
22. Zurzach, Switzerland	Sandstones and marls directly above crystalline	Not defined, possibly	<10	10−1000 nm	Cross-filtration, bulk water for SPC and	Silica, clay	Pumped from 470 m deep so disturbed. Note similarity of water type to

Site	Rock type and groundwater	Flow system	Colloid number (/l)	Size and form	Sampling and analytical methods	Colloid composition	Comments
	basement, Na-HCO_3-Cl-SO_4 water, strongly anoxic, pH 8.0.	fractures in sediments			colloids on membrane for XRD		Leuggern; likely that groundwater from the crystalline basement is being drawn in.
23. Ruprechtov, Czech Republic [xiv]	Clays (altered tuff), lignite and altered granite, Ca-HCO3 groundwater, I=0.003 to 0.02 mol/L, oxic to anoxic, pH 6.2−8.0.	Zones of higher hydraulic conductivity in the clay lignite [xv]	0.003 to 0.744	Most >45 nm	LIBD	No data	Samples from shallow boreholes (max. depth 37 m), some questions regarding Eh status of system (varies with time).
24. Alligator Rivers, Australia [xvi]	Quaternary sands over clay-rich zone of intensely-weathered schist grading into weathered schist. Mg-Ca-Si-HCO type groundwater, pH~7, oxic, I=1−1.5 mol/L.	Not described in detail, seems to be permeable zones in the sands and clays.	<0.05 102 to 105	Platelets, spheres, crystals (quartz, Fe-oxide) up to 1 µm diameter	Hollow-fibre ultrafiltration and direct ultrafiltration for ICP-MS and SEM/TEM/EDS	Quartz, Fe-rich colloids and clays. In highly weathered zone, colloidal clay is kaolinite, in less weathered zones, chlorite. Also uranyl silicate and lead	Uranium ore not mined, but over 100 exploration boreholes drilled. Site also experiences significant seasonal fluctuation of the water table.
26. Tsukinuno, Japan	Bentonite beds intercalated with shales.	Not described, but fractures likely.	None detected, presumed to be due to groundwater chemistry		Ultrafiltration and ICP-AES (colloid concentrations calculated from [Si, Mg and Al]	Assumed to be bentonite, but not presented	Bentonite deposit is mined, so highly disturbed site. Colloid detection limit is not presented.

Abbreviations:
AFM Atomic force microscopy
BSE-SEM Backscattering electron scanning electron microscopy
DOC Dissolved organic carbon
EDX (EDAX) Energy dispersive X-ray analysis
ESCA Electron spectroscopy for chemical analysis

ESEM Environmental scanning electron microscopy
EXAFS (XAFS) Extended X-ray absorption fine structure (spectroscopy)
ICP-AES (ICP-OES) Inductively coupled plasma-atomic (optical) emission spectroscopy
ICP-MS Inductively coupled plasma-mass spectrometry
LIBD Laser-induced breakdown detection
PCS Photon correlation spectroscopy
RBS Rutherford backscattering spectroscopy
SEM Scanning electron microscopy
SPC Single particle counting
STEM Scanning-tunnelling electron microscopy
TEM Transmission electron microscopy
TR-LFS Time-resolved laser fluorescence spectroscopy
XRD X-ray diffraction

Notes:

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Conclusions

Colloid NA studies played a significant role in developing an understanding of the potential impact of colloids on radionuclide transport (predominantly in the geosphere) and drove the development of sampling and analytical tools. Currently, as with the radionuclide retardation NA studies, those national programmes which have identified potential GDF sites are moving towards site-specific colloid studies with focussed work reported for the Forsmark (e.g. Nilsson & Degueldre 2007, Hallbeck & Pedersen 2008) and Olkiluoto (e.g. Luste et al. 2014, Luste & Kilponen 2020) sites.

Further development work needs to be carried out for near-field colloids and bentonite colloid studies are planned at a NA site in Japan and cement colloid studies have been proposed for a NA site in Jordan (see chapter 13 for details).

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8.4 Matrix diffusion – overview

Rock matrix diffusion is the process by which a solute, flowing in distinct fractures in a rock, penetrates the surrounding rock matrix. Diffusion into this matrix occurs in a connected system of pores or microfractures. The importance of matrix diffusion in the context of a radioactive waste repository is that it greatly enlarges the area of rock surface in contact with advecting radionuclides from just the fracture surface to a portion of the bulk rock (Figure 8.4-1).

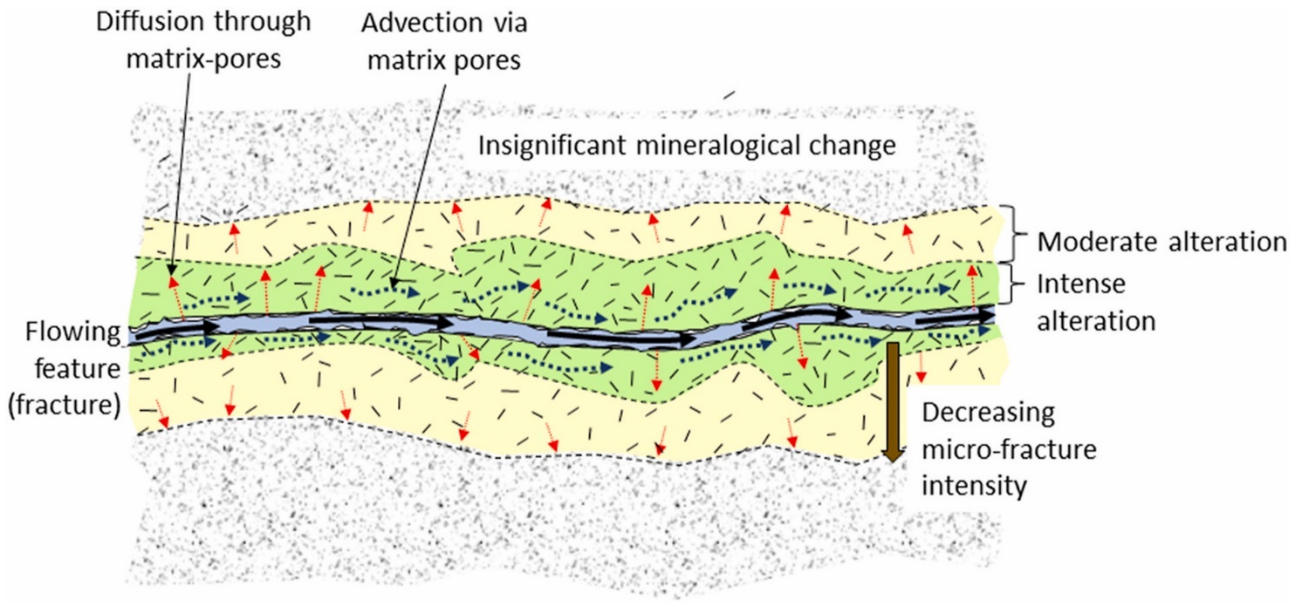

Figure 8.4-1: Conceptual model for radionuclide uptake in a fractured GDF host rock (Metcalfe et al. 2021)

The theoretical basis for matrix diffusion is fairly well established and it has since been verified both in laboratory (e.g. Garrels et al. 1949, Muuri et al. 2018) and URL (e.g. Birgersson & Neretnieks 1990, Möri et al. 2003) experiments. Both these approaches are relatively short-term, so much effort has been expended in examining long-term matrix diffusion via NA studies (e.g. Smellie et al. 1985, Suksi & Ruskeeniemi 1992). Here, the usual approach is to carry out studies on natural tracers in rock where perturbations to the average chemical composition of the bulk rock are used to indicate the presence of previous rock-water interaction.

In the 1990s, it was argued (von Marovic & Smellie 1996) that matrix diffusion had been studied in sufficient detail to provide a high level of confidence that understanding of the process was mature enough for its routine inclusion in SCs (e.g. Nagra 1994, JNC 2000). Nevertheless, there remains scope for further research in potential GDF host rocks (e.g. Havlová et al. 2020) and a recent study (Metcalfe et al. 2021) covers several host rock types of relevance to the UK programme. The preliminary results indicate that rock matrix alteration may play a role in influencing the degree of matrix accessibility[19] and this is being studied further within NWS' experimental programme. Currently, the Finnish national programme is producing detailed information on matrix diffusion in their Olkiluoto GDF host rock with laboratory (e.g. Sammaljärvi et al. 2017), URL (e.g. Poteri et al. 2018) and site characterisation studies (e.g. Posiva 2022) currently ongoing.

Conclusions

There is a massive body of NA work on matrix diffusion (see Miller et al. 2000, Posiva 2012, 2021, for details) and this is clearly a mature field of study. Nevertheless, as various national programmes move towards identifying specific GDF host formations, there is scope for future work focussed on the actual host rocks themselves.

[19] Studies in the Finnish national programme also indicate that anion exclusion (which is well documented in clay-rich sediments) is also a relevant process in crystalline rocks which contain sufficient clays (through various alteration mechanisms). See Alexander et al. (2022) for details.

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9 OTHER EBS MATERIALS

9.1 Longevity of other EBS materials - Overview

In addition to clay and cement based EBS there are other materials that might be considered depending on the design of the GDF. These may be related to structures of closure, room/tunnel seals, shaft/ramp seals, borehole seals or other engineered features. Examples of these include (White et al. 2008):

- magnesium oxide (MgO), which is used as a buffer material in the Waste Isolation Pilot Plant (WIPP) (Papenguth et al. 2000), the underground facility for disposal of US transuranic waste in New Mexico.
- crushed rock, particularly rock that has characteristics and behaviour similar to the host rock. For example, crushed salt is proposed for backfilling the excavated regions of a disposal facility for spent fuel in salt host rocks in Germany (see chapter 6). Backfill of this nature might comprise part of the spoil removed during excavation activities.

The choice of materials for engineered seals (for tunnels, shafts, and boreholes) within the GDF will depend upon the other materials used as engineered barriers, together with the characteristics of the host rock and the desired longevity of the seals. Designs might incorporate multiple and mixed materials, perhaps including (White et al. 2008):

- bitumen
- clay, including bentonite (see analogues for clays, chapter 5)
- concrete (see analogues for concrete, chapter 4)
- crushed rock

Sealing of the repository requires various types of materials that are emplaced at the GDF level and up to the surface. These materials need to last over long time scales and many of them have analogues in nature that can be useful for the performance assessment (see section 13.9). The relevant analogue studies depend on the selected design and materials considered during the generic phase may not be included in the final design and new materials may emerge.

A developed example from Posiva is provided in Figure 9.1-1 and this has been adapted to the properties of the Olkiluoto site. Some initial potential NAs for crushed rock and clay-aggregate mixtures have been considered in Posiva (2021).

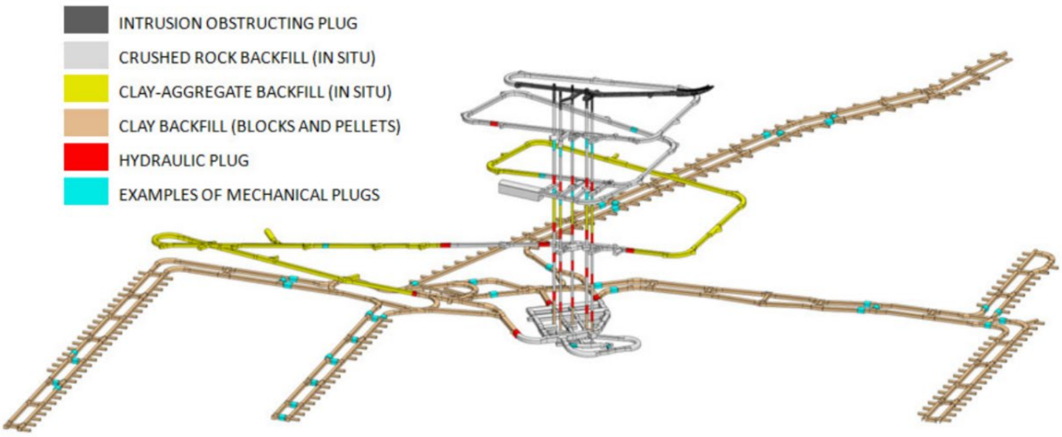

Figure 9.1-1. Example of a generic illustration of closure options for the planned GDF at Olkiluoto in Finland with potential plug locations, and potential backfill materials conforming to the closure requirements (Sievänen et al. 2012).

In addition to closing of the access ways to the repository, boreholes at the repository site have to be sealed. This has been considered in a dedicated RWM project (Sealing deep site investigation boreholes; Jefferies et al., 2018). For the borehole concepts various materials have been considered and the relevant natural analogues studies reviewed (Table 9.1-1). Alexander (2018) concluded that targeted NA studies at borehole sealing systems per se are all but missing, although qualitative input of existing knowledge is acknowledged. Several potential targets to obtain better qualitative and quantitative information from NAs were identified by Alexander (2018).

Some preliminary assessments of NAs for shaft sealing, including consideration of asphalt, has been reported by Kremer & Alexander (2015). NWMO has considered shaft seal designs that include a layer of asphalt as a redundant low-permeability seal. Although, no dedicated analogue studies were found, Kremer and Alexander (2015) reported several natural occurrences of bitumen of relevance (see Table 13.8-1, ID 9.1-15):

- The Athabasca oil sands, the largest known reservoir of crude bitumen in the world (Longstaffe 1993), indicating stability in likely brackish groundwater for over 10 million years
- The bitumen and gilsotine deposits in sandstone at Uinta Basin, Utah (Schamel 2009, Boden & Tripp 2012, respectively), both indicating long-term stability of bitumen in a saline environment for millions of years
- Fracture asphaltite from Forsmark (Drake et al. 2006), indicating long-term stability in saline conditions
- Dead sea asphalt blocks, that have been used in the preservation of Egyptian mummies (Rullkötter & Nissenbaum 1988), indicating potential durability in brines

Clearly then, a multitude of processes can be relevant depending on the material selected in the final GDF, hence, in the future, individual FEPs should be defined for detailed NA screening. Section 13.8 provides a set of examples but is not by no means exhaustive.

Table 9.1-1. Summary of relevant NA information on borehole sealing materials (Alexander et al. 2018) with updates as indicated by references in the table.

Components considered	**NA studies of relevance**	**Notes**
Bentonite HDBC (High density block concept)	For overall process understanding bentonite analogues can be used.	Physico-chemical data on natural bentonites from the vast majority of existing NA studies have little relevance to the HDBC where the seal material comprises well-fitting blocks of highly compacted bentonite, pre-dried to a water content of about 6% and then compacted to a dry density of 1,900 kg m-3
Bentonite pellets	Bentonite pellets are known to exist (e.g. Kato Moni, Alexander et al. 2017), but no dedicated studies available so far for borehole seals. Kato Moni micro pellets have provided initial information on potential shear displacement prevention. See Table 13.8-1, ID 9.1-3.	Potential impacts of coatings are mentioned as a potential field for investigations, but there is no existing literature.
Bentonite – cement reactions	Seal relevant studies are few and ambiguous. See Table 13.8-1, ID 9.1-4.	Process understanding benefits from general studies (i.e. bentonite is unstable under highly alkaline conditions). Short-term industrial analogues exist (e.g. Harpur Hill and Herbert's Quarry (UK) industrial analogue sites; see Milodowski et al., 2013 and Moyce et al., 2015, respectively, for details), but have been considered to be too young to benefit borehole sealing assessments.
Bentonite – metal reactions	Few NA data of relevance to the long-term impact of metal corrosion products on bentonite behaviour have been reported. See Table 13.8-1, ID 9.1-5.	Steel/iron material in the borehole, existing NA studies are not relevant enough for current designs, although general observations from natural systems and the NF-PRO URL experiment (Milodowski et al. 2009a,b) suggest uptake of iron could reduce swelling pressures. Qualitative data from the Kronan cannon are available and these could be more rigorously integrated with existing laboratory data.
Bentonite – host rock reactions	Kato Moni study (Alexander et al. 2017) provides some indication of long-term reaction between bentonite and the overlying limestone at a site on the north side of the Troodos Massif in Cyprus. See Table 13.8-1, ID 9.1-6 IBL project has identified sites to assess the processes in detail for bentonite – shale contacts in relevant settings (similar volumes to EBS components) (Reijonen & Alexander 2023b). See Table 13.8-1, ID 9.1-7	
Bentonite – groundwater reactions	Existing NA studies on bentonite-groundwater interaction, such as CNAP (see NA7.2.1) can be used. Illitisation is well understood and can be taken into account in the safety cases. Low salinity groundwaters and high salinity environments would benefit of more investigations, see chemical erosion (section 5.1.5) and stability in saline/brine conditions (section 5.1.6)	

Components considered	NA studies of relevance	Notes
	See Table 13.8-1, ID 9.1-8	
Bentonite – magnetite reactions	Magnetites are known to occur within bentonite, but no NA studies have been made so far. Table 13.8-1, ID 9.1-9	
Bentonite – sand mixtures	From CNAP (Alexander & Milodowski 2014), Perapedhi bentonite in Cyprus is an example of an analogue of a bentonite-sand mixture. CNAP study did not focus on this aspect of the analogue, but shows general stability ca. 90 million of years in saline environment. See Table 13.8-1, ID 9.1-10	Natural bentonites show a wide variation in the smectite content, even over short distances within the same deposit (cf. Alexander & Milodowski, 2014). As such, natural bentonites range in composition from those directly analogous to 'pure' industrial bentonites to those more akin to industrial bentonite-sand mixtures. However, few NA studies of bentonite have characterised the physical properties of the material in enough detail to allow direct comparison with either of these end-members.
Cementitious materials (OPC)	The NA studies on cements in general are applicable (see chapter 4 and section 13.3). However, quantitative data would be of interest. See also Table 13.8-1, ID 9.1-11	
Cementitious materials (Low alkali cements)	Some qualitative information from Roman cements, that are archaeological in age. See section 4.1.2 and Table 13.8-1, ID 9.1.1-12	
Other materials (barite)	Limited NA data from Jordan indicate that barite can co-exist long-term with cementitious minerals without significant reaction. See Table 13.8-1, ID 9.1.1-13	
Other materials (graded silica (Sandaband™)	No identified studies. See Table 13.8-1, ID 9.1-14	The physical properties of non-glacial, non-cemented loess may not be unlike Sandaband™.
Other materials (Evaporites)	No identified studies.	Industrial NA data are available for tunnel seals and plugs for WIPP, but the results are no more than qualitative. See also chapter 6.
Magnesium oxide	No identified studies.	

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10 OPERATIONAL ANALOGUES

Operational analogues refer to information that can help to support GDF design and construction as well as guiding the GDF operation in such a way that the disturbances to the system are minimised. Operational analogues may cover processes that take place during the operational phase (tens to hundred years), but, also long-term effects of the same processes can be considered. In addition, operational analogues may be considered from the worker safety point of view. Occupational safety is not the main focus of this report, but some examples presented here include this aspect.

Potential disturbances of the GDF can and should be estimated prior to the operations at the site. One example of such exercise is the study by Alexander & Neall (2007), which included NA considerations for potential perturbations of a GDF in Olkiluoto, Finland. Perturbations may be caused by physical changes to the system (such as excavation of disposal spaces) or due to chemical disturbance (materials used in GDF or stray materials introduced to the system). Lessons can be learnt through looking at analogous GDF projects, where operations have already been started and monitoring of the site has been ongoing for extended periods of time. The most extensively monitored site to date is Olkiluoto in Finland, where systematic monitoring of perturbations of operations has been in place since 2004 when underground construction commenced (see Posiva 2003, 2012a, 2021a), including monitoring of, for example:

- Rock mechanics
- Hydrogeology and hydrogeochemistry
- Other site properties (e.g. fracture mineralogy changes such as oxidation, formation of biofilms, precipitation of minerals)
- Effects and amounts of introduced materials (e.g. cement, explosives etc.)
- Environment
    - Biosphere in general
    - Landscape changes
    - Monitoring needed for environmental impact assessment (EIA[20])

NAs have not been traditionally considered regarding operational aspects, and hence the topic is discussed at a level of providing some example. In the NA work, it is likely that operational aspects may be considered as a part of wider NA project (such as host rock regional analogue studies), rather than as a main focus of the NA project. Here, brief topical overview is provided discussing host rock, EBS and other GDF materials, environmental implications of the GDF and hazards potentially affecting GDF, that could provide input as operational analogues.

Table 10-1. Examples of URL experiments that may be seen as operational NAs for host rock perturbations.

Type of perturbation	Analogues used	Reference	Implications for GDF development
Void spaces in GDF – mechanical integrity (crystalline)	AECL in situ experiments in the Whiteshell URL at the Lac du Bonnet batholith	Read (2004) Read & Chandler (2002)	Operational safety: Tunnel stability Long-term safety: Formation and extent of EDZ

[20] In the Finnish case, the EIA is separate study from the long-term safety assessment.

Type of perturbation	Analogues used	Reference	Implications for GDF development
Void spaces in GDF – mechanical integrity (crystalline)	SKB Äspö Pillar Spalling Experiment (APSE) in Äspö HRL in Sweden	Andersson (2007)	Operational safety: Tunnel stability Long-term safety: Formation and extent of EDZ
Void spaces in GDF – mechanical integrity (HSR)	Olkiluoto assessment	e.g. Valli et al. (2021) Posiva (2012b, 2021b) analogue discussion on mechanical integrity (also from other sites for comparison)	Long-term safety: Formation and extent of excavation damage
Void spaces in GDF – mechanical integrity (LSSR)	Not identified.		
Void spaces in GDF – mechanical integrity (evaporites)	See section 6.4.		Long-term safety: Creep leading to tunnel sealing
Excavation damage	Excavation damage depending on the rock type and excavation methods can be studied from other sites. Depends greatly on the host rock type.	Needs to be reviewed based on host rock (see section 13.9)	Operational safety: Tunnel stability Long-term safety: Formation and extent of EDZ
Hydrogeological and chemical perturbations (crystalline)	At Olkiluoto, perturbations of a controlled operation have been monitored throughout the operation of ONKALO facility.	Posiva (2012a, 2022a)	Operational safety: - Long-term safety: Stability of the groundwater conditions, maintaining site suitability
Hydrogeological and chemical perturbations (Sed)	Pyrite oxidation has been studied in > 100 years old Swiss tunnel quarry in Palfris Formation (W.R. Alexander, 2022, pers.comm.)		Information on the effects of long operational times (both long-term and operational potential consequences).
GDF ventilation during operation	The impact of ventilation on a HSR was studied in the Grimsel URL by examining physico-chemical changes in the near-surface tunnel wall.	Baertschi et al. (1991)	Long-term degradation of the tunnel walls. Mobility of reduced iron and uranium carbonate observed immediately behind the tunnel wall due

Type of perturbation	Analogues used	Reference	Implications for GDF development
			to ingress of atmospheric oxygen and carbon dioxide respectively.
GDF ventilation during operation	The impact of ventilation on a LSSR was studied in an underground quarry in the Palfris Formation[21] by examining physico-chemical changes in the near-surface tunnel wall.	W.R.Alexander (pers. comm. 2022)	Long-term degradation of the tunnel walls. None observed, despite the quarry having been open to the atmosphere for over a century. Pyrite in the rock was possibly protected by carbonate surface coating.
Naturally pressurised gas pockets	Not studied to date, but potential exists. See section 13.9, ID 10-4.		

Considering EBS, cement degradation studies may provide information of interest as operational analogues. Iron corrosion of concrete and cement degradation in general, are processes that may take place during long operation times.

In addition to operational safety and long-term safety, investigation, construction, operation and closure of a GDF can have implications to the environment in general. These implications can include e.g.:

- Air quality, including effects on existing air quality and sensitive receptors
- Noise, vibration and lighting, including effects on existing baseline levels of noise and sensitive receptors
- Biodiversity and nature conservation, including effects on flora and fauna, habitats and designated sites
- Climatic factors including effects of climate change and ability to use low carbon technologies and renewable energy sources.
- Historic environment implications, including effects on the historic landscape, heritage assets and their setting as well as archaeological and palaeontological assets
- Land use, including effects on and compatibility with existing land uses
- Landscape and visual implications, including effects on the character of the landscape, townscape and seascape (as appropriate)
- Waste management, including the ability to adhere to the waste management hierarchy and management of waste, such as spoil
- Resources, including the ability to utilise resources efficiently

Analogue studies can be used to obtain background information on these topics from other similar projects. However, depending on the site and GDF design, the needs for this type of data can only be assessed when site or site candidates have been selected.

The implications of natural and other external hazards are of concern during the operations and may cause also challenges for post-closure performance in case their effect of the site properties are of significant extent. Hazards usually considered in operational safety include at least:

- Storms or flooding
- Explosions and fires

[21] The potential GDF host formation at the Wellenberg site in central Switzerland.

- Leakages / spillages
- Tunnel collapse / rock fall
- Loss of services (power failure, shielding system failure, ventilation, and filter system failure)
- Inadvertent entry.

In detailed hazard identification, other types may be included. All the above-mentioned have happened in mines and other underground facilities, even for disposing radioactive waste (e.g. WIPP accidents). Analogue information can be used in operational safety assessments, but also in consideration of their potential long-term effects on the post-closure safety. See Alexander and Neall (2007) for an example of treatment of hazards in the perturbation assessment. No direct analogue studies were found in the literature on hazards, but some of the topics are clearly more potential for analogue studies in the future than others. Potential for explosions and fires can be assessed via existing experienced from mining industry (see section 13.9), tunnel collapse is closely related to overall analogue for rock mechanical stability (see section 10.1).

Conclusions

Considering the current status of NWS GDF programme, it is recommended that any work done under this topic, would be tied to other regional analogue work commenced. Further assessment can be made when more specific information is available of the potential site and GDF design details.

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11 WHOLE SYSTEM PERFORMANCE

11.1 Overview

A natural analogue of an entire GDF could provide extremely valuable long-term information for understanding its behaviour and performance into the far future. In early natural analogue studies, there was often the temptation to take the information and try to apply it to a complete GDF design. This was reflected to some extent in the approaches taken in the early studies of the Oklo and Poços de Caldas sites (for a SF/HLW GDF) and the Maqarin area (for a cementitious GDF). Generally, this approach has been of limited success because most NA studies are focussed on particular processes or mechanisms, indeed often looking at just one specific aspect of a GDF system. Even in the broader projects, such as Poços de Caldas, although there were multiple objectives for the study, they should not be thought of as covering all aspects of any particular GDF design.

At Oklo, in the Gabon, a total of 16 separate natural reactor cores (or zones) have been identified, across an area of ca. 2 km^2, with one found at Bangombé about 20 km to the south-east of the main group at Oklo/Okelobondo (see Figures 11.1-1 and 11.1-2). This would seem to be an ideal natural analogue for assessing the performance of a GDF through geological time, a location where predictions about rates of movement of various radionuclides could be rigorously tested.

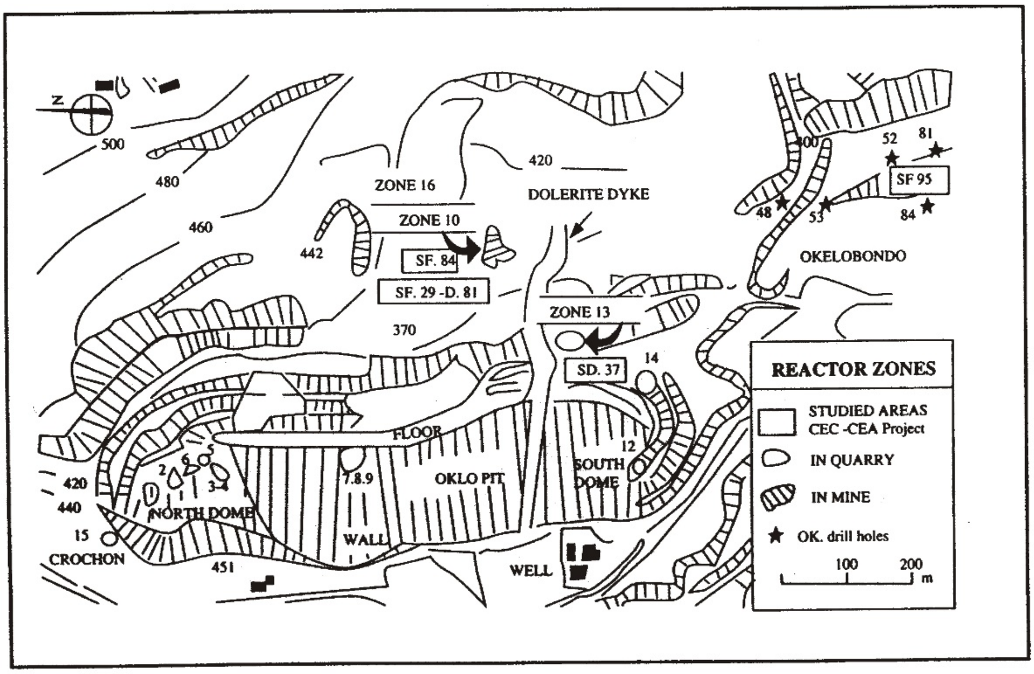

Figure 11.1-1. A map of the reactor zones in the Oklo area (Hollinger 1992).

Radionuclide migration can be traced from a well-defined source term (i.e. the reactor zone, which has been claimed to be a SF analogy), out through the surrounding clay (bentonite buffer analogy) and into the far-field sedimentary host rock which can represent either the fracture-flow character of a fractured crystalline host rock (i.e. the underlying sandstone formations) or a porous-flow clay-based host rock (i.e. the overlying clay-rich sediments).

Figure 11.1-2. A view of the main quarry at Oklo (Oklo pit at centre bottom of Figure 11.1-1) where the shallower reactor zones were accessed directly (the deeper ones were exploited by mining). (Miller et al. 2000).

However, as noted above, a complete analogue of a GDF system does not exist at Oklo or at any other location in the world. For example, even though the source-term chemistry at the Oklo site might be expected to show similarities to that resulting from the leaching of SF, quantitative analysis of this system is extremely difficult because of the highly complex geochemical and hydrothermal history of the region (Del Nero et al. 2002). And the fact that the environment around the reactors has changed numerous times in the ca. 2 billion years since criticality means that it is difficult to draw meaningful conclusions from the data. As noted in Milodowski et al. (2016):

"In the early stages of the *(Oklo)* study, safety case issues were largely ignored at the expense of 'interesting science'. Later stages saw a marked improvement in consideration in safety cases, to the extent that a special Oklo Safety Assessment Interface Group was formed in 1996, representing an integration of geoscientists (data gatherers) and performance assessors (data users). However, this was only partly successful and, to date, Oklo has been more or less ignored in safety cases."

However, perhaps one analogue study has come closer than most to being an analogy for an entire GDF, namely Cigar Lake in Canada (Figure 11.1-3). This uranium (U) ore body is one of the largest in the world, with proven reserves of over 200,000 tonnes of uranium. The ore is also unusually rich in U, with an average ore grade of 21% and a maximum of 60%. The deposit was located using geophysical methods and systematic drilling within a region that was known to host other major uranium ore bodies associated with the base of the Athabasca Sandstone. Here, U mineralisation occurs at the base of the Athabasca Sandstone, where it unconformably overlies crystalline metamorphic basement rocks.

Although Alexander et al. (2006) noted that "…and the ease with which explanation by analogy is generally understood compared to the subtleties of PA mathematical models." and used Figure 11.1-4 as an example to explain a multi-barrier GDF, this does not mean that the Cigar Lake orebody can be taken as a whole system analogue. Smellie and Karlsson (1996) rightly noted the many aspects of the Cigar Lake site which have safety case relevance but, as with the case at Oklo, the great age of the site (1300 million years) and the complexity of the system make any attempt to portray the site as a whole system analogue highly dubious.

Figure 11.1-3. Cigar Lake, Canada. At the surface, there are no significant radiological traces of one of the richest uranium ore bodies in the world (Milodowski et al. 2015).

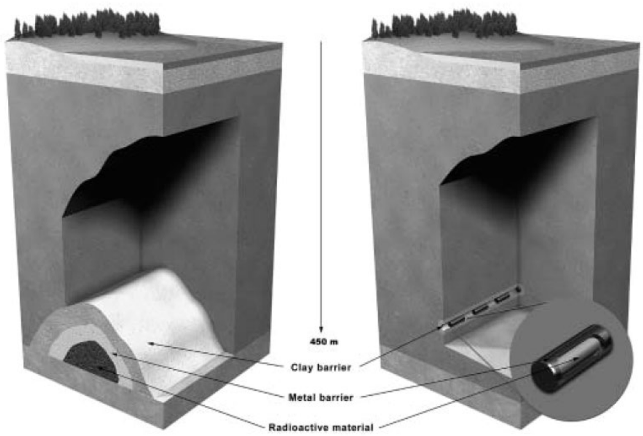

Figure 11.1-4. Comparison of the Cigar Lake uranium ore body (left) with the engineered barrier system (right) for a repository for high-level radioactive waste (HLW). In Cigar Lake, the radioactive waste is represented by the natural uraninite ore (dark grey core), the metal barrier by an iron oxide/hydroxide rich zone (light grey middle layer) and the clay barrier by a clay-rich, hydrothermal halo (mid-grey outer layer). Alexander et al. (2006).

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12 BIOSPHERE

12.1 Biosphere analogues – overview

The biosphere (Figure 12.1-1) is defined in the NWS glossary as follows:

“That part of the environment normally inhabited by living organisms. In practice, the biosphere is generally taken to include the atmosphere and the Earth’s surface, including the soil and surface water bodies, seas and oceans and their sediments. There is no generally accepted definition of the depth below the surface at which soil or sediment ceases to be part of the biosphere, but this might typically be taken to be the depth affected by basic human actions, in particular farming.”

Additionally, RWM (2016) has defined that “The biosphere comprises the atmosphere, surface and near-surface environment, normally inhabited by living organisms, and is taken to include any near-surface aquifers. The biosphere acts as the receptor for any contaminants released from the geosphere and does not constitute a barrier within the disposal system.”

Internationally, there are some terminological differences that are good to note, and may vary between national programmes, e.g. ‘surface environment’ is also sometimes used as a entity with wider scope than ‘biosphere’.

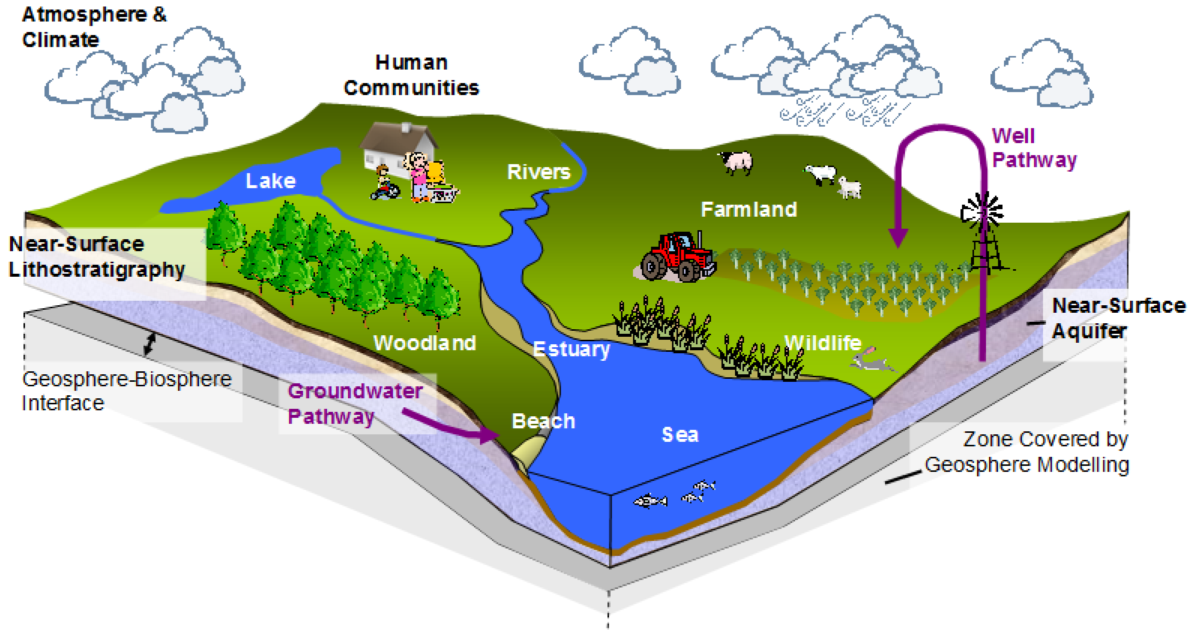

Figure 12.1-1. Principal components of the biosphere as identified (RWM 2016)

Depending on the methods used in dose assessment calculations for any potential releases from the repository it can be necessary to understand the surface environment more broadly than only in the immediate vicinity of the selected GDF site. NWS’s approach to biosphere assessment is defined as follows (RWM 2016) “Stylised assessment-level models of the biosphere are supported by more detailed process modelling which, in turn, builds on biosphere research and characterisation. An important consideration is the long timescales, meaning that research has included consideration of long-term climate change and landform evolution.” Overall relationships between biosphere research, characterisation and modelling is illustrated in Figure 12.1-2. Utilisation of regional analogues is related to the need arising from site characterisation. Biosphere characterisation is an ongoing work supporting the overall ESC development from the generic phase, through siting and to the finally selected site (Figure 3). Utilisation of regional analogues, e.g. for the climate predictions, is foreseen for the next phases of the NWS GDF programme, however, the site specific data will be in the focus towards the time after the site selection (see Figure 12.1-3).

Utilisation of regional analogues is well established within the international research community and the current NWS approach is based on the knowledge base developed in international projects (see RWM 2016). The usage of regional analogues is taken the furthest in Sweden and Finland, where the landscape evolution has a great emphasis in the safety assessments due to prominent process of land-uplift in the disposal site areas (Forsmark and Olkiluoto). Their adaptation of the landscape modelling approach that represents spatial variation in contaminant concentrations (see Avila et al. 2013 and Posiva 2014, 2023) has been acknowledged in NWS biosphere analysis approach (RWM 2016), but differencies remain in the level of simplification at the current NWS's generic assessment phase. In some cases, it can be difficult to define whether the biosphere studies are natural analogues or just a part of the scientific knowledge base (e.g. the MODARIA, see http://www-ns.iaea.org/projects/modaria/default.asp?l=116, and BIOPROTA, see http://www.bioprota.org/, projects, both discuss a wealth of data from biological sources that are used as analogue data in the ESC, but not necessarily seen as such, see also RWM 2016). In any case, there are many local considerations made regarding the data needs within the UK context. Therefore, it is not fruitful to list all regional analogues worldwide in this catalogue, but to mention those focused on the UK aspects.

The regional analogues supporting biosphere assessments are, in general, twofold:

- Those that help to understand future conditions on the surface environment at the site (due to external processes such as climate change).
- Those that help to understand radionuclide migration in case of releases.

For the former, work has been undertaken for UK context to estimate the evolution of the British landscape and its implications for the post-closure safety assessment of a GDF (Thorne & Towler 2017).

For the latter, NWS has been utilising the results of the NERC Lo-RISE: Studies of Speciation, Environmental Transport and Transfer of Key Radionuclides (C-14, U & Ra) in Naturally Contaminated Environments and Laboratory Studies) see RWM (2020) Section 1.2.3 and https://www2.bgs.ac.uk/rate/LO-Rise.html. The project studied ESC relevant radionuclides:

- Carbon-14, that occurs in nature but was also produced artificially due to nuclear weapon testing in 1950s and 1960s.
- Uranium, together with its decay product radium.

The project has produced a wealth of publications listed at: https://www2.bgs.ac.uk/rate/publications.html#LORISE. The review of the results of the Lo-RISE is planned to be undertaken and it is included in the current research and technology plan (RWM 2020, Task nr. 80.5.015).

The future research needs for the biosphere analogues will be defined in more detail after the site has been selected.

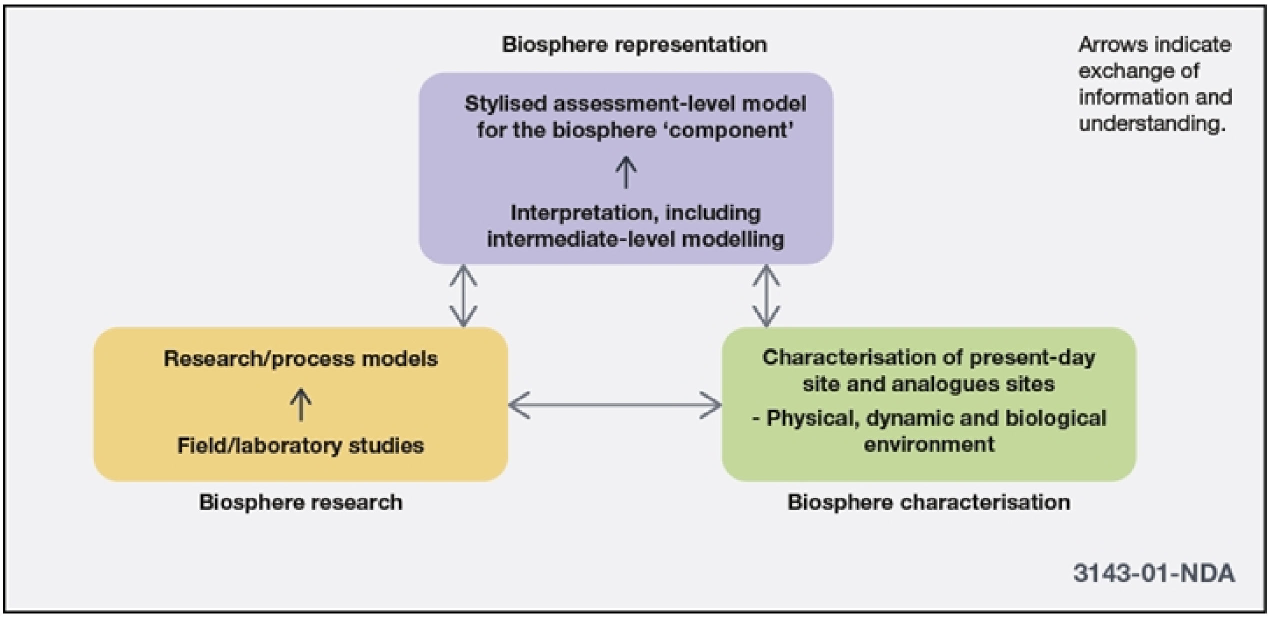

Figure 12.1-2. Relationship between biosphere research, characterisation and modelling (RWM 2016).

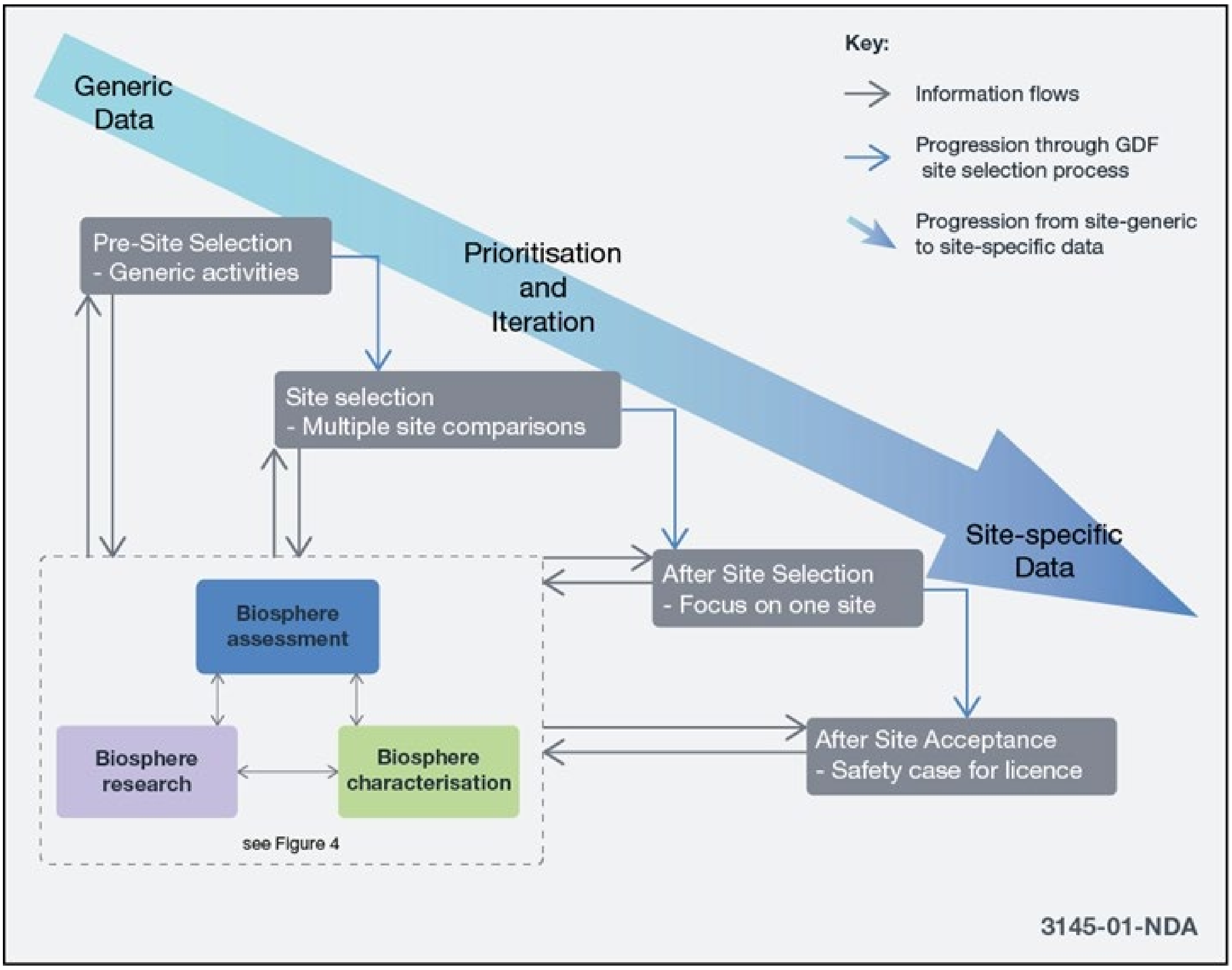

Figure 12.1-3. Prioritisation and iteration as the GDF site selection process moves forwards (RWM 2016).

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13 POTENTIAL FUTURE STUDIES

The NA catalogue contains examples of studies and related literature available for SC use as a part of the overall knowledge base. The very nature of the NA catalogue, as with any database, is such that it needs to be updated during the repository programme (see discussion in Reijonen & Alexander 2023a). While reviewing the existing literature is of importance, a gap analysis regarding the processes discussed in this report has also been undertaken. The gap analysis here has been focusing on pointing out potential sources of new NA information. The relevance of these potential future studies depends greatly on the focus and needs of the still evolving siting programme and safety case and this needs to be kept in mind when using this current version.

Topical potential future studies have been mentioned in the NA catalogue where appropriate. All proposed potential new work is listed here in tables corresponding to the chapters 2 to 11 of this report. Each main chapter has its own subsection here.

The recommendations for next steps are discussed in section 13.11.

13.1 Potential future studies - waste forms

Table 13.1-1. Potential future studies on the waste form processes.

ID number[22] and component in GDF	Processes of interest	Locality	Potential for new research	References
2.1.1-1 Waste form (glass)	Glass alteration	Broborg Hillfort, Knivsta, Sweden	Study funded by the USDoE in support of the safety case for the disposal of low-activity waste glasses at shallow depth at the Hanford site. Authors report an alteration layer on the 1500 year old glass and evidence of biological degradation of the glass. Of little relevance to GDF vitrified HLW.	Weaver et al. (2018)
2.1.1-2 Waste form (glass)	Glass alteration	Bet She'arim, Israel	The glass slab of Bet She'arim in Israel weighs some 8 tonnes and was fabricated around 1100 BP. Although it is unlikely that this particular example could be sampled for analysis, it was customary to break these slabs up into large chunks for transport to other workshops to be re-melted to make glass containers locally. It may be worth investigating sites of other glass foundries (such as at Bet Eli'ezer in Israel where 17 furnaces have been identified) to assess if a range of sizes of glass samples from the same block are available. Potentially, they could provide information on the influence of thermal cracking of vitrified waste by examining the effects of surface area on long-term alteration (although it should be noted	Freestone (2005)

[22] Refers to the section where mentioned in the main text of this report N.N.N and running number -N.

ID number[22] and component in GDF	Processes of interest	Locality	Potential for new research	References
			that the glass chemistry differs somewhat from vitrified HLW).	

References

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13.2 Potential future studies - containers

Table 13.2-1. Potential future studies on the waste form processes.

ID number[23] and component in GDF	Processes of interest	Locality	Potential for new research	References
3.1-1 Container (copper)	Corrosion	Michigan Keweenaw	Potential is being assessed in the MICA project.	Aaltonen et al. (2023) Included in the science and technology plan (RWM2020): B.5.2.3. (MICA)
3.1-2 Container (copper)	Corrosion under marine and higher salinity conditions	Mediterranean Sea	The world's oldest shipwreck (ca 3.6 ka old) was carrying copper ingots when it sank in the Aegean Sea. About 1.5 tonnes of copper has been recovered by the Akdeniz University Underwater Research Center, Turkey, but nothing has been reported to date.	
		Dead Sea	The world's oldest crown (ca. 6 ka old) is made of copper and was discovered on the shores of the Dead Sea. Nothing has yet been reported from the Dead Sea itself, but clearly significant amounts of copper were being produced in the area at the time, indicating the potential for future, more relevant, finds.	Moorey (1988)
3.1-3 Container (copper)	Microbially influenced corrosion (MIC)	Michigan, USA	Although not currently part of the MICA project, this would appear to be a suitable site to study MIC in the future.	Aaltonen et al. (2023)

[23] Refers to the section where mentioned in the main text of this report N.N.N and running number -N.

ID number[23] and component in GDF	Processes of interest	Locality	Potential for new research	References
3.2-1 Container (steel)	Corrosion	Broxmouth Hillfort, East Lothian, UK	Most NAs of steel corrosion are actually iron. However, steel artefacts were recovered from an Iron Age settlement in Scotland which was occupied between 2.2-2.8 ka ago, making this probably the oldest steel found to date. The steel is high carbon and these artefacts are the earliest evidence of sophisticated blacksmithing skills in the UK – and would appear to represent the oldest known steel in the world. As such, their potential significance for offering both technical support to those repository concepts which utilise steel for canisters or containers and as evidence of steel longevity for stakeholder communication purposes should not be overlooked.	Armit et al. (2013); Alexander (2023)
3.2-2 Container (steel)	Corrosion	Isle of Skye, UK	Approximately 61 million year old native iron microspherules are present in a meteoritic ejecta layer of volcanic ash altered to a potassium-rich clay not unlike bentonite. The iron spherules have native Fe(Si) cores, ferrosilicate glass mantles and oxidized FeO margins. These native iron spherules as significantly older than any previously reported native iron NAs and have possibly been protected by the bentonite-like host sediments. This combination is worth further examination to assess the possible role of the bentonite in protecting the iron from corrosion over time periods massively in excess of those of concern for a GDF.	Drake et al. (2018) Milodowski (2023)
3.2-3 Container (steel)	Corrosion	Mine waste waters	Green rust phases have been identified as specific secondary phases forming during the evolution of SF under GDF-relevant conditions (e.g., Curtius et al. 2010) and they are known to retard various radionuclides via a range of capture mechanisms (e.g., O'Loughlin et al. 2003; Pepper et al. 2003). According to King (2014), general corrosion of carbon-steel waste containers under the aerobic conditions assumed to exist immediately post-closure in a GDF is characterised by the formation of Fe(III) corrosion products. In Cl^-, SO_4^{2-}, or CO_3^{2-} containing waters, various forms of green rust (ferric oxide/hydroxide incorporating anions from the solution) may also form (Refait and Génin 1993). As the initially trapped O_2 is consumed, Fe(III) corrosion products will be transformed to magnetite, either by reaction with dissolved Fe(II) or by reductive dissolution coupled to C-steel dissolution and it is assumed that the previously entrapped radionuclides will be released to solution. However, recent examination of contaminated U mine waters (e.g., Johnson et al. 2015) indicates that green rust may persist for	Curtius et al. (2010) King (2014) O'Loughlin et al. (2003) Pepper et al. (2003) Refait & Génin (1993)

ID number[23] and component in GDF	Processes of interest	Locality	Potential for new research	References
			significant periods under anaerobic conditions. As such, future examination of green rust phases may reduce conservatism in current SF dissolution and release scenarios.	
3.2.2-1 Container (steel)	Corrosion	Experimental	The rate of corrosion is very different for laboratory studies where the iron surfaces are not confined (i.e. in free water), where it is constant, while, in soils, the confined surfaces indicate that the iron corrosion kinetics follow a parabolic different rate equation (time span ranging from 0.5 to 1700 years). Based on this it would be advisable to examine corrosion in the laboratory where samples are confined in bentonite.	Crossland (2005, 2006)

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13.3 Potential future studies - cementitious materials

Table 13.3-1. Potential future studies on the cementitious materials.

ID number[24] and component in GDF	Processes of interest	Locality	Potential for new research	References
4.1-1 Concrete containers, plugs and seals	Carbonation	Maqarin, Jordan	Neall and Johnson (2006) noted that, although the carbonation mechanism can be viewed as mainly a favourable phenomenon in the safety case which could "....to a large degree mitigate the potential for high pH alteration of the buffer.", it has generally been neglected in safety cases to date (although Höglund 2014 and Höglund et al. 2018 are rare cases where this has been taken into account to some degree). Recent, large-scale laboratory work (Collier et al. 2019) on forced carbonation of the porous grout Nirex Reference Vault Backfill (NRVB) has been carried out and carbonation was observed to impact both the mineral assemblage and porosity of the grout. It would be of value to support such short-term laboratory studies with NA data, but, currently, no directly relevant NA studies of carbonation exist, but the process could be studied at the Maqarin site in Jordan (cf. The preliminary study of Clark et al. 1994). At the Khushaym Matruk site in central Jordan, late-stage, carbonation products have been shown to be between 110,000 and 130,000 years old (Pitty & Alexander 2011), indicating the longevity of these carbonation phases.	Clark et al. (1994) Collier et al. (2019) Höglund (2014) Höglund et al. (2018) Neall & Johnson (2006) Pitty & Alexander (2011)
4.1.2-1 Low-pH concrete natural analogue for the long-term behaviour of GDF low-pH concretes	Longevity of low-pH concretes in marine and brine groundwaters	Puteoli, Italy	It has been speculated (Olsen et al. 2004) that the formation of natural concrete at sea level around Puteoli in Italy, formed when calcium-carbonate-saturated groundwaters seeped through pozzolana, may have suggested the formula for hydraulic mortar to Roman engineers.	Oleson et al. (2004)

[24] Refers to the section where mentioned in the main text of this report N.N.N and running number -N.

ID number[24] and component in GDF	Processes of interest	Locality	Potential for new research	References
			The long-term exposure of any such natural low-pH concretes at Puteoli to marine conditions (and possibly brines, due to the presence of many lagoons in the area) suggest these may be an appropriate analogy to examine the longevity of modern low-pH concretes when exposed to high salinity groundwaters (both marine and brines).	
4.1.2-2	Preservation of low-pH concrete	Multiple	Samples have been collected from a range of sites around the Mediterranean and the degree of preservation of the bulk concrete has been found to be remarkably high The noted differences in material handling (section 4.1.2) could be tested in two simple ways: • make modern low-pH concretes using the Roman handling methods as laid down in Vitruvius (27 BC) • make Roman concretes using today's handling methods (e.g. those used in Chandler et al. 2002). and then compare the physical and mechanical properties	This report, see section 4.1.2
4.1.3-1	Concrete longevity	Chile	The Maqarin, Jordan, site is currently difficult to access due to the ongoing conflict in neighbouring Syria. As such, the natural concretes which border the General Carrera Lake on the border of Chile and Argentina offer an alternative site to study concrete longevity. Currently, there is no detailed information available on the site.	Bell (2009)
4.1.3-2	Concrete stability under high stress	Jordan	Despite the point noted above, existing samples from Jordan (collated at the University of Jordan) could be used to study the impact of high stress on concrete. As noted above, there is no detailed information available on the site in Chile, so detailed assessment of the site would be necessary before initiating studies there.	Alexander et al. (2016) Bell (2009)
4.1.6-1	Microbial degradation of low-pH concrete	Oman	The results of the Oman microbial population study were produced some 35 years ago. They indicate that the alkaline conditions did not preclude the presence of iron- and sulphate-metabolising bacteria which are capable of causing iron corrosion and degradation of cementitious materials. It would be prudent to repeat such analyses using modern methods to re-assess the potential impact of such microbes on low-pH concretes.	Bath et al. (1987)
8.3-2	Cementitious colloids	Maqarin, Jordan	A preliminary assessment of cementitious colloids was carried out at the Maqarin site, but samples were collected at a highly alkaline (pH12.5) groundwater seep in an	Wetton et al. (1998)

ID number[24] and component in GDF	Processes of interest	Locality	Potential for new research	References
Colloid transport analogues - overview			open adit, so contamination with atmospheric CO_2 could not be avoided and introduced sampling artefacts. It would be worthwhile sampling again under controlled conditions at the original pH12.5 seep (Maqarin Eastern Springs site) and also at the pH12.9 seeps at the Maqaein Western Springs site.	

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13.4 Potential future studies - clays

Table 13.4-1. Potential future studies on the clays.

ID number[25] and component in GDF	Processes of interest	Locality	Potential for new research	References
5.1.2-1 Clay barriers (EBS, buffer / backfill)	Thermal alteration	Cabo de Gata, Spain	Bentonite outcrops occurr in the Cabo de Gata, Almería, southern Spain. These were formed when pyroclastic rocks (c. 11.6 million year old) were altered to bentonite by low temperature (<70 °C) saline waters and subsequently intruded by dacite intrusions around 11.3-10.8 million years ago. This site is of interest as an analogue because the smectite-rich rocks can be compared directly to bentonite backfill materials. Though the heat pulse through the bentonites probably lasted some tens of years, it has so far not been possible to establish thermal profiles away from the intrusions. Therefore, at the moment we cannot uniquely attribute observed changes in the bentonite properties to specific temperatures. Would be of value to sample again with focus on assessing the temperatures of reaction.	Pérez del Villar et al. (2005)
5.1.2-2 Clay barriers (EBS, buffer / backfill)	Thermal alteration	Ishrini, Libya	Bentonite showing alteration due to basalt dome and dykes. Alteration described only for parts experiencing temperatures > 190 °C. Bentonite outside the sampled range could be sampled for temperatures < 190 °C, with more relevance to the GDF context.	Kolaríková & Hanus (2008)
5.1.2-3 Clay barriers (EBS, buffer / backfill)	Thermal alteration	Busachi, Sardinia	Heat induced dissolution of smectite observed at 150 °C to 200 °C as well as precipitation of siliceous material (cementation). The relevant ground truthing of the site was not undertaken. To obtain better data from the analogue it would be advisable to apply a range of more relevant analytical techniques to better understand the site history and temperature profiles.	Pusch & Karnland (1988)
5.1.3-1 Clay barriers (EBS, buffer / backfill)	Deformation Shearing	Kato Moni, Cyprus Other localities with pelletal/granular bentonites	Further examination of the "pellet" bentonite at Kato Moni would be useful as the inherited structure appears to spread the shear through anastomising shear plane networks, potentially minimising disruption of the bentonite fabric. This could be an alternative bentonite design option, so avoiding a potential redesign of existing waste containers. In addition to Kato Moni, other bentonites with pelletal (or	Alexander et al. 2017

[25] Refers to the section where mentioned in the main text of this report N.N.N and running number -N.

ID number[25] and component in GDF	Processes of interest	Locality	Potential for new research	References
			otherwise heterogenous) textures can be considered.	
5.1.3-2 Clay barriers (EBS, buffer / backfill)	Deformation Shearing Self-sealing (homogenisation)	Tsukinuno, Japan	The IBL project (www.iblproject.com) focusses on studying long-term, safety-relevant processes, including studying micro-scale properties of sheared bentonites.	Reijonen & Alexander (2023b)
5.1.3-3 Clay barriers (EBS, buffer/backfill)	Deformation Shearing	e.g., Cyprus	Bentonites are investigated for their geotechnical significance routinely (e.g., in Cyprus) and collaboration with organisations collecting this data would be useful to form spatial coverage to the dataset in addition to targeted sampling.	Alexander et al. (2017)
5.1.4-1 Clay barriers (EBS, buffer / backfill) 8.3-2 Colloid transport analogues - overview	Cation exchange, chemical erosion	Tsukinuno, Japan	The IBL project (www.iblproject.com) focusses on studying long-term, safety-relevant processes, including cation exchange, chemical erosion and colloid transport aspects of bentonites. Similar studies would be possible also at other bentonite sites.	Reijonen & Alexander (2023b)
5.1.5-1	Stability of smectites in crystalline bedrock (including potentially dilute conditions)	Sweden and Finland	KINA project (Sweden) BROCTIO project (Finland) (https://www.gtk.fi/en/research-project/kyt-broctio-bentonite-rock-interaction/)	KINA (2022)
5.1.6-1	Saline reactions	Bentonite studies, several potential sites	Bentonite analogue studies in suitable formations where basinal brines occur. Proposals have been made for example in Laine & Karttunen (2010) regarding Wyoming bentonite, but other localities can be sought for. Reijonen & Alexander (2015) have also suggested studies on smectite occurrences in Michigan basin.	Laine & Karttunen (2010) Reijonen & Alexander (2015)
5.1.6-2	Saline reactions	Fracture filling mineral studies, several potential sites	Studying the sites where saline groundwaters /brines occur at depth together with fracture smectites have been proposed as an alternative way of studying the saline reactions for bentonite buffer (see e.g. Reijonen & Alexander 2015).	Reijonen & Alexander (2015)
5.1.7-1	Saturation/desaturation	Tsukinuno Japan (other sites also possible)	The IBL project focusses on studying long-term, safety-relevant processes, including saturation state – natural saturation states of bentonite in differing environments (on the surface and at varying depths underground, under dry and wet host rock conditions) for comparison with current SC assumptions (based on short-term, laboratory and underground rock laboratory tests);	Reijonen & Alexander (2023b)
5.1.8-1	Cu-bentonite interaction	Tasmania	Native copper occurs in clays in Tasmanian copper clays.	e.g. Corbett (2011)

ID number[25] and component in GDF	Processes of interest	Locality	Potential for new research	References
5.1.8-2	Fe-bentonite interaction	Sweden	KINA project.	Included in the science and technology plan (RWM 2020): B.5.4.4. (KINA)
5.1.9-1	Microbial activity in bentonites	Tsukinuno, Japan Sweden	The topic is included in both IBL and KINA project plans	Included in the science and technology plan (RWM 2020): B.5.4.4. (KINA) B.5.4.5. (IBL)

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13.5 Potential future studies - host rocks

HSR: In the current situation in the UK GDF programme, it is recommended that a considered approach is implemented. Although there are limitations on the use of existing geological data, those on HSR can be carefully extrapolated to provide initial information on what could be expected at GDF depths (taking, for example, the presence of secondary phases produced by weathering etc. into account). Potential topics for investigation are listed in Table 13.5-1 (IDs 6.2-1 to 6.2-8).

LSSR: (Mercia Mudstone Group) In the current situation in the UK GDF programme, it is recommended that a considered approach is implemented. Although there are limitations on the use of existing geotechnical data, those on the Mercia Mudstone Group mineralogy can be extrapolated to provide initial information on what could be expected at GDF depths (taking, for example, the presence of secondary phases produced by weathering etc. into account). Potential sites for investigations are listed in Table 13.5-1 (IDs 6.3.3-1 to 6.3.3-7).

LSSR: (Evaporite). In the current situation in the UK GDF programme, it is recommended that a considered approach is implemented. Although there are limitations on the use of existing geological data, those on evaporites can be carefully extrapolated to provide initial information on what could be expected at GDF depths (taking, for example, the presence of secondary phases produced by weathering etc. into account). Potential topics for investigation are listed in Table 13.5-1 (IDs 6.4-1 to 6.4-9).

Table 13.5-1. Potential future studies on the host rocks.

ID number[26] and component in GDF	Processes of interest	Locality	Potential for new research	References
6.2-1	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	HSR – outcrops in Cumbria and Lincolnshire	While the number of relevant sites is limited, outcrops do exist in Cumbria and Lincolnshire and these should be investigated to provide initial impressions for NWS' and contractors' staff. Clearly, the focus shall be on outcrops of relevant HSR, but preferably at some distance from the potential GDF sites As noted in section 6.3.3.3, the use of data (and/or future samples) from quarries and shallow boreholes must be treated with caution as certain processes which occur near-surface are irrelevant to GDF depths. As long as these limitations are kept in mind, examination of outcrops is always of value	Reijonen & Alexander (2023a, sections 3.3.1 and 3.3.2)
6.2-2	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	HSR – Road and rail tunnels	Setting aside the increased likelihood of accidental death and injury of field staff from vehicles, such environments are more likely to provide more relevant samples/information than surface outcrops Unlike in 6.3.3-2, the high formation strength of HSR means there is a higher probability of accessing unlined tunnels, especially when they are older tunnels. But if they are lined or shotcreted, drilling through the concrete to obtain sample cores is not difficult once agreement with the proprietors has been reached	Cantine (2021) Bradbury et al. (1990)
6.2-3	Formation properties (including	HSR – Hydro-power plant	As above, but with less danger from vehicles	

[26] Refers to the section where mentioned in the main text of this report N.N.N and running number -N.

ID number[26] and component in GDF	Processes of interest	Locality	Potential for new research	References
	geotechnical, lithological, mineralogical, geochemical etc.)	access and pipeline tunnels		
6.2-4	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	HSR – Resource exploration records	Although many cores and associated information are held at BGS, Keyworth, some material is not. Such information is generally deemed to be commercial-in-confidence by the owners and so difficult to access, but the first author is aware of two national WMOs which have reached agreement with resource exploration companies to exchange data for use confidentially. Crucially, this use of information was also agreed in advance with the relevant national regulators	
6.2-5	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	HSR – Abandoned mines	BGS, Keyworth, currently hold information on abandoned mine workings for haematite, gypsum, limestone, baryte and metalliferous minerals in Cumbria and Lincolnshire. Clearly this calls for a full occupational health safety assessment beforehand, but such facilities do exist and are worth detailed evaluation as the in situ conditions are much more likely to be GDF-relevant	Cumbria: https://data.gov.uk/dataset/096d8d11-b9ca-49db-8cef-9ea1dc57c06b/plans-of-abandoned-mines-other-than-coal-cumbria Lincolnshire: https://discovery.nationalarchives.gov.uk/details/c/F218065
6.2-6	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	HSR – Active mines		
6.2-7	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	HSR – Future mines		
6.2-8	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Comparison with other coastal sites internationally	As noted in section 6.2.1, the Olkiluoto site is not unique in displaying both long-term stability at GDF-relevant depths and significant hydrological and hydrogeochemical buffer capacity (section 6.2.3) against potential future disturbances. A useful stakeholder confidence building exercise would be to develop the current arguments on this further	Posiva (2023) Alexander et al. (2023)
6.3.3-1 LSSR	Formation properties (including	Mercia Mudstone Group –	While the number of relevant sites is limited, outcrops do exist in Cumbria and Lincolnshire and these should be investigated to provide initial	Reijonen & Alexander (2023a, sections 3.3.1 and 3.3.2)

ID number[26] and component in GDF	Processes of interest	Locality	Potential for new research	References
	geotechnical, lithological, mineralogical, geochemical etc.)	outcrops in Cumbria and Lincolnshire	impressions for NWS' and contractors' staff. Clearly, the focus shall be on outcrops in the relevant Mercia Mudstone Group depositional basins, but preferably at some distance from the potential GDF sites As noted in section 6.3.3.3, the use of data (and/or future samples) from quarries and shallow boreholes must be treated with caution as certain processes which occur near-surface are irrelevant to GDF depths. As long as these limitations are kept in mind, examination of outcrops is always of value.	
6.3.3-2 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Mercia Mudstone Group – Road and rail tunnels	Setting aside the increased likelihood of accidental death and injury of field staff from vehicles, such environments are more likely to provide more relevant samples/information than surface outcrops. The generally low formation strengths of the Mercia Mudstone suggest that most tunnels which intersect the host rock will be lined or shotcreted, but drilling through the concrete to obtain sample cores is not difficult once agreement with the proprietors has been reached.	Cantine (2021) Bradbury et al. (1990)
6.3.3-3 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Mercia Mudstone Group – Hydro-power plant access and pipeline tunnels	As above, but with less danger from vehicles	
6.3.3-4 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Mercia Mudstone Group – Resource exploration records	Although many cores and associated information are held at BGS, Keyworth, some material is not. Such information is generally deemed to be commercial-in-confidence by the owners and so difficult to access, but the first author is aware of two national WMOs which have reached agreement with resource exploration companies to exchange data for use confidentially. Crucially, this use of information was also agreed in advance with the relevant national regulators	
6.3.3-5 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Mercia Mudstone Group – Abandoned mines	Clearly this calls for a full occupational health safety assessment beforehand, but such facilities do exist in the Mercia Mudstone Group and are worth detailed evaluation as the in situ conditions are much more likely to be GDF-relevant	See 6.2-5 for details Macmillen, (2009)
6.3.3-6 LSSR	Formation properties (including geotechnical,	Mercia Mudstone Group –	There are currently no mines actively exploiting the Mercia Mudstone Group – it outcrops in the vicinity of the Boulby mine, but it is in the overlying strata. All	

ID number[26] and component in GDF	Processes of interest	Locality	Potential for new research	References
	lithological, mineralogical, geochemical etc.)	Active mines	mine workings are in the deeper (Permian) strata and the shaft is lined along its entire depth	
6.3.3-7 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Mercia Mudstone Group – Future mines	The nearby Woodsmith mine is driving two shafts (service and production) to a depth of 1600 m (Figure 13.5-1), also potentially allowing access to the Merci Mudstone Group above the evaporite deposits. As this construction work is currently ongoing, it is crucial to contact Anglo-American on this immediately to initiate and develop a mutually beneficial relationship	https://uk.angloamerican.com/the-woodsmith-project
6.3.3-8	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Comparison with other coastal sites internationally	As noted in section 6.2.1, the Olkiluoto site is not unique in displaying both long-term stability at GDF-relevant depths and significant hydrological and hydrogeochemical buffer capacity (section 6.2.3) against potential future disturbances. A useful stakeholder confidence building exercise would be to develop the current arguments on this further	Posiva (2023) Alexander et al. (2023)
6.4-1 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Evaporites – outcrops in Cumbria and Lincolnshire	As in 6.3.3-1 above, but note that any evaporite outcrops in the UK tend to be heavily weathered and probably unusable	
6.4-2 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Evaporites – Road and rail tunnels	As in 6.3.3-2 above	
6.4-3 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Evaporites – Hydro-power plant access and pipeline tunnels	As in 6.3.3-3 above	
6.4-4 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Evaporites – Resource exploration records	As in 6.3.3-4 above, but several other organisations are currently exploiting evaporites in the UK, providing more numerous opportunities for collaboration	www.compassminerals.com https://irishsaltmining.com https://www.icl-uk.uk

ID number[26] and component in GDF	Processes of interest	Locality	Potential for new research	References
6.4-5 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Evaporites – Abandoned mines	As in 6.3.3-5 above. In addition, as noted in section 6.4.1.3, future opportunities may exist to examine abandoned oil and gas storage facilities in evaporites (for example, to assess the evaporite host rock long-term stability and the stability of the overall setting).	
6.4-6 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Evaporites – Active mines	The Boulby mine is actively exploiting evaporite reserves (but see comment in 6.3.3-6 on the formation of interest) and they already collaborate with academia in their underground laboratory, suggesting the organisation is open to co-operation In addition, several other active mines (e.g. the Winsford mine in Cheshire) exist, providing more numerous opportunities for collaboration. In addition, as in 6.4-6, collaboration with operational oil and gas storage facilities could be advantageous.	https://www.icl-uk.uk/about/ https://www.icl-uk.uk/undergroundlab/ https://www.compassminerals.com/who-we-are/locations/winsford-cheshire-u-k-2/
6.4-7 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Evaporites – Future mines	The Woodsmith mine is driving two shafts (service and production) to a depth of 1600 m (Figure 13.5-1) and will exploit evaporite deposits. As noted in 6.3.3-7, construction work is currently ongoing, so it is crucial to contact AngloAmerican on this immediately to initiate and develop a mutually beneficial relationship	https://uk.angloamerican.com/the-woodsmith-project
6.4-8 LSSR	Formation properties (including geotechnical, lithological, mineralogical, geochemical etc.)	Alternative data sources	As noted in section 6.4.1.3, little attention has been paid to potential data sources in the oil and gas industries. An intensive data mining exercise of this resource could prove to be highly profitable	
6.4-9	Formation properties (including geotechnical, lithological, mineralogical,	Comparison with other coastal sites internationally	As noted in section 6.2.1, the Olkiluoto site is not unique in displaying both long-term stability at GDF-relevant depths and significant hydrological and hydrogeochemical buffer capacity (section 6.2.3) against potential future disturbances. A useful stakeholder confidence building exercise would be to develop the current arguments on this further.	Posiva (2021) Alexander et al. (2022)

ID number[26] and component in GDF	Processes of interest	Locality	Potential for new research	References
	geochemical etc.)			

Figure 13.5-1. artists impression of the service (far left) and production (middle) shafts in the Woodsmith mine at Dove's Nest Farm, near the village of Sneaton, Yorkshire. Image courtesy Anglo-American plc.

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13.6 Potential future studies - post-closure processes affecting the host rock and/or repository

Table 13.6-1. Potential future studies on the post-closure processes affecting the host rock and /or GDF.

ID number[27] and component in GDF	Processes of interest	Locality	Potential for new research	References
7.1.3-1 Host rock	Post-closure processes affecting host rock Seismicity, glacially induced seismicity	UK	A significant amount of research has been carried out in this field in northern Fennoscandia. Glacially induced faults could be potentially studied in UK as well (although no sites have been identified in this report).	

References

13.7 Potential future studies - radionuclide retardation

Table 13.7-1. Potential future studies on radionuclide retardation.

ID number28 and component in GDF	Processes of interest	Locality	Potential for new research	References
8.2-1 **Host rock**	^{226}Ra retardation in the GDF host rock	Same formation as the GDF host rock	Although significant improvements in the understanding of ^{226}Ra retardation processes have been made in the past few years, it is clear that short-term laboratory experiments (and the associated modelling studies) require additional support from NA studies to provide data of direct relevance to a GDF SC. To do this successfully, the distribution of ^{226}Ra in the groundwater, porewater and rock of a potential GDF host rock formation would be studied to provide direct evidence of the likely sites and mechanisms of ^{226}Ra retardation at the actual repository site itself. This regional analogue approach examines the actual GDF host rock formation at a site nearby the actual or proposed GDF and has the clear advantage that the processes and mechanisms controlling ^{226}Ra retardation at the regional analogue will be the exact same as those at the GDF site itself.	Alexander (2022) Yamada & Ota (2015)

[27] Refers to the section where mentioned in the main text of this report N.N.N and running number -N.
[28] Refers to the section where mentioned in the main text of this report N.N.N and running number -N.

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13.8 Potential future studies - other EBS materials

Table 13.8-1. Potential future studies on the other EBS materials.

ID number[29] and component in GDF	Processes of interest	Locality	Potential for new research	References
9.1-1 Other EBS materials for sealing: crushed rock	Stability	Several potential sites	Clastic sediments can provide useful information regarding the geochemical evolution of these materials, but as noted by SKB (EBSSR30), no specific natural analogues have been investigated concerning the geochemical processes expected in excavated tunnels and backfilled with crushed rock. However, the processes will be equivalent to those occurring in organic matter-bearing aquifers, as gravel aquifers or backfilled abandoned mines where organic matter is present (Postma and Jakobsen 1996, Jakobsen and Postma 1999, Banwart 1999, Hartog et al. 2004, Massmann et al. 2004, Park et al. 2006, Jakobsen and Cold 2007). In these systems, reducing conditions are maintained through different types of bacterially mediated organic matter degradation reactions. The specific type of organic matter degradation depends on the type and amount of organic matter as well as on the dominant electron acceptor in groundwater.	SKB (2010) Postma & Jakobsen (1996) Jakobsen & Postma (1999) Banwart (1999) Hartog et al. (2004) Massmann et al. (2004) Park et al. (2006) Jakobsen & Cold (2007)
9.1-2 Other EBS materials for	Stability	Several potential sites	Many natural bentonites and clay formations with a swelling clay component contain various mixtures of clastic materials.	See Posiva (2021) for short overview

[29] Refers to the section where mentioned in the main text of this report N.N.N and running number -N.

ID number[29] and component in GDF	Processes of interest	Locality	Potential for new research	References
sealing: clay aggregate mixtures			Depending on the selected design, it is possible to look for NA sites that focus on materials closer to the mixtures than pure clays.	
9.1-3 Other EBS materials for sealing: bentonite pellets	Pellet stability	Several potential sites	The Kato Moni (Cyprus) study identified micro pellets that affect the rheological properties of the bentonite. More information would be useful to assess the potential of pellet use in shear displacement prevention (especially for bentonite seals). In addition, potential impact of pellet coating has been identified as an area of potential NAs (proof of concept needed). Reworked lapilli-derived bentonites identified, but proof of concept needed.	Alexander (2018)
9.1-4 Other EBS materials for sealing: bentonite	Bentonite-cement reactions	Khushaym Matruk site in central Jordan	A focussed study of potential bentonite-OPC reaction at the Khushaym Matruk site in central Jordan should be undertaken if NA studies of bentonite-OPC reaction are required.	Alexander (2018)
9.1-5 Bentonite	Bentonite – metal reactions	Several potential sites	For bentonite-iron interaction: observations from a study in the Philippines made *en passant* may be of relevance, as could a study from Spain, which could address bentonite uptake of iron from groundwaters, rather than corroding materials in the borehole. For bentonite-copper interaction, the work on the Littleham Cove copper-uranium concretions could be re-assessed with focus on the enveloping mudstone, rather than on the copper corrosion products as per the original study. NWS is already involved in the KINA study of bentonite-iron interaction.	Alexander (2018)
9.1-6 Bentonite – host rock reactions	Limestone	Cyprus	There are suggestions that reaction between the bentonite and the overlying limestone has degraded the bentonite to some extent, as the bentonite immediately below the limestone has been reported to be more friable island-wide (A.Siathas, pers. comm., October 2015). More data would be needed for assessing the observation both areally and against distance from the limestone/bentonite contact. Similar assessments could include alternative host-rock types (e.g. underlying pillow lavas). Observation also made on more Na-bearing bentonite at depth underlying the Ca-bentonites at Kato Moni site.	Alexander (2018) Alexander et al. (2017)
9.1-7 Bentonite – host rock reactions	Shale	Tsukinuno, Japan	IBL site is being studied further.	Reijonen & Alexander (2023b)

ID number[29] and component in GDF	Processes of interest	Locality	Potential for new research	References
9.1-8 Bentonite groundwater interaction	Various groundwater chemistries	Several sites available	Specifically, dilute and brine groundwater compositions could be further studied via analogues.	Alexander (2018) Reijonen & Alexander (2015)
9.1-9 Bentonite – magnetite reactions	Rare occurrence of magnetite rich bentonites	One site identified in Greece Kiruna, Sweden	NWS also involved in the KINA project	Alexander (2018)
9.1.1-10 Bentonite-sand mixtures	Smectite – quartz interaction; Gas permeability; Saturation; erosion	Identified in Cyprus, but occurs elsewhere	Focussed studies on various bentonite – sand mixtures yet to be made. It is possible in the future to find analogous bentonites for many compositional variations. In addition to mineralogical interaction, natural bentonites (with or without sand) could be studied for the gas and water uptake/migration processes (also in connection to erosion).	Alexander (2018)
9.1.-11 OPC in boreholes	Longevity, precipitation, carbonation	Jordan Scawt Hill in Northern Ireland	Further understanding on precipitation of secondary cement phases (and pore blocking) could be obtained from the natural OPC sites in Jordan and Scawt Hill in Northern Ireland. See also section 13.3 in general.	Alexander (2018)
9.1-12 Low alkali cements	Longevity	Natural low alkali cements could be located	Italy is the most likely site, no proof of concept.	Alexander (2018)
9.1-13 Barite stability with cements	Longevity	Jordan	A targeted examination of the barite would be necessary to provide quantitative NA support. In addition, there would appear to be barite-natural cement zones in the North Pennine Orefield (UK) which could benefit from more detailed examination.	Alexander (2018)
9.1-14 Graded silica	Longevity	No specific sites mentioned	The physical properties of non-glacial, non-cemented loess may not be unlike Sandaband™(graded silica used in oil borehole seals). Although little information currently exists regarding the behaviour of such loess in boreholerelevant settings, it is suggested that enough background information exists on the geotechnical properties of the material that an appropriate setting could be established where the long-term properties of the material could be assessed as an analogy for Sandaband™.	Alexander (2018)
9.1-15 Other EBS materials for sealing: bitumen	Durability of bitumen	Athabasca Basin Utah Sweden Dead Sea	Several localities are known, but no dedicated studies have been undertaken.	Kremer & Alexander 2015

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13.9 Potential future studies – operational analogues

For NWS, potential exists to include investigations mines that are in similar rock types as the potential repository sites (see also Chapter 6). From such sites, valuable knowledge could be gained regarding the effects of the underground openings on the overall host rock conditions, specifically considering mechanical and groundwater stability issues (and gas in some cases).

Table 13.9-1. Potential future studies for operational analogues.

ID number[30] and component in GDF	Processes of interest	Locality	Potential for new research	References
10-1 Concrete (container, tunnel supports, plugs and seals)	Microbial degradation	Maqarin, Jordan	The microbial studies at the Maqarin site were carried out to assess the activity of microbes under alkaline conditions (NB pH of the groundwaters is between 12.5 and 12.9). The fact that the system is aerobic and that the alkaline conditions proved no hinderance to microbial activity suggests that further work at the site would be of use in assessing potential microbial degradation of concrete during any extended GDF operational phase.	West et al. (1992) Coombs et al. (1998)
10-2 GDF	The implications of the investigation, construction, operation and closure of a GDF on the Environment.	Other GDF sites	Site investigation and construction of other GDF's (e.g Olkiluoto), underground laboratories, mining operations etc, can be used as analogues to provide insight of the potential environmental impacts.	
10-3 GDF	The implications of natural and other external hazards	Not defined here, depends greatly on process in question	Regional analogues (for example impact of GDF construction and operational phase hazards on the host rock and EBS) could be studied for overview on the potential processes of interest.	See Alexander & Neall (2007) for example (Olkiluoto case study)
10-4 GDF	The impact of naturally pressurised gas pockets	Not defined here, depends greatly on process in question	Any mining experiences of similar geological environments as the planned host rock can provide valuable information on potential effects of formation gas.	

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[30] Refers to the section where mentioned in the main text of this report N.N.N and running number -N.

13.10 Potential future studies – whole system performance

No new studies of whole system performance are currently foreseen.

13.11 Potential future studies – biosphere

As discussed in chapter 12, the future research needs for the biosphere analogues will be defined in more detail after the site has been selected.

14 CONCLUSIONS

14.1 NA Catalogue update

The catalogue of NAs presented here provides an update based on a review of the existing catalogue (Milodowski et al. 2015) and added information from the literature. The update has been based on the overall guidelines, that arose from the strategic review of NA requirements in the future UK national programme (Reijonen & Alexander 2023a), resulting in the following updates:

- NA data presented is assessed based on its relevance to the present status of the GDF program (at the time of writing, generic safety case)
- Topical additions have been made on the subjects that could benefit from NAs in the future, or that were not been included in the discussion in the earlier version
- The catalogue is compiled in a form that can be applied to both traditional report formats and interactive content management tools (such as Visi)
- The information presented can be linked to other parts of the ESC in the future or other documentation related to this part of the overall knowledge base

During the update, relevance screening was carried out, meaning that some information has been substituted[31] as it was felt to be less relevant to the current and foreseen requirements of the UK national programme. Some of the information in Milodowski et al. (2015) has been retained, but its role in the catalogue may have changed. Component level gap analysis has been performed leading to additions at the topical level. In addition to this, the international FEP database (NEA 3.0) has been mapped to the contents of the catalogue. This mapping is a first step towards integration of the NA catalogue to the overall knowledgebase that is linked to the other related components within it.

The catalogue is supported by a chapter on potential future studies (chapter 13) that provides insight on NA research needs in general, based on the current and foreseen requirements of the UK national programme. The potential future work presented does not place the items in order of merit, since this will depend on the overall safety case research requirements in the future.

14.2 Way forward

The catalogue is not a static database, rather the contents should be reviewed regularly in line with the rest of the knowledge base. Any potential future development of the catalogue should be based on the updated needs arising from the national GDF programme.

A strategy for implementing NA work during the forthcoming years by NWS has been discussed in Reijonen & Alexander (2023a). This strategy is based on the continuous update of the NA catalogue / database in a systematic manner.

[31] While, at the same time, ensuring the substituted information is clearly recorded in the system (Reijonen & Alexander, 2023a)

New work on NA research needs to be assessed together with NWS' overall research and technical development plans. However, some aspects here are foreseen to be of specific interest regarding the site selection phase.

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