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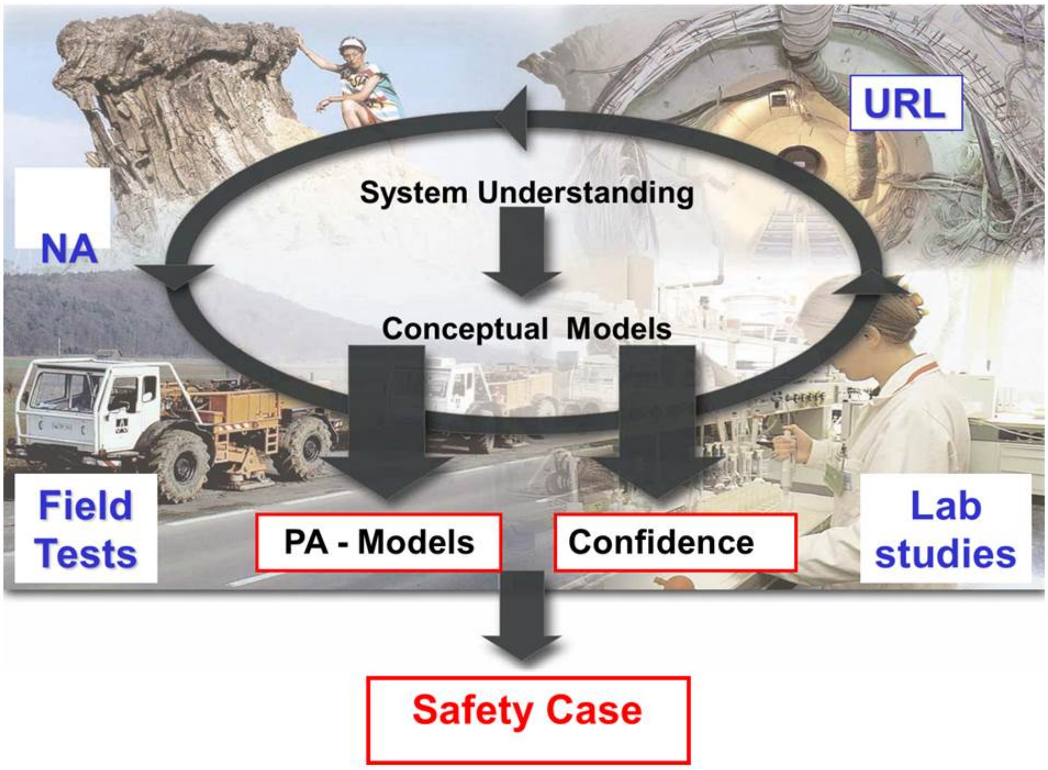
A Catalogue of Analogues for Radioactive Waste Management

Minerals and Waste Programme

Commissioned Report CR/15/106



BRITISH GEOLOGICAL SURVEY

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A Catalogue of Analogues for Radioactive Waste Management

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Key words

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Front cover

Illustration showing the interaction between natural analogue studies, field and laboratory experiments, and their input to system understanding and the development of conceptual models (©Bedrock Geosciences)

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Foreword

This report is the published product of a study by the British Geological Survey (BGS) commissioned by Radioactive Waste Management (RWM). The report is a catalogue of examples from the natural environment, archaeological and man-made systems that illustrate aspects of the performance of potential geological disposal facility (GDF) systems for radioactive waste over long time scales, and which can be used to support the safety case. This report presents a series of summary descriptions as stand-alone data sheets for each analogue system, with references to additional sources of information where more detailed accounts can be found.

Information from a wide range of relevant national and international programme published reports have been used to prepare this catalogue, which is intended for a general readership.

Acknowledgements

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Contents

Summary

Natural, archaeological and older industrial systems can provide an important source of supplementary evidence that can be used in support of a safety case for a geological disposal facility (GDF) for radioactive wastes. These systems may not exactly mimic a GDF. However, they provide insights and information on the long-term processes, and physical and chemical behaviour, affecting many aspects of the engineered and geological barrier, over the very long timescales relevant to the post-closure timeframe for a geological disposal facility. Analogues can be helpful in demonstrating understanding of aspects of GDF performance and provide evidence that certain materials can persist for long periods. However, they do not provide conclusive proof that these materials will maintain their required functions for the required periods in the environments of a particular GDF, as the conditions under which the analogue material has persisted may not match those expected to occur or evolve in a GDF.

This catalogue of analogues presents examples from the natural environment (including archaeological sites and older industrial sites) that illustrate aspects of the performance of potential GDF systems over long time scales, and which can be used to support a safety case. Specifically, it presents a series of summary descriptions as stand-alone data sheets for each analogue system, with references to additional sources of information where more detailed accounts can be found. The analogues are grouped according to the main GDF safety barrier functions which they demonstrate applicability. The catalogue does not aim to provide a comprehensive list of all known analogues; it presents a spread of examples that relate to the main safety barrier functions of a GDF.

The catalogue is presented at a level that is appropriate for an audience involved in the waste management process who are not necessarily specialists in analogue systems. It is also suitable for the general scientific audience and may prove a useful background resource for undergraduates.

1 Introduction

1.1 OVERVIEW

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 will contain a collection of arguments and evidence, both quantitative and qualitative, that collectively aim to demonstrate long-term safety can be achieved and maintained.

It is not possible to simulate in, or extrapolate from laboratory studies, all of the very long-term processes that might affect the safety performance of a geological disposal facility (GDF) for radioactive waste. In this context, some natural systems (including archaeological and older industrial systems) can be helpful as 'analogues' in demonstrating understanding of aspects of GDF performance and can provide evidence that certain materials can persist for long periods relevant to the post-closure timescale for a GDF, or that e.g. certain processes can be inferred to occur at rates that are slow in comparison with timescales considered in the safety case.

The generally accepted definition of the term "natural analogue" is "*...an occurrence of materials or processes which resemble those expected in a proposed geological waste repository*" [1]. This has subsequently been refined by an International Atomic Energy Agency review group [2]. The progressive refinement of the definition reflects a maturation in the understanding and appreciation of natural analogues. In essence, natural analogue 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 repository to develop and test models appropriate to performance assessment work.

Analogues, whether natural, archaeological and industrial, can be helpful in demonstrating understanding of aspects of GDF performance and can provide evidence that certain materials can survive for long periods. However, they do not provide conclusive proof that these materials will survive for the required periods in the environments of a particular GDF, as the conditions under which the analogue material has survived may not match those expected to occur or evolve in a GDF. Therefore, analogues should only be used with caution, and can only ever provide supporting arguments in a safety case. Nevertheless, appropriate analogues can be helpful in providing a long-term practical demonstration to support the theoretical and mathematical arguments.

For this reason, natural, archaeological and industrial analogue studies are often used as one of several multiple lines of reasoning that, when combined, help to build confidence in process understanding as considered in the safety case. Information derived from investigations of the natural system at actual GDF sites (termed 'self-analogues') rather than other locations can also

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1 Côme, B. & Chapman, N.A. (*editors*) (1986) Natural Analogue Working Group; First Meeting, Brussels, November 1985. *CEC Nuclear Science and Technology Report*, EUR 10315, Commission of the European Communities, Luxembourg.

2 IAEA (1989) Natural Analogues in Performance Assessments for the Disposal of Radioactive wastes. *IAEA Technical Report*, **304**, International Atomic Energy Agency, Vienna.

contribute valuable information to the safety case in regard to the long-term performance of the geological barrier.

Radioactive Waste Management Limited (RWM) commissioned the British Geological Survey (BGS) to compile this catalogue of analogue examples from natural, archaeological and industrial systems to illustrate aspects of the performance of potential disposal systems over long time scales, and which can be used to support the safety case. Information from a wide range of relevant national and international programme published reports have been used to prepare this catalogue. A range of analogues has been selected to illustrate different components of a GDF system that could be used to support a safety case and as such the catalogue is not an exhaustive list of all known analogues.

1.2 USE OF NATURAL ANALOGUES IN A SAFETY CASE

Analogues can be used in support of a safety case in several ways, with the input ranging from qualitative to quantitative. Examples cover many aspects of the safety case:

- Analogues can increase our confidence in the safety case by identifying mechanisms or processes that could be relevant to the GDF and its long term evolution.
- Analogues provide qualitative understanding of the impact of processes that may occur over long (geological) time scales but which cannot be readily studied under laboratory conditions or within laboratory experimental timescales.
- Analogues can be used to test model predictions or extrapolations from laboratory experiments, in regard to the performance of the GDF host rock and engineered barrier materials over long timescales.

In general, most safety cases prepared over the last 30 years have included analogues in some form or another, whether to support conceptual model development, to test models or with direct input of quantitative data.

Some examples of the use of analogues in a safety case (after Alexander and McKinley, 1999 and Grundfelt and Smellie, 2004, with additional sources of information):

Safety case/safety assessment	Conceptual model development	Model testing	Direct data input
KBS-3 (1983)	Radiolytic oxidation of spent fuel		Maximum rate for pitting of copper. Bentonite stability at T<100°C
Projeckt Gewähr (1985)	Borosilicate glass stability Cement and concrete stability Bitumen stability Radionuclide migration		Long-term corrosion rates of iron Spent fuel corrosion rates Estimates of rates of illitisation of bentonite
SKB-91 (1992)	Long-term stability of bentonite Matrix diffusion concept Defining relevance of colloids	Redox front propagation Radionuclide solubilities	Radiolytic oxidation rates
TVO (1992)	Definition of glacial impact on the GDF Copper corrosion processes Impact of colloids and microbes	Spent fuel dissolution	Matrix diffusion depths
Kristallin-1 (1994)	Temperature dependence of illitisation of bentonite Radiolytic oxidation of the canister Glass corrosion rates Radiolytic oxidation of spent fuel Microbial radionuclide retardation	Radionuclide solubilities Canister corrosion rates Redox front development	Thermal alteration of bentonite Long-term corrosion rates of iron Matrix diffusion depths Estimates of redox front development rates

AECL EIS (1994)	Spent fuel and copper canister corrosion rates Long-term behaviour of bentonite Radionuclide retardation	Radionuclide solubilities Colloid and organic complexation of radionuclides Copper corrosion rates	Spent fuel stability Radiolysis parameters Copper canister corrosion rates Bentonite illitisation rates Matrix diffusion depths
NRC IPA (1995)	Development of GDF disruption scenarios Source-term model development Gas phase transport Relative importance of small- and large-scale fractures on radionuclide migration	Radionuclide transport in unsaturated media Radionuclide transport in fractured media	Definition and relevance of secondary phases following spent fuel corrosion
SFR (1998)	Long-term stability of cementitious materials Development of a hyperalkaline disturbed zone around a cementitious GDF	Blind Predictive Model (BPM) testing of thermodynamic databases for hyperalkaline conditions	Development of secondary CSH, CASH and zeolites within the hyperalkaline disturbed zone pH buffering by reaction with aluminosilicates in the host rock K/Na/CaOH release parameters
TILA-99 (1999)	Support for the assumed conservativism of the spent fuel dissolution model		Copper canister corrosion rates
SR-97 (1999)	Inclusion of permafrost data in the glacial scenarios Inclusion of post-glacial tectonics information in the glacial scenarios	Radiolytic oxidation of spent fuel Radionuclide retardation via matrix diffusion Redox front propagation Mixing of different groundwaters	Bentonite illitisation rates Bentonite thermal stability Bentonite as a barrier to microbial activity Low colloid populations in deep groundwaters Gas transport in the host rock Maximum depth penetration of oxidising surface waters Long-term redox buffer capacity of the host rock
H-12 (2000)	Temperature dependent mineralisation of the bentonite		Conservative corrosion rates for steel canister Conservative dissolution rates for vitrified waste Matrix diffusion depths Bedrock stability from Tono site
Opalinus Clay (2002)	Interaction of the hyperalkaline leachates from the near-field with the far-field High temperature interaction of the host rock and bentonite Chemical alteration of bentonite Impact of radiolysis		Radionuclide solubilities Corrosion rates of the steel canister Dissolution rates of spent fuel
TRU-II (2007)	Impact of secondary mineral crystallisation on radionuclide retardation on cementitious materials		
Posiva (2012) Posiva (2013). Safety Case-2012: Complementary Considerations. *Posiva Report* **2012-11**, Posiva, Eurajoki, Finland.	Use of complementary data from natural analogues for uranium migration, copper corrosion, iron corrosion, and thermal, mechanical chemical alteration of bentonite buffers, and cement-rock interactions for input to the safety case for the disposal of spent nuclear fuel at Olkiluoto.		Copper canister corrosion rates
SKB: Forsmark (2014) Sidborn, M.,	Development of evolutionary models for a hyperalkaline plume from OPC grouts, and its interaction with bentonite backfill	Integration of information from natural analogue studies with laboratory, URL	

Marsic, Crawford, N.J., Joyce, S., Hartley L., Idiart, A., de Vries, L.M., Maia, F., Molinero, J., Svensson, U., Vidstrand, P. and Alexander, W.R. (2014). Potential alkaline conditions for deposition holes of a repository in Forsmark as a consequence of OPC grouting. *SKB Report* **SKB R-12-17**, SKB, Stockholm, Sweden.	material, and the development of the geochemical environment within an alkaline disturbed zone in the host rock for a GDF Development of conceptual models to evaluate the impact of climate change.	and modelling studies	

Other useful examples	
Recent general overviews of the use of analogues to support national disposal programmes	Alexander, W.R., McKinley, I.G. and Kawamura, H. (2013). The process of defining an optimal natural analogue programme to support national disposal programmes. Proc. NEA-GRS Workshop on natural analogues for Safety Cases of repositories in rock salt. 4 – 6 September, 2012, Braunschweig, Germany. NEA/OECD, Paris, France.
	Alexander, W.R., Reijonen, H.M., McKinley, I.G. (2015). Natural analogues: studies of geological processes relevant to radioactive waste disposal in deep geological repositories. Swiss Journal of Geosciences 108, 75-100.
	Reijonen, H.M. and Alexander, W.R. (2015). Bentonite analogue research related to geological disposal of radioactive waste – current status and future outlook. Swiss Journal of Geosciences 108, 101-110.
Cyprus Natural Analogue Project (CNAP)	Milodowski, A.E., Norris, S. and Alexander, W.R. (2016). Minimal alteration of montmorillonite following long-term interaction with natural alkaline groundwater: implications for geological disposal of radioactive waste. *Applied Geochemistry*, **66**, 184-197.
Stakeholder communication	Alexander, W.R. (2013). An assessment of the long-term durability of proposed shaft seal materials under highly saline groundwater conditions using natural analogues. Bedrock Geosciences Technical Report BG13-04 for NWMO, Toronto, Canada (in press).

Unfortunately, not all safety cases note where analogue input has been used and much material is only utilised implicitly, with some relevant reports remaining as unpublished supporting documentation.

Analogues are also heavily used to build confidence in the output of any safety case. Analogues also provide clear examples of GDF processes and mechanisms which can be used to communicate complex issues, or geological processes that operate over long timescales, in a simple manner.

1.3 OBJECTIVES AND SCOPE OF THE ANALOGUE CATALOGUE

The main objective of the Analogue Catalogue is to produce examples of data from analogue systems that can be used to support a safety case for a GDF. Its scope includes all aspects of disposal relevant to the UK situation; a range of waste types and potential GDF host rocks are considered and examples are grouped into four main sections - the engineered barrier system, natural barrier system, radionuclide migration in natural systems, and natural analogues and the safety case.

For each analogue example, the following information is provided:

- A description of the specific aspects of components of a GDF that the analogue system represents, or to which it is applicable to;
- A summary description of the geoscientific characteristics of the analogue example;
- Key safety-relevant observations;
- A summary of limitations of the use of the analogue;
- Images of systems that can be used in RWM publications, subject to appropriate acknowledgements and copyright criteria; and,
- A list of references where further information can be obtained.

1.4 CATALOGUE ORGANISATION

The examples are grouped into four sections that are then subdivided according to their main safety barrier functions:

1. The Engineered Barrier System:
    - Wasteforms;
    - Container performance;
    - Near-field barrier materials.
2. The Natural Barrier System:
    - Long-term performance of clay host rocks;
    - Long-term performance of fractured crystalline host rocks;
    - Long-term performance of salt host rocks;
    - Long-term isolation concepts.
3. Radionuclide migration in natural systems:
    - Retardation in natural systems;
    - Colloid migration in natural systems.
4. Whole system performance.

2 The Engineered Barrier System

2.1 WASTEFORMS

Natural glasses as analogues of vitrified high-level waste

Natural glasses as analogues of vitrified high-level waste

Overview

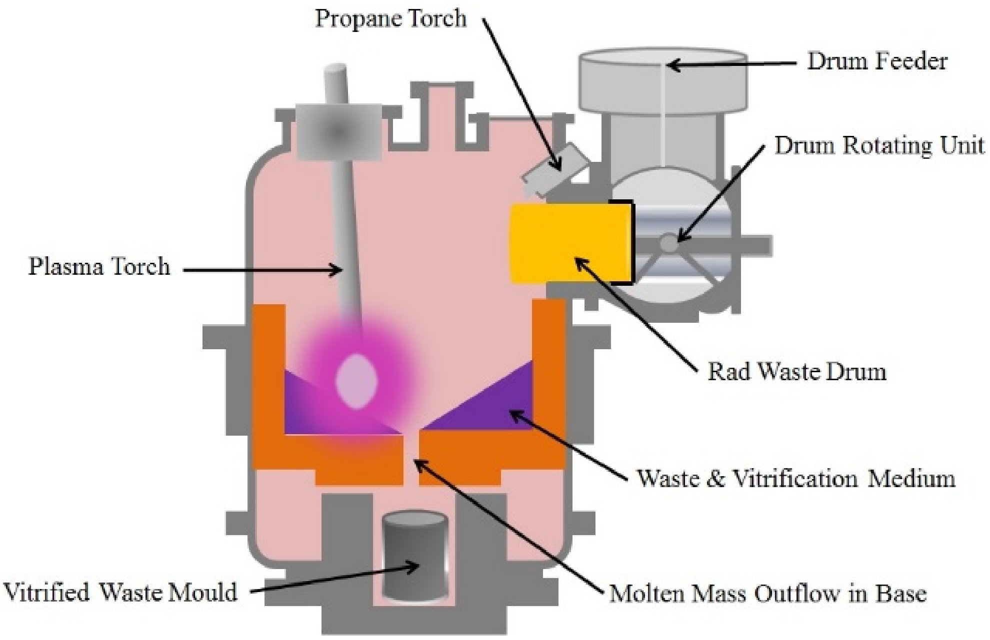
Glass was first proposed as a matrix for high-level radioactive waste (HLW) disposal in the 1950s. The current disposal route for HLW generated within the UK is to dissolve it in borosilicate glass (vitrification). Vitrification plants are currently in operation at Sellafield (UK), Marcoule and Cap de la Hague (France), Savannah Rivers (USA) and at Rokkasho (Japan). Plasma-oven vitrification of low- and intermediate-level waste (L/ILW) is also currently ongoing in Taiwan and Switzerland.

Why put waste in glass?

Vitrification incorporates liquid HLW into the glass and the vitrified wastes are encapsulated in metal containers for storage prior to final disposal. The attraction of glass as a wasteform stems from its physical and chemical durability under conditions expected in a deep geological disposal facility (GDF), its ease of production and the relative insensitivity of the vitrification process to waste stream composition.

Borosilicate glass (incorporating 15-25 wt. % B_2O_3) is the most common vitrified wasteform 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 wasteform, all glasses degrade with time and there is a significant body of laboratory and modelling work concerned with the durability of borosilicate glass wasteforms under GDF conditions.

Vitrified HLW in a section of steel canister (http://nuclearstreet.com/images/img/dw117.jpg)



Schematic diagram of the plasma-oven vitrification plant for L/ILW at the Swiss Interim Storage Facility, ZWILAG (modified after www.zwilag.ch)

Natural analogues of waste glasses

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

Obsidian from the Ross of Mull, Scotland. Note the grey-white spherical zones of devitrification within the otherwise glassy matrix in this approximately 60 million year old glass (© Bedrock Geosciences).

Most natural glasses have similar bulk compositions to those of 'normal' igneous rocks, ranging from silica-poor (basaltic composition) to silica-rich (obsidian). 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. 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.

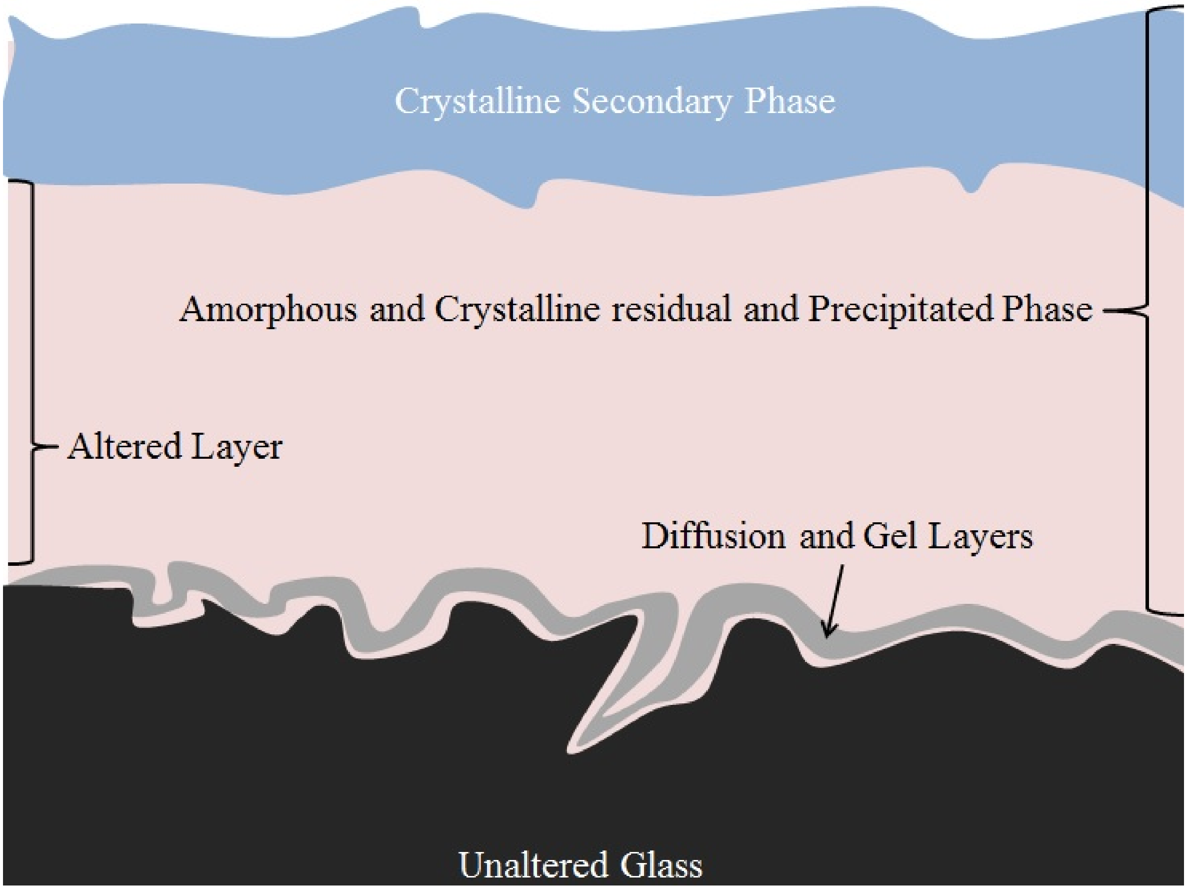
Like archaeological glasses, natural glasses lack the high B_2O_3 and radionuclide content of vitrified HLW. Although some natural glasses enriched in uranium have been reported, no systematic natural analogue study of these glasses has been carried out to date. The surface degradation products on marine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

Natural glasses 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 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.

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 (© Bedrock Geosciences).

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 – 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 two million years old, but some were as old as 40 million years. 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.



Schematic diagram of three alteration layers that form when glass dissolves in groundwater. The outer layer may become thick enough that it effectively seals the glass, so stopping further degradation (modified after Lutze and Ewing, 1988).

Uncertainties and differences

- 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;

- No natural glasses with a high radionuclide content have been examined to date, so the direct analogy to vitrified HLW is weakened.

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;
- Because of the more aggresive environments in which the natural glasses studied react, 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.

Further reading

ANDERSON, E.M. AND RADLEY, E.G. 1915 The pitchstones of Mull and their genesis. *Quarterly Journal of the Geological Society*. **71**, 205-217.

HAVLOVA, V., LACIOK, A., CERVINKA, R. AND VOKAL, R. 2008 Natural analogue evidence relevant to UK HLW glass waste forms. *UK Nirex Report 509009, RWM Ltd, Harwell, UK.*

JUDD, J.W. AND COLE. G.A.J. 1883 On the Basalt-Glass (Tachylyte) of the Western Isles of Scotland. *Quarterly Journal of the Geological Society* **39**, 444-465.

LUTZE, W. AND EWING, R.C. (editors). 1988. *Radioactive Waste Forms for the Future*. North Holland, New York, USA.

MacDougall, J.D. 1977. Uranium in marine basalts: concentration, distribution and implications. *Earth and Planetary Science Letters*, **35**, 65-70

MARSHALL, R.R. 1961 Devitrification of natural glass. *Bulletin of the Geological Society of America*, **72**, 1493-1520.

MILLER, W.M., ALEXANDER, W.R., CHAPMAN, N.A., MCKINLEY, I.G. AND SMELLIE, J.A.T.. 2000. *Geological Disposal of Radioactive Wastes and Natural Analogues*. Waste Management Series, Vol. 2, Pergamon, Amsterdam, The Netherlands.

2.2 CONTAINER PERFORMANCE

Littleham Cove, south Devon, United Kingdom: corrosion of native copper in Permian mudstones

Roman legionary nails from Inchtuthil: iron corrosion

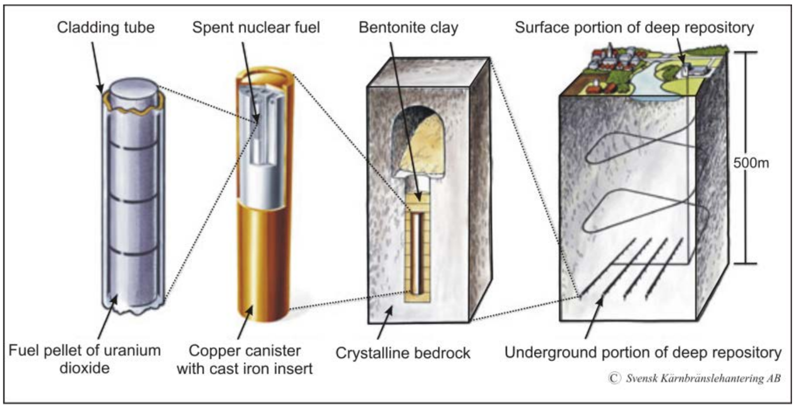
Littleham Cove, south Devon, United Kingdom: corrosion of native copper in Permian mudstones

Overview

Copper is one of the materials that may be used in a geological disposal facility (GDF) for radioactive waste to contain high-level waste (HLW) and spent fuel.

The use of copper waste canisters in a GDF

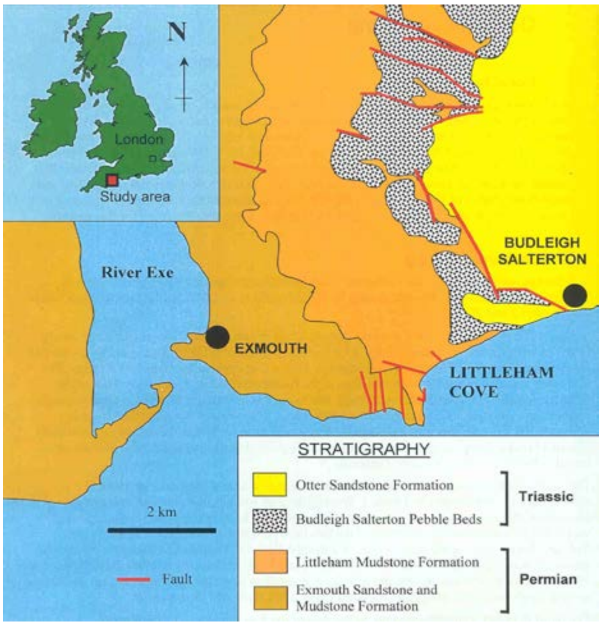
- The Swedish (KBS-3), Finnish and Canadian GDF concepts for the disposal of HLW and spent nuclear fuel, consists of copper canisters with a cast iron insert containing the waste;



- Each canister is emplaced into a hole bored in granitic rock at depths of 400-700 m, and sealed in place with compacted bentonite (a type of clay) which protects the container;
- 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 this GDF environment. As a result, the copper will be expected to isolate and protect the waste for long periods of time.

The Littleham Cove natural analogue study

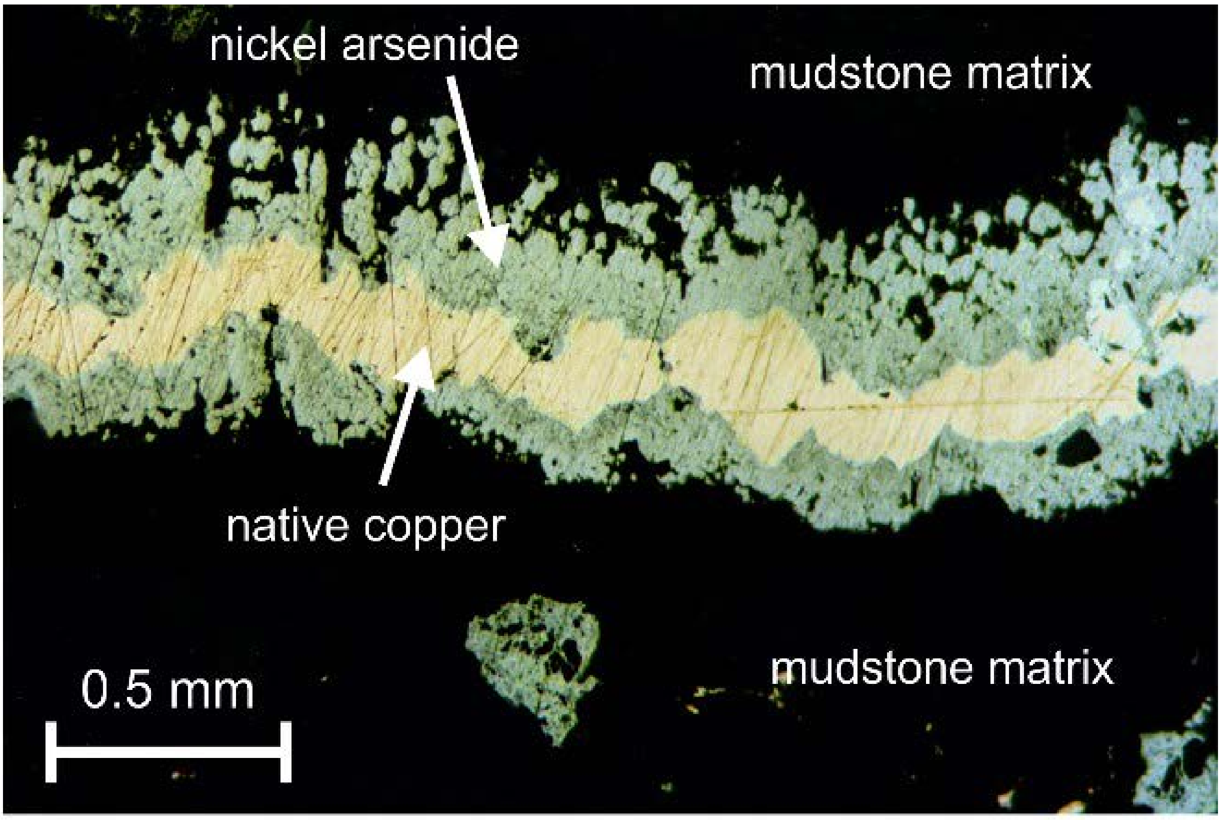
Naturally occurring copper sheets are preserved in the Permian age (c 300 to 250 Ma) Littleham Mudstone Formation, at Littleham Cove, in south Devon, South West England. They have been studied to understand the long-term stability of copper enclosed in clay – such as would be found in a GDF where copper canisters are used.



***LEFT:** Location of the Littleham Cove Natural Analogue Site (©British Geological Survey).*

***ABOVE:** 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).



Reflected light microscopy image of a thin section of a copper concretion showing a thin sheet of native copper within mudstone that has been corroded and partially replaced by grey-silver nickel arsenide (from 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;
- Between 30 and 80 % of the original thickness of the copper remains 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.

Uncertainties and differences

- 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 greater permeability 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 similar age elsewhere in the UK but at greater depths are are highly saline brines. Furthermore, halite and anhydrite deposits and matrix cement minerals are known to have been formerly present in the overlying Triassic strata, and are still preserved in the deeper parts of the basin to the east. Therefore, the porewater in the Permian 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 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 for radioactive waste.

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 years;
- 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 by the present near-surface weathering environment. This is well in excess of the timescales (up to one million years) considered in radioactive waste management safety cases;
- The preservation of copper metal in this natural environment provides support to the prediction that copper canisters can potentially resist corrosion within a GDF environment for tens of thousands of years.

Further reading

ARCOS, D., GRANDIA, F. AND DOMENECH, C. 2006. Geochemical evolution of the near field of a KBS-3 repository. *SKB Technical Report*, **TR-06-16**, 90pp. Svensk Kärnbränslehantering AB (SKB) - Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden.

HARRISON, R.K. 1975. Concretionary concentrations of the rarer elements in Permo-Triassic red beds of south-west England. Bulletin of the Geological Survey of Great Britain, **52**. 1-26.

KING, F., AHONEN, L., TAXÉN, C., VUORINEN, U. AND WERME, L. 2001. Copper corrosion under expected conditions in a deep geologic repository. *SKB Technical Report*, **TR-01-23**. Svensk Kärnbränslehantering AB (SKB) - Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden. [Also published as *Posiva Oy, Report*, **POSIVA 2002-01**, Helsinki]

MILODOWSKI, A.E., STYLES, M.T., HARDS, V.L. 2000. A natural analogue for copper waste canisters: The copper-uranium mineralised concretions in the Permian mudrocks of south Devon, United Kingdom. *SKB Technical Report*, **TR-00-11**, 90pp. Svensk Kärnbränslehantering AB (SKB) - Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden.

MILODOWSKI A.E., STYLES M.T., HORSTWOOD, M.S.A. AND KEMP, S.J. 2002. Alteration of uraniferous and native copper concretions in the Permian mudrocks of south Devon, United Kingdom. *SKB Technical Report*, **TR-02-09**. Svensk Kärnbränslehantering AB (SKB) - Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden.

WERME, L. 1998. Design premises for canister for spent nuclear fuel. *SKB Technical Report*, **TR-98-08**. Svensk Kärnbränslehantering AB (SKB) - Swedish Nuclear Fuel and Waste Management

Roman legionary nails from Inchtuthil: iron corrosion

Iron and steel may be used as canister materials in a geological disposal facility (GDF) for radioactive waste for the containment of high-level waste (HLW), spent fuel and low- and intermediate-level wastes (L/ILW). The archaeological excavation of a distant outpost of the Roman Empire, an archaeological analogue, has given us an insight into the stability of iron over a time period of thousands of years.

Overview

One of the multiple layers of the protective barriers intended to prevent early exposure and mobilisation of radionuclides from HLW and L/ILW repositories is a metal canister to contain various radioactive waste types, including spent nuclear fuels. The metal of these canisters must be resistant to:

- Corrosion – the deterioration of metals caused by oxidation, chemical or electro-chemical reactions;
- Pressure – the canister will be buried at depth and will be exposed to compression. Some waste products may generate gasses, so internal pressurisation is also possible;
- Thermal effects – some of the contained waste materials are heat-producing and may potentially generate temperatures up to around 125 ˚C;
- Radiation – bombardment of the metal by radiation can affect its physical properties.

Resistance must be long enough for shorter-lived radioactive fission products to have largely decayed. Metals based on iron and copper are the main candidates for canister construction because both appear to have many of the required properties. Metals are also likely to be used in many of the construction components of any GDF for radioactive waste.

The use of iron and steel

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 canisters may be sealed by and enclosed in compacted clay (bentonite) backfill or encased in a cement. 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 iron under the warm, mildly alkaline and reducing chemical environment that will persist in a GDF.

Inchtuthil as a natural analogue study

The site

An apparently unremarkable area of pasture situated on the banks of the River Tay near Dunkeld in Perthshire, Scotland, 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. 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), 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. During the abandonment of the fort, in a (successful) attempt to put the nails out of the reach of the local tribes, the nails had been buried in a 3.66 m deep pit dug into fluvio-glacial deposits and covered by a 1.83 m depth of gravel.


The site of the Roman legionary Fort at Inchtuthil. ©NDA 2009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The nails

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. 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 uses. The degree of corrosion does not systematically reflect differences in composition.

What has happened?

The reaction of the outer nails with water in the ground 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 cause rusting.

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.

Uncertainties and differences

- The nails are of different compositions and internal structures to the iron-based metals likely to be used in repositories;
- The nail burial environment is different to that of a GDF – it is shallow and not deep, exposed to surface waters (more reactive), at lower temperatures and in relatively high permeability sediment;
- The nails were discovered during an archaeological dig. Consequently there has been no systematic study of the corrosion profile both within the hoard and also the surrounding sediment. Similarly there is no information on the chemistry of the groundwater, soils and sediments;

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

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 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, gives us confidence in predicting that iron-based structures in a GDF will survive for thousands of years (e.g. Posiva, 2012)

Further reading

ANGUS, N.S., BROWN, G.T. AND CLEERE, H.F. 1962. The iron nails from the Roman legionary fortress at Inchtuthil, Perthshire. *Journal of Iron and Steel Institute*, **200**, 956-968.

CROSSLAND, I. *Corrosion of Iron-Based Alloys – Evidence from Nature and Archaeology,* Report prepared for United Kingdom Nirex Limited, Crossland Report CCL/2006/2, 2006.

MAPELLI, C., NICODEMI, W., RIVA, R.F., VEDANI, M. AND GARIBOLDI, E. 2009. Nails of the Roman Legionary at Inchtuthil. *La Metallurgia Italiana*, January 2009, 51-58.

MILLER, W.M., ALEXANDER, W.R., CHAPMAN, N.A., MCKINLEY, I.G. AND SMELLIE, J.A.T.. 2000. *Geological Disposal of Radioactive Wastes and Natural Analogues*. Waste Management Series, Vol. 2, Pergamon, Amsterdam, The Netherlands.

PITTS, L. AND ST JOSEPH, A. 1985. Inchtuthil: The Roman Legionary Fortress Excavations 1952-65. *Britannia Monograph Series* **No. 6**. Allan Sutton Pub. Ltd.

POSIVA. 2012. Safety Case for the Disposal of Spent Nuclear Fuel at Olkiluoto – Complementary Considerations 2012. *Posiva Report*, **2012-11**, Posiva Oy, Olkiluoto, FI-27160 Eurajoki, Finland.

The Story of Inchtuthil: http://www.glasgowsteelnail.com/romans2.HTM

Ordnance Survey Historical Map: *Roman Britain*. 5th Edition 2001. ISBN 978-0-319-29029-3

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2.3 NEAR-FIELD BARRIER MATERIALS

Archaeological cements: longevity of cementitious materials

Cement from Hadrian's Wall: longevity of cementitious materials

Northern Ireland: a cement analogue

Maqarin: longevity of calcium silicate hydrate phases

Maqarin: an analogue of the alkali disturbed zone

Oman: survival of microbes in cementitious environments

Maqarin, Jordan: survival of microbes in cementitious environments

The Dunarobba Forest, Todi, Italy: long-term isolation properties of clay

The Philippines: long-term isolation properties of clay

Cyprus: long-term isolation properties of clay

Mudrocks altered by igneous intrusions: thermal stability of clay barriers

Engineered barrier system: colloids

Bentonite: is erosion possible at GDF depths?

Radiolysis

Archaeological cements: longevity of cementitious materials

Overview

Cement and concrete will be used as part of the multi-barrier containment system in many design concepts for a geological disposal facility (GDF) for radioactive waste, particularly for low- and intermediate-level wastes (L/ILW).

Cement and concrete in a GDF

Cement and concrete will be present as:

- tunnel liners
- plugs and seals in shafts and tunnels;
- a solidification matrix for some L/ILW;
- concrete waste containment packages;
- a cementitious buffer and backfill;
- concrete silos for waste emplacement.

The actual quantities of cement 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 up to 1.5 million tonnes of cement, which will be approximately 90 % of the total mass of all materials emplaced in the GDF. This quantity of cement is comparable to that used in other major infrastructure projects, e.g. 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 cement durability are useful, the very slow rates of transformation or degradation mean that long-term supporting data are also required. The oldest man-made concrete known to date is some 9,000 years old, and makes up the floors of a Neolithic building in modern-day Galilee. Therefore, the study of such archaeological cements can provide valuable insights into cement longevity.

Man-made cements and concretes

The oldest man-made concrete known to date is some 9,000 years old, and makes up the floors of a Neolithic building in modern-day Galilee. Although the Egyptians and the Greeks had various forms of cements, the first truly resistant material was developed by the Romans. This pozzolanic lime concrete used fine siliceous and aluminous materials (the 'pozzolans') that caused the cement to set and harden without drying.

Hydrated modern Portland-type cements are dominated by calcium silicate hydrates (CSH), calcium aluminate hydrates (CAH) and calcium hydroxide (portlandite, $Ca(OH)_2$), and complex hydrated calcium alumino-sulphates such as ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$) if sulphate is also present (cf. Hewlett, 1988), However, lime-based and pozzolanic archaeological cements can provide an analogy to the low-pH cements currently being developed for use alongside bentonites and other clays in the engineered barrier system of a GDF.

There are many examples of extant Roman cements and concretes, one of the most famous being Hadrian's Wall in northern England. 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.

A section of the 1,900 year old Hadrian's Wall in northern England. The massive stone blocks are cemented by Roman mortar (Miller et al., 2000).

BELOW: A close up of Hadrian's Wall (top) showing the mortar binding the stone blocks with (bottom) a section of core drilled through the wall (Jull and Lees, 1990).

ABOVE: Roman aqueduct, Aqua Claudia, which supplied Rome with water. Started by Emperor Caligula in AD 38, it was finished in AD 52 in the reign of Emperor Claudius.

There are many examples of extant Roman cements and concretes, one of the most famous being Hadrian's Wall in northern England. 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 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.

Uncertainties and limitations

- All studies of archaeological mortars so far have been focussed on the similarities with modern-day (Portland) cements because they were carried out before the current interest in low-pH cements. This makes some of the information difficult to extrapolate to low-pH cements;
- None of the material studied has been from an environment of relevance to a deep GDF, so once again, extrapolation of data is difficult;
- 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.
- Cement degradation can occur via other mechanisms such as attack by sulphate, chloride and magnesium (cf. Hewlett, 1998) that have not been observed or studied here.

Relevance – what we have learnt

- 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 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 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.

Further reading

CROSSLAND, I. *Long-term Properties of Cement - Evidence from Nature and Archaeology,* Report prepared for United Kingdom Nirex Limited, Crossland Report CCL/2006/01, 2006.

GANI, M.S.J. 1997. *Cement and Concrete*. Chapman and Hall, London, UK.

HARRIS, A. W., *A review of ancient and historical analogues for cementitious materials,* A report produced for UK Nirex Ltd, TE 2867 Task Sheet 39, RWMD(02)P020 Issue 1, 2002.

HEWLETT, P.C. 1998. *Lea's Chemistry of Cement and Concrete (Fourth Edition).* Arnold, London, UK.

HODGKINSON, E. S. AND HUGHES, C.R. 1999.The mineralogy and geochemistry of cement/rock reactions: high resolution studies of experimental and analogue materials. In: METCALFE, R. AND ROCHELLE, C. A. 1999. *Chemical containment of waste in the Geosphere*. Geological Society of London, Special Publication, **157**, 195-211.

JULL, S.P.AND LEES, T.P. 1990. Studies of historic concrete. *CEC Nuclear Science and Technology Report,* **EUR 12972**, CEC, Luxembourg.

MILLER, W.M., ALEXANDER, W.R., CHAPMAN, N.A., MCKINLEY, I.G. AND SMELLIE, J.A.T. *2000 Geological disposal of radioactive wastes and natural analogues.* Waste Management Series, Vol. 2, Pergamon, Amsterdam, The Netherlands.

POLLIO, M.V. ca. 27 BC. *De Architectura, Books I to X*. Translated as *"Ten Books on Architecture"* by MORGAN, M.H. (1914), Harvard University Press, Cambridge, USA

RAYMENT, D. L. AND PETTIFER, K. 1987. Examination of durable mortar from Hadrian's Wall. *Materials Science and Technology*, **3**, 997-1004.

SAVAGE, D. *Analogue Evidence Relevant to the Alkaline Disturbed Zone*, Report prepared for United Kingdom Nirex Limited, QRS-1300A-1, Version 2.0, 2005.

SMELLIE, J. A. T. AND KARLSSON, F. 1999.The use of natural analogues to assess radionuclide transport. *Engineering Geology*, **52**, 193-220.

Cement from Hadrian’s Wall: longevity of cementitious materials

Examination of Roman cement still surviving in Hadrian’s Wall has given us valuable information about the stability of cement for time periods of hundreds to thousands of years.

Overview

Large quantities of concrete and cement will be present as part of the built infrastructure in all types of designs for a geological disposal facility (GDF) for radioactive waste, however the actual amount will depend on the final concept. There are two main roles that they perform:

- Physical support and containment - concrete will have widespread use as a tunnel and disposal cavern liner. Additionally, concrete will be used to plug or backfill GDF caverns in some designs, and cement is expected to be used to seal natural fractures exposed in the GDF host-rocks;
- Chemical containment - highly alkaline waters will evolve from cements and concretes used in a GDF as a result of the initially high concentrations of potassium, sodium and hydroxide ions (typical pH > 12), and will interact with the other materials in the GDF. Because many radioactive elements are poorly soluble in alkaline conditions, these waters will reduce their mobility. The cement itself also offers a large surface area for radioactive element sorption.

It is also likely that cement and concrete will be present as part of the waste itself (for example, from reactor decommissioning).

What are cements and concretes?

Cements 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 matter, e.g. volcanic ash);
- Cements harden through hydration reactions that generate calcium silicate hydrate (CSH) compounds of varied compositions;
- These CSH compounds initially form as gels that bind the intermixed aggregates (sand and gravel);

- CSH gels are unstable (thermodynamically) and are expected to transform into more crystalline forms which may impact buffering properties of the GDF environment;
- The rates of the expected transformations are typically too slow to measure experimentally;
- The transformations are very difficult to predict and model;
- Ultimately it is the properties of the gels and their evolved compounds that determine the physical and chemical properties of the cements and concretes.

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

Remains of milecastle 39 near Sycamore Gap ©NDA 2009

Hadrian's Wall analogue study

Samples were taken from the heart of the Wall at a site near Sycamore Gap where the remains of the original Roman mortar survive from a period of reconstruction around 200 AD under Emperor Septimus Severus. Several researchers have analysed these samples using a wide range of techniques (optical and electron microscopy, electron probe microanalysis, X-ray diffraction, wet chemistry) and found:

- The cement nearest the edges of the wall is extensively carbonated (a process of conversion to carbonate minerals);
- Cement 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;
- The CSH compounds include hydrous gels and crystalline to semi-crystalline phases possessing fibrous to crumpled sheet morphologies;
- Evidence for some reaction between the cement and the wall aggregate, giving rise to both decreased and increased porosities.

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 significant silicate material (as chert – a poorly crystalline form of silica) that could have fortuitously produced calcium silicates (as found in Portland cement) during the manufacture of the cement.

Uncertainties and limitations

- Observations from studying intact archaeological structures are biased to behaviour of cements under near surface conditions and therefore may not be directly applicable to behaviour in a GDF environment;
- The compositions of the CSH compounds are subtly different to modern cements, which typically have higher calcium / silicon molar ratios (1.2-2.0);
- The cement is exposed to the atmosphere and not surrounded by large amounts of silicate minerals and associated fluids, as is expected in a GDF;
- Archaeological cements contain little or no analogue species for most radionuclides. Consequently they provide little information on chemical containment in the GDF;
- Cement degradation can occur via other mechanisms such as attack by sulphate, chloride and magnesium (cf. Hewlett, 1998) that have not been observed or studied here.

Relevance - what we have learnt

- The compounds identified in the Hadrian's Wall mortar 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 cement to be considered a good analogue;
- CSH compounds, despite their theoretical instability, have been shown to survive essentially intact for nearly 2,000 years;
- Carbonation (a process of conversion to carbonate minerals) is the main mechanism for the alteration of cement exposed to the atmosphere;
- Where protected from carbonation, CSH gels can survive and stabilise cement and concrete over periods of hundreds to thousands of years.

Further reading

CROSSLAND, I. *Long-term Properties of Cement - Evidence from Nature and Archaeology*, Report prepared for United Kingdom Nirex Limited, Crossland Report CCL/2006/01, 2006.

HARRIS, A. W., *A review of ancient and historical analogues for cementitious materials*, A report produced for UK Nirex Ltd, TE 2867 Task Sheet 39, RWMD(02)P020 Issue 1, 2002.

HEWLETT, P.C. 1998. *Lea's Chemistry of Cement and Concrete (Fourth Edition)*. Arnold, London, UK.

HODGKINSON, E. S. AND HUGHES, C.R. 1999.The mineralogy and geochemistry of cement/rock reactions: high resolution studies of experimental and analogue materials. In: METCALFE, R. AND ROCHELLE, C. A. 1999. *Chemical containment of waste in the Geosphere*. Geological Society of London, Special Publication, **157**, 195-211.

RAYMENT, D. L. AND PETTIFER, K. 1987. Examination of durable mortar from Hadrian's Wall. *Materials Science and Technology*, **3**, 997-1004.

SAVAGE, D. *Analogue Evidence Relevant to the Alkaline Disturbed Zone*, Report prepared for United Kingdom Nirex Limited, QRS-1300A-1, Version 2.0, 2005.

SMELLIE, J. A. T. AND KARLSSON, F. 1999.The use of natural analogues to assess radionuclide transport. *Engineering Geology*, **52**, 193-220.

Northern Ireland: a cement analogue

Overview

The use of cements and concrete in a GDF

Cements and concrete will be extensively used in some concepts for a geological disposal facility (GDF) for low- and intermediate-level radioactive 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:

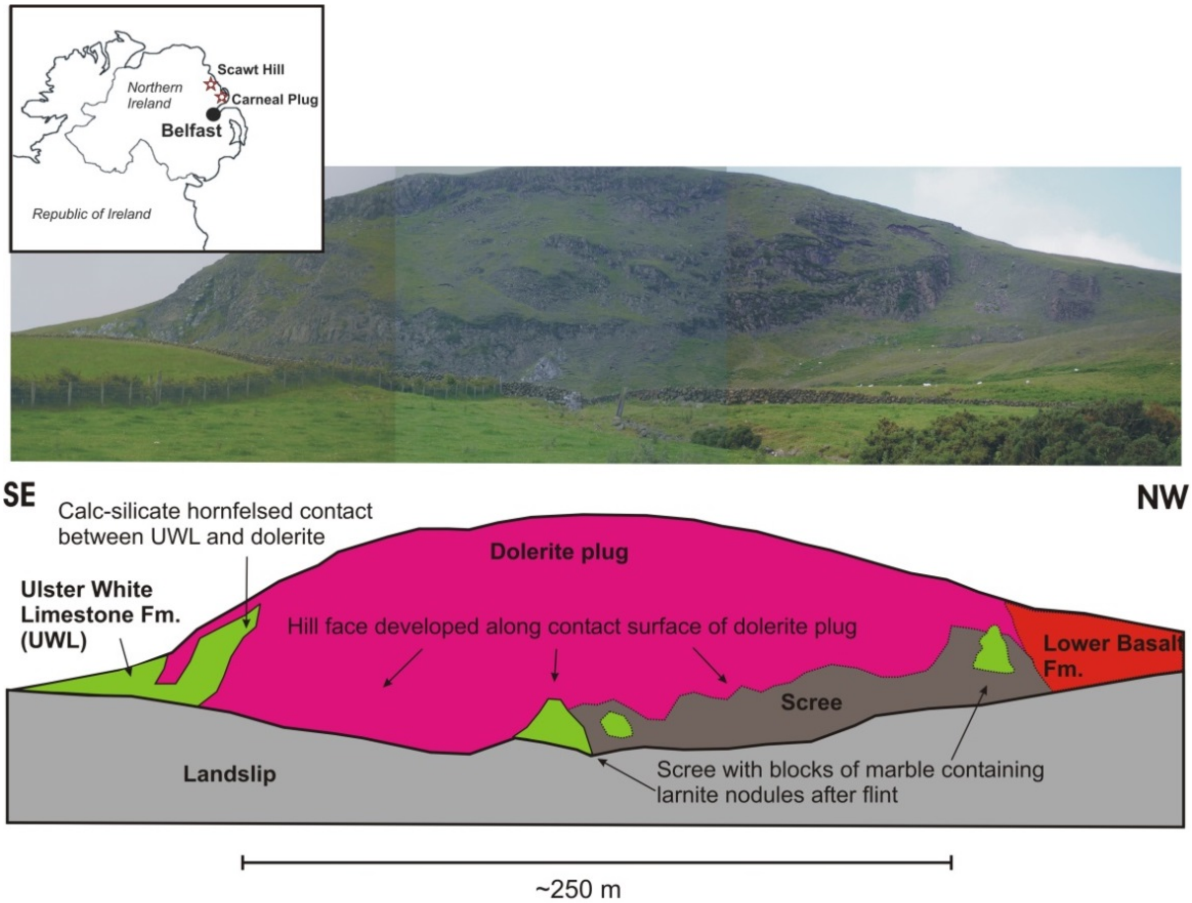
- Cement and concrete will be used for *structural purposes*: as tunnel liners, seals and grouts, where their structural integrity (mechanical strength) and hydraulic properties (sealing against groundwater movement) of the cement are important;
- Cements and concretes may be used in *containment*: for 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). The solubility of many radioactive elements is very low in high pH alkaline porewaters, and therefore radionuclide migration will be restricted;
- Cement offers a large surface area for radioactive element sorption. It will also play a role in colloid mitigation;
- In addition, alkaline porewaters leaching from the cement in a GDF will potentially interact with the adjacent host rock. This may result in the dissolution 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 a GDF.

Amorphous calcium silicate hydrate (CSH) phases are major components of cements, and after the dissolution of any free portlandite ($Ca(OH)_2$), the dissociation of CSH phases will provide the main buffering capacity to maintain a high pH (Atkinson, 1985; Atkinson and Hearne, 1989). Therefore, the longevity of these phases in the GDF environment is important for understanding the geochemical evolution and the phases likely to control pH within the near-field environment.

Scawt Hill and Carneal Plug analogue sites

The Tertiary (Palaeogene) Antrim Lava Group of Northern Ireland is intruded by at least thirty dolerite plugs. 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 parallel to the orientation of the main Palaeogene dyke swarm. 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 Upper Cretaceous Ulster White Limestone Formation. Within the thermal aureole of these intrusions, high-temperature (~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 (β-Ca_2SiO_4). These larnite nodules have been hydrated through reaction with groundwater, resulting in the formation of natural CSH gel and minerals analogous to phases found in Portland cement clinker. Larnite and its associated CSH alteration products (which include crystalline tobermorite and amorphous CSH gels) at Scawt Hill and Carneal Plug have been studied as natural analogues to investigate the occurrence and longevity of CSH (Milodowski et al., 1989).

Scawt Hill in County Antrim is a very conspicuous feature at the edge of the east-facing Antrim basalt escarpment. It is formed by a moderately large dolerite plug that intrudes both the limestones and early Palaeogene lavas. Carneal Plug is much smaller, some 100-120 m in diameter, located to the south of Larne. The eastern margin of the plug is sheared, and this shearing also affects a large metasomatised xenolith of host limestone included within the dolerite.



Location of the analogue sites, and a simplified geological cross-section of Scawt Hill (from Milodowski et al., 2011(©British Geological Survey).

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 Portland cement clinker.

At Scawt Hill the mineralogy of these nodules is relatively simple, comprising either largely unaltered cores of coarsely crystalline quartz and calcsilicate minerals (either larnite, or larnite and spurrite ($Ca_5(SiO_4)_2CO_3$). At Carneal Plug, a more complex mineral assemblage is present because of metasomatism by iron- and magnesium-fluids introduced from the dolerite. The nodules comprise recrystallised quartz cores surrounded by a reaction rim of quartz and a range of other minerals including carbonate bearing minerals.

Very hydrous gel-like phase formed by hydration and alteration of a calcsilicate (larnite) nodule, which was revealed in a freshly broken open block of marble from Scawt Hill (©British Geological Survey).

Hydration of the larnite nodules has produced reaction rims containing crystalline and amorphous CSH phases, and minerals analogous to those found in Portland cement clinker. These phases in turn may be replaced by calcium carbonates. Dating the hydration and carbonation events is difficult. However, two phases of carbonation are recognised by Milodowski et al. (1989):

- The earliest phase of carbonate formation appeared to be texturally contemporaneous with the CSH gel formation. A study of the stable C and O isotopes of these early calcium carbonates showed them to be comparable with the carbonates formed during metamorphism;
- Later iron oxyhydroxide-stained calcite replaces the CSH, and with a stable isotope signature that suggests a meteoric origin. This has been interpreted to have formed much later and at shallower depths when the CSH phases were in contact with oxidising groundwaters.

This evidence was interpreted by Milodowski et al. (1989) to infer an age for the formation of the CSH phases during retrograde hydration, probably shortly after intrusion (i.e. ~58 Ma).

Uncertainties and limitations

- The natural analogue study has not dated the CSH gels directly. Based on geological, geomorphological and petrographical considerations the CSH gels are interpreted to predate the late carbonation and alteration by atmospheric carbon dioxide or oxidising shallow groundwater;
- Late-stage carbonation of the CSH hydration rims is most likely to have occurred when the larnite 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 BP), when the ice support to the steep slopes of the Larne Plateau was lost (Mitchell, 2004; Milodowski et al., 2009; 2011);
- The boundary conditions of this natural analogue system are poorly-constrained. In particular, the timing and composition of past groundwaters interacting with the CSH 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.

Relevance - what we have learnt

- CSH compounds, despite their theoretical instability, have been shown to survive essentially intact, possibly for several million years, without evolving to more crystalline forms. This natural analogue study extends our knowledge of the persistence of CSH phases in the natural geosphere environment beyond the timescale of archaeological cements;
- Carbonation (a process of conversion to carbonate minerals) is the main mechanism for the alteration of cement exposed to the atmosphere;
- Where protected from carbonation, even poorly-crystalline CSH gels may survive for many millions of years;
- 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 over the long-term.

Further reading

ATKINSON, A. 1985 The time-dependence of pH within a repository for radioactive waste disposal. *UKAEA*

ATKINSON, A. AND HEARNE, J.A. 1989. The hydrothermal chemistry of Portland cement and its relevance to radioactive waste disposal. *Nirex Report*, **NSS/R187**.

CROSSLAND, I. *Long-term Properties of Cement - Evidence from Nature and Archaeology,* Report prepared for United Kingdom Nirex Limited, Crossland Report CCL/2006/01, 2006.

HARRIS, A. W., *A review of ancient and historical analogues for cementitious materials,* A report produced for UK Nirex Ltd, TE 2867 Task Sheet 39, RWMD(02)P020 Issue 1, 2002.

HEWLETT, P.C. 1998. *Lea's Chemistry of Cement and Concrete (Fourth Edition).* Arnold, London, UK.

MILODOWSKI, A.E., NANCARROW, P.H.A. AND SPIRO, B. 1989. A mineralogical and stable isotope study of natural analogues of Ordinary Portland cement (OPC) and CaO-SiO_2-H_2O (CSH) compounds. *Nirex Report*, **NSS/R340**.

MILODOWSKI, A.E., LACINSKA, A. AND WAGNER, D. 2009. A natural analogue study of CO_2-cement interaction: carbonate alteration of calcium silicate hydrate-bearing rocks from Northern Ireland. *British Geological Survey Report*, **CR/09/096**, 28p.

MILODOWSKI, A.E., ROCHELLE, C.A., LACINSKA, A. AND WAGNER, D. 2011. A natural analogue study of CO_2-cement interaction: Carbonation of calcium silicate hydrate-bearing rocks from Northern Ireland. *Energy Procedia*, **4**, 5235-5242.

MITCHELL, W.I. 2004. *The Geology of Northern Ireland*. Geological Survey of Northern Ireland, Belfast.

SABINE, P.A. 1975. Metamorphic processes at high temperatures and low pressure: the Petrogenesis of the metasomatized and assimilated rocks of Carneal Plug, Co. Antrim. *Philosophical Transactions of the Royal Society, London*, **280(A)**, 225-265.

SABINE, P.A., BECKINSALE, R.D., EVANS, J.D. AND WALSH, J.N. 1982. Geochemical and strontium-isotope studies of reactions between basic magma, Chalk, and flint, and the role of groundwater, in the Carneal Plug, Co. Antrim, Northern Ireland. *Journal of Petrology*, **23**, 427-446.

SABINE, P.A., STYLES, M.T. AND YOUNG, B.R. 1985. The nature and paragenesis of natural bredigite and associated minerals from Carneal and Scawt Hill, Co. Antrim. *Mineralogical Magazine*, **49**, 663-670.

SAVAGE, D. *Analogue Evidence Relevant to the Alkaline Disturbed Zone*, Report prepared for United Kingdom Nirex Limited, QRS-1300A-1, Version 2.0, 2005.

TILLEY, C.E. AND ALDERMAN, A.R. 1934. Progressive metamorphism in the flint nodules of the Scawt Hill contact-zone. Mineralogical Magazine, 23, 513-518.

TILLEY, C.E. AND VINCENT, H.C.G. 1948. The occurrence of an orthorhombic high-temperature form of Ca_2SiO_4 (bredigite) in the Scawt Hill contact-zone and as a constituent of slags. Mineralogical Magazine, 28, 255-271

Maqarin: longevity of calcium silicate hydrate phases

Overview

The use of cements and concrete in a GDF

Cements and concrete will be extensively used in some concepts for a geological disposal facility (GDF) for low- and intermediate-level radioactive 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). The solubility of many radioactive elements is very low in high pH alkaline porewaters, and therefore radionuclide migration will be restricted;
- Cement offers a large surface area for radioactive element sorption. It will also play a role in colloid filtration;
- In addition, alkaline porewaters leaching from the cement in a GDF will potentially interact with the adjacent host rock. This may result in the dissolution 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 a GDF.

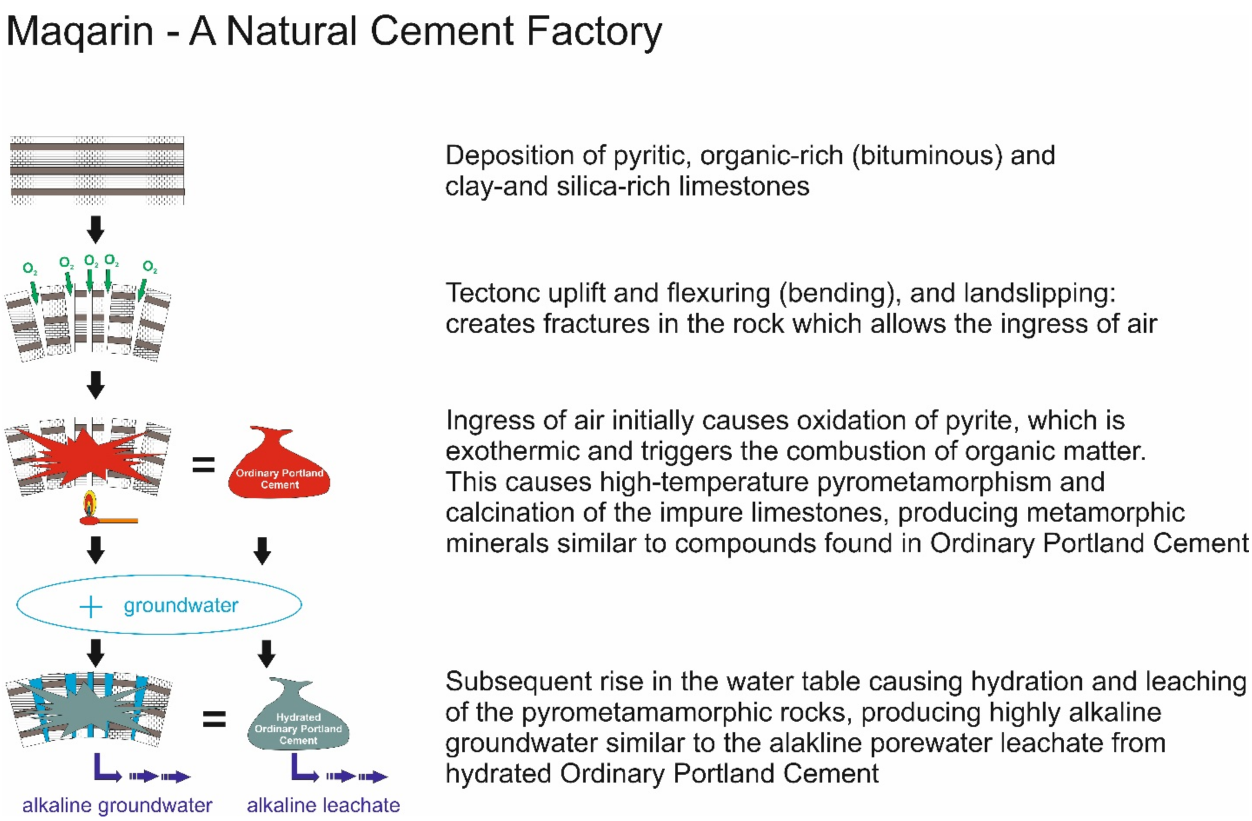
Amorphous calcium silicate hydrate (CSH) phases are major components of cements, and after the dissolution of any free portlandite ($Ca(OH)_2$), the dissociation of CSH phases will provide the main buffering capacity to maintain a high pH (Atkinson, 1985; Atkinson and Hearne, 1989). Therefore, the longevity of these phases in the GDF environment is important for understanding the geochemical evolution and the phases likely to control pH within the near-field environment.

The Maqarin analogue

The Maqarin study area is located in the Yarmouk River valley at the Syrian-Jordanian border, 16 km north of the provincial town of Irbid. 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 "*naturally-occurring cement-like*" rocks are found within the Upper Cretaceous and Lower Tertiary sedimentary sequence at Maqarin, and also in several other places in central Jordan and in Israel. They have been formed by high-temperature, low-pressure thermal metamorphism of organic rich, muddy-limestones ("marls") 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 (pyrometamorphism).

Combustion took place within highly fractured zones that allowed oxygen ingress into the rock mass, and was probably triggered by spontaneous exothermic pyrite oxidation, and possibly due to tectonic activity or landslides initiating such oxidation. The pyrometamorphism produced marble "pods" with complex calcium silicate and calcium aluminate-ferrite mineral assemblages.

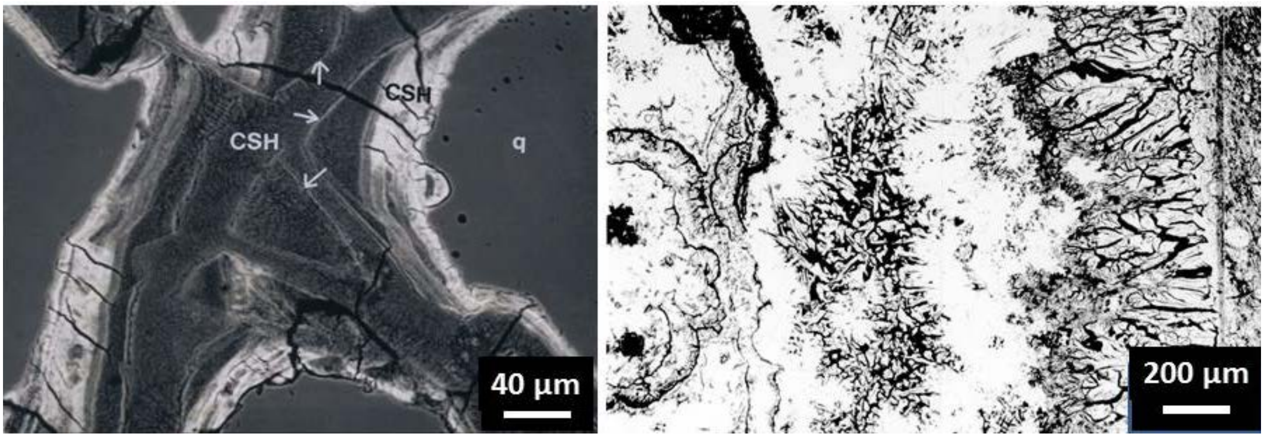


Schematic representation of the production of the natural analogue cements at Maqarin and in central Jordan.

Subsequent groundwater percolation through the metamorphic rocks has resulted in the hydration, alteration and leaching of the metamorphic assemblage. The hydration products include a wide variety of cement-analogue hydrated CSH minerals and gels, which closely resemble phases found in hydrated Portland cements (these include: crystalline CSH minerals such as tobermorite ($Ca_5Si_6O_{16}[OH]_2.2\text{-}8H_2O$), jennite ($Ca_9H_2Si_6O_{18}[OH]_8.6H_2O$) and afwillite ($Ca_3(SiO_3OH)_2{\cdot}2H_2O$); amorphous CSH gels and aluminous CSH gels (CASH); and crystalline calcium alumino-sulphates and silico-sulphates such as ettringite (Ca_6Al_2 $[SO_4]_3[OH]_{12}.25H_2O$) and thaumasite ($Ca_6Si_2[SO_4]_2[CO_3]_2[OH]_{12}.24H_2O$))..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.

Longevity and alteration characteristics of natural cement phases

CSH and CASH minerals and amorphous gels occur as low-temperature retrograde hydration products forming directly from high-temperature pyrometamorphic minerals (e.g. larnite, spurrite, and ellestadite) within the marble "pods". They also occur as vein minerals which are precipitated as high-pH groundwaters leach from the metamorphic rocks, and flow along fractures in the surrounding marls and chalk host rocks.



LEFT: Backscattered scanning electron microscope image of growth-zoned tobermorite-type CSH gel formed by interaction of high-pH groundwater with a fractured chert (flint) nodule. The banding represents variations in the degree of hydration and Ca:Si ratio of the gel.

RIGHT: Backscattered scanning electron microscope image of a complex banded vein showing repeated alternations between dense jennite (white) and fibrous thaumasite and ettringite (grey).

Some of the CSH and CASH mineralisation exhibits complex banded or zoned vein fabrics reflecting the evolution of the groundwater system. Alternations between CSH and ettringite-thaumasite mineral phases, and late stage replacement by calcium carbonate phases, result from pulses of different groundwater types discharged through the fractures in response to repeated fracture reactivation.

Uncertainties and limitations

- The precise age of the combustion metamorphism at Maqarin is uncertain. However, it must have occurred after the rocks had been fractured as a result of uplift or landslip activity. It must also have occurred when the rocks were above the water table and unsaturated, in order to allow the ingress of air to facilitate combustion

- The timing of the late-stage carbonation of the vein-filling cement minerals (CSH and portlandite) and their replacement by calcite and aragonite replacement is unclear. The carbonate mineralisation contains detectable ^{14}C, which implies a maximum age of about 50,000 years (i.e. equivalent to between 8 to 9 half-lives of ^{14}C (5,700 years half-life), which is the practical limit for measurement). However, the source of the ^{14}C is not known and consequently, the carbonation alteration could be much more recent. For example, the carbonate minerals could have precipitated from mixed sources of bicarbonate: e.g. diffusion and dissolution of modern (^{14}C-bearing) atmospheric CO_2 into groundwater containing geologically-old bicarbonate ('dead' to ^{14}C).
- Only limited dating of the CSH mineralisation has been undertaken because of the difficulty of being able to separate pure mineral phases for radiometric analysis. $^{230}Th/U$ dating of secondary fracture minerals has shown that the hyperalkaline groundwater fracture-flow system has been operative for the order of 80 000 to 100 000 years, and that some of the metastable CSH minerals have therefore persisted for this length of time.
- Although reaction between sulphate and CSH and CASH minerals has been observed at Maqarin, cement degradation can occur via other mechanisms such as attack by chloride and magnesium (cf. Hewlett, 1998) that have not been observed here.

Relevance - What we have learnt

- CSH and CASH (including supposedly metastable amorphous phases and gels) appear to be stable for tens to hundreds of thousands of years, provided they remain isolated from the groundwater, in particular from sulphate-rich and bicarbonate groundwaters;
- CSH and CASH minerals and gels react with sulphate-rich groundwaters, to form ettringite, thaumasite and gypsum as alteration products. Trace metals, including uranium, caesium and strontium, incorporated within the CSH and CASH phases are released during this process and not taken up by the secondary sulphate minerals. In contrast, metals such chromium are concentrated within the secondary minerals;
- Replacement of CSH and CASH by ettringite and thaumasite leads to sealing of the fractures and therefore cessation of alkaline groundwater flow. Reactivation of the fractures by tectonic or landslip activity may rejuvenate the groundwater flow and result in renewed mineralisation or alteration;
- CSH, CASH, ettringite and thaumasite are altered to calcium carbonates when exposed to bicarbonate groundwaters. Calcium carbonate has been identified as an alteration product produced by carbonation reaction;
- The Maqarin natural analogue study significantly extends our knowledge of the persistence of CSH phases in the natural geosphere environment beyond the timescale of archaeological cements, and supports safety case arguments for the potential long-term stability of CSH phases in the natural environment, and the associated long-term buffering of high pH.

Further Reading

ALEXANDER, W.R. (editor). 1992. A natural analogue study of cement buffered, hyperalkaline groundwaters and their interaction with a repository host rock. I: definition of source terms. *Nagra Technical Report*, **NTB 91-10**, Nagra, Wettingen, Switzerland.

ALEXANDER, W.R. AND SMELLIE, J.A.T. 1998. Maqarin natural analogue project. ANDRA, CEA, Nagra, Nirex and SKB synthesis report on Phases I, II and III. *Nagra Unpublished Project Report*, **NTB 98-08**, Nagra, Wettingen, Switzerland.

ATKINSON, A. 1985 The time-dependence of pH within a repository for radioactive waste disposal. *UKAEA*

Technical Report, **AERE-R11777**, Harwell, U.K.

ATKINSON, A. AND HEARNE, J.A. 1989. The hydrothermal chemistry of Portland cement and its relevance to radioactive waste disposal. *Nirex Report*, **NSS/R187**.

CLARK, I.D., FRITZ, P., MILODOWSKI, A.E. AND KHOURY, H.N. 1992. Sampling and analytical methods in W.R.Alexander (editor) A natural analogue study of cement buffered hyperalkaline groundwaters and their interaction with a repository host rock. *Nagra Technical Report*, **NTB 91-10**, Wettingen, Switzerland.

CLARK, I., FIRTZ, P. SEIDLITZ, H., KHOURY, H., TRIMBORN, P., MILODOWSKI, A.E., AND PEARCE, J. 1993. Recarbonation of metamorphosed marls, Jordan. *Applied Geochemistry*, **8**, 473-481.

CROSSLAND, I. *Long-term Properties of Cement - Evidence from Nature and Archaeology,* Report prepared for United Kingdom Nirex Limited, Crossland Report CCL/2006/01, 2006.

HARRIS, A. W., *A review of ancient and historical analogues for cementitious materials,* A report produced for UK Nirex Ltd, TE 2867 Task Sheet 39, RWMD(02)P020 Issue 1, 2002.

HEWLETT, P.C. 1998. *Lea's Chemistry of Cement and Concrete (Fourth Edition).* Arnold, London, UK.

KHOURY, H.N. SALAMEH, E., CLARK, I., FRITZ, P., BAJJALI, W., MILODOWSKI, A., CAVE, M. AND ALEXANDER, W.R. 1992. A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan 1:Introduction to the site. *Journal of Geochemical Exploration*, **46**, 117-132.

LINKLATER C.M. (EDITOR). 1998. A natural analogue study of analogue cement buffered, hyperalkaline groundwaters and their interaction with a repository host rock: Phase II. *Nirex Science Report*, **S-98-003**, UK Nirex, Harwell, U.K.

MILODOWSKI A.E., PEARCE J.M., HUGHES C.R. AND KHOURY H.N. 1992. A preliminary mineralogical investigation of a natural analogue of a cement-buffered hyperalkaline groundwater interaction with marl, Maqarin, northern Jordan – *Nagra Internal Report*. Nagra, Wettingen, Switzerland.

MILODOWSKI, A.E., HYSLOP, E.K., KHOURY, H.N., HUGHES, C.R., MÄDER, U.K., GRIFFAULT, L.Y. AND TROTIGNON, L. 2001. Mineralogical alteration by hyperalkaline groundwater in northern Jordan. *Proceedings of the 10th International Water Rock Interaction Symposium, Villasimius, Italy (June 10-15, 2001).* Balkema, Amsterdam, The Netherlands.

PITTY, A.. AND ALEXANDER, R. (EDITORS). 2011. A natural analogue study of cement buffered, hyperalkaline groundwaters and their interaction with a repository host rock IV: an examination of the Khushaym Matruk (central Jordan) and Maqarin (northern Jordan) sites. *NDA Technical Report*, NDA, Moor Row, UK

SAVAGE, D. *Analogue Evidence Relevant to the Alkaline Disturbed Zone*, Report prepared for United Kingdom Nirex Limited, QRS-1300A-1, Version 2.0, 2005.

SMELLIE, J.A.T. (Editor). 1998. Maqarin natural analogue study: Phase III, *SKB Technical Report*, **TR-98-04**, Volumes I and II, SKB, Stockholm, Sweden.

Maqarin: an analogue of the alkali disturbed zone

Overview

The use of cements and concrete in a GDF

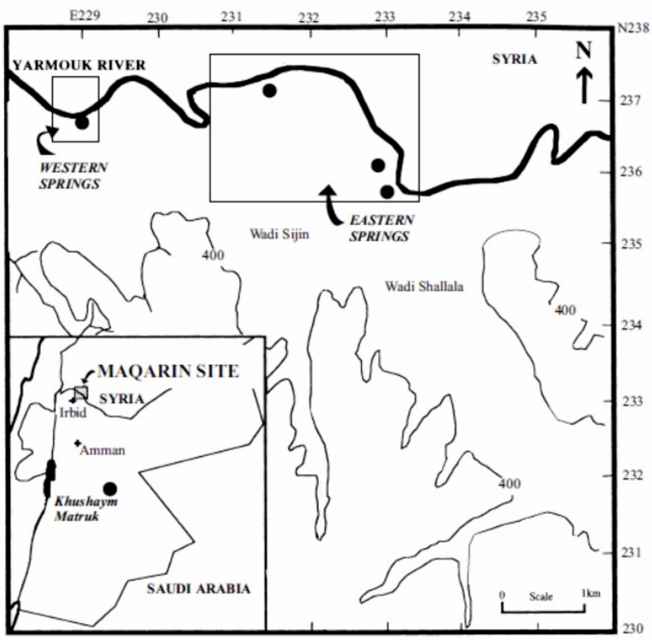
Cements and concrete will be extensively used in some GDF concepts for low- and intermediate-level waste (L/ILW) and will also be used in some parts of a GDF for high-level waste (HLW) and spent fuel (SF). Cement and concrete may also form part of the waste itself, e.g. waste from reactor decommissioning.

- 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). The solubility of many radioactive elements is very low in high pH 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. 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.

Natural cements (*ca* 0.5 to 2 Ma old) and their associated hyperalkaline 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 natural analogues of the long-term evolution of a cementitious GDF for radioactive wastes.

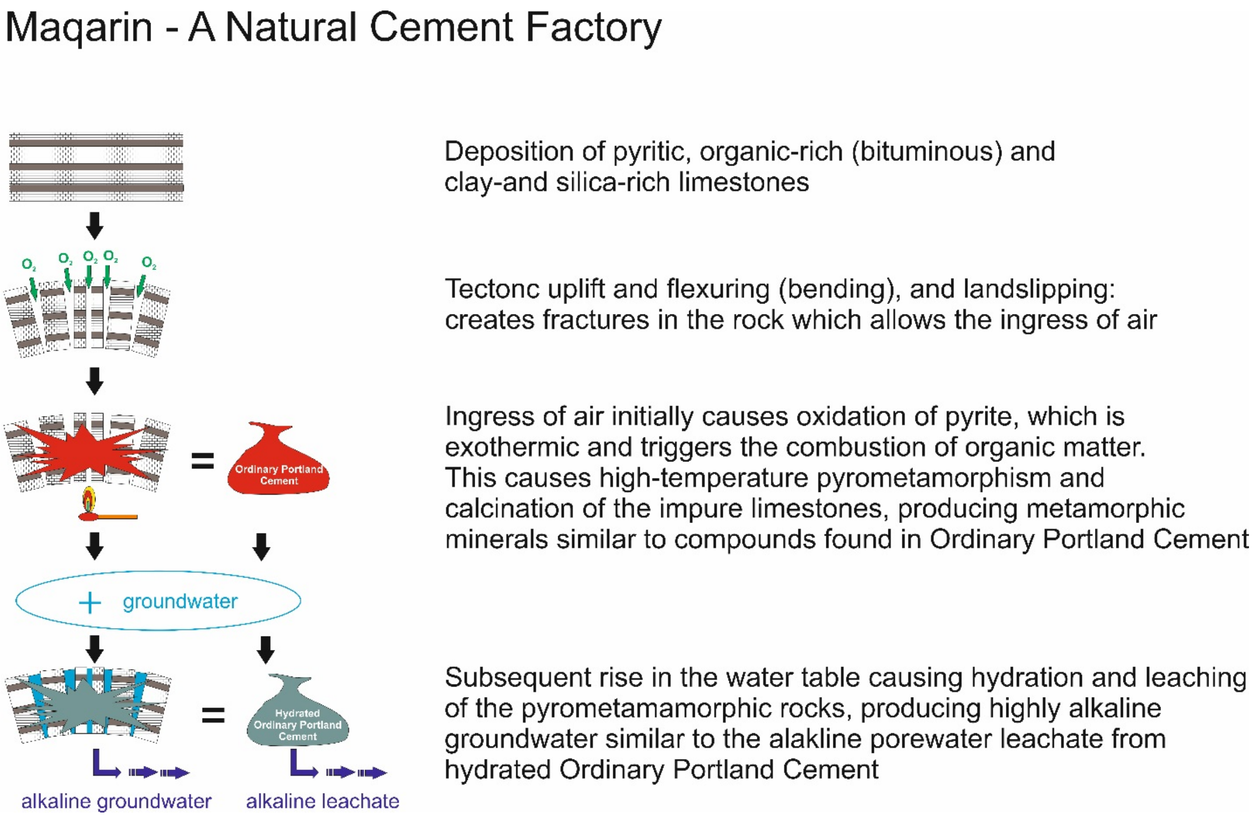
The Maqarin natural analogue



The Maqarin natural analogue study area is located in the Yarmouk River valley at the Syrian-Jordanian border, 16 km north of the provincial town of Irbid.

Discontinuous lenses of "*naturally-occurring cement-like*" rocks are found within the Upper Cretaceous and Lower Tertiary sedimentary sequence at Maqarin, and also in several other places in central Jordan and in Israel. They have been formed by high-temperature, low-pressure thermal metamorphism of organic rich, muddy-limestones ("marls") 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 (pyrometamorphism).

Combustion took place within highly fractured zones that allowed oxygen ingress into the rock mass, and was probably triggered by spontaneous exothermic pyrite oxidation, and possibly due to tectonic activity or landslides initiating such oxidation. The pyrometamorphism produced marble "pods" with complex calcium silicate and calcium aluminate-ferrite mineral assemblages.



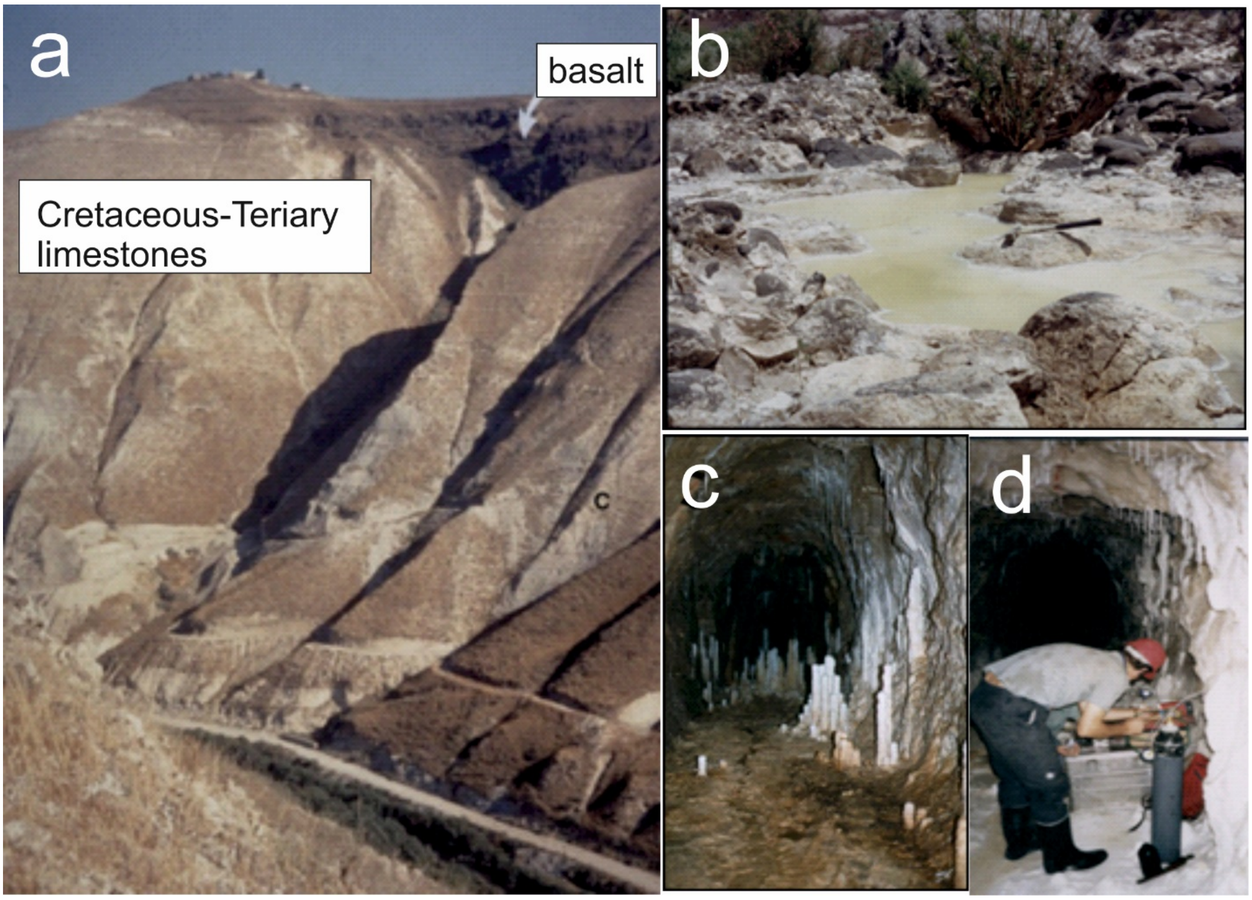
Schematic representation of the production of the natural analogue cements at Maqarin and in central Jordan.

Subsequent groundwater percolation through the metamorphic rocks has resulted in the hydration, alteration and leaching of the metamorphic assemblage. The hydration products include a wide variety of cement-analogue hydrated CSH minerals and gels, which closely resemble phases found in hydrated Portland cements (these include: crystalline CSH minerals such as tobermorite ($Ca_5Si_6O_{16}[OH]_2.2\text{-}8H_2O$), jennite ($Ca_9H_2Si_6O_{18}[OH]_8.6H_2O$) and afwillite ($Ca_3(SiO_3OH)_2{\cdot}2H_2O$); amorphous CSH gels and aluminous CSH gels (CASH); and crystalline calcium alumino-sulphates and silico-sulphates such as ettringite ($Ca_6Al_2\ [SO_4]_3[OH]_{12}.25H_2O$) and thaumasite ($Ca_6Si_2[SO_4]_2[CO_3]_2[OH]_{12}.24H_2O$)). These hydrous secondary minerals now buffer the chemistry and high pH of the groundwater. 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.

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

Hydrochemistry

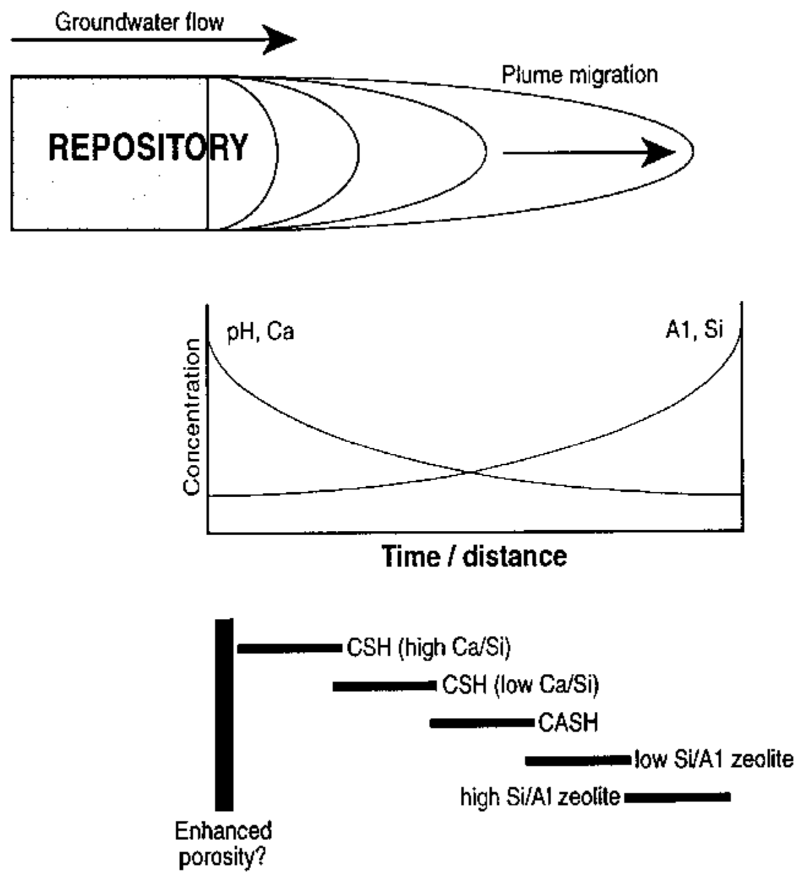
Two hydrochemically distinct high pH groundwater systems have been identified that are associated with two separate metamorphic zones and hydrological drainage systems, and are referred to as the "Western Springs" and the "Eastern Springs".



The Maqarin area, northern Jordan: (a) The Yarmouk Valley (Wadi Yarmouk) looking towards Syria, showing basalt lava flows filling depressions in the palaeo-land surface on top of the Cretaceous to Tertiary sequence of organic rich, muddy-limestones ("marls") and chalks (the Bituminous Marl Formation); (b) Hyperalkaline 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) Hyperalkaline 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 colloids in Adit-6.

The Western Springs are characterised by higher pH (12.9), K, Na, Ca, OH^-, SO_4^{2-}, and are heavily mineralised with high concentrations of Cr. Se, Re and several other metals are particularly enriched in these waters. 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 (referred to as "Young Cement Leachate");

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



Conceptual model of the evolution of a cement leachate plume from a GDF for L/ILW (from Smellie, 1998)

Uncertainties and limitations

- The precise age of the combustion metamorphism at Maqarin is uncertain. However, it must have occurred after the rocks had been fractured as a result of uplift or landslip activity. It must also have occurred when the rocks were above the water table and unsaturated, in order to allow the ingress of air to facilitate combustion. However, with regard to the timescale for the hydration of the metamorphic minerals, uranium disequilibrium series dating of CSH mineralisation indicates the hyperalkaline groundwater fracture-flow system has been operative for the order of 80,000 to 100,000 years. Some of the metastable CSH minerals have therefore persisted for this length of time;
- Although the Maqarin (and other similar pyrometamorphic 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. Therefore is it 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.

Relevance - What we have learnt

- Detailed geomorphological reconstructions at Maqarin, together with natural uranium decay dating of CSH and CASH fracture mineralisation associated with the high pH groundwaters, show that the pyrometamorphic rocks – the "natural cement zone" – are about 0.5 to 2 Ma old, and the hyperalkaline groundwater system has been operative for at least 80,000 to 100,000 years. These timescales are directly relevant to the safety case timescales considered for a GDF;

- Hyperalkaline pore fluid conditions, generated by minerals analogous to those envisaged for cements, 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 nearfield and geosphere;
- Data from the Maqarin site have proved extremely valuable for testing and validating the applicability of available thermodynamic data to hyperalkaline 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;
- Reaction between hyperalkaline 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 – even in the high flow gradient conditions at Maqarin;
- The reaction and mineral precipitation sequences observed at Maqarin correspond closely to the observed and predicted behaviour of industrial cements (i.e. the "*source-term*"), and the evolutionary sequence of mineralogical reactions associated with the propagation of a hyperalkaline plume. 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.

Further Reading

ALEXANDER, W.R. (editor). 1992. A natural analogue study of cement buffered, hyperalkaline groundwaters and their interaction with a repository host rock. I: definition of source terms. *Nagra Technical Report*, **NTB 91-10**, Nagra, Wettingen, Switzerland.

ALEXANDER, W.R. AND SMELLIE, J.A.T. 1998. Maqarin natural analogue project. ANDRA, CEA, Nagra, Nirex and SKB synthesis report on Phases I, II and III. *Nagra Unpublished Project Report*, **NTB 98-08**, Nagra, Wettingen, Switzerland.

ATKINSON, A. 1985 The time-dependence of pH within a repository for radioactive waste disposal. *UKAEA*

Technical Report, **AERE-R11777**, Harwell, U.K.

ATKINSON, A. AND HEARNE, J.A. 1989. The hydrothermal chemistry of Portland cement and its relevance to radioactive waste disposal. *Nirex Report*, **NSS/R187**.

CLARK, I.D., FRITZ, P., MILODOWSKI, A.E. AND KHOURY, H.N. 1992. Sampling and analytical methods in W.R.Alexander (editor) A natural analogue study of cement buffered hyperalkaline groundwaters and their interaction with a repository host rock. *Nagra Technical Report*, **NTB 91-10**, Wettingen, Switzerland.

CLARK, I., FIRTZ, P. SEIDLITZ, H., KHOURY, H., TRIMBORN, P., MILODOWSKI, A.E., AND PEARCE, J. 1993. Recarbonation of metamorphosed marls, Jordan. *Applied Geochemistry*, **8**, 473-481.

CROSSLAND, I. *Long-term Properties of Cement - Evidence from Nature and Archaeology,* Report prepared for United Kingdom Nirex Limited, Crossland Report CCL/2006/01, 2006.

HARRIS, A. W., *A review of ancient and historical analogues for cementitious materials*, A report produced for UK Nirex Ltd, TE 2867 Task Sheet 39, RWMD(02)P020 Issue 1, 2002.

KHOURY, H.N. SALAMEH, E., CLARK, I., FRITZ, P., BAJJALI, W., MILODOWSKI, A., CAVE, M. AND ALEXANDER, W.R. 1992. A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan 1: Introduction to the site. *Journal of Geochemical Exploration*, **46**, 117-132.

LINKLATER C.M. (EDITOR). 1998. A natural analogue study of analogue cement buffered, hyperalkaline groundwaters and their interaction with a repository host rock: Phase II. *Nirex Science Report*, **S-98-003**, UK Nirex, Harwell, U.K.

MILODOWSKI A.E., PEARCE J.M., HUGHES C.R. AND KHOURY H.N. 1992. A preliminary mineralogical investigation of a natural analogue of a cement-buffered hyperalkaline groundwater interaction with marl, Maqarin, northern Jordan – *Nagra Internal Report*. Nagra, Wettingen, Switzerland.

MILODOWSKI, A.E., HYSLOP, E.K., KHOURY, H.N., HUGHES, C.R., MÄDER, U.K., GRIFFAULT, L.Y. AND TROTIGNON, L. 2001. Mineralogical alteration by hyperalkaline groundwater in northern Jordan. *Proceedings of the 10th International Water Rock Interaction Symposium, Villasimius, Italy (June 10-15, 2001)*. Balkema, Amsterdam, The Netherlands.

PITTY, A. AND ALEXANDER, R. (EDITORS). 2011. A natural analogue study of cement buffered, hyperalkaline groundwaters and their interaction with a repository host rock IV: an examination of the Khushaym Matruk (central Jordan) and Maqarin (northern Jordan) sites. *NDA Technical Report*, NDA, Moor Row, UK

SAVAGE, D. *Analogue Evidence Relevant to the Alkaline Disturbed Zone*, Report prepared for United Kingdom Nirex Limited, QRS-1300A-1, Version 2.0, 2005.

SMELLIE, J.A.T. (Editor). 1998. Maqarin natural analogue study: Phase III, *SKB Technical Report*, **TR-98-04**, Volumes I and II, SKB, Stockholm, Sweden.

Oman: survival of microbes in cementitious environments

Overview

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. 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). The solubility of many radioactive elements is very low in high pH 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. 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;
- Cement offers a large surface area for radioactive element sorption. It will also play a role in colloid mitigation;
- 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 Oman provide an opportunity to study established microbial communities in these environments.

Microbial degradation

- 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 assessments of a 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 calcium silicate hydrate (CSH) gel and $Ca(OH)_2$. Direct anaerobic corrosion of concrete 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.

The Oman natural analogue study

- 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 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 very reducing, with the result that hyperalkaline springs, containing hydrogen gas, flow from the lower areas of the mountains;

- Analysis of the water from some of the springs show them to be Na-Cl-Ca-OH solutions with pH levels between 10 and 11.45;
- Microbial populations were found in the alkaline waters, although these were low (10^1 to 10^3 cells/mL^{-1}). However, a wide range of species were detected that had adapted to the environment; some species are capable of producing acid. Interestingly, biological activity was controlled not by the alkaline pH but by the availability of carbon and phosphorus, which are needed as nutrients.

Uncertainties and differences

- The pH in the near-field environment and alkaline disturbed zone (ADZ) of a cementitious GDF may be greater than pH 13 at an early stage after closure, as potassium hydroxide is initially leached from the cement. This will then fall and be maintained at around pH 12.5 for several tens of thousands of years after the potassium hydroxide has been depleted and the cement porewater is buffered by the calcium hydroxide. This is much higher than the pH of between 10 to 11.45 recorded from the groundwater in the Oman natural analogue system.
- Detection of the microbes in Oman spring waters does not imply that they will prove viable in the cement pore waters of a GDF;
- The chemistry of Oman is not directly analogous to cementitious material in a GDF. The alkaline conditions relate to the alteration of ultramafic minerals, not to naturally occurring cement minerals;
- The conditions within / around a radioactive waste repository (particularly one at greater depths) may well differ from the conditions within the analogue and therefore the microbial populations within a repository may differ considerably from those that have been studied here.

Relevance – what we have learnt

- This 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 natural analogue shows that an alkaline pH up to 11.45 will not guarantee microbial sterility. However, it is important to bare-in-mind the pH in the GDF is expected to remain above pH 12 for tens of thousands of years. The observations from the Oman study do not tell us whether bacteria will be viable in the GDF under this higher pH;
- The observations provide some justification for researching the possible effects of microbes on engineered barrier performance in cementitious repositories;
- Some of the microbial groups, including as iron- and sulphate-metabolising bacteria found living 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 engineered barrier materials.

Further reading

BATH, A. H., CHRISTOFI, N., NEAL, C., PHILP, J. C., CAVE, M. R., MCKINLEY, I.G. AND BERNER, U. 1987. Trace element and microbiological studies of alkaline groundwaters in Oman, Arabian Gulf: a natural analogue for cement pore-waters. *British Geological Survey, Technical Report,* **FLPU 87-2**.

SAVAGE, D. *Analogue Evidence Relevant to the Alkaline Disturbed Zone*, Report prepared for United Kingdom Nirex Limited, QRS-1300A-1, Version 2.0, 2005.

Maqarin, Jordan: survival of microbes in cementitious environments

Overview

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. 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). The solubility of many radioactive elements is very low in high pH 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. 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;

- Cement offers a large surface area for radioactive element sorption. It will also play a role in colloid mitigation;

- 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 Maqarin provide an opportunity to study established microbial communities in these environments.

Microbial degradation

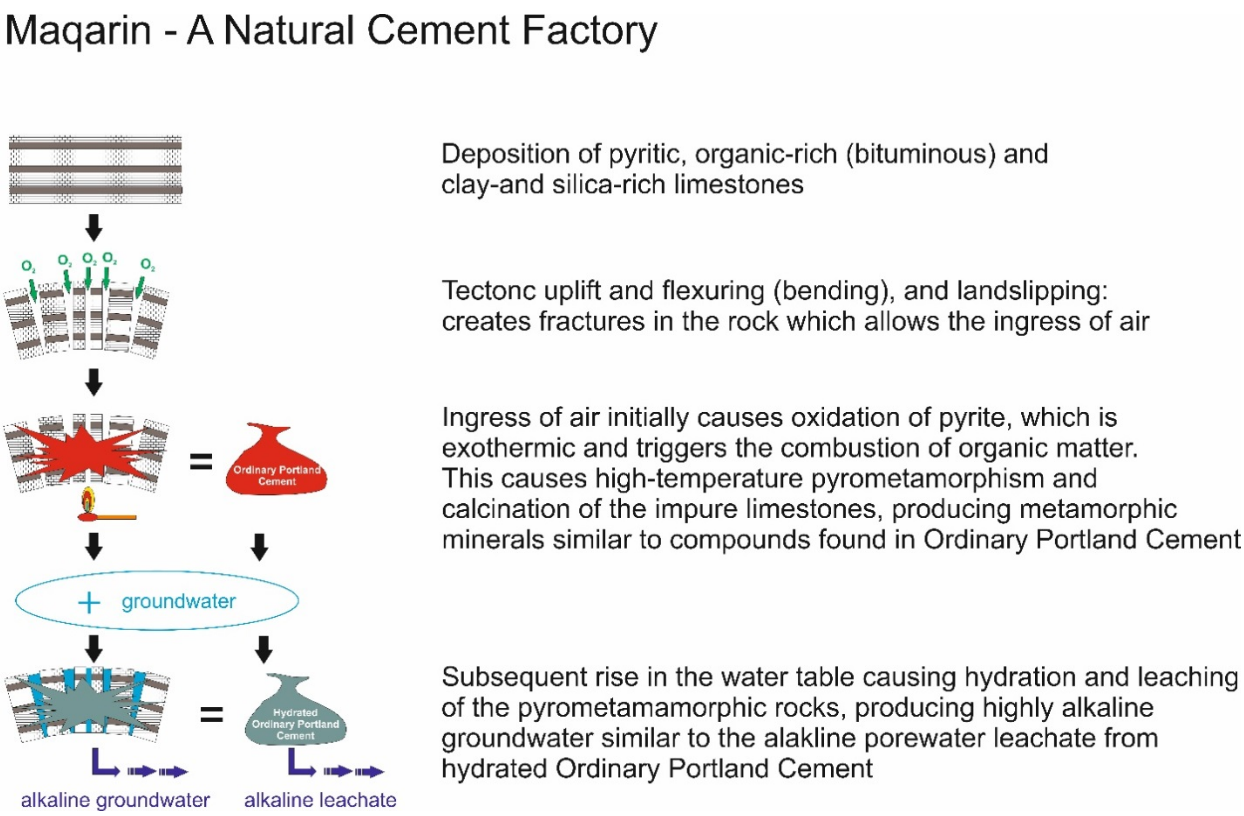
- Microbial degradation of cements and concretes is commonly observed under aerobic conditions and could occur during the early phase of a GDF, thus undermining the performance of the GDF in the short-term. This needs to be considered when carrying out safety case evaluations;
- Microbial degradation is achieved by microbes oxidising sulphur, sulphide and thiosulphate, resulting in the production of sulphuric acid, which attacks the concrete matrix by dissolving calcium silicate hydrate (CSH) gel and $Ca(OH)_2$. Direct anaerobic corrosion of concrete 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.

Maqarin natural analogue

- The Maqarin study site is located in northern Jordan in an area with clay- and organic-rich limestones, where hyperalkaline springs are associated with the retrograde alteration and hydration of thermally-metamorphosed zones created by spontaneous combustion (pyrometamorphism) of the organic-rich rocks. The pyrometamorphic rocks and their hydrated alteration products have a similar mineralogy to kilned 'cement clinker' with portlandite ($Ca(OH)_2$), a critical component of many GDF cements and concretes, comprising a major rock-forming mineral in the hydrated altered rocks. This makes the Maqarin site a particularly close analogue of a cementitious GDF;

- Analysis of the water from these springs 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/cement 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 waters 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}). However, a wide range of species were detected that were shown to be metabolically active, albeit at a low level. 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.



Schematic representation of the production of the natural analogue cements at Maqarin and in central Jordan.

Uncertainties and differences

- 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;
- Another important difference between the post-closure environment of a cementitious GDF and the Maqarin natural analogue, 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 cement pore waters of a GDF over long time periods;
- The conditions within / around a radioactive waste repository (particularly one at greater depths) may well differ from the conditions within the analogue and therefore the microbial populations within a repository may differ considerably from those that have been studied here.

Relevance – what we have learnt

- The mineralogy and chemistry of the pyrometamorphic marbles and their hydrated alteration products at Maqarin natural analogue site are a very close analogue for Portland-type cements used in a GDF, This is in marked contrast to the Oman alkaline natural analogue site, where the alkaline groundwaters are produced by low-temperature serpentinisation of ultramafic igneous rocks;
- The pH of the Maqarin alkaline groundwaters range between pH 12.3 and pH 12.9, buffered by portlandite. 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 cements will be around pH 12.5, 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 Portland cement, also provides some degree of analogue comparison for the early stages of pH evolution in the GDF environment;
- 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.
- 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;
- The observations provide some justification for researching the possible effects of microbes on engineered barrier performance in cementitious repositories.

Further reading

COOMBS, P., GARDNER, S., ROCHELLE, C.A AND WEST, J.M. 1998. Natural analogue for geochemistry and microbiology of cement porewaters and cement porewater host rock. Near-field interactions. In: Linklater, C.M. (Ed.). *A natural analogue study of cement buffered, hyperalkaline groundwaters and their interaction with a repository host rock Phase II*. Nirex Report, **S/98/003,** UK Nirex, Harwell, Oxon., UK.

PEDERSEN, K., ARLINGER, J., ERLANDSON, A-C. AND HALLBECK. L. 1998. Culturability and 16S rRNA gene diversity of microorganisms in the hyperalkaline groundwaters of Maqarin. In: Smellie. J. (Ed.), *Maqarin Natural Analogue Study: Phase III*. SKB Technical Report, **TR-98-04**, Sweden. (Volumes I and II).

PEDERSEN, K., NILSSON, E., ARLINGER, J., HALLBECK, L. AND O'NEILL, A. 2004. Distribution, diversity and activity of microorganisms in the hyper-alkaline spring waters of Maqarin in Jordan. *Extremophiles*, 8 (2), 151-164.

SAVAGE, D. *Analogue Evidence Relevant to the Alkaline Disturbed Zone*, Report prepared for United Kingdom Nirex Limited, QRS-1300A-1, Version 2.0, 2005.

WEST, J. M., DEGUELDRE, C., BRUETSCH, R., GARDNER, S., INCE, S. AND MILODOWSKI, A. E. 1992. Microbial and colloidal populations in the Maqarin groundwaters. In: Alexander, W.R. (Ed.). *A natural analogue study of cement-buffered hyperalkaline groundwaters and their interaction with a sedimentary host rock - I: Source-term description and geochemical code database validation*. NAGRA Technical Report, **NTB 91-10**, Nagra, Wettingen, Switzerland.

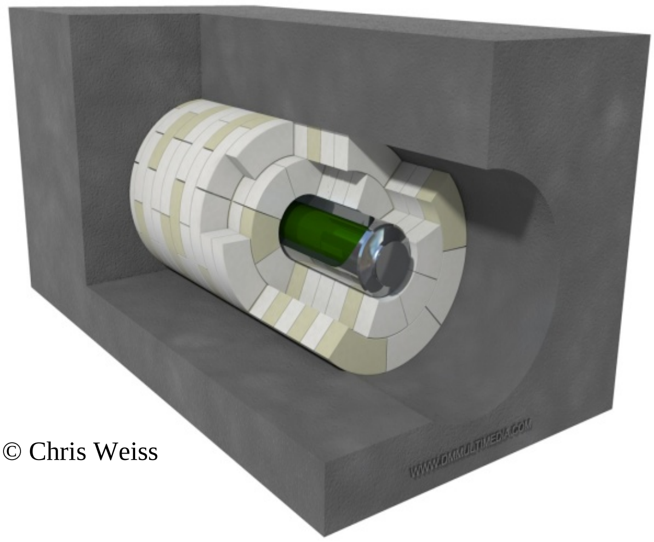
WEST, J.M., COOMBS, P., GARDNER, S.J. AND ROCHELLE, C.A. 1995. The microbiology of the Maqarin site, Jordan. A natural analogue for cementitious radioactive waste repositories. *Scientific Basis for Nuclear Waste Management*, **XVIII**, 181-189.

The Dunarobba Forest, Todi, Italy: long-term isolation properties of clay

Overview

The use of bentonite buffer

The engineered barrier system (EBS) of a Geological Disposal Facility (GDF) for radioactive waste is characterised by the use of large quantities of rather simple, well-understood materials. For example, many high-level wastes, spent fuel and some low- to intermediate wastes GDF designs specify the use of compacted bentonite clay as a backfill or buffer around waste packages or canisters. The functions of the bentonite are:



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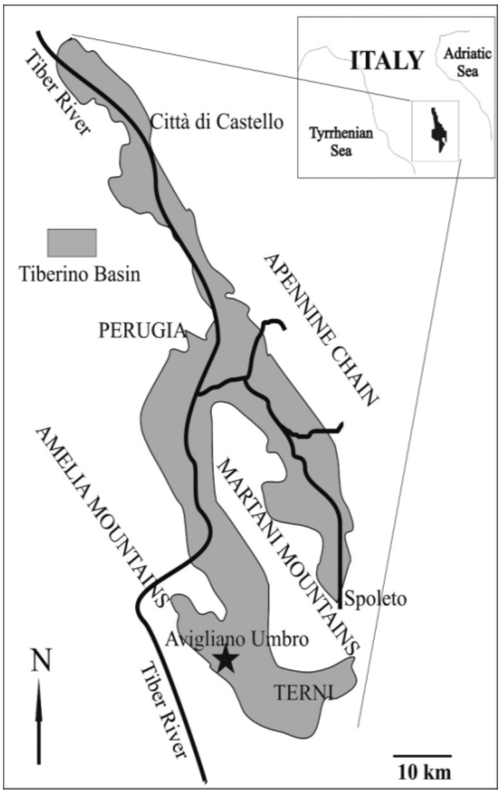
Example of an engineered barrier system in a clay host rock

- 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 montmorillonite clay in the bentonite swells when hydrated, producing a material with an extremely low hydraulic conductivity;
- To slow the migration of radionuclides from the waste (because of low hydraulic conductivity of the bentonite), so much so that the vast majority of radionuclides generated 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 resaturation;
- High retardation of radionuclides in the backfill because of the good radionuclide sorption properties of the bentonite.

The Dunarobba Forest natural analogue study

During the 1970s, in the Dunarobba and Cava Topetti quarries in Umbro, Italy, 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. The trees originally grew in the swampy margins of a coastal lake and the soils and clays in which they stand have been dated to the Upper Pliocene, making the trees approximately 2.5 million years old. Most amazingly, they are not petrified; rather they still consist of wood.

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



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

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 current attempts to shelter the trees from the elements, the trees have started to degrade because of the natural weathering process, which the clays protected them against for so many millennia.

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.

A Dunarobba Forest log being sampled. From Miller et al (2000).

Example of fossil wood, Dunarobba Forest (From Baldanza et al (2009).

Relevance – what we have learnt

- Unlike the engineered bentonite clay buffer in current GDF designs, the natural clays surrounding the trees at the Dunarobba Forest were not specially 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, could be minimised in a GDF near-field.

Further reading

AMBROSETTI, P., BASILICI, G., CIANGHEROTTI, A.D., CODIPIETRO, G., CORONA, E., ESU, D., GIROTTI, O. LO MONACO, A., MENEGHINI, M., PAGANELLI, A. AND ROMAGNOLI, M. 1995. The Dunarobba Fossil Forest (Terni, Umbria, central Italy): lithostratigraphic, sedimentologic, palynologic, dendrochronologic and paleomalacologic characteristics. *Italian Journal of Quaternary Sciences*, **8**, 465-508.

AMBROSETTI, P., BARBIERI, M. ET AL. 1995. Analysis of the geoenvironmental conditions as morphological evolution factors of the sand-clay series of the Tiber Valley and Dunarobba Forest preservation (activity period: July 1993-July 1994). *Commission of the European Communities, Nuclear Science and Technology: Migration of radionuclides in the geosphere (Mirage Project-3rd Phase)*. Proceedings of the final meeting, Brussels, 15-17 November 1994. Report EUR 16218 EN, Luxembourg.

BALDANZA, A., SABATINO, G., TRISCARI, M. CRISTINA DE ANGELIS, M. 2009. The Dunarobba Fossil Forest (Umbria, Italy): mineralogical transformations evidences as possible decay effects. *Per. Mineral*. **78**, 51-60.

MILLER, W.M., ALEXANDER, W.R., CHAPMAN, N.A., MCKINLEY, I.G. AND SMELLIE, J.A.T. 2000 *Geological Disposal of Radioactive Wastes and Natural Analogues*. Waste Management Series, Vol. 2, Pergamon, Amsterdam. The Netherlands.

WILSON, J. SAVAGE, D. BOND, A. WATSON, S. PUSCH, R .AND BENNET. D. 2011. Bentonite: a review of key properties, processes and issues for consideration in the UK context. *Quintessa Report*, **QRS-1378ZG-1.1**. Quintessa, Henley-on-Thames, UK.

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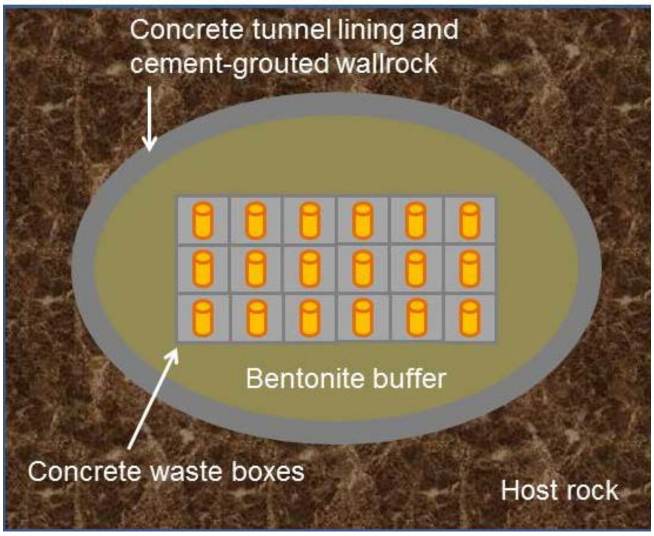
The Philippines: long-term isolation properties of clay

Overview

The use of bentonite backfill



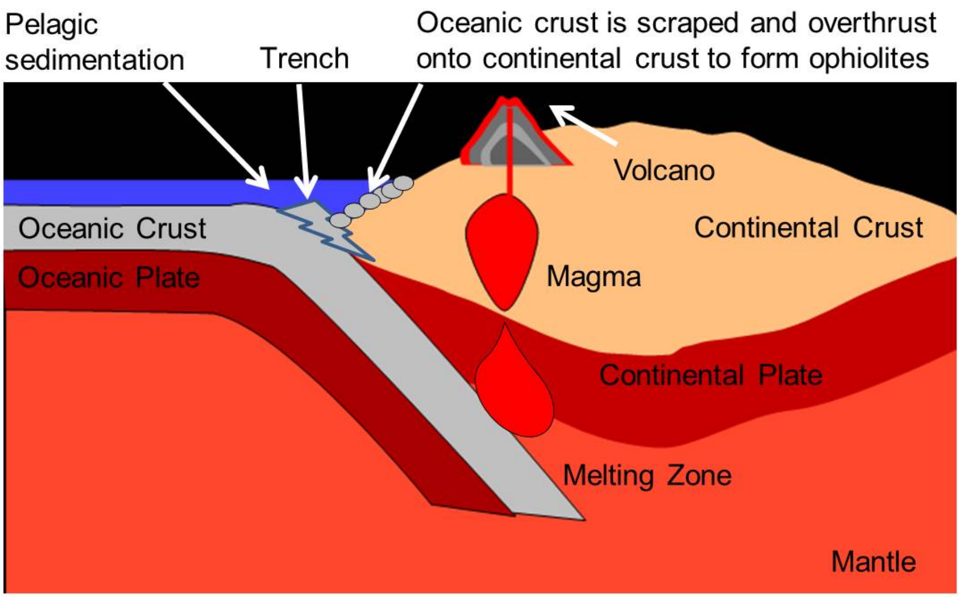
Cross-section through a potential GDF tunnel. Here, the cemented waste (orange) is placed in concrete boxes (grey) which are then surrounded by a protective layer of bentonite (green). Note also concrete tunnel liners (grey), necessary for staff safety during the construction and operational phase.

The engineered barrier system (EBS) of a Geological Disposal Facility (GDF) for radioactive waste is characterised by the use of large quantities of rather simple, well-understood materials. For example, many high-level wastes, spent fuel and some low- to intermediate wastes GDF designs specify the use of compacted bentonite clay as a backfill or buffer around waste packages or canisters. Bentonite plays a significant barrier role in the design of many GDF's , where it has been chosen because of its favourable properties such as plasticity, swelling capacity, colloid filtration, low hydraulic conductivity and its stability in relevant geological environments. In some designs, bentonite may be used alongside concrete, which could be problematic in the future. This is because bentonite is unstable under the high-pH of leachates derived from concrete construction materials (e.g. tunnel liners (although some may be removed prior to closure), grouts, etc.) and cementitious wastes in a GDF. This fact has led several national programmes to assess alternative construction and sealing materials such as low-pH cements. Recently, it has been assumed that the lower pH (typically between pH 10 and 11) leachates of such cements will degrade bentonite to a lesser degree than 'standard' OPC (Ordinary Portland Cement)-based cement leachates (generally with an initial pH >13). Laboratory experiments are currently testing this hypothesis (e.g. Heikola et al., 2013), but these short-term experiments need to be supported by long-term natural analogues that can assess bentonite reaction over thousands to millions of years.

The Philippines Natural Analogue Study

Natural alkaline groundwater

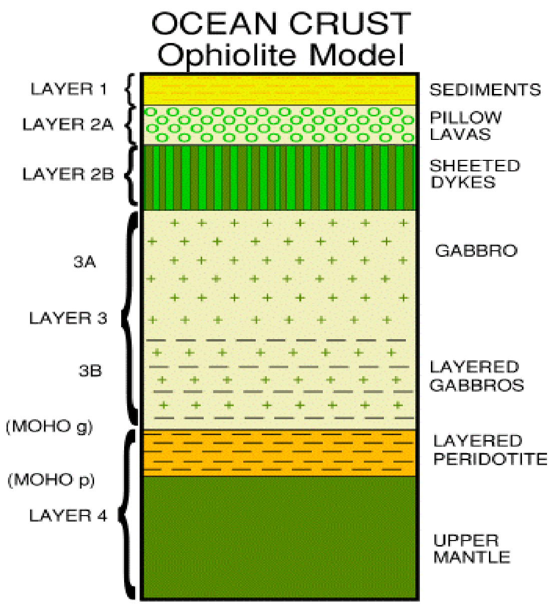
Natural groundwaters with the same pH-range as low-pH cements are found associated with certain igneous rock-types known as ophiolites in many areas of the world. Ophiolites are sequences of rocks that are formed when ancient ocean crust encounters one of the many deep ocean trenches found around the world (in this case the deepest known, the Marianas Trench). Normally, this crust is drawn down into the Earth's mantle where it melts and returns in the form of the many volcanoes which stud the so-called 'Circum-Pacific Ring of Fire'. However, not all ocean crust is consumed in this fashion, sometimes pieces are 'scraped off' the sinking plate and end up exposed on land, as ophiolites.



Ophiolites are produced as a result of plate tectonics, where oceanic plates are dragged down in deep oceanic trenches and subducted beneath overriding continental crust. The oceanic crust and overlying sediments are scraped up onto continents to form ophiolites.

Reaction of near-neutral pH groundwater with minerals present in an ophiolite produces the natural alkaline (and often hydrothermal) groundwaters that are a common feature of ophiolites worldwide.

A common feature of ophiolites is the presence of bentonite, usually lying on top of the upper-most layer of oceanic crust. This serendipitous combination of alkaline groundwaters and bentonite make such areas a suitable natural laboratory to study the long-term reaction of bentonite in an environment almost identical to that in a GDF using low-pH cement and bentonite together.

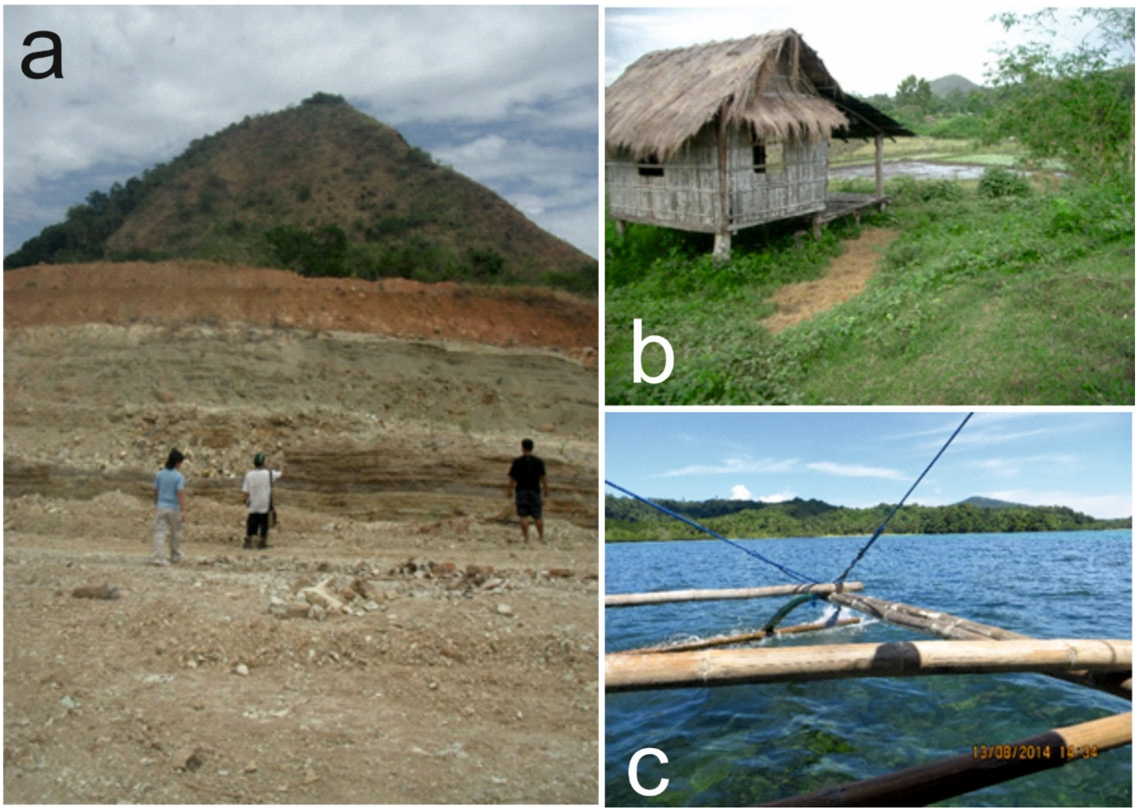


Schematic cross-section of an ophiolite. Layer 1 contains the bentonite and the hyperalkaline groundwater is produced in the igneous layers 2-4.

In the Philippines there are at least 20 known occurrences of ophiolites with associated alkaline groundwaters and bentonite clays.

One of the best places to examine the bentonite is in the Mangatarem area of western Luzon, about 150 km north of the capital, Manila. Here, the mineral-rich Zambales ophiolite produces copious amounts of alkaline groundwater, which appears to have reacted to a very small extent with the base of the widespread bentonite.

Following work at Mangatarem (see Tsukada et al., 2012; Fujii et al., 2014, for details), drilling was carried out at Bigbiga, some 30 km further south and despite clear evidence for alkali groundwaters below the bentonite layer here too, little sign of significant change to the bentonite has been found. The results to date indicate that minimal reaction of the bentonite has occurred over millions of years, something that compares well with the results from the Cyprus natural analogue study. As in Cyprus, this does not seem to have been enough to damage the bentonite in any significant way, suggesting that using low-pH cements and bentonite together in a GDF may well be feasible.



The Philippines Natural Analogue Project: (a) The Mangaatatem site - despite some degree of reaction of the bentonite at its base, thick deposits remain unperturbed at Mangatarem (courtesy of Sailes Industries, Manila); (b) Typical paddy field terrain at the Bigbiga (Luzon) site. Drilling around the paddy fields of the small village of Bigbiga (Luzon) has been extensive but, despite encountering alkali groundwaters below the bentonites, little indication of any reaction or alteration of the clay have been observed (©Bedrock Geosciences); (c) Ulugan Bay, Palawan: some of the analogue sites are only accessible from the sea (©Bedrock Geosciences).

Research at these sites in continuing, and the current focus for the project team is a raft of sites on the island of Palawan in south west Philippines. Here, some of the sites need to be approached by fishing boat, weaving a path through the dense mangrove forest on the shore. At other sites, it is possible to access the area by foot and sample by drilling boreholes or digging trenches into the sediments to examine the potential zone of reaction in the bentonite.

The island of Palawan in southwest Philippines: (a) small drilling rig employed to sample the bentonite (©Bedrock Geosciences); (b) Narra, Palawan: despite monsoonal rains, samples can be collected from trenches dug by JCB excavators and finished by hand (©Bedrock Geosciences).

Uncertainties and limitations

- No dates for the reaction times of the bentonite are currently available, so there remains some uncertainty as to the timing of events;
- The spatial extent of reactions is a function both of the permeability and reactivity of the bentonite and the minimal extent of reaction observed in the ophiolite may in part be attributed to the low permeability of the bentonite rather than the lack of reactivity with the alkaline water;
- In addition, no estimation of the volume of alkali groundwater involved in these reactions has been calculated so far, so it is currently impossible to compare the system directly with a GDF where the volume of cement porewater produced will be precisely known.

Relevance – what we have learnt

- To date, bentonite in contact with natural alkali groundwaters has been sampled at a range of sites across the Philippines and, despite minimal reaction at the base of the bentonite, the vast majority of the material remains unchanged. This suggests that the use of cement and concrete for construction in repository designs which utilise a bentonite clay barrier will not be deleterious to the bentonite;
- This suggests that GDF designs which combine bentonite barrier materials and low-pH cement and concrete, necessary for construction and safety, would be possible;

Further reading

ALEXANDER, W.R., ARCILLA, C.A,. MCKINLEY, I.G., KAWAMURA, H., TAKAHASHI, Y., AOKI K. AND MIYOSHI S. 2008 A new natural analogue study of the interaction of low-alkali cement leachates and the bentonite buffer. *Scientific. Basis for Nuclear Waste Management*, **XXXI**, 493-500.

FUJII, N., YAMAKAWA, M., SHIKAZONO, N. AND SATO, T. 2015. Geochemical and mineralogical characterisation of bentonite interacted with alakaline fluids generating in Zambales Ophiolite, northwestern Luzon, Philippines. *Journal of the Geological Society of Japan*, **120**, 361-375 (*in Japanese with English abstract*)

HAWORTH, A., SHARLAND, S.M., TASKER, P.W. AND TWEED, C.J. 1987. Evolution of the groundwater chemistry around a nuclear waste repository. *Scientific. Basis for Nuclear Waste Management*, **XI**, 425-434

HEIKOLA, T., KUMPULAINEN, S., VUORINEN, U., KIVIRANTA, L. AND KORKEAKOSKI, P. 2013. Influence of alkaline and saline solutions on chemical, mineralogical and physical properties of two different bentonites – batch experiments at 25 °C. *Clay Minerals* **48**, 309-329.

METCALFE, R. AND WALKER, C. 2004. Proceedings of the International Workshop on Bentonite-Cement Interaction in Repository Environments 14–16 April 2004, Tokyo, Japan. *NUMO Technical Report*, **NUMO-TR-04-05**, NUMO, Tokyo, Japan.

REIJONEN, H.M. AND ALEXANDER, W.R. 2015. Bentonite analogue research related to geological disposal of radioactive waste – current status and future outlook. *Swiss Journal of* Geosciences, **108**, 101-110. [DOI 10.1007/s00015-015-0185-0]

TSUKADA, Y., NAKABAYASHI, R. ET AL. 2012. Natural analogue study for interaction between alkaline groundwater and bentonite at Mangatarem region in the Philippines. *Clays in natural and engineered barriers for radioactive waste confinement – 5 (book of abstracts), Montpellier, September, 2012*. ANDRA, Paris, France. https://inis.iaea.org/search/search.aspx?orig_q=RN:44048905

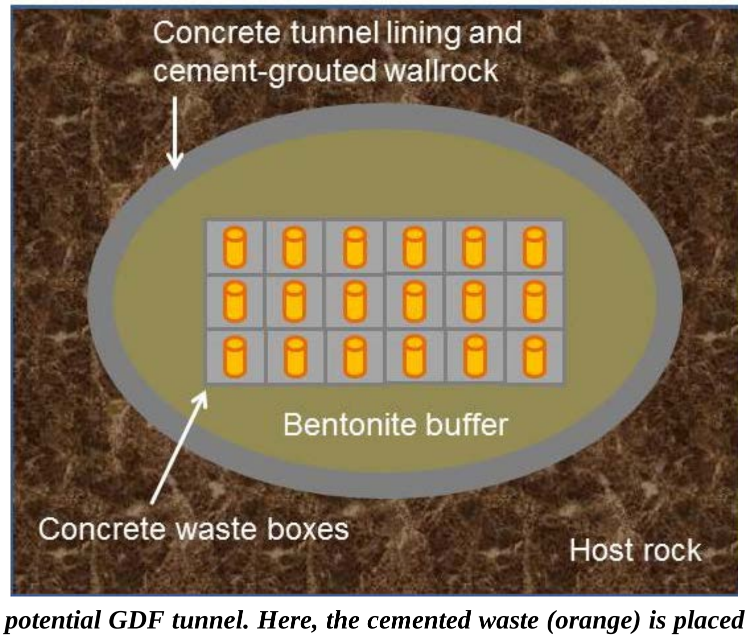
WILSON, J. SAVAGE, D. BOND, A. WATSON, S. PUSCH, R .AND BENNET. D. 2011. Bentonite: a review of key properties, processes and issues for consideration in the UK context. *Quintessa Report*, **QRS-1378ZG-1.1**. Quintessa, Henley-on-Thames, UK.

Cyprus: long-term isolation properties of clay

Overview

The use of bentonite backfill

The engineered barrier system (EBS) of a Geological Disposal Facility (GDF) for radioactive waste is characterised by the use of large quantities of rather simple, well-understood materials. For example, many high-level wastes, spent fuel and some low- to intermediate wastes GDF designs specify the use of compacted bentonite clay as a backfill or buffer around waste packages or canisters. is chosen because of its favourable properties such as plasticity, swelling capacity, colloid filtration, low hydraulic conductivity and its stability in relevant geological environments. In some designs, bentonite may be used alongside concrete, which could be problematic in the future. This is because bentonite is unstable under the high-pH of leachates derived from concrete construction materials (e.g. tunnel liners (although some may be removed prior to closure), grouts, etc.) and cementitious wastes in a GDF. This fact has led several national programmes to assess alternative construction and sealing materials such as low-pH cements. Recently, it has been assumed that the lower pH (typically between pH 10 and 11) leachates of such cements will degrade bentonite to a lesser degree than 'standard' OPC (Ordinary Portland Cement)-based cement leachates (generally with an initial pH >13). Laboratory experiments are currently testing this hypothesis (e.g. Heikola et al., 2013), but these short-term experiments need to be supported by long-term natural analogues that can assess bentonite reaction over thousands to millions of years.



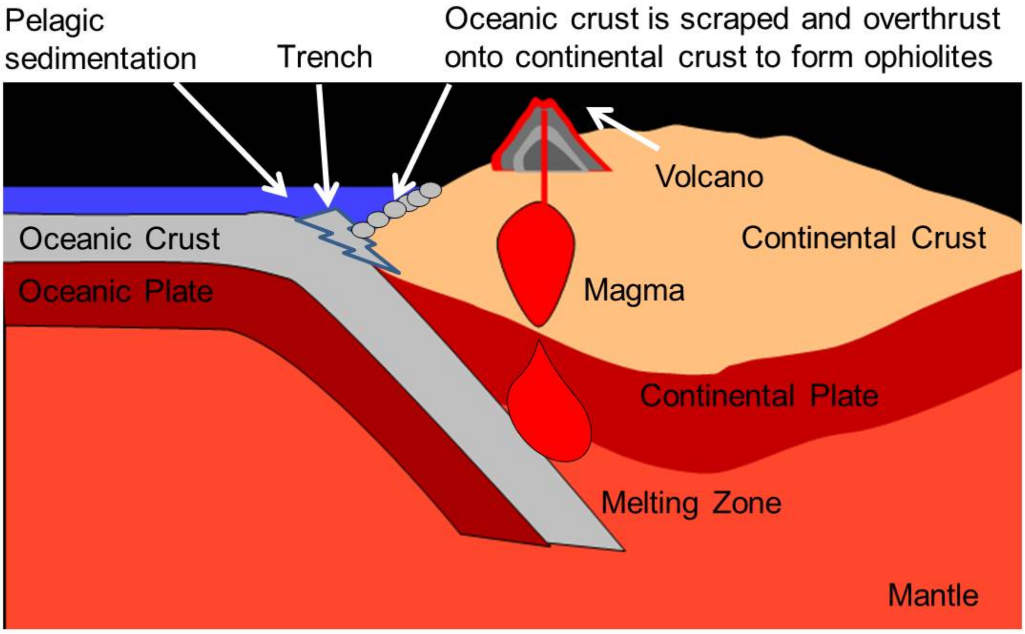
Cross-section through a potential GDF tunnel. Here, the cemented waste (orange) is placed in concrete boxes (grey) which are then surrounded by a protective layer of bentonite (green). Note also concrete tunnel liners (grey), necessary for staff safety during the construction and operational phase.

The Cyprus Natural Analogue Study

Natural alkaline groundwater

Natural groundwaters with the same pH-range as the low-pH cements are found within the Troodos Ophiolite Complex on the Island of Cyprus. Ophiolites are formed when ancient ocean crust has been 'scraped off' and thrusted (obducted) onto the edge of continental plates, and subsequently end up exposed on land as ophiolites.

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

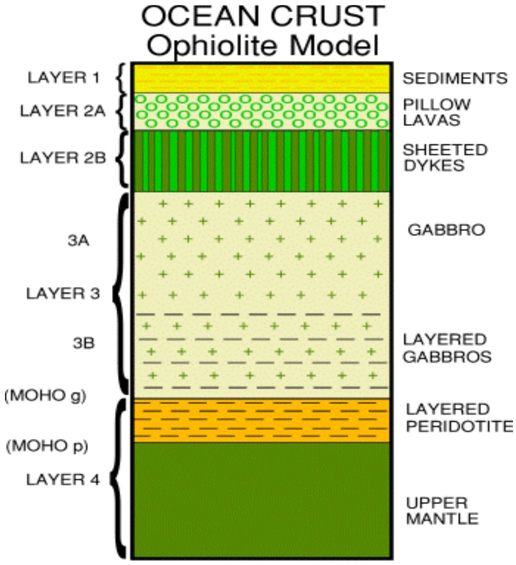


Ophiolites are produced as a result of plate tectonics, where oceanic plates are "scraped-up" and thrust onto continental crust. The oceanic crust and overlying sediments are scraped up onto continents to form ophiolites.

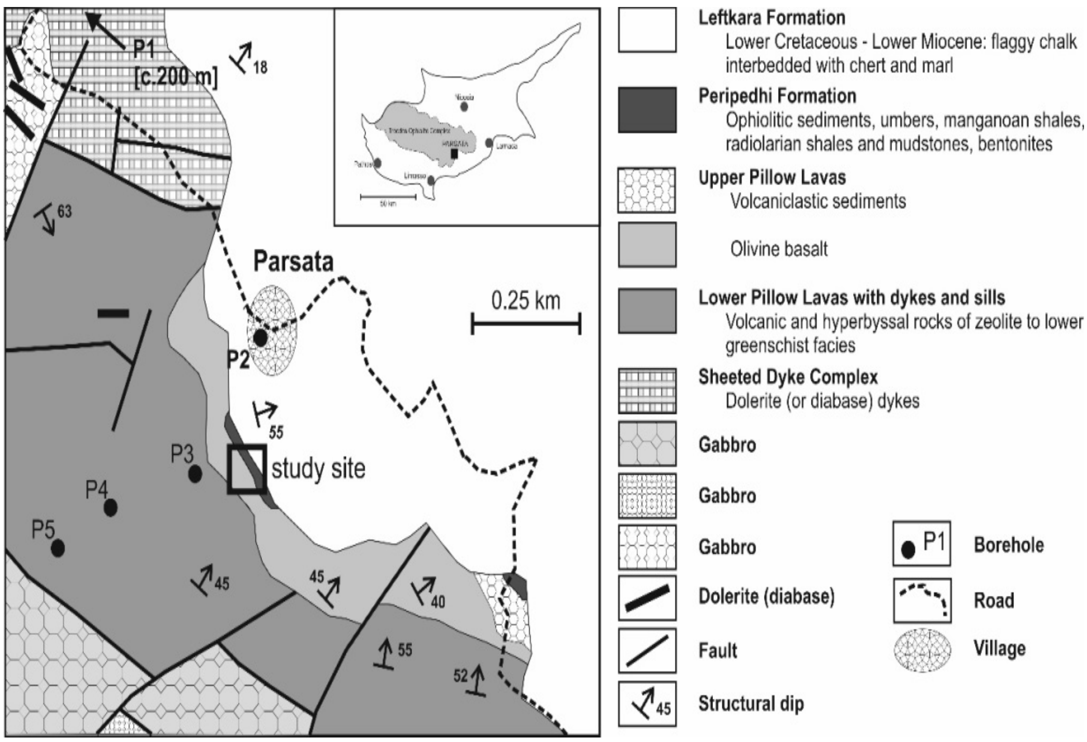
Alkaline groundwater discharging with artesian flow through a steeply inclined fracture in harzbergite. Travertine (tufa) is deposited over the harzbergite surface as the Ca-rich alkaline groundwater reacts with atmospheric CO_2. The brown staining is caused by biofilms or bacterial mats coating the surface of the travertine deposit. Allas Springs, Troodos Mountains (from Alexander and Milodowski, 2011).

Geological setting: the Parsata site

Bentonites are often present within the sedimentary sequence deposited on top of the upper-most layer of igneous rock forming the oceanic crust. This situation is found on the southern flanks of the Troodos Massif in Cyprus. 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.

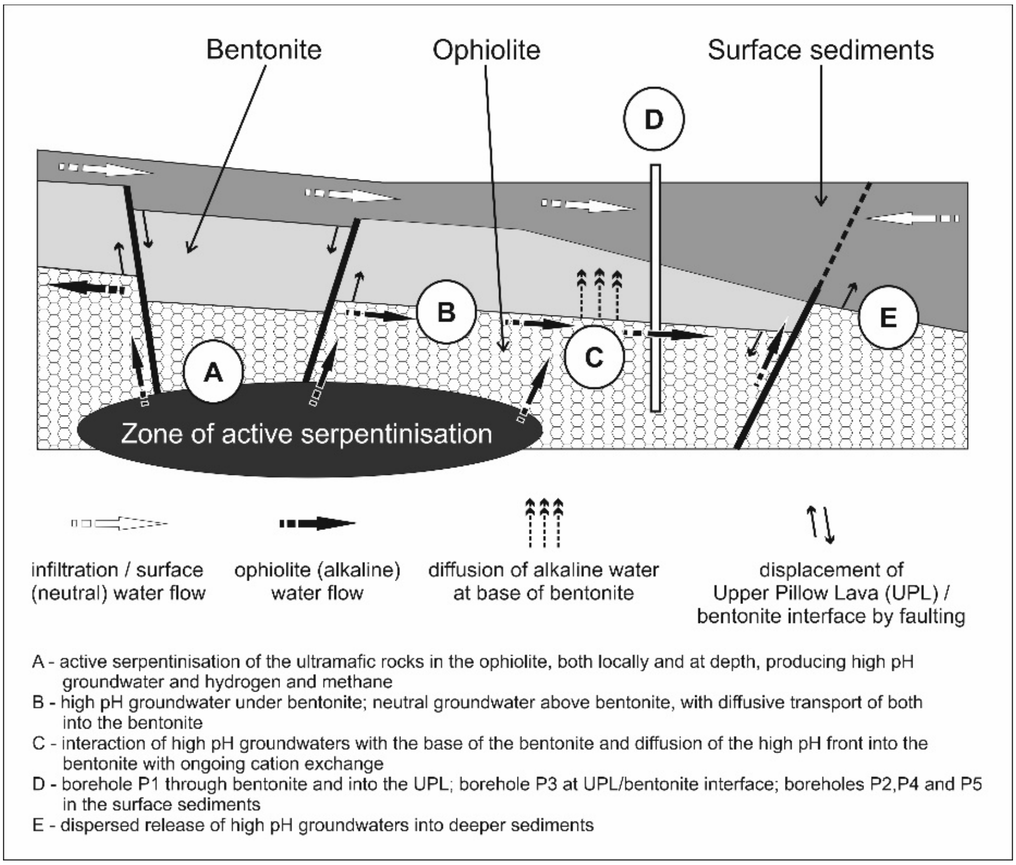


Schematic cross-section of an ophiolite. Layer 1 contains the bentonite and the hyperalkaline groundwater is produced in the igneous layers 2-4.



Location map and bedrock geology of the Parsata area showing the location of study site and irrigation boreholes used for groundwater sampling (Alexander and Milodowski, 2015).

The analogue site is located around the abandoned village of Parsata, east-northeast of Limassol. The village sits on a plateau above the Vasilikos valley, which drains the Limassol Forest. At Parsata, Upper Cretaceous bentonite-rich sediments (Peripedhi Formation) infill palaeo-depressions in the highly irregular surface of the olivine basalts, which form the Upper Pillow Lavas at the top of the ophiolite sequence. Alkaline (pH ≤11) groundwaters produced by currently active low-temperature serpentinisation within the underlying ultrabasic rocks discharge through the fractured and permeable pillow lavas, penetrating into the base of the overlying bentonite. A series of trenches and boreholes were dug and sampled across this interface to study the interaction between the alkaline groundwater and bentonite.



Schematic overview of the alkaline groundwater flow system in the Cyprus analogue.

Uncertainties and limitations

- Palygorskite is identified as an alteration product of bentonite by alkaline groundwater in the Cyprus natural analogue. 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 silica and glass which is different to the typical bentonite formulations proposed for use in a GDF;

- 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 Ordovician, andesitic meta-volcanic rocks from the Sellafield area of the UK (Moyce et al., 2014);

- Thermodynamic data and mineralogical observations from other natural occurrences suggest that palygorskite is only stable under very high dissolved silica activities. Therefore, its formation in the Parsata analogue site may be due to the high concentration of amorphous (biogenic) silica and present relict glass, which would dissolve in the high-pH groundwater, producing the high silica activities required to stabilise palygorskite;
- Although, high silica contents are not to be expected in most processed bentonites, typical requirements for processed bentonite for repositories 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. In these designs, bentonite would not be required to swell. Unfortunately, models of bentonite reaction do not currently include the dissolution of silica sand, amorphous materials and/or glasses.

Relevance – what we have learnt

- The field conditions of this analogue are considered to realistically simulate those expected in a GDF;
- The results indicate that minimal mineralogical alteration of bentonite by alkaline groundwater has occurred over a period of 10^5-10^6 years. Only very minor alteration and replacement of smectite to fibrous palygorskite was observed, typically along micro-fractures;
- 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;
- 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.

Further reading

ALEXANDER, W.R. AND MILODOWSKI, A.E. 2008. Low-alkali cement leachate/bentonite interaction natural analogue study. Cyprus Natural Analogue Project (CNAP) Phase I. *Bedrock Geosciences Technical Report*, **BG08-01**, Bedrock Geosciences, Auenstein, Switzerland.

ALEXANDER, W.R. AND MILODOWSKI, A.E. 2009. Cyprus Natural Analogue Project (CNAP) Phase II Reconnaissance Trip Report November-December 2008. *Bedrock Geosciences Technical Report*, **BG08-02**, Bedrock Geosciences, Auenstein, Switzerland.

ALEXANDER, W.R. AND MILODOWSKI, A.E. (EDITORS). 2011. Cyprus Natural Analogue Project (CNAP) Phase II Final Report. *Posiva Working Report,* **WR 2011-08**, Posiva, Eurajoki, Finland.

ALEXANDER, W.R., MILODOWSKI, A.E. AND PITTY, A.F. (EDITORS) 2011. Cyprus Natural Analogue Project (CNAP) Phase III Final Report. *Posiva Working Report,* **WR 2011-77**, Posiva, Eurajoki, Finland.

ALEXANDER, W.R. MILODOWSKI, A.E. CONSTANTINOU, C.A. RIGAS, M. TWEED, C. SELLIN, P. KORKEAKOSKI, P. AND PUIGDOMENECH . I. 2011. Reaction of bentonite in low-alkali cement leachates: results from the Cyprus Natural Analogue Project. *Proceedings of ICEM 2011 Conference, Reims, France, September, 2011,* ASME, Washington, USA.

ALEXANDER, W.R. MILODOWSKI, A.E. PITTY, A.F. HARDIE, S. KORKEAKOSKI, P. RIGAS, M. SELLIN, P. AND TWEED, C. 2012. Reaction of bentonite in low-alkali cement leachates: results from the Cyprus Natural Analogue Project. Extended abstract in: *Proceedings of the Conference on the Geological Disposal of Radioactive Waste: Underpinning Science and Technology for Radioactive Waste 18 - 20 October 2011, Loughborough, UK.* Mineralogical Magazine, December *2012*, **76(8)**, 149–152.

ALEXANDER, W.R. AND MILODOWSKI, A.E. (EDITORS). 2013. Cyprus Natural Analogue Project (CNAP) Phase IV Final Report. *Bedrock Geosciences Technical Report*, **BG13-02**, Bedrock Geosciences, Auenstein, Switzerland.

ALEXANDER, W.R. AND MILODOWSKI, A.E. (EDITORS). 2013. Cyprus Natural Analogue Project (CNAP) Phase IV Final Report. *Posiva Working Report*, Posiva, Eurajoki, Finland (in press).

ALEXANDER, W.R. MILODOWSKI, A.E. PITTY, A.F., HARDY, S.M.L., KEMP, S.J., RUSHTON, J.C., SIATHAS, A., SIATHAS, A., MACKENZIE, A.B., KORKEAKOSKI, .P., NORRIS, S., SELLIN, P. AND RIGAS, M. 2013. Bentonite reactivity in alkaline solutions: results of the Cyprus Natural Analogue Project (CNAP). *Clay Minerals*, **48**, 235–249.

GASS, I.D., MACCLEOD, C.J., MURTON, B.J., PANAYIOTOU, A., SIMONIAN, K.O. AND XENOPHONTOS, C. 1994. The Geology of the Southern Troodos Transform Fault Zone. *Geological Survey Department Memoir*, **No.9**, Geological Survey Department, Lefkosia, Cyprus.

HEIKOLA, T., KUMPULAINEN, S., VUORINEN, U., KIVIRANTA, L. AND KORKEAKOSKI, P. 2013. Influence of alkaline and saline solutions on chemical, mineralogical and physical properties of two different bentonites – batch experiments at 25 °C. *Clay Minerals* **48**, 309-329.

MILODOWSKI, A. E**.**, NORRIS, S. AND W.R. ALEXANDER, 2016. Minimal alteration of montmorillonite following long-term interaction with natural alkaline groundwater: Implications for geological disposal of radioactive waste. *Applied Geochemistry*, 66. 184-197.

MOYCE, E.B.A., ROCHELLE, C.A., MORRIS, K., MILODOWSKI, A.E., CHEN, X., THORNTON, S., SMALL, J.S. AND SHAW. S. 2014. Rock alteration in alkaline cement waters over 15 years and its relevance to the geological disposal of nuclear waste. *Applied Geochemistry*, **50**, 91-105.

WILSON, J. SAVAGE, D. BOND, A. WATSON, S. PUSCH, R .AND BENNET. D. 2011. Bentonite: a review of key properties, processes and issues for consideration in the UK context. *Quintessa Report*, **QRS-1378ZG-1.1**. Quintessa, Henley-on-Thames, UK.

Mudrocks altered by igneous intrusions: thermal stability of clay barriers

Overview

Radioactive decay generates heat energy. In natural systems the decay of naturally-occurring radioactive elements (principally uranium, thorium and potassium) is what keeps the inside of planets like the Earth hot. The radioactive decay in high-level radioactive wastes (HLW) and spent nuclear fuel also still generates some heat. Rocks are relatively good insulators and so spent fuel and HLW are likely to warm up once stored deep underground; potentially warming to around 100 °C in some design concepts for a Geological Disposal Facility (GDF) for radioactive waste. As heating might change the mechanical and chemical properties of backfill materials surrounding storage canisters, and potentially the surrounding rocks, it is important to design a deep GDF where long-term warming is taken into account. 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.

The thermal phase after GDF closure may persist for a few thousand years. 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.

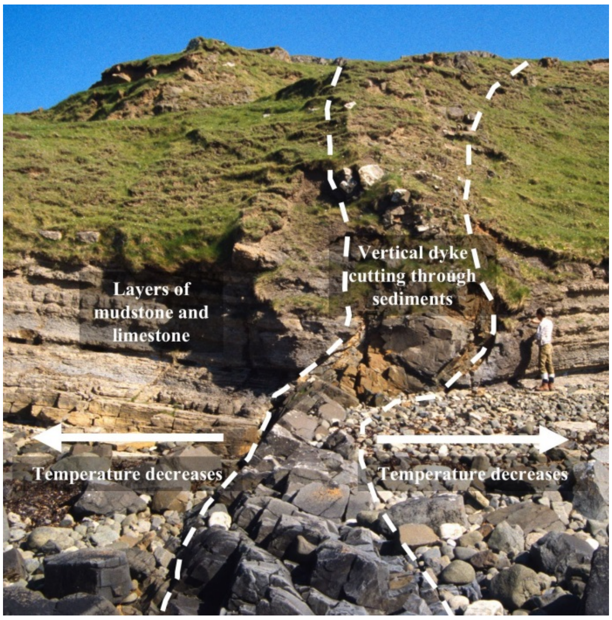
If we are to understand how materials used in a GDF and the surrounding rocks will behave with long-term warming we need to study natural thermal analogues that have undergone similar warming over tens, hundreds or thousands of years.

Clay thermal analogues: nature's experiments

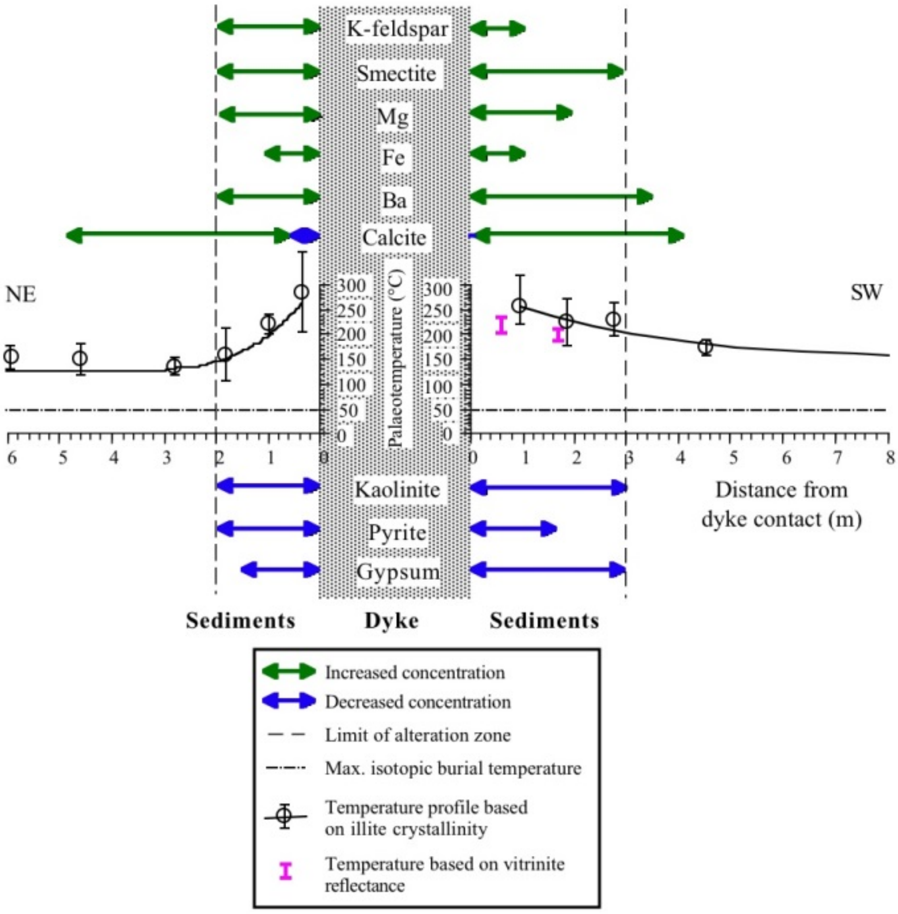
Several examples of clays and mudstones intruded by igneous rocks have been studied as analogues for the thermal impact on engineered clay barriers in a GDF. The intrusion of molten rocks at about 800-1,200 °C into clay-rich sedimentary rocks causes a locally high thermal gradient, parts of which could 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 temperatures. Samples can be taken from these zones and tested to assess if there have been changes in the bentonite properties.

Isle of Skye, Scotland

Several examples of Tertiary basaltic dykes and sills cutting Jurassic mudrocks were studied on northern Skye, Scotland. These approximately 70 million year old intrusions vary from 20 cm to several metres in thickness (see image, right). Samples taken from the clays show that heating occurred within about one dyke-width of the intrusion. Although smectite is unstable at high temperatures, the smectite content of the mudstones increases towards the contact with some intrusions, indicating that a post-heating or back-reaction event caused smectite to form once the rocks had cooled down. As a result, both high and low temperature mineral assemblages are found together, showing the complex nature of some of these analogues. Field observations also reveal that the physical properties of the mudstones changes near to their contact with the intrusions (e.g. becoming harder and more brittle). Networks of cracks within the mudstones were also observed, possibly resulting from thermal contraction of the clays. If similar cracking occurred adjacent to a GDF then enhanced radionuclide migration might result. However, evidence from Skye also shows that minerals (e.g. calcite and silica) precipitate in these cracks resulting in the cracks becoming sealed.



Tertiary dolerite dyke intruded into Jurassic interbedded mudstones and limestones, Isle of Skye (© British Geological Survey).

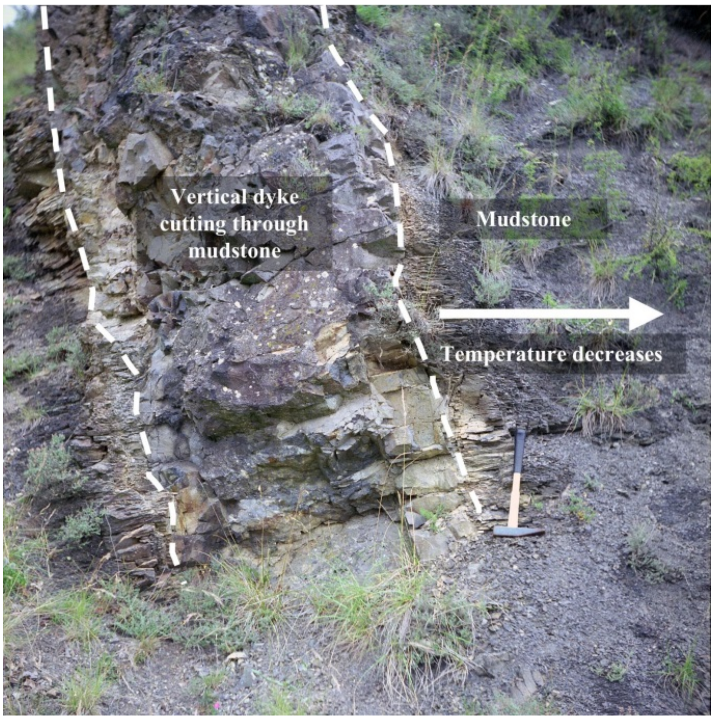


Mineralogical alteration profile observed in the Jurassic mudstone at the contact with the dolerite dyke, Isle of Skye (© British Geological Survey).

Col du Perthus, southern France

This site is approximately 50 km WNW of Montpellier, in southern France. About 1 km west of the village of Lauroux, Jurassic clays have been cut by a 1 m wide basaltic dyke that was intruded approximately 2 million years ago.

Samples taken from the clays show that heating is evident within about one dyke-width of the intrusion, similar to that observed on Skye. Heating within this zone was probably 100-250 °C but probably lasted for only a few years. Within this zone the illite-smectite mudrock is altered to a more illitic composition, resulting in a lower swelling capacity compared to the original clay. Reduced swelling capacity within the backfill in a GDF environment would equate to a reduction in sealing efficiency.

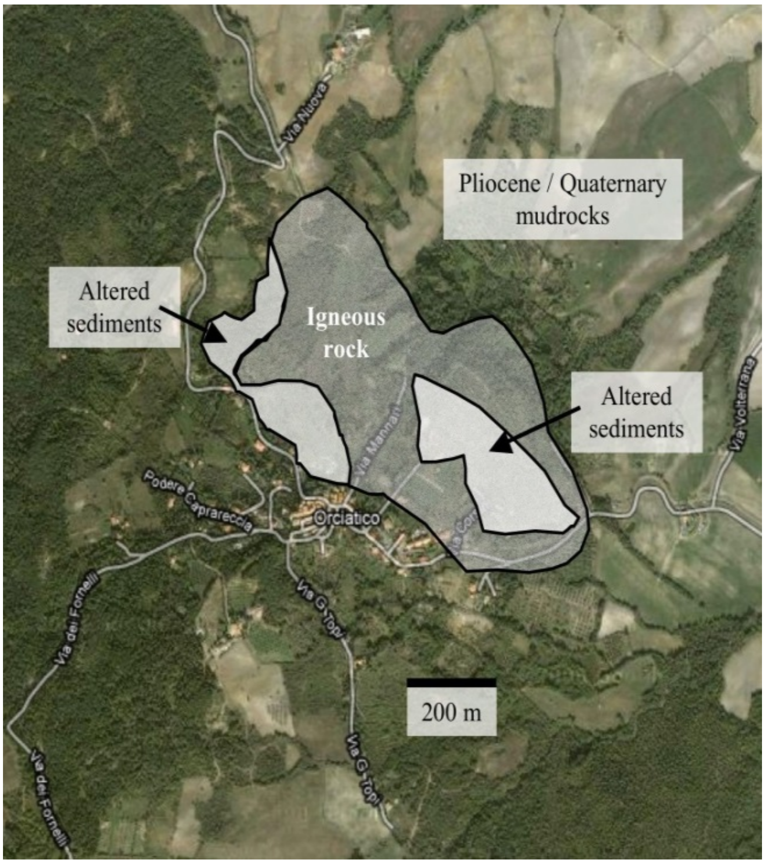


Basic dyke intruded into mudstone at the Col du Perthus site, southern France.

Orciatico, central Italy

The village of Orciatico is about 40 km SE of Pisa, Italy. Immediately north and east of the village is a small sill/laccolith that was intruded at shallow depth into marine Pliocene sediments around 4 million years ago.

Boreholes have been drilled into the mudrocks on the SE side of the intrusion to sample rocks heated to different temperatures. The illite-rich clays were altered up to several metres away from the intrusion. Similar to the analogue site on Skye, there are increases in the swelling clay content very close to the contact with the intrusion, where original temperatures were highest, because of later low-temperature rehydration reactions. The thermally altered zone is much larger than for the analogues above, and allowed several large samples to be taken across the temperature range of interest. These were tested for their mechanical properties, with results showing that heating increased the strength and overconsolidation of the clay. However, the heated clay is also less plastic and more prone to brittle failure, and has a higher permeability compared to the original clay.



The main geological features of the Orciatico site, central Italy.

Cabo de Gata, southern 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 very 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 can not uniquely attribute observed changes in the bentonite properties to specific temperatures.

Uncertainties and limitations

- 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 models they 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;

- 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 smectite-rich rocks. Identification and investigation of additional examples of the latter would improve understanding of thermal effects on bentonite buffer/backfill materials.

Relevance – what we have learnt

Despite the difference in intrusion size and original mudstone composition, initial mineralogical and geochemical data suggest that similar processes have operated at the above sites. Studies show:

- That heated clays are less plastic and more prone to brittle fractures and consequently results in higher permeability in comparison with the original clay;
- Heating increases strength and over-consolidation of the clay;
- Heating reduces the swelling capacity of the clay due to illitisation of smectite in these analogue environments. However illitisation may be due to hydrothermal processes that might not be relevant to a GDF environment.

Further reading

GERA, F., HUECKEL T. AND PEANO, A. 1996. Critical issues in modelling the long-term hydro-thermo-mechanical performance of natural clay barriers*. Engineering Geology*, **41**, 17-33.

Güven, N. 1990. Longevity of bentonite as buffer material in a nuclear-waste repository. *Engineering Geology,* **28,** 233-247.

Horseman, S.T. and McEwen, T.J. 1996. Thermal constraints on disposal of heat-emitting waste in argillaceous rocks. *Engineering Geology*, **41**, 5-16.

Pellegrini, R., Horseman, S., Kemp, S., Rochelle, C., Boisson, J.-Y., Lombardi, S., Bouchet A., and Parneix J.-C., 1999. Natural analogues of the thermo-hydro-chemical and thermo-hydro-mechanical response of clay barriers. Final report of EC project no. FI-4W/CT95/0014. *Nuclear Science and Technology Series*, **EUR 19114, ISBN 92-828-7317-X**, Office for Official Publications of the European Communities, 110p.

Pérez del Villar, L., Delgado, A., Reyes, E., Pelayo, M., Fernández-Soler, J.M., Cózar, J.S., Tsige M. and Quejido, A.J. 2005. Thermochemically induced transformations in Al-smectites: A Spanish natural analogue of the bentonite barrier behaviour in a radwaste disposal. *Applied Geochemistry*, **20**, 2252-2282.

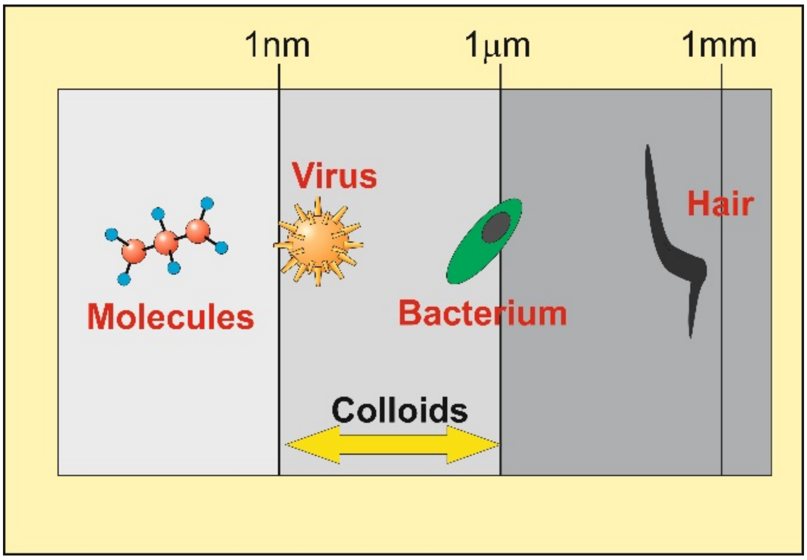
WILSON, J. SAVAGE, D. BOND, A. WATSON, S. PUSCH, R .AND BENNET. D. 2011. Bentonite: a review of key properties, processes and issues for consideration in the UK context. *Quintessa Report,* **QRS-1378ZG-1.1**. Quintessa, Henley-on-Thames, UK.

Engineered barrier system: colloids

Overview

Why study EBS colloids?

There is some evidence from laboratory and underground research laboratory experiments that colloids (or nano-particles) may be generated in the engineered barrier system (EBS) of a deep Geological Disposal Facility (GDF) for radioactive waste. These could include cement and metal colloids from the waste, containers and backfill of a low- and intermediate-level waste (L/ILW) repository, or glass, metal and clay colloids from similar sources in a high-level waste (HLW) GDF, produced as the materials degrade over time. Colloids may be produced from the bentonite and cement backfill through erosion by flowing groundwater. If radionuclides are associated with these colloids, and the colloids are mobilised and transported by groundwater flow, the ability of the EBS to contain radionuclides may decrease. This may lead to an increase in the flux of radionuclides from the EBS into the surrounding host rock. Consequently, it is important for a safety case to assess the significance of colloids generation and the potential impact of their mobilisation on radionuclide migration from the GDF.

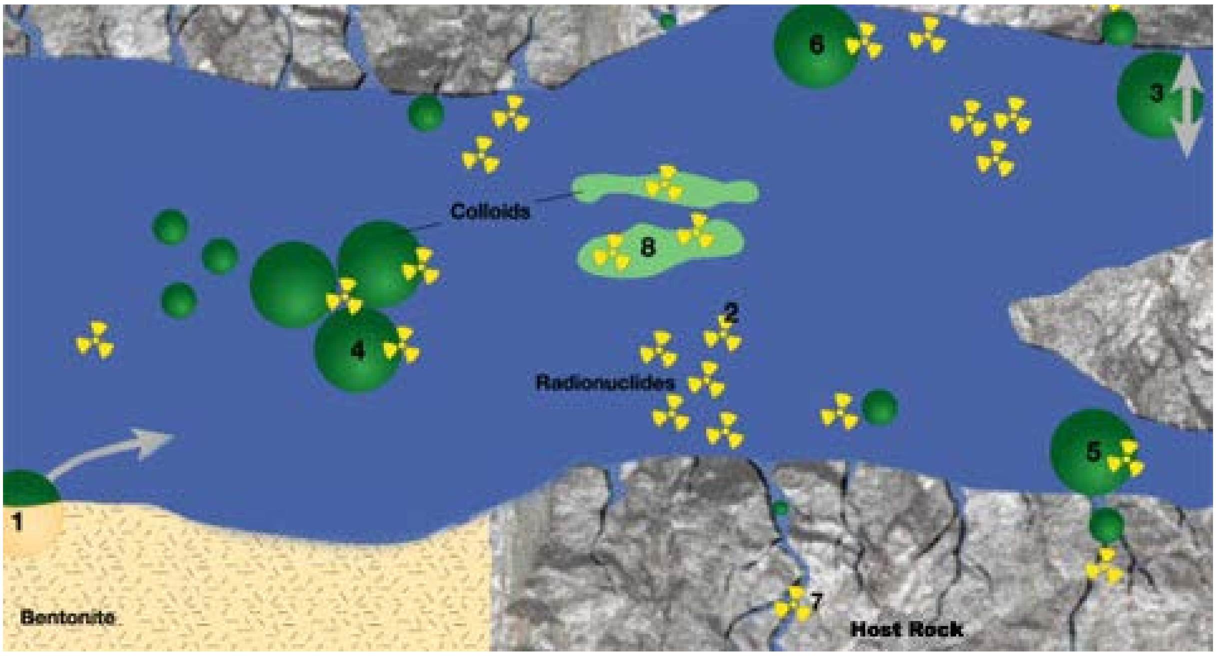


Schematic illustration to show the scale range relationship of colloids

Importance of colloids

Colloids can potentially influence the mobility of radionuclides dissolved in the EBS porewater and groundwater. For example:

- Sorption/de-sorption of natural and GDF-derived colloids onto/from rock surface;
- Sorption of radionuclides onto inorganic colloids (e.g. bentonite, rust from the canister, cement);
- Filtration of colloids in pores and micro-fractures in the EBS and the host rock;
- Colloid size prevents penetration into smaller pores in the EBS and the host rock;
- Diffusion of radionuclides into the pores in the EBS and the host rock;
- Sorption of radionuclides onto organic colloids (e.g. from cellulose-rich waste or from the groundwater), or incorporation of radionuclides into organic colloids.



Potential production mechanisms of colloids (for example at the bentonite barrier/host rock interface in a HLW GDF) and subsequent transport of radionuclides in fractures in the host rock (Möri, 2003).

Colloids can affect the transport of radionuclides in porewater and groundwater in the EBS in several ways (above), some of which (e.g. sorption on colloids) could increase transport rates while others (e.g. filtration of colloids after sorbing radionuclides) would decrease the overall transport through the EBS. 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 the EBS porewaters (and deep host rock groundwaters) means that it has so far proven very difficult to quantitatively define the likely impact of colloids on radionuclide release from a deep GDF.

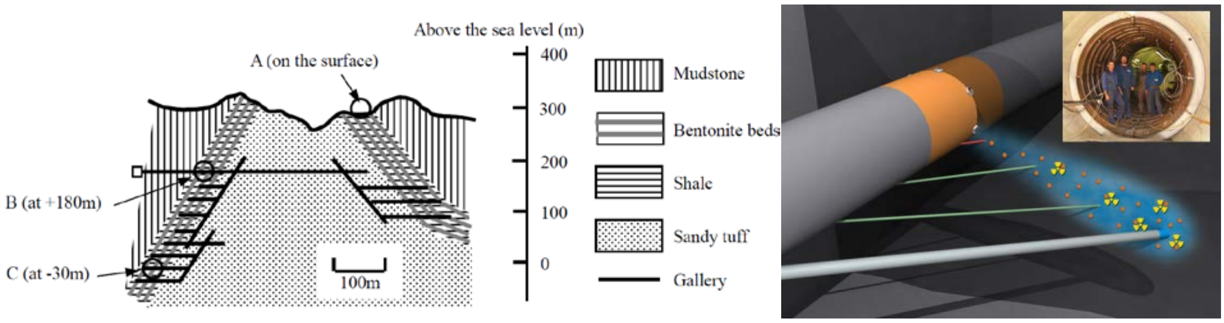
Natural analogues of EBS colloids

Few attempts have been made to study EBS colloids, either in the laboratory or in the field. In the recent past, work has been undertaken on cement colloids from L/ILW GDF. More recently the focus has been on the production of bentonite colloids from HLW GDF backfill materials.

Natural analogues of colloids in HLW systems

In general, It is reasonable to postulate that any glass or metal colloids produced during the degradation of the waste and container may be filtered out by the very fine pore spaces in the bentonite. This would need testing in a site-specific safety case. As such, the focus has very much been on the production of bentonite colloids, either by physical erosion by flowing groundwater, or by deflocculation because of the presence of very dilute glacial water pumped to great depth at the front of an advancing ice sheet.

Bentonite erosion has been studied in the laboratory for several years and is once more under the microscope as part of ongoing colloid studies at the Grimsel Underground Rock Laboratory in Switzerland. A natural analogue study of bentonite erosion in the Tsukinuno bentonite mine in Japan found very low concentrations of colloids in groundwaters collected at various depths in the tunnels. However, this would be expected in sodium-rich groundwaters because under these conditions colloids tend to coagulate and precipitate out of the groundwater.



Left: Schematic cross-section through the Tsukinuno bentonite mine, Japan. A-C are groundwater sampling points (Kuno et al., 2002). Right: Bentonite has been placed in a borehole (grey cylinder, foreground) in the presence of radionuclides in a fracture at Grimsel. Groundwater will be collected in the tunnel (orange cylinder, background) to assess the degree of bentonite erosion and colloid production (www.grimsel.com).

Natural analogues for colloids in L/ILW systems

A handful of laboratory studies of cement colloids have been undertaken over the last 15 years and only one natural analogue study. This was part of the Jordan Natural Analogue Study in which groundwater samples were collected at the cement/host-rock interface in tunnels through the natural cement zone. The colloid populations observed in the field were between one and three orders of magnitude lower than those observed in the laboratory.

Colloids were collected under primitive conditions in a tunnel through the natural cement at Maqarin, northern Jordan. The thick white material coating the tunnel wall is carbonate which precipitates when the calcium-rich, CO_2-poor hyperalkaline cement water contacts the air (Bedrock Geosciences).

Uncertainties and limitations

- The very limited number of EBS colloid natural analogue studies carried out to date means that the data are not statistically significant;
- Sampling colloids in the field is never easy and it is almost impossible to avoid artifacts of some form or another;
- It is very difficult to compare EBS colloid analogue data with those from laboratory experiments, because of the fact that there are no agreed experimental protocols for the

laboratory work. Consequently, the wide spread in measured colloid populations in the laboratory cannot easily be explained;

- Laboratory EBS colloid experiments are generally a very poor copy of a GDF and little weight can be given to their results.

Relevance – what we have learnt

- Despite the difficulties of field sampling, the data from natural systems are currently much more relevant to a deep GDF than any laboratory system studied to date;
- As such, the low colloid populations observed in the field are probably more realistic than the higher values measured in the laboratory;
- More GDF-relevant analogue studies of the EBS are required. One of the issues identified is that different research groups wokring on EBS analogues have employed varying methodologies which makes intercomparisons difficult. Therefore, agreed laboratory protocols are essential to allow meaningful intercomparison of data from different sources.

Further reading

AUQUÉ, L.F., GIMENO, M.J., GÓMEZ, J.B., PUIGDOMENECH, I. SMELLIE, J.A.T. AND TULLBORG, E-L. 2006.s Groundwater chemistry around a repository for spent nuclear fuel over a glacial cycle. Evaluation for SR-Can. *SKB Technical Report*, **TR-06-31**, SKB, Stockholm, Sweden.

Grimsel URL – www.grimsel.com (see CRR and CFM projects)

KUNO, Y., KAMEI G. AND OHTANI, H. 2002. Natural Colloids in Groundwater from a Bentonite Mine - Correlation between Colloid Generation and Groundwater Chemistry. *Material Research Society Symposium Proceedings*, 713

MÖRI, A. (ed). 2003. The CRR final project report series: 1 - description of the field phase - methodologies and raw data. *Nagra Technical Report*, **NTB 03-01**. Nagra, Wettingen, Switzerland.

Nantes (2010) Proc. Conference on Clays in natural and engineered barriers for radioactive waste confinement. 4th International meeting, March, 2010, Nantes, France. *Special Issue of Andra's Science and Technology Report Series*, Andra, Paris, France.

PUURA, E. 2010. Impact of the changes in the chemical composition of pore water on chemical and physical stability of natural clays: a review of natural cases and related laboratory experiments and the ideas on natural analogues for bentonite erosion/non-erosion. *SKB Technical Report*, **TR-10-24**, SKB, Stockholm, Sweden.

SWANTON, S.AND ALEXANDER, W.R. 2010. Review of the behaviour of colloids in the near field of a cementitious repository. *NDA Technical Report* (in press), NDA, Moor Row, UK

SWANTON, S. BERRY, J.A. KELLY, M.J. AND ALEXANDER, W.R. 2010. Review of colloids in the geosphere and their treatment in performance assessment. *NDA Technical Report* NDA, Moor Row, UK.

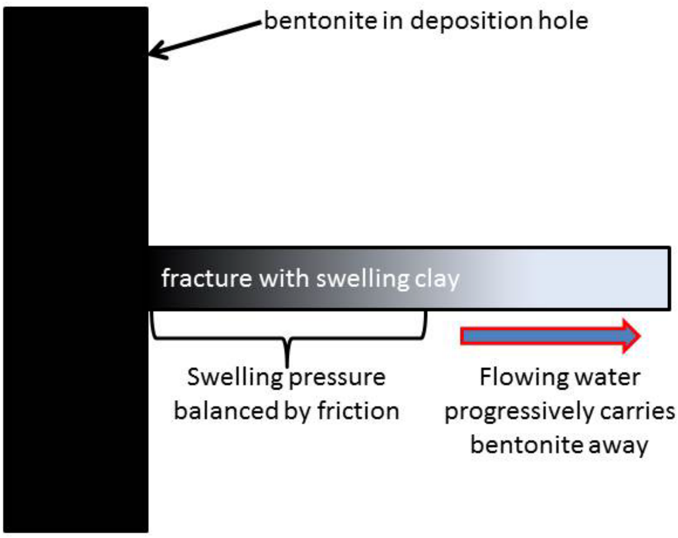
Bentonite: is erosion possible at GDF depth?

Overview

The role of bentonite in a GDF

The engineered barrier system (EBS) of a Geological Disposal Facility (GDF) for radioactive waste is characterised by the use of large quantities of rather simple, well-understood materials. For example, many high-level wastes, spent fuel and some low- to intermediate wastes GDF designs specify the use of compacted bentonite clay as a backfill or buffer around waste packages or canisters. The choice of bentonite results from its favourable properties for the isolation and containment of waste; such as plasticity, swelling capacity, colloid filtration, low hydraulic conductivity, high retardation of key radionuclides, and its stability in relevant geological environments. However, the longevity of bentonite under changing groundwater conditions, especially the swelling clay component (smectite) that contributes to its essential barrier functions, has been little studied (Reijonen and Alexander, 2015).

Stability of bentonite across a range of groundwater salinities is of interest, as dilute groundwaters could induce bentonite erosion and saline groundwaters could induce a reduction in bentonite swelling pressure in the EBS. For example, any high latitude GDF site could be glaciated in the far future, if this happens dilute surface waters under the glacier could be forced down into the bedrock by the high pressures experienced beneath the thick body of ice (i.e. hundreds to thousands of metres). In addition, deep groundwater could potentially be diluted by copious volumes of surface water, produced during an extended temperate climate period, entering the deep bedrock.



Bentonite in the EBS will swell and could extrude into fractures in the GDF host rock, so reducing the overall bentonite density. This could allow gas breakthrough and/or bentonite erosion and colloid generation at the bentonite / groundwater interface

What are the exact concerns?

Bentonite used in a GDF will initially be compacted and dry and will then saturate by drawing in groundwater from the surrounding rock, inducing a high swelling pressure in the material. This may cause the swelling bentonite to penetrate into any nearby fractures in the surrounding rock.

If the density of the bentonite becomes very low, due to extrusion into fractures, the individual colloid-sized clay particles in the bentonite may dissociate, float free and be removed from the main mass of bentonite in the EBS either by moving groundwater, or by diffusion of free particles in stagnant groundwater.

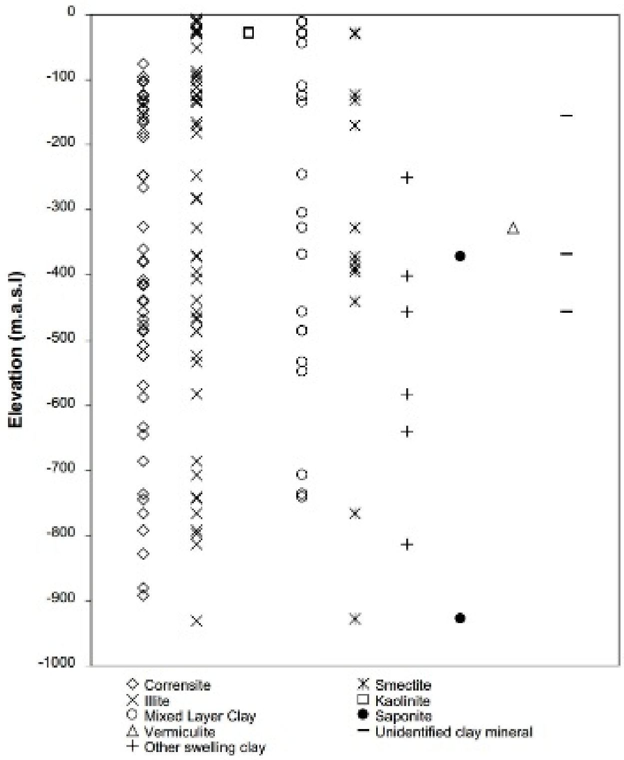
The generation of these clay particles in a region where the bentonite comes into contact with groundwater, can be important for several reasons:

- If a large enough mass of the bentonite is removed by this erosion process, the barrier properties of the bentonite might be compromised. For example, low-swelling pressure may allow any gas produced by the waste to escape from the EBS, potentially carrying radionuclides released from the waste along with it;
- As the vast majority of radionuclides released from the waste packages are expected to strongly sorb onto the bentonite, any release of bentonite colloids could impact migration of radionuclides through the GDF host rock to the surface (Alexander et al., 2011);
- Physical erosion and removal of bentonite from around waste canisters may allow the groundwater to have greater access to the canisters and result in faster corrosion.

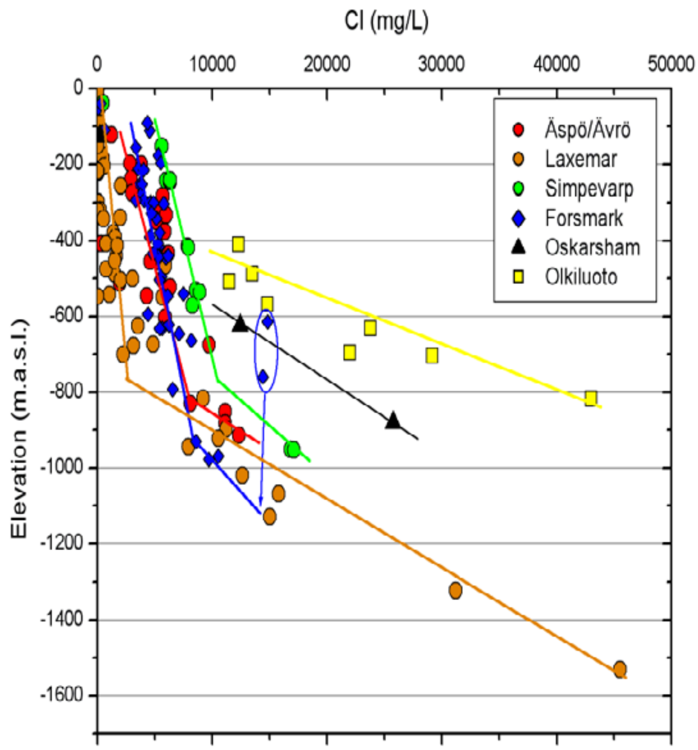
Natural analogue studies of bentonite erosion

Reijonen and Alexander (2015) noted that natural analogue studies of bentonite erosion are rare, but that the erosional histories during glacial periods, or infiltration of surface waters in bentonite deposits could be of interest. Bentonite deposits are often vast and erosional processes are mostly controlled by relatively fast surface water drainage and the resulting instability of the slopes (Figure 1). Thus, in most surface bentonite deposits, the amount of erosion due to colloidal transport is difficult, if not impossible, to assess. As such, studying underground bentonite deposits, where very slow groundwater flow rates are expected, would probably be more informative because the conditions are likely to closely replicate those expected in a GDF.

Examples of erosion in surface bentonite deposits in North Dakota, USA. On the left, the deep channels in the bentonite show that fast flowing surface water can remove lots of material. This can be seen more clearly on the right where the original surface of the bentonite is around 3 metres higher than the person on the right of the shot (images from Bluemle, 1991).



Depth distribution of different clay minerals identified by XRD in Forsmark Sweden (Sandström et al. 2008).



Current groundwater chlorinities (i.e. salinity) at various sites in Sweden and Finland as a function of depth (Smellie et al. 2008)

In the only natural analogue study of bentonite colloids to date, Kuno et al. (2002) examined erosion of bentonite by groundwater flow through a bentonite mine in Japan and found levels were too low to measure with their analytical equipment. While this is promising, the study is of limited value as the analytical detection limit for colloids was high (1 mgL^{-1} - see discussion in

Alexander et al., 2011), also precise groundwater flow velocities were not measured. The latter point is understandable in that access and sampling in a working mine is always difficult, also bentonite mines are, in any case, rare. Consequently, this led to an alternative approach to examining the likely consequences of bentonite erosion in a GDF.

The potential for using natural host rock smectite (the main clay mineral in bentonite) to assess the likely impact of bentonite erosion on the EBS was initially raised by Arthur and Savage (2012) when reviewing information on the potential GDF site at Forsmark in Sweden. They noted that:

"Site mineralogical data…show that smectite and calcite occur at all depths in Forsmark fractures, with no evidence for removal/dissolution by previous glacial episodes. This natural analogue implies that these minerals may not have been dissolved/eroded during previous glacial episodes."

In other words, the continued presence of smectite at Forsmark despite glacial influence suggests that it may well be stable in dilute systems after all. To date, smectites have been reported from candidate GDF sites in several countries, including Finland, Sweden, Switzerland and Canada. For example, in Finland, smectite has been reported from fracture material sampled at the proposed GDF site at Olkiluoto in western Finland along with four other areas examined as potential GDF sites.

At the proposed GDF site at Forsmark, investigations have shown that smectites occur throughout the host rock (Figure 4). Dating of the fracture systems at Forsmark suggest that the smectites have been present for at least 250 million years.

Indeed, smectites have been identified in the host rock of at least five other potential GDF sites in Finland and Sweden, showing the widespread abundance of the mineral in the hard crystalline rocks of the Fennoscandian Shield. Deep groundwater systems in the bedrock at these sites (Figure) have been studied in great detail during GDF site investigations. The data indicate where dilute waters have been present, they can also be compared to the bedrock mineralogy to see where smectites have survived in the presence of dilute waters.

This information supports conclusions from short-term laboratory experiments and ongoing URL studies, which suggest that bentonite erosion by dilute waters should not be a significant problem in a GDF, even during possible future glaciation events.

Uncertainties and limitations

- The data from the Kuno et al. (2002) study are incomplete and so of little use other than as a general indicator that EBS bentonite erosion may not be an issue;
- As the data collected during a GDF site characterisation studies in Sweden and Finland were not intended to support an examination of bentonite erosion processes, they are not focussed enough to be of direct use. For example, it is necessary to know about the swelling ability and grain size of the smectites so these can be compared with the EBS bentonite (and the existing laboratory and URL experiments) but these parameters were never measured;
- Although smectites at the Forsmark site have been dated, little is known about the age of smecitites at other GDF sites and hence their relevance to the very long timescales applicable to a GDF (thousands to hundreds of thousands of years);
- For a UK-based GDF, it would be useful to assess the longevity of natural smectites at the potential site. However, as both deep groundwaters and the types of clays present in the bedrock will likely be examined during site characterisation, it will require little

additional effort to provide locally relevant data for comparison with existing laboratory, URL and natural analogue data.

Relevance – what we have learnt

- Based on currently available evidence it appears unlikely that the erosion of bentonite in the EBS of a GDF will be an issue. However, the data collected to date are too general to be conclusive;
- A fully focussed study of natural smectites present at potential GDF sites is required for more conclusive proof and such a study was recently proposed by Reijonen and Alexander (2015) for sites in Finland, Sweden and Canada. Such a study would significantly improve the natural analogue database in support of existing laboratory and ongoing URL experiments.

Further reading

ALEXANDER, W.R., BERRY, J.A., KELLY M.J. AND SWANTON, S. 2011. Review of colloids in the geosphere and their treatment in performance assessment. *Serco Report* **Serco/TAS/002924/01**, Serco, Didcot, UK.

ARTHUR, R. AND SAVAGE, D. 2012. Equilibrium constraints on buffer erosion based on the chemistry and chemical evolution of glacial meltwaters. *Proceedings of the 5th International meeting on Clays in Natural and Engineered Barriers for Radioactive Waste* Confinement. 22-25 October, 2012, Montpellier, France.

BLUEMLE, J.P. 1991. The face of North Dakota, revised edition: *North Dakota Geological Survey Educational Series* **21**, North Dakota Geological Survey, USA.

CHAPMAN, N.A. BALDWIN, T. NEALL, F. MATHIESON, J. AND WHITE, M. 2009. Design Options for the UK's HLW Geological Disposal Facility. *Radwaste Solutions*, **16**, 44-54.

KUNO, Y., KAMEI G. AND OHTANI, H. 2002. Natural Colloids in Groundwater from a Bentonite Mine - Correlation between Colloid Generation and Groundwater Chemistry. *Material Research Society Symposium Proceedings*, 713MISSANA, T. (EDITOR) 2015. Proceedings of the 3rd annual workshop of the EU BELBAR project. Ciemat, Madrid, Spain. ISBN: 978-84-7834-831-5.

MÖRI, A. (EDITOR). 2004. The CRR final project report series I: description of the field phase – methodologies and raw data. *Nagra Technical Report*, **NTB 03-01**, Nagra, Wettingen, Switzerland.

NERETNIEKS, I. LIU, L. AND MORENO L. 2009. Mechanisms and models for bentonite erosion. *SKB Technical Report* **TR-09-35**, SKB, Stockholm, Sweden.

POSIVA 2012. Safety case for the disposal of spent nuclear fuel at Olkiluoto – Design Basis 2012. *Posiva Report*, **R-2012-03**. Posiva, Eurajoki, Finland.

REIJONEN, H.M. AND ALEXANDER, W.R. 2015. Bentonite analogue research related to geological disposal of radioactive waste – current status and future outlook. *Swiss Journal of Geosciences*, **108**, 101-110. [DOI 10.1007/s00015-015-0185-0*]*

SANDSTRÖM, B., TULLBORG, E-L, .J. SMELLIE, .A.T., MACKENZIE, A.B. AND SUKSI, J. 2008. Fracture mineralogy of the Forsmark site: final report. *SKB Technical Report*, **R-08-102**, SKB, Stockholm, Sweden.

SCHATZ, T. KANERVA, N. MARTIKAINEN, J. SANE, P. AND KOSKINEN, K. 2013. Buffer erosion in dilute groundwater. *Posiva* Report, **WR-2012-44**. Posiva, Eurajoki, Finland.

SMELLIE, J.A.T., TULLBORG, E-L., NILSSON, A-C., SANDSTRÖM, B., WABER, H.N., GIMENO, M. AND GASCOYNE, M. 2008. Explorative analysis of major components and isotopes. SDM-Site Forsmark. *SKB Report*, **R-08-84**, SKB, Stockholm, Sweden.

VIDSTRAND, P. FOLLIN, S. AND ZUGEC, N. 2010. Groundwater flow modelling of periods with periglacial and glacial climate conditions – Forsmark. *SKB Report*, **R-09-21**, SKB, Stockholm, Sweden.

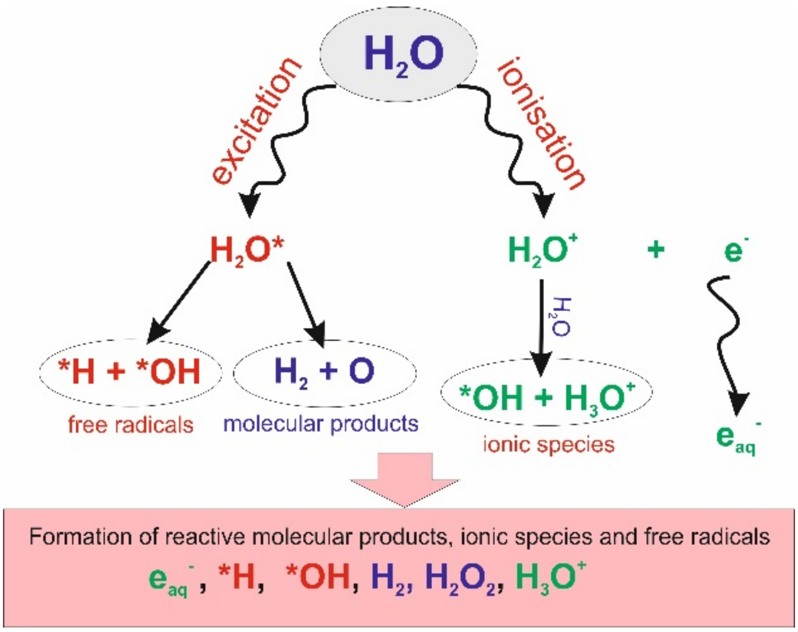
WILSON, J. SAVAGE, D. BOND, A. WATSON, S. PUSCH, R .AND BENNET. D. 2011. Bentonite: a review of key properties, processes and issues for consideration in the UK context. *Quintessa Report*, **QRS-1378ZG-1.1**. Quintessa, Henley-on-Thames, UK.

Radiolysis

Overview

The nature of radiolysis

Significant radiation fields may exist within the near-field of geological disposal facilities (GDFs) for spent fuel, high-level waste (HLW) and certain forms of high-activity intermediate-level waste (ILW); these may cause radiolysis of a number of materials (e.g. cellulose, bitumen and other organic materials) in the waste or in the engineered barrier system (EBS). A potentially significant issue would be the radiolysis of groundwater, which will re-saturate the GDF after closure and therefore be present 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. For this to be significant, the groundwater must be able to come into contact with the waste in the canister. This could be achieved by ingress of water through vented canisters in some ILW designs, or cracks or holes in completely sealed canisters for HLW and spent fuel.



Schematic illustration showing the formation of reactive species by the radiolysis of water (modified after Nilson, 2008)

Most safety cases assume that a net build up of oxidents (oxygen, hydrogen peroxide, hydroxide, etc.) 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, would be more reactive and diffuse away more slowly. This might result in the creation of a slowly moving redox (from REDuction and OXidation) front that migrates outwards from the waste into the EBS and eventually, the host rock. A redox front is a boundary that separates oxidising rock and groundwater (full of oxidants) on one side with reducing rock and groundwater (full of reductants) on the other. The extent of redox front migration would be controlled by the balance between oxidant production within the canister by radiolysis and oxidant consumption by iron-rich material in the EBS (e.g. the steel of the waste canister, pyrite mixed in the bentonite buffer) and the rock (e.g. pyrite).

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 will stay in solution longer; possibly long enough to diffuse through the bentonite and out into the host rock, thus increasing radionuclide loss from a GDF.

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

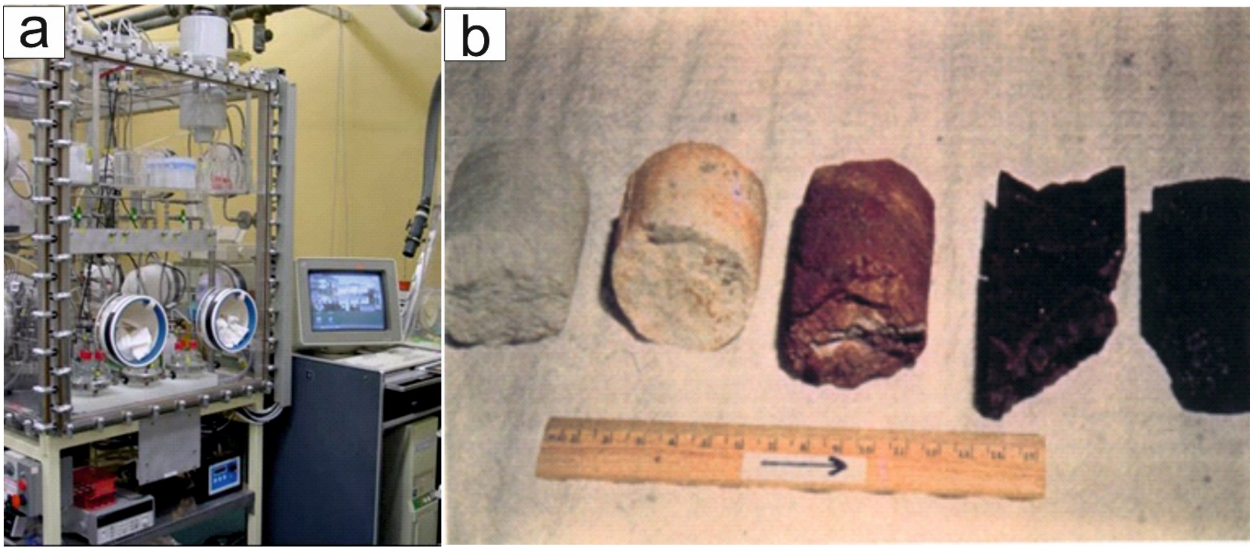
The issues of most relevance to radiolysis that could be addressed in natural analogue studies are:

- 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.

Analogue studies of radiolysis

The first detailed analogue investigation of radiolysis under GDF-relevant conditions was carried out at the Oklo natural fission reactors. 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 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 sped up some of the reaction rates) mean that the data cannot be used directly in a GDF safety case assessment. However, the results suggest that this process could occur in a GDF.



(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 (©John Smellie, Conterra).

Radiolysis studies at Cigar Lake, Canada, 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 spent fuel corrosion. If the corrosion of spent fuel passes a certain threshold level 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 natural analogue data to develop and improve SA 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.

Uncertainties and limitations

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

Relevance – what we have learnt

- Testing previous-generation spent fuel corrosion models against natural analogue data showed that they significantly over-estimated corrosion rates, which were based on short-term laboratory data. This led to improved models which can more closely approximate the natural data.

Further reading

FINCH, R.J. AND EWING, R.C. 1992. The corrosion of uraninite under oxidising conditions. *Journal Nuclear Materials*, **190**, 133-156.

HOFMANN, B.A. 1999. Geochemistry of natural redox fronts - a review. *Nagra Technical Report*, **NTB 99-05**, Nagra, Wettingen, Switzerland.

NILSON, S., 2008 Influence of fission products and irradiation on the rate of spent nuclear fuel –matrix dissolution. Licentiate thesis KTH Stockholm.

SMELLIE, J.A.T. AND KARLSSON, F. (eds) 1996. The Cigar Lake analogue project: a re-appraisal of some key issues and their relevan.e to repository performance assessment. *SKB Technical Report*, **TR 96-08**, SKB, Stockholm, Sweden.

WABER, N., SCHORSCHER, H.D., MACKENZIE A.B. AND PETERS T. 1990. Mineralogy petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil I: Osamu Utsumi uranium mine. *SKB Technical Report*, **TR 90-11**, SKB, Stockholm.

POSIVA 2012. Safety case for the disposal of spent uclear fuel at Olkiluoto synthesis. *Posiva Technical Report*. **2012-12**. Posiva Oy, Olkiluoto, FI-27160 Eurajoki, Finland.

3 The Natural Barrier System

3.1 LONG-TERM PERFORMANCE OF FRACTURED CRYSTALLINE HOST ROCKS

Sellafield Site: using palaeo-hydrogeology to predict future climate change impacts on groundwater systems

Äspö and Laxemar, SE Sweden: long-term stability of a deep groundwater system

The Lupin Mine: a natural analogue for a permafrost environment

Tono: a natural analogue for host rock stability

Sellafield site: using palaeo-hydrogeology to predict future climate change impacts on groundwater systems

Overview

An important requirement of a safety case for a geological disposal facility (GDF) for radioactive waste is to be able to demonstrate that climatic changes will not adversely affect the chemistry of the groundwater system at GDF depth over the period of time during which the waste will be a hazard, typically up to one million years. The potential impact of future climate change on deep groundwater systems is therefore of major concern to the safety case for a GDF. The last 2.6 million years (Quaternary Period) saw the climate in northern Europe vary between extremes of ice ages and conditions warmer than today.

The present-day climate is not representative of that which existed for much of the Quaternary, 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 Quaternary climate changes (i.e. '*palaeohydrogeology*') may therefore provide valuable information on how the modern groundwater system might respond to future climate changes. Of particular concern in the UK is the potential for oxidising groundwater to penetrate to GDF depth during periods of glaciation, thereby increasing the mobility of some transuranic radionuclides.

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

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

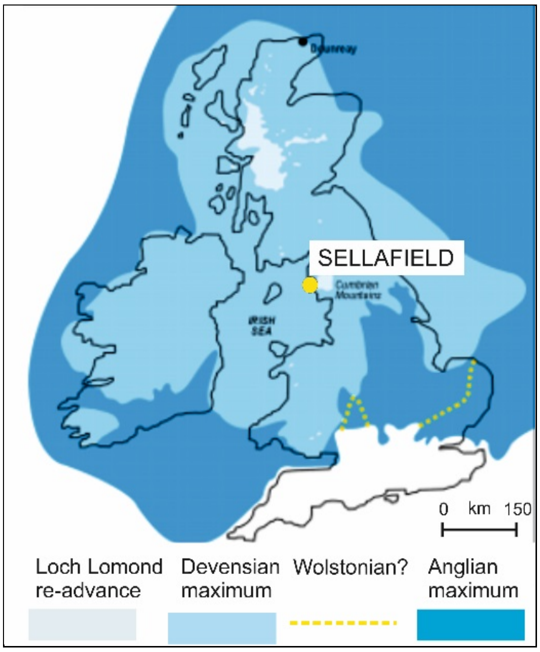
The Sellafield site

The Sellafield site 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 Quaternary. Sellafield has been at the forefront of palaeohydrogeology studies, initially for UK Nirex Ltd and more recently in the EC-funded 'EQUIP' and 'PADAMOT' projects.

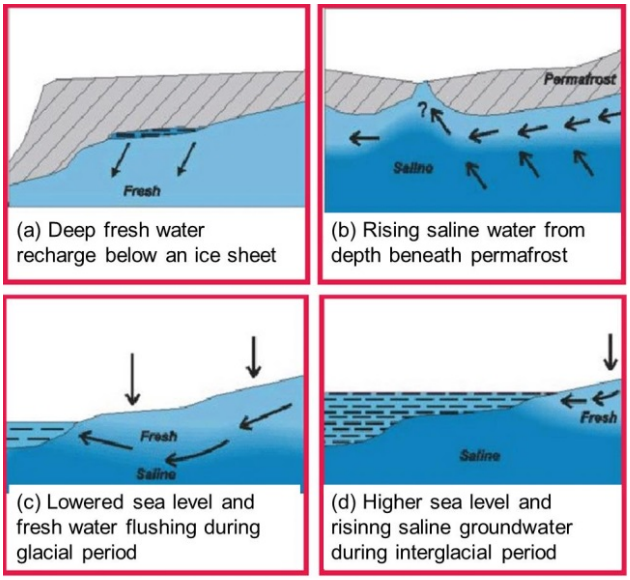
Detailed petrological analysis of fracture mineralisation in 23 deep boreholes drilled through a sequence of Permo-Triassic, Carboniferous and Ordovician strata at Sellafield, west Cumbria identified a complex sequence of mineralization events referred to as ME1-ME9. Much of the mineralization is geologically-old (Palaeozoic-Mesozoic) but the distribution of the latest (ME9) calcite ($CaCO_3$) mineralisation correlates closely with modern groundwater flows. In addition, detailed investigations of groundwater geochemistry including 36-chlorine studies have been used to shed light on the origin and timing of past groundwater movement.

Groundwater scenarios

Chemical composition and groundwater flow are the key factors influencing the performance of a GDF and radionuclide containment; affecting radionuclide mobility, and the rate (if any) of movement in groundwater, potentially (dependent on site characteristics) including movement from GDF relevant depths to the land surface.



Locations of the Sellafield site. West Cumbria in relation to the extent of Quaternary glaciations in the British Isles (from Milodowski et al., 2005).



Illustrations of some general scenarios for how groundwaters in a coastal region in northern Europe might change in response to changing climate states (from Milodowski et al., 2005).

Palaeohydrogeological studies at Sellafield

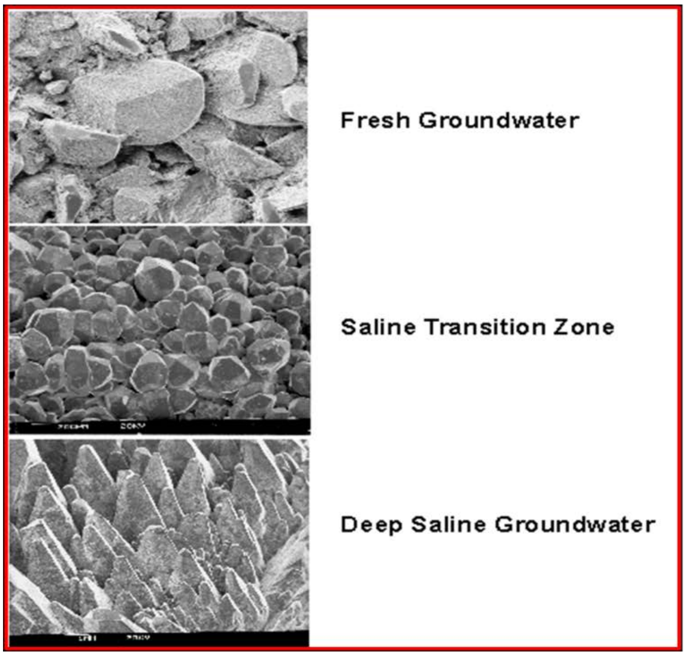
Palaeohydrogeology studies to date focused mainly on the youngest (ME9) calcite mineralisation, which is closely associated with the present-day groundwater system and is well developed in fractures across the site, to a depth of at least 1.5 km. Calcite is an ideal target because crystals grow at low temperature within the depth range and timescale of interest, and can record information on past groundwater conditions in various ways, including:

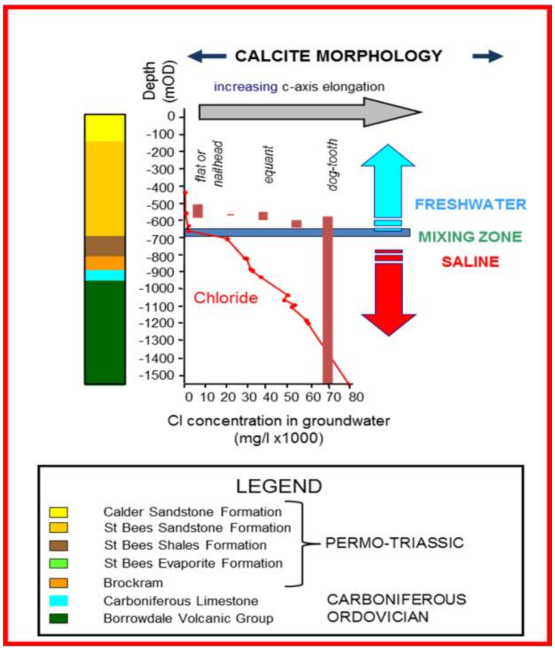
- Crystal shape changes systematically with groundwater salinity
- Growth zones preserve a physical and chemical record of groundwater composition
- Crystals dissolve in certain groundwater conditions, creating corrosion surfaces
- Trace elements reflect the oxidation ('redox') state of groundwater
- 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.

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.

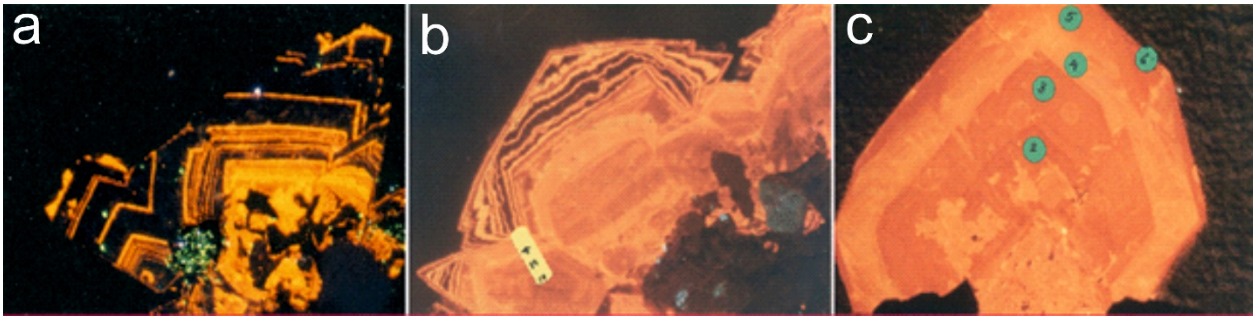
Petrographical and microchemical analyses of these late calcite crystals reveals that they are strongly growth zoned, reflecting variations in Fe and Mn. The variation in cathodoluminescence and chemical zoning characteristics also correlates closely with the position of the modern-day freshwater and 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.





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 ©British Geological Survey.



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) (from 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 (REE) 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, clearly show that the groundwater has remained reducing during mineralisation, regardless of the input of any glacially-recharged water.

Uncertainties and differences

- Future climate evolution may not follow the patterns and impacts of the past.
- Anthropogenic influences, in particular greenhouse gas emissions, could significantly modify the natural patterns of climate variation in the future and the magnitude of their impact in the geosphere.
- Although the late (ME9) calcite mineralisation can be clearly demonstrated to have formed during the Quaternary and correlated to the modern groundwater flow system, precise dating of individual growth zones has not yet been possible. This means that the impacts of specific glaciation events cannot be differentiated.

Relevance – what we have learnt

- For the UK, present-day climate is not representative of much of the Quaternary Period, in terms of either temperature or rainfall. We must look to past climate variability and its effects to inform predictions of future changes and impacts.
- Palaeohydrogeology studies 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 drivers.

  The distribution of much of the present-day fracture porosity in deep groundwater systems is of secondary origin, controlled by the distribution and dissolution of the pre-existing, geologically-old (Mesozoic), reactive or soluble fracture minerals, rather than controlled by primary fracture structure and regional stress patterns.

- The location and geometry of groundwater flow pathways evolved continuously as pre-Quaternary minerals dissolved and Quaternary minerals grew. These processes continue today, and propagate from east to west following the meteoric groundwater flow-gradient.
- The latest calcite mineralisation preserves evidence showing that the depth of the fresh–saline groundwater boundary has fluctuated since Tertiary uplift, with a net increase in depth of this interface of several 10's of metres in central and eastern parts of the site. However, fresh water has not reached a significantly greater depth than at the present day.
- The range in groundwater salinity values across the site as a whole has remained broadly stable during the Quaternary, 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. Moderately reducing conditions have been the norm beneath the freshwater zone.
- Studies at Sellafield have shown that glacially-recharged groundwater can penetrate to GDF depths but that groundwater can remain reducing 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 Forsmark (Sweden), Olkiluoto (Finland) and Horonobe (Japan). 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.

Further reading

AMANO, K., NIIZATO, T., YOKOTA, H., OTA, K., LANYON, B. AND ALEXANDER, W.R. 2011. *Development of comprehensive techniques for coastal site characterisation: integrated palaeohydrogeological approach for development of site evolution models.* Proc. ICEM 2011 Conference, Reims, France, September, 2011, ASME, Washington, USA.

BATH, A., MILODOWSKI, A.E., RUOTSALAINEN, P., TULLBORG, E.-L., CORTÉS RUIZ, A. AND ARANYOSSY, J.-F. 2000. *Evidence from mineralogy and geochemistry for the evolution of groundwater systems during the Quaternary for use in radioactive waste repository safety assessment (EQUIP project).* **Report EUR 19613**, D-G for Research, European Commission, Brussels.

BATH, A.H., RICHARDS, H., METCALFE, R., MCCARTNEY, R., DEGNAN, P., LITTLEBOY, A. 2006. Geochemical indicators of deep groundwater movements at Sellafield, UK. *Journal of Geochemical Exploration*, **90**, 24-44.

DEGNAN, P., BATH, A., CORTES, A., DELGADO, J., HASZLEDINE, R.S., MILODOWSKI, A.E., PUIGDOMENECH, I., RECREO, F., SILAR, J., TORRES, T. AND TULLBORG, E.-L. 2005. PADAMOT: Project Overview Report. *PADAMOT Project Technical Report, EU FP5 CONTRACT NO. FIKW-CT2001-20129*. 105 pp.

METCALFE, R., CRAWFORD, M.B., BATH, A.H., LITTLEBOY, A.K., DEGNAN, P.J. AND RICHARDS, H.G. 2007. Characteristics of deep groundwater flow in a basin marginal setting at Sellafield, Northwest England: 36Cl and halide evidence. *Applied Geochemistry*, **22**, 128-151

MILODOWSKI, A.E., GILLESPIE, M.R. AND METCALFE, R. 1997. Relationship between mineralogical transformations and groundwater chemistry at Sellafield, NW England: a tool for studying Quaternary palaeohydrogeology. In: HENDRY, J., CAREY, P., PARNELL, J., RUFFELL, A. AND WORDEN, R. (editors), *GEOFLUIDS II '97: Contributions to the Second International Conference on Fluid Evolution, Migration and Interaction in Sedimentary Basins and Orogenic Belts (Belfast, Northern Ireland, March 10th – 14th, 1997).* Queens University, Belfast, 30-33.

MILODOWSKI, A.E., GILLESPIE, M.R., NADEN, J., FORTEY, N.J., SHEPHERD, T.J., PEARCE, J.M. AND METCALFE, R. 1998. The petrology and paragenesis of fracture mineralization in the Sellafield area, west Cumbria. *Proceedings of the Yorkshire Geological Society*, **52**, 215-241.

MILODOWSKI, A.E. TULLBORG, E.-L., BUIL, B., GÓMEZ, P., TURRERO, M.-J., HASZELDINE, S., ENGLAND, G., GILLESPIE, M.R., TORRES, T., ORTIZ, J.E., ZACHARIÁŠ, SILAR, J., CHVÁTAL, M., STRNAD, L., ŠEBEK, O. BOUCH, J.E., CHENERY, S.R, CHENERY, C., SHEPHERD, T.J. AND MCKERVEY, J.A. 2005. Application of Mineralogical, Petrological and Geochemical Tools for Evaluating the Palaeohydrogeological Evolution of the PADAMOT Study Sites. *PADAMOT Project Technical Report, WP2, EU FP5 CONTRACT NO. FIKW-CT2001-20129.*

NIREX 1997. Sellafield Geological and Hydrogeological Investigations: An assessment of the influence of basinal processes on the hydrogeology of the Sellafield area. *United Kingdom Nirex Limited Report,* **SA/97/055**.

SHAW, R.P.; AUTON, C.A.; BAPTIE, B.; BROCKLEHURST, S.; DUTTON, M.; EVANS, D.J.; FIELD, L.P.; GREGORY, S.P.; HENDERSON, E.; HUGHES, A.; MILODOWSKI, A.E.; PARKES, D.; REES, J.G.; SMALL, J.; SMITH, N.; TYE, A.; WEST, J.M.. 2012 *Potential natural changes and implications for a UK GDF*. British Geological Survey, 198pp. (CR/12/127).

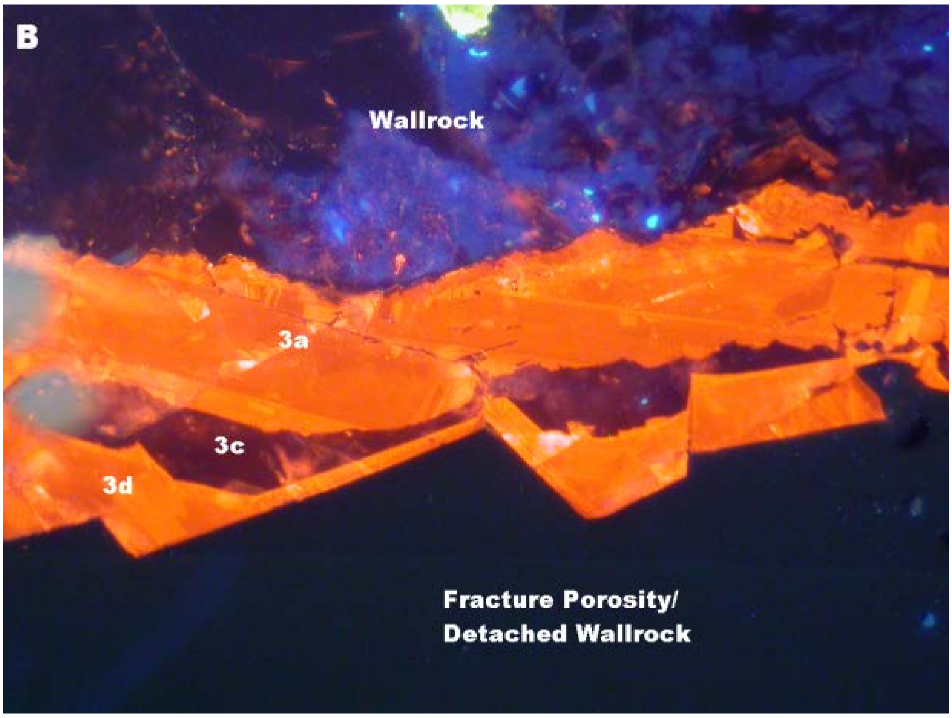
Äspö and Laxemar, SE Sweden: long-term stability of a deep groundwater system

Overview

An important requirement of a safety case for a geological disposal facility (GDF) for radioactive waste is to be able to demonstrate that climatic changes will not adversely affect the chemistry of the groundwater system at GDF depth over the period of time during which the waste will be a hazard, typically up to one million years. The potential impact of future climate change on deep groundwater systems is therefore of major concern to the safety case for a GDF. The last 2.6 million years (Quaternary Period) saw the climate in northern Europe vary between extremes of ice ages and conditions warmer than today. Of particular concern in northern Europe is the potential for oxidising groundwater to penetrate to GDF depth during periods of glaciation, thereby increasing the mobility of some transuranic radionuclides. It is therefore important to demonstrate that reducing conditions can be maintained for a long period of time at the depths of a potential GDF.

Geological background

Äspö and Laxemar are situated on the Baltic coast of southeast Sweden. The Swedish Nuclear Fuel and Waste Management Company (SKB) has constructed an underground rock laboratory on the low-lying island of Äspö, where it is carrying out a programme of investigations to develop and test methodologies for its programme of research into the disposal of spent nuclear fuel. SKB have also carried out regional studies in relation to GDF site investigations. The Äspö and Laxemar sites have been at the forefront of palaeohydrogeology research, initially for SKB and more recently in the EC-funded ‘EQUIP’ and ‘PADAMOT’ projects.



Cathodoluminescence microscopy image of zoned luminescent and non-luminescent late-stage calcite coating a fracture surface from Laxemar.

Detailed geochemical, mineralogical, stable isotope and uranium-series disequilibrium studies of the fracture filling minerals have identified a long history of fracturing, fluid movement and associated mineralisation events. Most of these are geologically old features, but the most recent mineralisation is associated with the Quaternary groundwater circulation.

The majority of the fractures in the Laxemar-Simpevarp-Äspö area were formed before the Palaeozoic (see Event 15, table below) and have subsequently been reactivated. Calcite mineralization associated with these fracture events is characterised by hydrothermal stable isotope signatures. During the Palaeozoic the region was covered with a thick sequence of marine and molasse sediments. This cover remained for at least 400 Ma, although from the Carboniferous-Permian onwards it was successively reduced, until finally being removed during the late Tertiary or early Quaternary. Low temperature clay minerals, zeolites and calcite were deposited in the fractures at this time, possibly with some gypsum and pyrite (Event 6, table below).

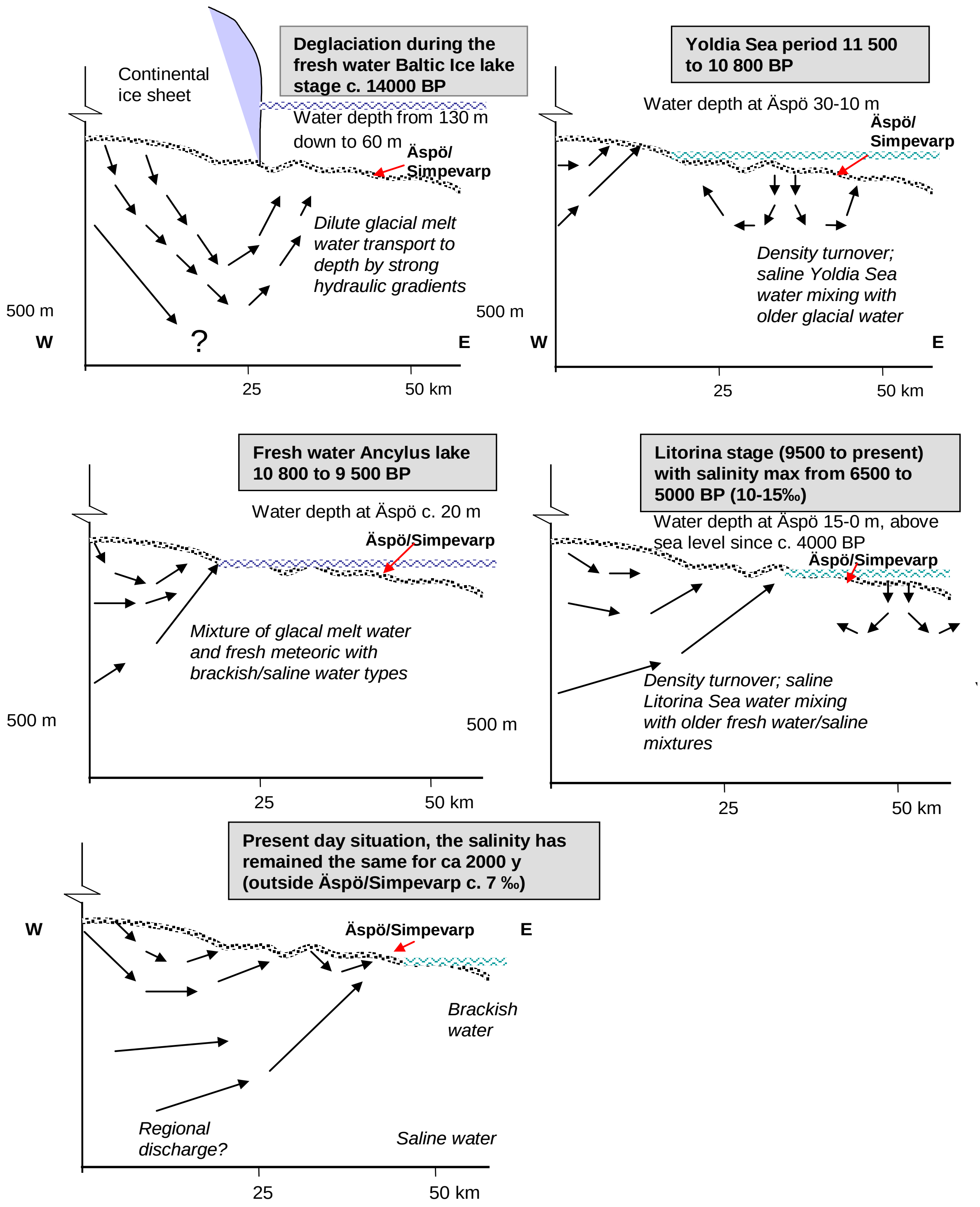
Subsequent low temperature fracture mineralization was dominated by calcite (with some pyrite) at depth, and close to the surface by goethite related to the percolation of oxidizing meteoric groundwater alteration (i.e. weathering) (Event 7, table below).

Summary sequence of geological events and fracture mineralization history for Äspö and Laxemar (from Milodowski et al., 2005).

Event	Effect/Mineralization	Comment
0	Formation of the Äspö Granitoids	c. 1800 Ma (Kornfält et al.,1997)
1	Regional deformation	1660-1450 Ma
2	Mylonitization; formation of fine-grained epidote, muscovite and quartz recrystallization.	Some mylonites probably belong to last phase of event 2.
3	Reactivation of mylonites and formation of idiomorphic epidote and fluorite.	Intrusion of the anorogenic Götemar Intrusion c. 1450 Ma (Åhäll, 2001).
4	Growth of idiomorphic quartz, muscovite, hematite, fluorite, calcite and spherulitic chlorite.	Late-magmatic hydrothermal circulation associated with the Götemar Intrusion.
5	Prehnite, laumontite, calcite, chlorite and fluorite.	Low-temperature burial metamorphism probably Late Proterozoic.
6	Illite-dominated mixed-layer clay, calcite, chlorite.	Low-temperature burial metamorphism and mineralization associated with burial beneath Post-Caledonian sedimentary cover in Sweden.
7	Calcite, Fe-oxyhydroxide, pyrite, clay minerals? (kaolinite, smectite, illite-smectite and corrensite)	Mineralization probably associated with Recent/Quaternary groundwater circulation.

Groundwater scenarios

Since the Äspö-Laxemar area is situated on the low-lying Baltic Sea coast, the postglacial evolution of the area has been strongly influenced by a complex interplay between global sea-level changes, fresh water run-off from the surrounding terrain, and glacio-isostatic fluctuations in the land surface. Consequently, the sites have experienced several different episodes during which either fresh or brackish water environments developed after the last glaciation, and which have had a large influence on the present groundwater chemistry.



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 stage, and e) present day Baltic Sea stage. (from Milodowski et al., 2005)

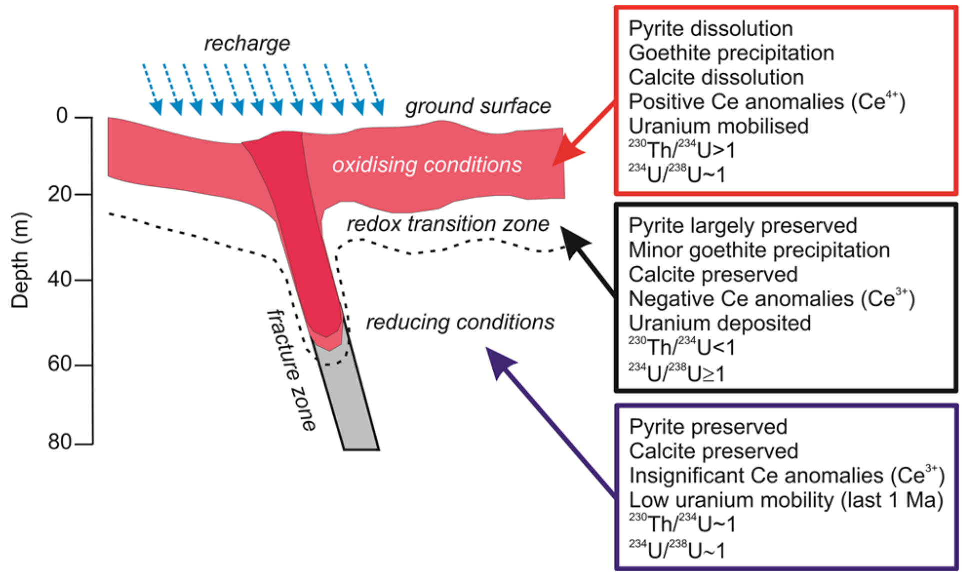
Uncertainties and limitations

- Reactivation of fractures is very common in the Äspö-Laxemar area, and the present- water-conducting features and their associated mineralisation usually have a very long and complex history.
- Since the hydraulically conductive 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: (i) the amounts of minerals produced can be very small; (ii) unsaturated chemical conditions and/or lack of flow may result in periods of non-deposition, and; (iii) periods of mineral dissolution may have destroyed traces of previous groundwater regimes.

Relevance – what we have learnt

- Useful palaeohydrogeological information has been obtained from studying the geochemistry of late-stage calcite mineralisation, detailed mapping of the distribution of redox-sensitive minerals such as pyrite and secondary iron oxides and iron oxyhydroxides (e.g. goethite), and uranium-series disequilibrium of fracture-coatings;
- Past groundwaters have left precipitates from which the different groundwater regimes can be traced;
- Late-stage calcite mineralisation can be correlated with present-day groundwater flow paths;
- The morphology of the latest calcite mineralisation reflects the salinity of the groundwater from which it precipitated: (i) crystallographic *c-a*xis elongated or "dog-tooth" crystal forms characterise saline or brackish groundwater zones; (ii) crystallographic *c*-axis flattened or "nailhead-shaped" and equant crystal forms characterise dilute groundwater zones;
- 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;
- 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. Uranium series disequilibrium studies show that this has been the case for at least the past 1 Ma;
- The calcite at depth contains reduced iron (Fe^{2+}) and manganese (Mn^{2+}). This, together with the absence of any positive cerium anomaly (i.e. any concentration of tetravalent (oxidised) cerium relative to other trivalent rare earth elements), demonstrates that conditions have been maintained reducing during groundwater circulation;
- 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 sheer). In other areas, the actual depth range will depend upon site-specific characteristics.



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)

Further reading

BATH, A., MILODOWSKI, A.E., RUOTSALAINEN, P., TULLBORG, E.-L., CORTÉS RUIZ, A. AND ARANYOSSY, J.-F. 2000. *Evidence from mineralogy and geochemistry for the evolution of groundwater systems during the Quaternary for use in radioactive waste repository safety assessment (EQUIP project).* **Report EUR 19613**, D-G for Research, European Commission, Brussels.

DIDERIKSEN, K., CHRISTIANSEN, B.C., BAKER, J.A., FRANDSEN, C., BALIC-ZUNIC, T., TULLBORG, E.-L., MØRUP, S. AND STIPP, S.L.S. 2007. Fe-oxide fracture fillings as a palaeo-redox indicator: structure, crystal form and Fe isotope composition. *Chemical Geology*, **244**, 330-343.

DEGNAN, P., BATH, A., CORTES, A., DELGADO, J., HASZLEDINE, R.S., MILODOWSKI, A.E., PUIGDOMENECH, I., RECREO, F., SILAR, J., TORRES, T. AND TULLBORG, E.-L. 2005. PADAMOT: Project Overview Report. *PADAMOT Project Technical Report, EU FP5 CONTRACT NO. FIKW-CT2001-20129*. 105 pp.

DRAKE, H AND TULLBORG E.-L. 2004. Fracture mineralogy and wall rock alteration. Results from drill core KSH01A+B. Oskarshamn site investigation. *SKB Report*, **P-04-250**. Svensk Kärnbränslehantering AB, Stockholm, Sweden

DRAKE, H. AND TULLBORG, E.-L. 2008. Oskarshamn site investigation. Fracture mineralogy. Results from drillcore KLX15A. *SKB Report*, **P-08-12**, Svensk Kärnbränslehantering AB, Stockholm, Sweden.

DRAKE, H. AND TULLBORG, E.-L. 2008. Oskarshamn site investigation. Mineralogy in water conducting zones. Results from boreholes KLX07A+B and KLX08. *SKB Report*, **P-08-42**, Svensk Kärnbränslehantering AB, Stockholm, Sweden.

DRAKE, H., AND TULLBORG, E.-L. 2009. Palaeohydrogeological events recorded by stable isotopes, fluid inclusions and trace elements in fracture minerals in crystalline rock, Simpevarp area, SE Sweden. *Applied Geochemistry*, **24**, 715-732.

DRAKE, H., TULLBORG, E.-L. AND MACKENZIE, A.B. 2009. Detecting the near-surface redox front in crystalline bedrock using fracture mineral distribution, geochemistry and U-series disequilibrium. *Applied Geochemistry*, **24**, 1023-1039.

MILODOWSKI A E, GILLESPIE M R, PEARCE J M, METCALFE R, 1998. Collaboration with the SKB EQUIP programme; Petrographic characterisation of calcites from Äspö and Laxemar deep boreholes by scanning electron microscopy, electron microprobe and cathodoluminescence petrography, *British Geological Survey, Technical Report*, **WG/98/45C**: British Geological Survey, Keyworth, Nottingham.

MILODOWSKI, A.E. TULLBORG, E.-L., BUIL, B., GÓMEZ, P., TURRERO, M.-J., HASZELDINE, S., ENGLAND, G., GILLESPIE, M.R., TORRES, T., ORTIZ, J.E., ZACHARIÁŠ, SILAR, J., CHVÁTAL, M., STRNAD, L., ŠEBEK, O. BOUCH, J.E., CHENERY, S.R, CHENERY, C., SHEPHERD, T.J. AND MCKERVEY, J.A. 2005. Application of Mineralogical, Petrological and Geochemical Tools for Evaluating the Palaeohydrogeological Evolution of the PADAMOT Study Sites. *PADAMOT Project Technical Report, WP2, EU FP5 CONTRACT NO. FIKW-CT2001-20129.*

TULLBORG, E.-L. 2004. Palaeohydrogeological evidences from fracture filling minerals - Results from the Äspö/Laxemar area. Material Research Society Symposium, Vol **807**, 873–878.

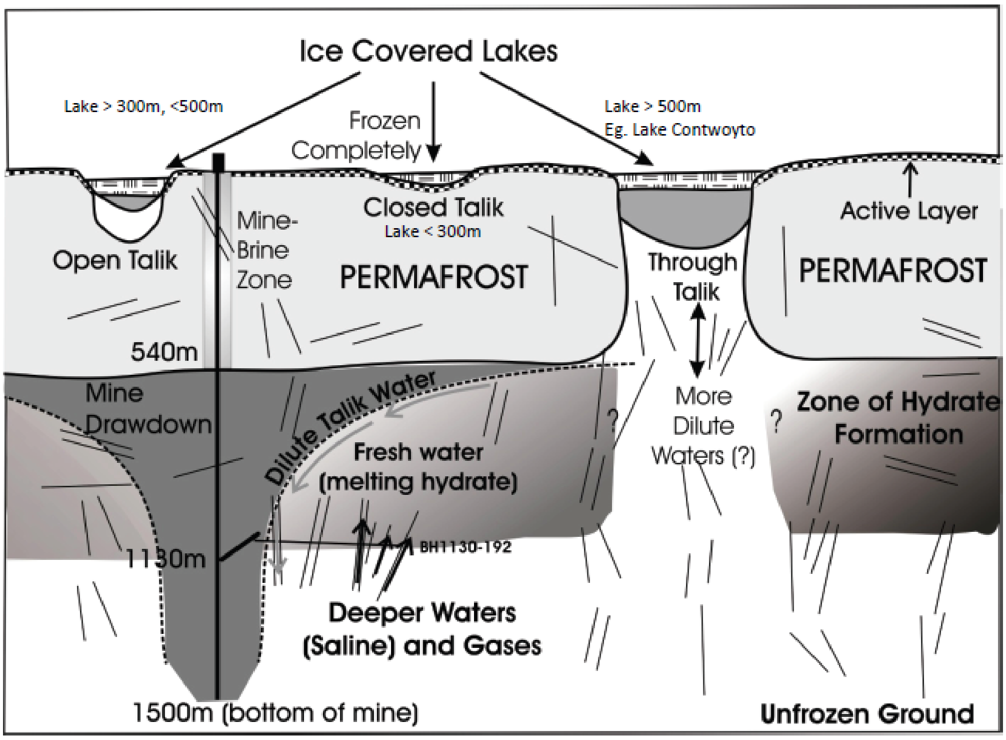
WALLIN, B. AND PETERMAN Z, 1999. Calcite fracture fillings as indicators of Paleohydrology at Laxemar at the Äspö Hard Rock Laboratory, southern Sweden. *Applied Geochemistry*, **14**, 939-952.

The Lupin Mine: a natural analogue for a permafrost environment

Overview

The safety case for deep geological disposal facilities (GDF) for radioactive waste must demonstrate that the performance of natural and engineered barriers will not be adversely affected by changes in groundwater flow and chemistry caused by possible future climate-driven events such as glaciation and sea-level change, over timescales in the order of up to one million years. Today, permafrost covers ~24 % of the Northern Hemisphere. However, under future long-term climate change, most climate models suggest that the Northern Hemisphere will return to glacial cycles several times over the next million years. Consequently, permafrost will form in northern and central Europe and northern America under dry conditions. Therefore, the effects of permafrost on the long-term safety of a GDF must be included in any safety case assessment of a site (Ruskeemiemi et al., 2002).

What and where is permafrost?



Conceptual model of Lupin mine (from Stotler et al., 2009a).

- Permafrost is defined as soil, unconsolidated deposits, and bedrock, in which temperatures below 0 °C exist for two years or more (Williams, 1970);
- Permafrost is classified based on percentage areal coverage into continuous (90-100 %), discontinuous (50-90 %), sporadic (10-50 %) and isolated (<10 %) (French, 2007).

What are the influences of permafrost on a GDF?

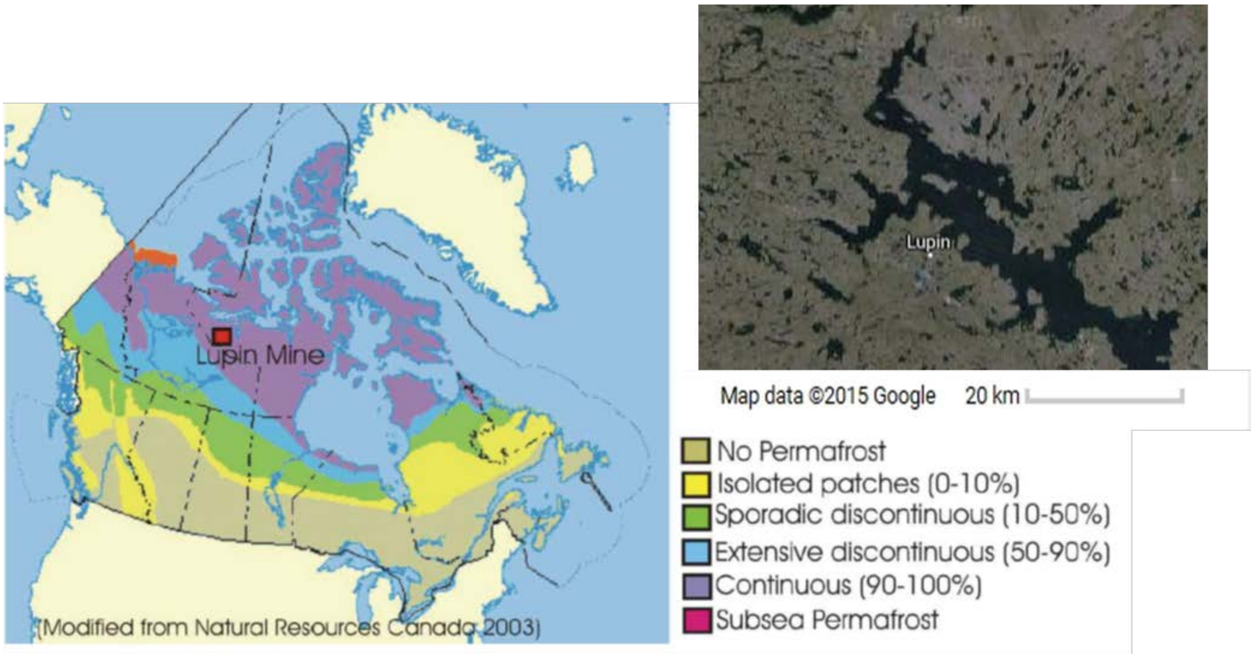
Possible impacts of permafrost on a GDF include:

- Influence on groundwater flow direction and magnitude;
- Reduction of recharge and discharge;

- Focussing of groundwater flow through *taliks* underneath surface water bodies and around high permeability fracture zones;
- Changes in the chemical composition of groundwater, as a result of salinity increase because of freeze out of solutes and the formation of *cryopegs*, which are defined as unfrozen zones that are perennially below 0 °C;
- Mechanical effects of freezing and thawing on rock and soil stability are of importance (Ruskeemiemi et al., 2002).

Lupin Mine: a present day analogue for a permafrost environment

The potential impacts of permafrost in a fractured rock environment have been studied at the Lupin gold mine in Nunavut, Canada which was active from 1982-2005. The Lupin mine is positioned in an Archean metaturbidite sequence that has undergone regional and contact metamorphism. Amphibolite facies metamorphism has partly destroyed the primary sedimentary structures and produced crystalline rock types (Stotler et al., 2009a).



Location of Lupin mine in relation to the distribution of permafrost zones from Stotler et al. (2009a) and satellite image (Google Earth).

The Lupin Mine is situated in the continuous permafrost zone and the permafrost depth of the Lupin Mine area extends to between 400-600 m below ground surface. Local variations of permafrost depth are because of differences in porosity and thermal conductivity of the main rock types (Stotler et al., 2009a).

The depth of permafrost at the Lupin Mine is estimated at 540 m (Ruskeemiemi et al., 2002). However, due to the warming effects of surface water bodies, unfrozen zones below these lakes and rivers can be found.

Underneath small lakes, a *sub-permafrost talik* can be found: these are an unfrozen zone overlying the permafrost. Underneath larger lakes, a *through-talik* can be found that penetrates the entire thickness of the permafrost and provides a sub-permafrost groundwater – surface water connection. Lake Contwoyto near Lupin Mine is more than 100 km long and the width close to

Lupin varies from 2 to 5 km. Here a talik boundary located 30-60 m from the shoreline has been identified from a survey using ground penetrating radar (Stotler et al., 2009b).

Influence of permafrost distribution on groundwater flow

Permafrost acts as an impermeable barrier, because the pore spaces are generally filled with ice within the zone of saturation.

- Ice- and water-saturation in permafrost is important for the groundwater flow, because the hydraulic conductivity in frozen media decreases over the freezing interval by several orders of magnitudes (Kleinberg and Griffin, 2005);
- The low hydraulic conductivity of permafrost hinders recharge and discharge of water to and from the aquifers beneath permafrost to the unfrozen zones that perforate the permafrost (Williams, 1970; French, 2007).

As sub-permafrost waters at the Lupin Mine had a wide range of salinities, it was unclear what impact water recharged through the open talik has on the deep groundwater (Stotler et al., 2009b).

Changes in chemical composition of groundwater due to permafrost

At Lupin Mine, the mining company has used large amounts of salt solution when operating within the permafrost, and sodium and calcium chloride have been added to the flushing water to prevent freezing (Ruskeeniemi et al. 2002). Consequently, this complicates interpretation of the groundwater chemistry:

- Groundwater within the permafrost is typically Na-Cl or Na-Cl-SO_4 type with highly variable SO_4 concentrations and high NO_3 concentrations. These fluids are thought to be mixtures of drilling salt, chemical residuals from blasting and natural fluids (Stotler et al., 2009a);
- Deep groundwater is distinct from the contaminated permafrost waters and may represent uncontaminated deep groundwater at the site. Deep groundwater is characterised by Na-Ca or Ca-Na-Cl with wide ranges of TDS values from 2 to 36 g/L (Stotler et al., 2009a).
- Basal permafrost waters show similar salinities to the most dilute deep sub-permafrost waters. *In situ* cryogenic concentration due to ice and methane formation may have concentrated the remaining fluids. Introduction of mine-brine, mine-induced drawdown and gas hydrate melting complicated the direct investigation of freezing effects on the groundwater chemistry (Stotler et al., 2009b).

Mine dewatering has created an artificial hydraulic gradient, depressurising the area immediately surrounding the mine. This under-pressure is the likely cause of the presence of an unsaturated zone beneath the base of the permafrost. In addition, it has been hypothesised that the drawdown caused by the mine dewatering has encouraged the downward flow of relative dilute permafrost and/or talik water. As the fluids were not found to be contaminated at depths between 890-1130 m, the primary dilute water source at this depth has been suggested to be related to melting of gas hydrates due to anthropogenic mine depressurization. However, underneath the *through-talik*, methane hydrates would not exist due to the warmer subsurface temperatures (Stotler et al., 2009a; Stotler et al., 2009b).

Stability of permafrost methane hydrate

An important feature of permafrost when considering groundwater flow and chemistry is the presence of methane hydrates:

- Methane hydrates form under low temperature and pressure conditions in areas of sufficient gas concentrations. These crystalline structures of stabilised gas and water affect the fluid geochemistry and the permeability (Stotler 2011);
- Methane is the dominant hydrocarbon gas associated with the deep subpermafrost groundwater and isotopic analysis suggests a thermogenic origin with an age of millions to billions of years (Stotler et al., 2009b);
- Pressure and temperature measurements indicate that methane hydrates were stable at the sites prior to the mining activities;
- Modelling of the subsurface pressures and temperatures over the last 120 ka glacial cycle indicates that glacial loading increased subsurfaces pressures, which resulted in an increase in the hydrate stability field during glacial periods with the stability field extending to the land surface;
- The existence of gas hydrates would have limited recharge during glacial periods (Stotler et al., 2010).

Uncertainties and limitations

The effects of 20 years of mining activity prior to the research conducted at Lupin mine influenced the results obtained. Contamination of groundwater with drilling fluids complicates the investigation of any influence of permafrost on groundwater chemistry. In addition, low hydraulic pressures attributed to mine dewatering resulted in an unsaturated zone beneath the permafrost:

- Investigation in a borehole 160 km north of Lupin mine indicated that the salinity of the non-drilling fluid component within the permafrost was <20000 mg/L with $\delta^{18}O$ values ~5% lower than that of local surface water. Thus the fluid isotopic composition has been hypothesised to be influenced by ice formation. Piezometric heads at the undisturbed site were near land surface, and thus the unsaturated zone at the Lupin mine results from dewatering of the mine (Stotler et al., 2011);
- Groundwater sampling for geochemical analysis has proved problematic, due to freezing of the sampling line, which prevented the collection of uncontaminated samples (Stotler et al., 2011).

Relevance – what we have learnt

The study of the Lupin Mine site has revealed a number of important findings:

- No brines were found beneath the permafrost at the Lupin site, thus it appears that *in situ* freeze-out during permafrost or methane hydrate formation is not able to create such highly concentrated fluids;
- Through-taliks, formed through surface insulation, heat advection or heat from a GDF, will have a major role in the regional scale groundwater system. Heat generated from a GDF could have the potential to form such a through-talik groundwater flow pathway. It will be important for a safety case for a GDF to understand how such taliks may affect the deep groundwater flow system in permafrost influenced regions;
- Methane hydrates are currently present underneath the permafrost at Lupin, and during ice sheet covered times can extend to the land surface. Similar to ice, the existence of gas hydrates reduces the hydraulic conductivity and thus subglacial recharge is limited when gas hydrates exist near the surface. As long as the gas hydrates are in the solid phase,

their effects on the performance of a GDF is small, however their destabilisation can release large quantities of methane (Ruskeemiemi et al., 2002; Stotler et al., 2010).

Further reading

BUSBY, J.P., LEE, J.R., KENDER, S., WILLIAMSON, P. AND NORRIS, S., 2016. Regional modelling of permafrost thicknesses over the past 130 ka: implications for permafrost development in Great Britain. *Boreas*, *45*(1), pp.46-60.

BUSBY, J.P., LEE, J.R., KENDER, S., WILLIAMSON, J.P. AND NORRIS, S., 2015. Modelling the potential for permafrost development on a radioactive waste geological disposal facility in Great Britain. *Proceedings of the Geologists' Association*, *126*(6), pp.664-674.

FRENCH, H. M. 2007. *The Periglacial Environment*, Wiley-Blackwell.

KLEINBERG, R.L., AND GRIFFIN, D.D. 2005. NMR measurements of permafrost: unfrozen water assay, pore-scale distribution of ice, and hydraulic permeability of sediments, *Cold Regions Science and Technology*, *42*, 63-77, [doi:10.1016/j.coldregions.2004.12.002].

RUSKEEMIEMI, T., PAANANEN M., AHONEN, L., KAIJA, J., KUIVAMÄKI, A., FRAPE, S., MOREN, L. AND DEGNAN, P. 2002. Permafrost at Lupin. Report of Phase I, *Permafrost Project GTK-SKB-POSIVA-NIREX-OPG*, Geological Survey of Finland, Nuclear Waste Disposal Research.

SHAW, R.P.; AUTON, C.A.; BAPTIE, B.; BROCKLEHURST, S.; DUTTON, M.; EVANS, D.J.; FIELD, L.P.; GREGORY, S.P.; HENDERSON, E.; HUGHES, A.; MILODOWSKI, A.E.; PARKES, D.; REES, J.G.; SMALL, J.; SMITH, N.; TYE, A.; WEST, J.M.. 2012 *Potential natural changes and implications for a UK GDF*. British Geological Survey, 198pp. (CR/12/127).

STOTLER, R.L., FRAPE, S.K., RUSKEEMIEMI, T., AHONEN, L., PAANANEN, M., HOBBS, M. Y., LAMBIE, K. E. AND ZHANG, M.. 2009a. Hydrogeochemistry of Groundwaters at and Below the Base of the Permafrost at Lupin: Report of Phase III. *NWMO*, **TR-2009-10**.

STOTLER, R.L., FRAPE, S.K., RUSKEEMIEMI, T., AHONEN, L., ONSTOTT, T.C. AND HOBBS, M.Y. 2009b. Hydrogeochemistry of groundwaters in and below the base of thick permafrost at Lupin, Nunavut, Canada, *Journal of Hydrology*, **373**, 80-95 [doi:10.1016/j.jhydrol.2009.04.013].

STOTLER, R.L., FRAPE, S.K., AHONEN, L., CLARK, I., GREENE, S., HOBBS, M., JOHNSON, E., LEMIEUX, J.M., PELTIER, R. PRATT, L. RUSKEENIEMI, T., SUDICKY, E. AND TARASOV, L. 2010. Origin and stability of a permafrost methane hydrate occurrence in the Canadian Shield. *Earth and Planetary Science Letters*, **296**, 384-394, [doi:10.1016/j.epsl.2010.05.024].

STOTLER, R.L., FRAPE, S.K., FREIFELD, B.M., HOLDEN, B., ONSTOTT, T.C., RUSKEENIEMI T. AND CHAN, E. 2011. Hydrogeology, chemical and microbial activity measurement through deep permafrost, *Ground Water*, **49**, 348-364 [doi:10.1111/j.1745-6584.2010.00724.x].

WILLIAMS, J. 1970. Ground water in the permafrost regions of Alaska. *Geological Survey Professional Paper*, **696**.

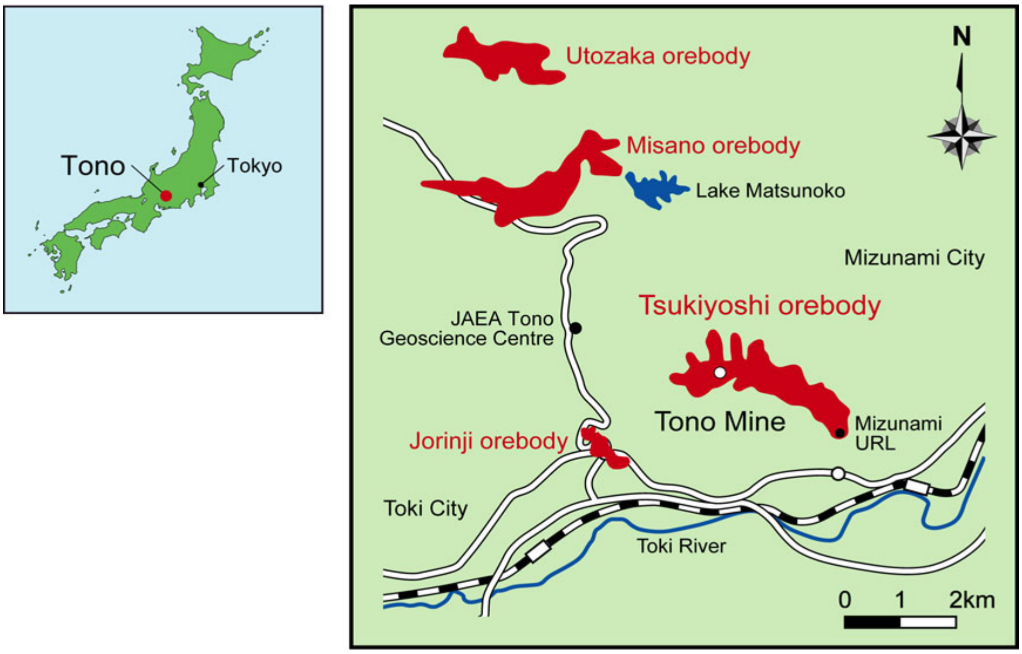
Tono: a natural analogue for host rock stability

Overview

Why host rock stability?

The main role of a host rock of a geological disposal facility (GDF) for radioactive waste is to provide a suitable environment which will guarantee the longevity and performance of the GDF engineered barrier system (EBS). The three most important safety features provided by the geosphere are mechanical protection, adequate geochemical conditions (i.e. near-neutral pH and low oxygen levels) and sufficiently low groundwater flow rates.

As such, the assurance of geological stability is essential for deep geological disposal, and is of special concern in areas of active tectonics (e.g. host rocks which experience lots of earthquakes). It is thus important in many geological disposal programmes to assess the potential impact of geological phenomena such as uplift/erosion and fault activity on long-term GDF safety and to identify key factors (conditions, processes, etc.) governing geological stability.

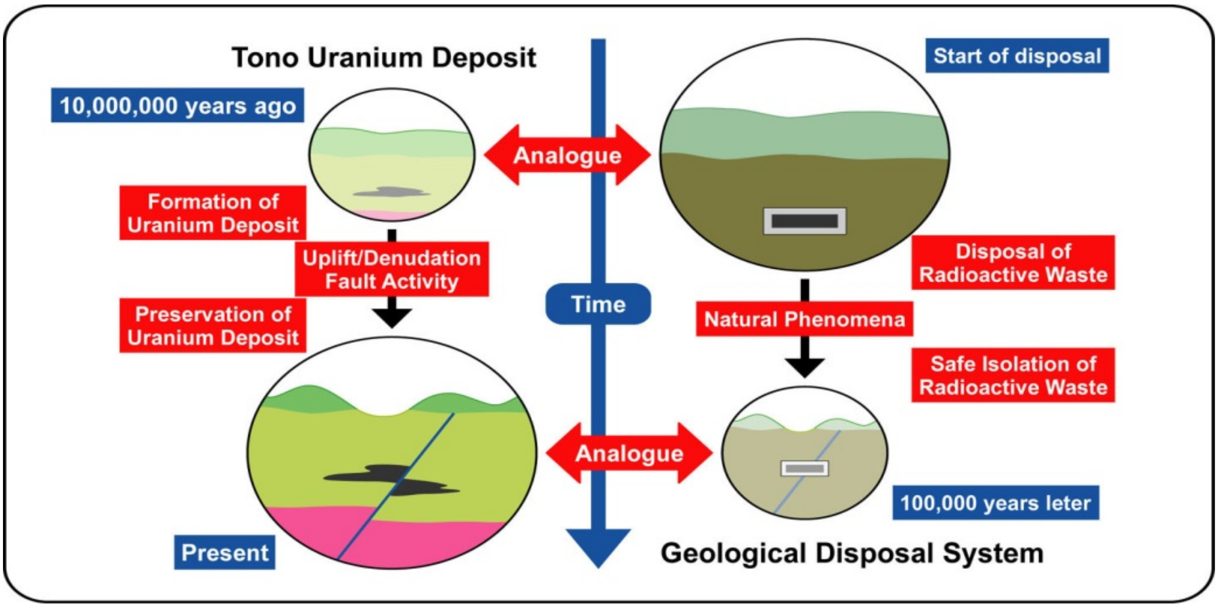


Location map of the Tono uranium orebody in central Japan (JAEA).

Host rock stability and Tono

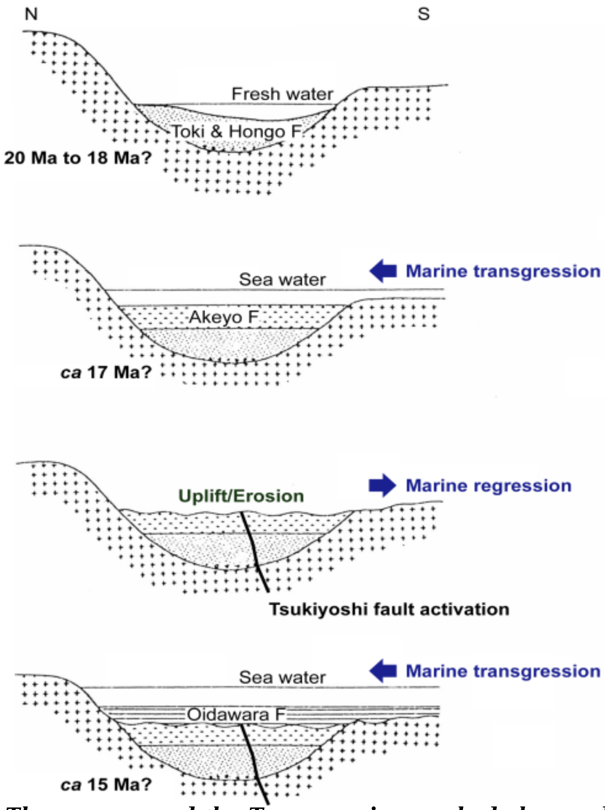
The very old Cigar Lake uranium ore body is often presented as evidence that a GDF should be able to isolate waste for millions of years if necessary. However, akin to the tectonic setting of the UK, Cigar Lake, lies in a stable intraplate setting and even the main fractures at the site are several hundred million years old. A more appropriate example for host rock stability in an active tectonic environment can be found in Japan, part of the Circum-Pacific ‘Ring of Fire’. Here, in the centre of the country, a group of uranium ore bodies occur which have persisted despite many periods of disturbance and change. Situated near the small town of Mizunami (the site of JAEA’s URL), 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.

This 10 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 over the last 20 million years.

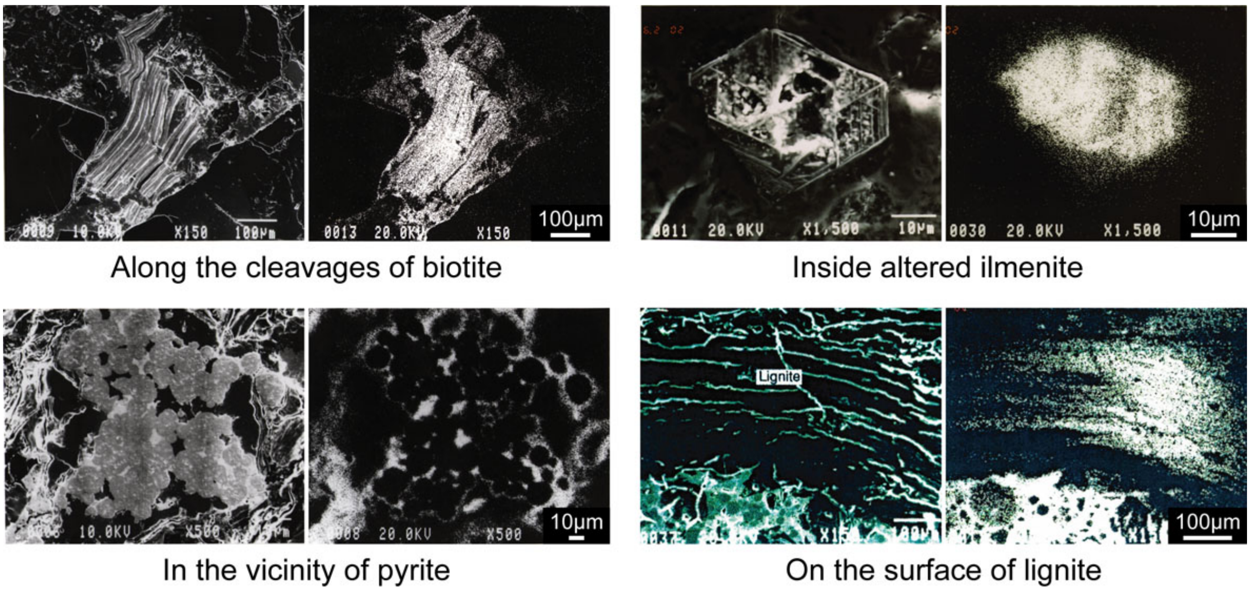


Comparison between the Tono uranium deposit and a GDF

Surface installations and underground galleries at the Tono Mine



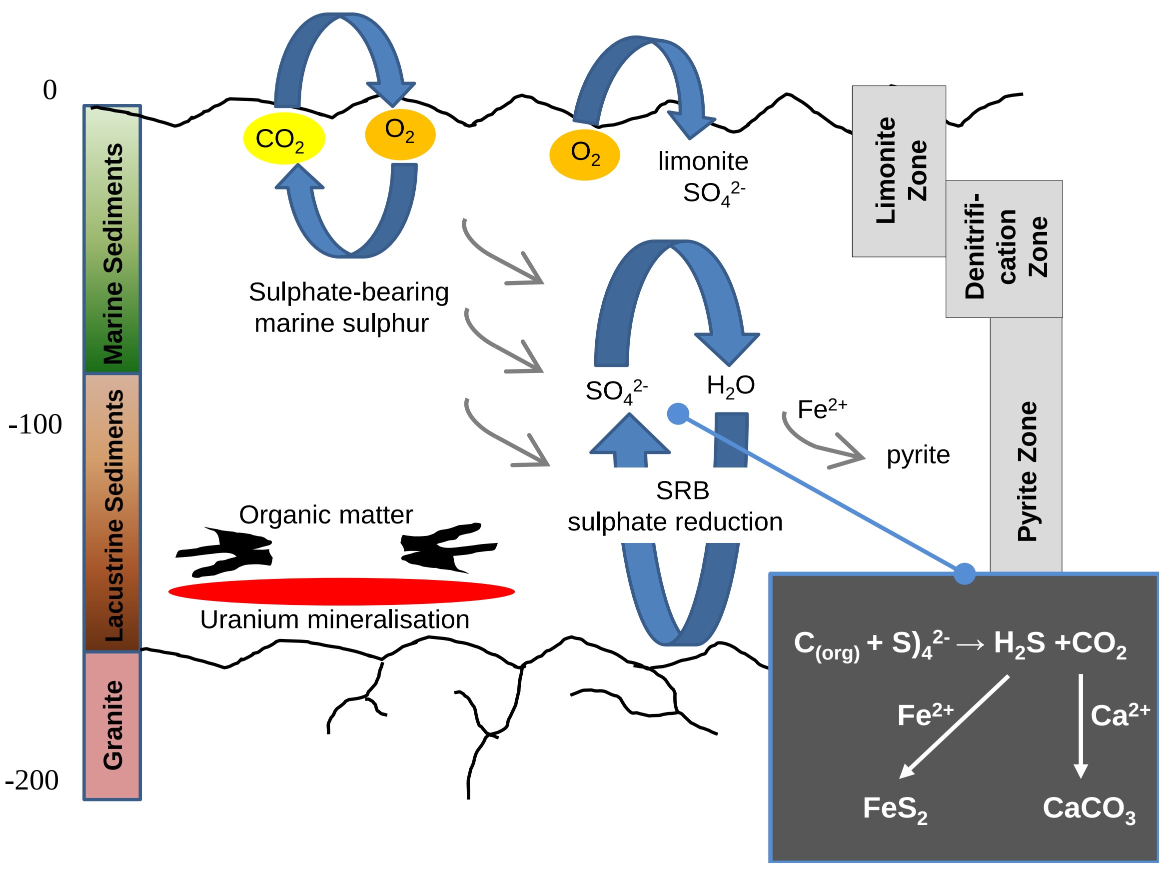
The area around the Tono uranium orebody has undergone many perturbations over the last 20 million years (JAEA).



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 (JAEA).

The area has been inundated by the sea several times, 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. Despite this, the Tono uranium ore body (and several others nearby) has survived intact for up to 15 million years, showing that deep geological disposal can be expected to work even in areas which are not perfectly stable.

Detailed examination of the ore body 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. An important part of this trapping mechanism is that the rock and groundwaters contain little or no available oxygen, which maintains reducing conditions and limits the mobility of uranium. 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 radionuclides) which might be released from the EBS.



A range of geochemical processes contribute to the low oxygen levels in the orebody (modified from JAEA).

Uncertainties and limitations

- The Tono study is a useful analogue for a deep GDF provided the GDF is expected to be located in a chemically reducing environment that would persist for millions of years in the surrounding host rock;
- The low oxygen levels in the rock and groundwater are known to be important for trapping the uranium, but it is unclear if these low levels are primarily because of the presence of the organic material, lignite, at the site – something unlikely in most GDF host rocks;

- The Tono analogue study suffers from the general limitation that applies to all natural uranium ore body studies, i.e. the primary mineral assemblage does not mimic exactly the solid phase compositions to be found in spent fuel rods;
- 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 ore body? How analogous was it to today's waste?

Relevance – what we have learnt

- Despite an incredibly complex history of repeated, regional and local perturbations at the Tono site, the Tsukiyoshi and neighbouring ore bodies are still present after millions of years, clearly showing that a less stable host rock can still guarantee the longevity and performance of a GDF;
- Several specific uranium trapping processes have been identified at the site, but it is known that this does not explain all the observations. Nevertheless, the data back the mechanisms elucidated in 'standard' laboratory experiments, so increasing confidence in their use in GDF safety cases.

Further reading

ALEXANDER, R., GIERE, R., HIDAKA, H AND H. DORA YOSHIDA (EDS). Thematic edition on the Tono Analogue Project. *Geochemistry: Exploration, Environment, Analysis* **6**

JAPAN NUCLEAR CYCLE DEVELOPMENT INSTITUTE. 2000. H12 Project to Establish Technical Basis for HLW Disposal in Japan - Supporting Report 1, Geological Environment in Japan. *JAEA Technical Report*, **JNC TN1410 2000-002**, JAEA, Tokai, Japan.

MIZUNO, T. AND IWATSUKI, T. 2005. Study on long-term stability of geochemical environments at deep underground. *Proceedings of the 15th Symposium on Geo-environments and Geo-Technics, December 2005, Japan*, pp 51–54. Chiba, Japan: Japanese Society of Geo-Pollution Science, Medical Geology and Urban Geology (in Japanese with English abstract).

SASAO, E., OTA, K., IWATSUKI, T., NIIZATO, T., ARTHUR, R.C., STENHOUSE, M.J., ZHOU, W., METCALFE, R., TAKASE, H. AND MACKENZIE, A.B. 2006. An overview of a natural analogue study of the Tono uranium deposit, central Japan. *Geochemistry: Exploration, Environment, Analysis* **6**, 5–12.

3.2 LONG-TERM PERFORMANCE OF SALT HOST ROCKS

Natural analogues for a GDF in a salt host rock

Natural analogues for a GDF in a salt host rock

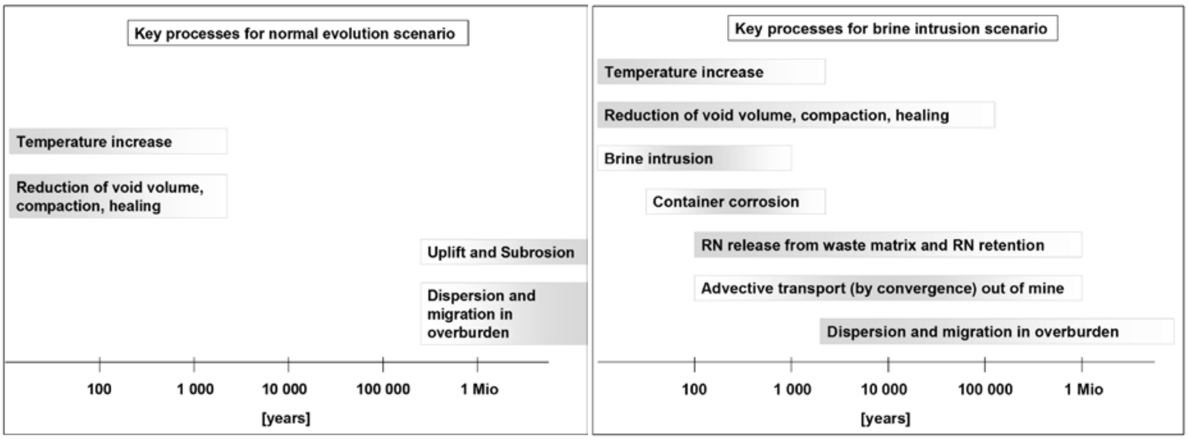
Overview

Why put waste in salt?

There have been several major investigations of rock salt (halite) host rock systems for geological disposal of radioactive wastes, including Morsleben and Gorleben (Germany), and WIPP (USA). For geological disposal facility (GDF) concepts in halite, the geological barrier 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 very long time periods (millions to 10s of millions of years). This is because the salt, which behaves plastically over time, will slowly close in around the waste and any engineered barrier system (EBS). As a result all voids will be closed, effectively sealing the GDF. Therefore, natural analogue observations indicating that the salt host rock (be it in a salt diapir or in layered evaporites) is stable and maintains a high integrity over geological time frames are crucial for the safety case.

LLW in the Morsleben GDF in Germany, built in a salt host rock (www.kernenergie.de)

The only significant alternative scenario considered is that of brine intrusion. Soon after GDF closure, as heat from the waste increases the salt 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 salt is assumed to be at its highest.



Key processes for the normal evolution and for a brine intrusion scenario for a GDF in rock salt. The shading of the bars indicates the importance of the process at a distinct point of time: grey = high importance, white = low importance.

Natural analogues of salt host rocks

A suite of NA studies have been identified to support the safety case for a GDF in salt and, of these, the greatest effort recently has been on the role of the salt host rock as a barrier to radionuclide transport.

Subsystem	Analogue for	Natural Analogue
Radionuclide retardation in the near field	**Element retardation in secondary phases during alteration of glass matrix**	**Element distribution in basaltic glasses and alteration phases**
	Retardation of radionuclides by uptake in precipitating salt minerals	**Co-precipitation of natural elements during formation of salt deposits**
Barrier function of the salt host rock	**Backfilled voids reach properties of salt in the long term**	**Areas in salt where brine solutions have migrated**
	Long-term integrity of salt against fluids and gases	**Fluid/brine inclusions in salt**
	Convergence/compaction of backfill material in the long term	**Current conditions of old, open and backfilled drifts**
	Tectonic/mechanical long-term behaviour of salt domes	**Healing of fissures and joints in salt rock**
Radionuclide retardation in the far field	**Transport of radionuclides through overlying sediments**	**Radionuclide interaction with sediments of overburden of salt domes**

Much of this work has been conducted on so-called ‘anthropogenic analogues’ – or man-made (rather than ’natural’) analogues such as abandoned mine workings. These have shown, as significant, a 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.

Brine and gas inclusions from salt diapirs across Germany have been analysed for their chemistry and Core through 20 year old compacted salt (from the Riedel mine, Germany) to assess void reduction efficiency with time. (Brasser et al., 2000).

'True' natural analogues have included work on the natural brine inclusions which are present in all salt deposits worldwide. These show that, while brines near the outer edge of the salt deposits have reacted with local groundwaters, those brines found in the centre of the deposits are very old and were formed at the same time as the original deposits, some 250 million years ago, demonstrating that there has been little or no movement of groundwater through the salt. This has been supported by work on gas bubbles in salt crystals which also indicate that there has been little interaction with groundwaters from outside the salt bodies.

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 much less clear, so weakening any natural analogue arguments.

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.

Further reading

BEIN, A., HOVORKA, S., ET AL. 1991. Fluid inclusions in bedded Permian halite, Palo Duro basin, Texas: Evidence for modification of seawater in evaporite brine-pools and subsequent early diagenesis. *Journal of Sedimentary Petrology* 61(1): 1-14.

BRASSER, T., DROSTE, J., MÜLLER-LYDA, I., NELES, J., SAILER, M., SCHMIDT G., AND STEINHOFF M. 2008. Endlagerung wärmeentwickelnder radioaktiver Abfälle in Deutschland. Final report from GRS and the Öko-Institut under contracts 02E9783 and 02E9793 from the Bundesministeriums für Wirtschaft und Technologie (BMWi), Berlin. PTKA-WTE, Forschungszentrum Karlsruhe, Karlsruhe, Germany, (in German).

HERRMANN, A.G. AND RÜHE, S. 1995. Lösungseinschlüsse in Zechsteinevaporiten – Neue Perspektiven in der anwendungsorientierten. Grundlagenforschung. - *Kali und Steinsalz*, **11**, 345-354, (in German).

KRONE, J., MÜLLER-HOEPPE, N., BREWITZ, W., MÖNIG, J. WALLNER, M. AND WEBER, J.R. 2008. Developing an advanced safety concept for a HLW repository in salt rock. Appendix in *NEA (2008) Safety Cases for Deep Geological Disposal of Radioactive Waste: Where Do We Stand? Symposium Proceedings, Paris, France, 23-25 January 2007*. NEA Report No. 6319, NEA, Paris, France.

ROEDDER, E. AND H. E. BELKIN 1980. *Thermal gradient migration of fluid inclusions in single crystals of salt from the waste isolation pilot plant site (WIPP). Scientific basis for nuclear waste management*. C. J. M. Northrup. N.Y., Plenum Publishing Corporation. 2: 453 - 464.

ROTHFUCHS, T., WIECZOREK, K., OLIVELLA S. AND GENS, A. 2003. Lessons Learned in Salt. *European Commission CLUSTER Conference on the Impact of EDZ on the Performance of Radioactive Waste Geological Repositories. 3-5 November 2003, Luxembourg*. European Commission Report EUR 21028 EN, CEC, Luxembourg.

3.3 LONG-TERM ISOLATION CONCEPTS

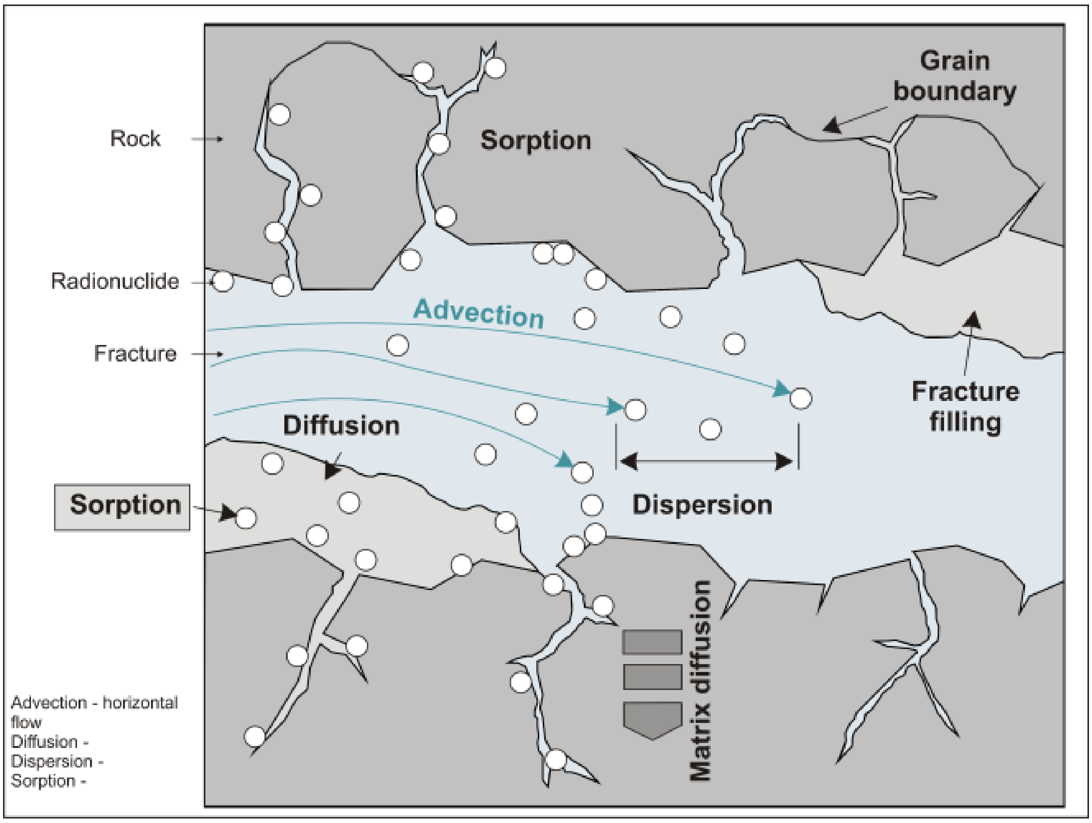
Matrix diffusion: long-term isolation properties of the host rock

MATRIX DIFFUSION: LONG-TERM ISOLATION PROPERTIES OF THE HOST ROCK

OVERVIEW

THE NATURE OF MATRIX DIFFUSION

When studying the long-term fate of radioactive wastes, it is assumed that some radionuclides will eventually migrate from the waste into the host rock surrounding a geological disposal facility (GDF). Once there, two main processes lead to the retention of radionuclides in the rock, namely sorption on the rock minerals and diffusion into the rock matrix. The term *matrix diffusion* is applied to the process by which radionuclides, flowing with the groundwater in fractures in the rock, penetrate the surrounding rock matrix. Diffusion into this rock occurs through a connected system of pores or micro-fractures.



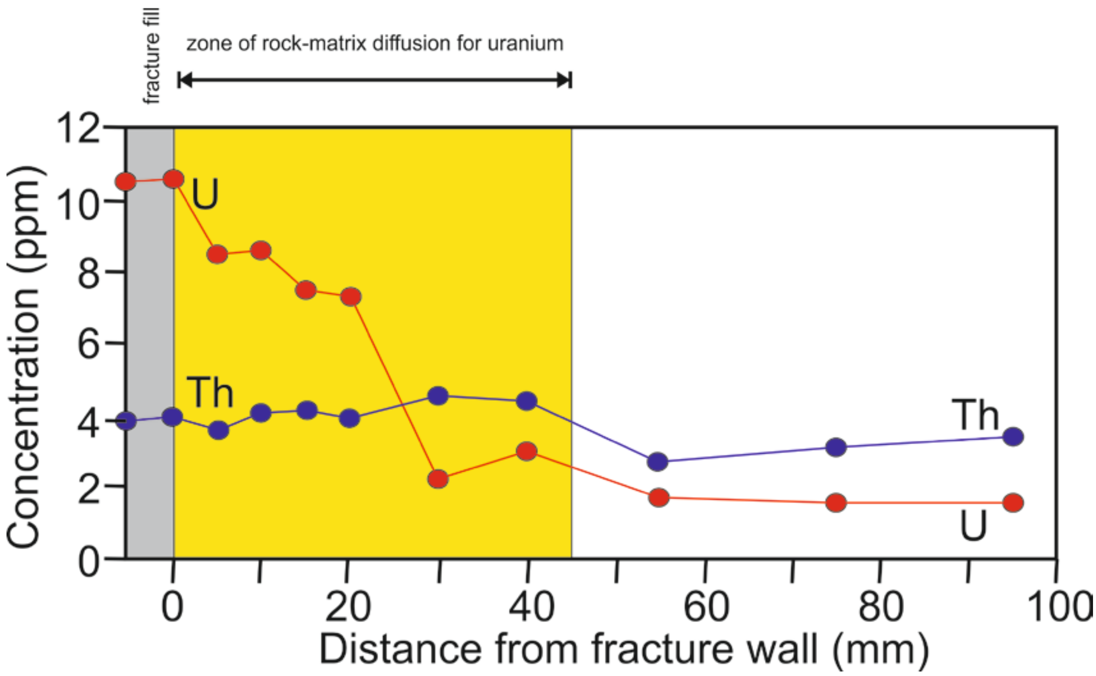
Schematic showing the means of radionuclide mobility in a fracture (diffusion, dispersion and sorption)

The importance of matrix diffusion is that it potentially provides a mechanism for greatly enlarging the area of rock surface in contact with radionuclides dissolved in the groundwater, from that of the fracture surfaces, to a much larger portion of the bulk rock. The degree of radionuclide 'capture' in a rock mass by this diffusion process is often underestimated due to difficulties in measuring various properties of the matrix. These assumptions of limited radionuclide retardation in the matrix may lead to significant overestimation of the transport of radionuclides through the host rock to the Earth's surface. This is especially so for non-sorbing radionuclides such as ^{129}I, because these species would otherwise be transported at the same rate as the groundwater.

Although the theoretical basis for matrix diffusion was fairly well established over six decades ago, the matrix diffusion concept required experimental verification before it could be included in a GDF safety case. Laboratory experiments of diffusion processes are very slow and take years to complete and, as such, are rare. Additionally, the process of drilling and transporting rock cores to the laboratory causes significant changes (increased porosity, new fracture paths) in the rock matrix, which generally means that laboratory data are not relevant to the natural conditions in the GDF host rock. Here, natural analogues offer clear benefits: drillcores are taken through fractures (in which groundwater is flowing) and into the rock matrix and the chemistry and structure of the rock core are examined.

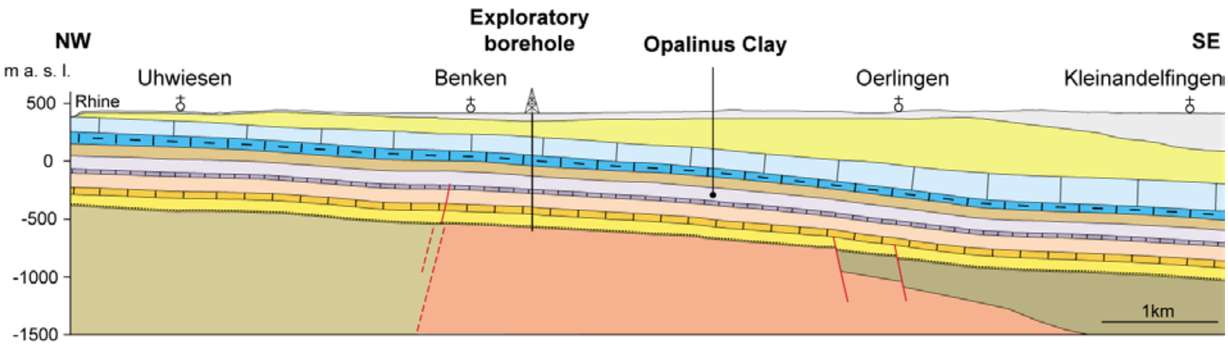
NATURAL ANALOGUE STUDIES OF MATRIX DIFFUSION

The standard natural analogue approach to the assessment of matrix diffusion is to examine natural tracers (for example, uranium, thorium etc.) in the rock. Here, it is assumed that the average chemical composition of the host rock is broadly comparable throughout and any deviations from this are used to indicate the presence of previous rock-water interaction (which might add or remove uranium above the average value, for example).



Geochemical profiles showing the variation in concentration for uranium (U) and thorium (Th) in granodiorite as a function of distance from a water-conducting fracture, from the Kamaishi Granite, Kamaishi Iron Mine, Honshu, Japan (based om Ota et al., 1998)

The distribution of a range of indicator elements is examined along a profile, usually away from a known water-conducting fracture in the host rock, as in the example illustrated above from studies of rock-matrix diffusion undertaken by the JAEA their *in situ* test site in the Kamaishi Granodiorite at the Kamaishi Iron Mine, in Japan. In an ideal world, matrix diffusion would result in a smooth concentration profile away from the fracture, but variability of the rock will complicate this picture a little. Here it can be seen that the relatively immobile thorium shows little variation across the profile whereas uranium, which can be transported in groundwater, shows signs that it has entered the rock matrix from the fracture on the left and moved inwards to a depth of at least 30 cm. This interpretation is of the geochemical profile is also supported by uranium ($^{234}U/^{238}U$) and thorium ($^{230}Th/^{234}U$) isotopic ratios which confirm that ^{234}U uranium has been added to the matrix as a result of migration from the fracture into the wallrock from the fracture, whilst thorium remains unaffected.



Cross-section through the Benken borehole, northern Switzerland

More recently, the work on metre-scale cores across individual fractures has been supplemented by looking at diffusion processes across entire rock formations – on the scale of hundreds of metres. Here, a deep borehole has been drilled through the Opalinus Clay Formation (grey in the figure above) in northern Switzerland. The Opalinus Clay was laid down in a deep ocean some 160-176 million years ago and, as it is highly impermeable, has retained much of the original seawater in its matrix porosity.

The over- and under-lying rock formations are much more permeable and the seawater was rapidly washed out of their matrix and replaced by fresh groundwater. The resultant chemical gradient between the Opalinus Clay and the neighboring rocks meant that the chloride in the matrix began to move out of the Opalinus, towards the over- and under-lying rocks. Modelling of the data from this analogue would suggest that diffusive transport began around 0.5 million years ago, which is entirely consistent with other geological evidence from the area. More importantly, it shows that the matrix diffusion mechanism can work over distances of hundreds of metres and not just the few tens of centimetres previously observed. More recent work from deep crystalline rock in Sweden and Switzerland and siliceous mudstones in Japan show similar matrix availability, suggesting this could be a widespread phenomenon.

Uncertainties and Limitations

- Although natural analogue studies more closely replicate the actual conditions deep in a GDF host rock and avoid the perturbations of laboratory studies, a lack of information on many boundary conditions means that completely unambiguous results may not always be available;
- Most studies to date have been at generic sites and greater certainty could be provided with GDF site-specific data;
- Few truly mechanistic studies of the matrix diffusion process have been carried out in deep rock formations.

Relevance – What We Have Learnt

- Matrix diffusion has been shown to be a relevant radionuclide retention process in both fractured crystalline rock (e.g. Kamaishi) and highly impermeable sediments (e.g. Opalinus Clay) - and at numerous other sites around the world;

- Early GDF safety cases assumed either no matrix diffusion at all or only a very limited amount (1-10 cm into the rock) and recent natural analogue studies have now shown that distances up to several hundred metres are possible;
- This implies that future safety cases should include realistic matrix diffusion depths, especially when assessing the likely degree of retention of non-sorbing radionuclides such as ^{129}I, ^{14}C, etc;
- Matrix diffusion parameters are among the few natural analogue datasets used quantitatively in SA (e.g. in Kristallin-1 in Switzerland and H12 in Japan), possibly in part due to the very simple and direct nature of the data.

FURTHER READING

GARRELS, R.M., DREYER, R.M. AND HOWLAND, A.L. 1949. Diffusion of ions through intergranular spaces in water saturated rocks. *Bulletin of the Geological Society of America*, **60**, 1809–1924.

KUNIMARU, T., OTA, K., YAMAMOTO, H. AND ALEXANDER, W.R. 2010. Hydrochemistry of the groundwaters from JAEA's Horonobe URL: Data Freeze I - preliminary evaluation of boreholes HDB9, 10 and 11. *JAEA Report*, **2008-007**, JAEA, Tokai, Japan.

MAZUREK, M., GAUTSCHI, A., MARSCHALL, P., ALEXANDER, W.R., VIGNERON, G., LEBON, P. AND DELAY, J. 2006. Transferability of features and processes from underground rock laboratories and natural analogues - use for supporting the Swiss and French Safety Cases in argillacaeous formations. P*roceedings AMIGO II workshop, NEA, Paris, 2005*. NEA/OECD, Paris, France.

MILLER, W.M., ALEXANDER, W.R., CHAPMAN, N.A., MCKINLEY, I.G. AND SMELLIE, J.A.T.. 2000. *Geological Disposal of Radioactive Wastes and Natural Analogues*. Waste Management Series, Vol. 2, Pergamon, Amsterdam, The Netherlands.

NERETNIEKS, I. 1980. Diffusion in the rock matrix: an important factor in radionuclide migration? *Journal of Geophysical. Research*, **85**, 4379-4397.

OTA, K. AMANO, K. AND ANDO, T. 1998. Brief overview of in situ contaminant retardation in fractured crystalline rock at Kamaishi *in situ* test site. *Proceedings of International Workshop for the Kamaishi in situ Experiments, Japan, August 24-25, 1998, Tokai-mura, Ibaraki-ken, Japan*: Japan Nuclear Cycle Development Institute, 67-76

WABER, H.N.AND SMELLIE, J.A.T. 2008. Characterisation of pore water in crystalline rocks. *Applied Geochemistry*, **23**, 1834-1861.

4 Radionuclide migration in natural systems

4.1 RETARDATION IN NATURAL SYSTEMS

Poços de Caldas, Osamu Utsumi mine and Morro do Ferro, Brazil - Introduction

Poços de Caldas, Morro do Ferro, Brazil – radionuclide migration

Poços de Caldas, Osamu Utsumi mine, Brazil – radionuclide migration

Poços de Caldas – Osamu Utsumi mine, Brazil – redox fronts

The El Berrocal Project - uranium mobilisation and migration

Needle’s Eye, Scotland - uranium mobilisation and migration

Broubster, Scotland - uranium mobilisation and migration

South Terras Mine: uranium mobilisation and migration

Alligator River, Australia - uranium mobilisation and migration

Loch Lomond, Scotland - a study of halogen migration

Poços de Caldas: Osamu Utsumi mine and Morro do Ferro, Brazil – Introduction

Overview

The multi-barrier system of a geological disposal facility (GDF) is designed to ensure long-term containment of radioactive waste. Were degradation in the functioning of a component of the barrier to occur, the design of the multi-barrier system could instead rely on very slow movement of radionuclides in the near- and far-field into the rock without adversely affecting the surface environment. However, chemical elements react in different ways in the environment according to their chemical form (species) and their interactions with other elements/compounds. Some become more mobile, whilst others are immobilised.

View of Osamu Utsumi mine, Brazil

Elemental solubility and speciation

- The transport and retardation of radionuclides in near- and far-field environments of a GDF are influenced by many factors, including the solubility and their chemical species (speciation). For the near-field, a number of geochemical models and codes can use element analyses of the groundwater (and associated databases) to predict the solubility and speciation of important elements and radionuclides which can be used in assessing the safety case for a GDF. Such predictions are also possible for the far-field;
- Changes in chemistry of a GDF environment caused by, for example, the development of redox fronts (see redox front sheet) will mean that some elements and radionuclides will become mobilised whilst others will be immobilised. These changes in chemistry are complex and need to be understood, using geochemical modelling codes, when assessing GDF safety case performance;
- The geochemical databases, which are used in geochemical models, must be validated demonstrating that they are appropriate for the use envisaged. Natural analogues provide an invaluable way to test, or validate, the results from various geochemical model predictions. Where there is agreement between model predictions of, say, major groundwater elements

with those observed at a relevant natural analogue, this shows that the databases used may be applicable to a GDF;

- The safety of a GDF is demonstrated using a safety case which shows it complies with regulatory targets associated with radionuclide releases into the environment. So understanding and evaluating radionuclide migration and retardation is an important part of a safety case.

Osamu Utsumi mine and Morro do Ferro

- The Osamu Utsumi mine and Morro do Ferro studies formed part of the Poços de Caldas Natural Analogue Project (1986-1990). Both sites are located in a caldera of Mesozoic age comprising alkaline igneous rocks containing variable amounts of uranium (U), Thorium (Th) and Rare Earth Elements (REE);
- Well characterised groundwater compositions from both sites were used in studies by several organisations to calculate, in blind test, the solubility and speciation of a number of trace elements of relevance to radioactive waste disposal (uranium, thorium, lead, strontium and nickel). The results from the various organisations were comparable and fairly consistent with the measured geochemical data. Thorium solubility was lower than expected. However, there was disagreement with predictions on speciation of these elements in water.

Uncertainties and differences

- The nature of both sites means that it was difficult to establish boundary conditions for the processes studied. This means that uncertainty remains as to how relevant the results are to a GDF environment;
- There will be differences in the host rock mineralogy, chemistry and physical properties of the host rock at both sites when compared to actual GDF environments;
- The geochemical modelling comparison exercise showed that the codes had limited predictive success.

Relevance – what we have learnt

- Although the host rock was originally crystalline in origin, hydrothermal alteration has transformed some areas into clay minerals. This means that the site provides data relevant to radionuclide migration in bentonite backfill and/or clay based host rock environments;
- Geochemical models are used in the assessment of safety cases and the studies at Osamu Utsumi mine were able to rigorously test them, resulting in improvements to thermodynamic databases, e.g. Th solubility was lower than expected;
- Most of the information from this study is semi-quantitative or qualitative and useful in scenario development and method development, particularly when studying the evolution of redox fronts and their role in radionuclide mobilisations;
- The time scale addressed by the study is geological, extending to over 2 million years (2 Ma) ago so falls within safety case periods.

Further reading

BRUNO, B., CROSS, J.E., EIKENBERG, J., MCKINLEY, I. G., READ, D., SANDINO, A. AND SELLIN, P. 1990. Testing of geochemical models in the Poços de Caldas analogue study. *SKB Technical Report* **TR90-20**, SKB, Stockholm, Sweden; *Nagra Technical Report*, **NTB90-29**, Nagra, Wettingen, Switzerland; *UK DoE Technical Report* **WR 90-051**.

BRUNO, J., DURO, L. AND MIREIA, G. 2002. The applicability and limitations of thermodynamic geochemical models to simulate trace element behaviour in natural waters. Lessons learned from natural analogue studies. *Chemical Geology 190* (2002) 371– 393.

CHAPMAN, N.A., MCKINLEY, I.G., SHEA, M. AND SMELLIE, J. A. T. (Editors) 1992. The Poços de Caldas project: Natural analogues of processes in a radioactive waste repository. *Journal of Geochemical Exploration (Special Edition)*. **45** (1-3).

CHAPMAN, N.A., MCKINLEY, I.G., SHEA, M. AND SMELLIE, J. A. T. (Editors) 1992. The Poços de Caldas project: Natural analogues of processes in a radioactive waste repository. Journal of Geochemical Exploration (Special Edition). Volume **46** (1).

MILLER, W.M., ALEXANDER, W.R., CHAPMAN, N.A., MCKINLEY, I.G. AND SMELLIE, J.A.T.. 2000. *Geological Disposal of Radioactive Wastes and Natural Analogues*. Waste Management Series, Vol. 2, Pergamon, Amsterdam, The Netherlands.

NORDSTROM, D.K., PUIGDOMENECH, I. AND MCNUTT, R. H. 1990. Geochemical modelling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue study sites. *SKB Technical Report*, **TR90-23**, SKB, Stockholm, Sweden; *Nagra Technical Report*, **NTB90-32**, Nagra, Wettingen, Switzerland; *UK DoE Technical Report* **WR 90-054**.

NAGRA 1993 *Poços de Caldas: Nature's Experiments*. Nagra Bulletin **1/93**

SMELLIE, J. *Analogue evidence from uranium orebodies,* Report to Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2009.

Poços de Caldas: Morro do Ferro, Brazil – radionuclide migration

Overview

The multi-barrier system of a geological disposal facility (GDF) is designed to ensure long-term containment of radioactive waste. Were degradation in the functioning of a component of the barrier to occur, the design of the multi-barrier system could instead rely on very slow movement of radionuclides in the near- and far-field into the rock without adversely affecting the surface environment.

Radionuclide migration in a GDF

- Over a long period of time, the engineered barriers of a GDF will degrade and, eventually, the waste will be exposed to the groundwater and will begin to degrade. Some radionuclides will dissolve in very slow moving groundwater but their transport away from the GDF will be retarded by interactions with the rock and any corrosion products from the engineered barriers. Dilution of the radionuclides in the groundwater will also occur;
- The safety of a GDF is demonstrated using a safety case, which shows it complies with regulatory targets associated with radionuclide releases in the environment. So understanding and evaluating radionuclide migration and retardation is an important part of a safety case.

Morro do Ferro

- The study at Morro do Ferro (Iron Hill) formed part of the Poços de Caldas Natural Analogue Project (1986-1990). Morro do Ferro is located in a caldera of Mesozoic age comprising alkaline volcanic and plutonic rocks containing variable amounts of uranium (U), Thorium (Th) and Rare Earth Elements (REE). The site has long been recognised as one of the most radioactive surface localities in the world;
- Morro do Ferro is a roundish hill rising 140 m above the surrounding plateau, and is about 5 km north of the Osamu Utsumi mine. The original rock is believed to have been carbonatite but it has been heavily weathered to a depth of at least 100 m. The hill is now composed of kaolinite and illite, gibbsite and iron and manganese oxyhydroxides that tend to form distinct layers;
- There are many magnetite veins (metres thick) and Th and REE mineralisation extends from the south down the south side of the hill. This is enriched; up to about 3 wt % ThO_2 and up to 20% wt % total REE in some parts. No U mineralisation is known at Morro do Ferro. Most of the mineralisation lies above the water table and is subject to tropical weathering;
- Two technical objectives focussed the studies at Morro do Ferro, one to test geochemical codes and databases used to evaluate rock/water interactions and solubility/speciation of trace elements and the second to examine colloidal transport of radionuclides and its significance on radionuclide transport processes.

View of Morro do Ferro, Brazil.

Uncertainties and limitations

Morro do Ferro is a site with features at variance to those expected in a clay-based GDF environment. It has a near-surface environment with different mineralogy and oxidising groundwater, in contrast to the reducing environment expected within the host rock around a deep GDF.

Relevance – what we have learnt

- The deep weathering at Morro do Ferro provides a close comparison with a clay-based GDF (and bentonite backfill). This means that the site provides data relevant to radionuclide migration in bentonite backfill and/or clay based host rock environments;
- Morro do Ferro can be considered a worst case scenario for a GDF – near-surface mineralisation, tropical weathering processes (oxidising), and a different mineralogy (illite) to most clay-based disposal concepts. However, its shows that mineralisation still remains, demonstrating the inherent efficiency of the 'clay' based rock to immobilise Th and REEs;
- The known source of Th, REEs and colloids means that the near- and far-field transport and retardation of these elements could be evaluated along known groundwater flow pathways. The efficient filtering of colloid material by the clay based host rock was also demonstrated;
- The main source of the Th and REE is located in the unsaturated zone above the water table so the analogue has relevance to unsaturated disposal concepts;
- Most of the information from this study is semi-quantitative or qualitative and useful in scenario development, particularly when evaluating the role of colloids;
- The time scale addressed by the study is geological, extending to over 2 million years (2 Ma) ago so falls within safety case assessment periods.

Further reading

BRUNO, J., DURO, L. AND MIREIA, G. 2002. The applicability and limitations of thermodynamic geochemical models to simulate trace element behaviour in natural waters. Lessons learned from natural analogue studies. *Chemical Geology 190* (2002) 371– 393.

CHAPMAN, N.A., MCKINLEY, I.G., SHEA, M., SMELLIE, J. A. T. (EDITORS) 1992. The Poços de Caldas project: Natural analogues of processes in a radioactive waste repository. *Journal of Geochemical Exploration (Special Edition)*. **Volume 45** (1-3).

CHAPMAN, N.A., MCKINLEY, I.G., SHEA, M., SMELLIE, J. A. T. (Editors) 1992. The Poços de Caldas project: Natural analogues of processes in a radioactive waste repository. *Journal of Geochemical Exploration (Special Edition)*. **Volume 46** (1).

MILLER, W.M., ALEXANDER, W.R., CHAPMAN, N.A., MCKINLEY, I.G. AND SMELLIE, J.A.T.. 2000. *Geological Disposal of Radioactive Wastes and Natural Analogues*. Waste Management Series, Vol. 2, Pergamon, Amsterdam, The Netherlands.

NAGRA 1993 Poços de Caldas: Nature's Experiments. *Nagra Bulletin* **1/93**

SMELLIE, J. *Analogue evidence from uranium orebodies*, Report to Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2009.

Poços de Caldas: Osamu Utsumi mine, Brazil – radionuclide migration

Overview

The multi-barrier system of a geological disposal facility (GDF) is designed to ensure long-term containment of radioactive waste. Were degradation in the functioning of a component of the barrier to occur, the design of the multi-barrier system could instead rely on very slow movement of radionuclides in the near- and far-field into the rock without adversely affecting the surface environment.

Radionuclide migration in a GDF

- Over a long period of time, the engineered barriers of a GDF will degrade and, eventually, the waste will be exposed to the groundwater and will begin to degrade. Some radionuclides will dissolve in very slow moving groundwater, but their transport away from the GDF will be retarded by interactions with the rock and any corrosion products from the engineered barriers. Dilution of the radionuclides in the groundwater will also occur.
- The safety of a GDF is demonstrated using a safety case, which shows it complies with regulatory targets associated with radionuclide releases in the environment. So understanding and evaluating radionuclide migration and retardation is an important part of a safety case.

Osamu Utsumi mine

- The Osamu Utsumi mine study formed part of the Poços de Caldas Natural Analogue Project (1986-1990). The mine is located in a caldera of Mesozoic age comprising alkaline volcanic and plutonic rocks containing variable amounts of uranium (U), Thorium (Th) and Rare Earth Elements (REE). Some of the rock minerals have been transformed into clay minerals during hydrothermal alteration processes. The mine has been commercially exploited for uranium;
- Intense weathering has altered the uppermost rock, leached the primary uranium and other trace elements and led to secondary deposition of uranium along prominent, distinct redox fronts;
- The depth of the redox fronts, formed by the percolation of oxygenated surface water into the rock, is controlled by fractures which are easily observed within the mine (unoxidised rock is blue-grey, oxidised rock is red-brown as iron in the rock is oxidised). The secondary uranium is also clearly seen because it occurs as centimetre sized nodules of pitchblende in unoxidised rock just ahead of the redox front, often with secondarily formed iron. Any primary uranium behind the front is associated with iron oxyhydroxides;
- Three technical objectives focussed the studies at the mine, firstly to test geochemical codes and databases used to evaluate rock/water interactions and solubility/speciation of trace elements; secondly to test models of the geochemical and biological evolution of redox fronts especially with regard to long-term, large-scale movements of redox-sensitive natural series radionuclides; and thirdly to model the migration of REEs and U-Th series radionuclides during hydrothermal activity that may be found in some GDF designs.

View of Osamu Utsumi mine, Brazil

Uncertainties and differences

- The nature of the site and mine meant that it was difficult to establish boundary conditions for the processes studied. This means that uncertainty remains as to how relevant the results are to a GDF environment;
- There will be differences in the host rock mineralogy, chemistry and physical properties of the host rock at Osamu Utsumi mine when compared to other clay-based host rocks;
- The formation and movement of the redox fronts could not be modelled, which underlined the inadequacy of the coupled codes used. Additionally the complex geochemical systems meant that no clear understanding of radionuclide retardation processes emerged although microbially mediated reactions did play a role.

Relevance

- Although the host rock was originally crystalline in origin, hydrothermal alteration has transformed some areas into clay minerals. This means that the site provides data relevant to radionuclide migration in bentonite backfill and/or clay based host rock environments;
- The study is relevant to the near- and far-field interface saturated zone (initiation, propagation and retardation potential of redox fronts; high temperature gradients) and the far-field (mobilisation and transport of radionuclides under high temperatures);
- Geochemical models are used in assessing the safety case and the studies at Osamu Utsumi mine were able to rigorously test them, resulting in improvements to thermodynamic databases, e.g. Th solubility was lower than expected;
- Most of the information from this study is semi-quantitative or qualitative and useful in scenario development and method development, particularly when studying the evolution of redox fronts and their role in radionuclide mobilisation;
- The time scale addressed by the study is geological, extending to over 2 million years (2 Ma) ago so falls within safety case periods.

Further reading

BRUNO, J., DURO, L. AND MIREIA, G. 2002. The applicability and limitations of thermodynamic geochemical models to simulate trace element behaviour in natural waters. Lessons learned from natural analogue studies. *Chemical Geology,* **190**, 371-393.

CHAPMAN, N.A., MCKINLEY, I.G., SHEA, M., AND SMELLIE, J. A. T. (Editors) 1992. The Poços de Caldas project: Natural analogues of processes in a radioactive waste repository. *Journal of Geochemical Exploration (Special Edition).* **45** (1-3).

CHAPMAN, N.A., MCKINLEY, I.G., SHEA, M., AND SMELLIE, J. A. T. (Editors) 1992. The Poços de Caldas project: Natural analogues of processes in a radioactive waste repository. Journal of *Geochemical Exploration (Special Edition)*. **46** (1).

MILLER, W.M., ALEXANDER, W.R., CHAPMAN, N.A., MCKINLEY, I.G. AND SMELLIE, J.A.T.. 2000. *Geological Disposal of Radioactive Wastes and Natural Analogues*. Waste Management Series, Vol. 2, Pergamon, Amsterdam, The Netherlands.

NAGRA 1993 Poços de Caldas: Nature's Experiments. *Nagra Bulletin* **1/93**

SMELLIE, J. *Analogue evidence from uranium orebodies*, Report to Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2009.

Poços de Caldas: Osamu Utsumi mine, Brazil – redox fronts

Overview

The normal condition of rocks and groundwaters at depth is reducing because there is little oxygen present. Reducing conditions ensure that radionuclides remain immobile and will not migrate from a geological disposal facility (GDF) for radioactive waste. However, when air and oxidising groundwaters are introduced during the excavation and operation of a GDF, exposed rock will be oxidised and a redox front will be established which will change radionuclide mobility.

Redox fronts

- Redox fronts are created at the boundary between two rock/groundwater systems with different oxidation environments. The development of redox fronts in the near- and far-fields of GDFs of all designs is usually unavoidable;
- If an excavated GDF is left open for any length of time (say for monitoring or for retrievability reasons), the continuous supply of oxygen in the air will cause the redox front to migrate from the excavation walls into the rock. After GDF closure the oxygen will be dissolved in the groundwater and will be used in redox processes. Eventually the near-field will become reducing;
- Redox fronts may occur in the far-field where surface groundwaters containing oxygen infiltrate downwards meet deeper reducing waters;
- For HLW and spent fuel repositories, redox fronts will be caused by waste-induced radiolysis (splitting) of water generating oxidising ions;
- GDF engineered barriers such as steel and bentonite can act as redox buffers, scavenging oxidising ions to maintain reducing conditions;
- The chemistry of many radionuclides is strongly influenced by redox and so their capacity to be transported changes across a redox front. In general, oxidising conditions enhance radionuclide mobility;
- The safety of a GDF is demonstrated using a safety case, which shows it complies with regulatory targets associated with radionuclide releases to the environment. So understanding and evaluating the effects of redox front processes on radionuclide migration and retardation is an important part of a safety case. Consequently, there is great interest in developing geochemical codes capable of modelling redox processes.

Osamu Utsumi mine

- The Osamu Utsumi mine study formed part of the Poços de Caldas Natural Analogue Project (1986-1990). The mine is located in a caldera of Mesozoic age comprising alkaline volcanic and plutonic rocks containing variable amounts of uranium (U), Thorium (Th) and Rare Earth Elements (REE);
- Intense weathering has altered the uppermost rock, leached the primary uranium and other trace elements and led to secondary deposition of uranium along prominent, distinct redox fronts;
- The depth of the redox fronts, formed by the percolation of oxygenated surface water into the rock, is controlled by fractures and they are easily observed within the mine

(unoxidised rock is blue-grey, oxidised rock is red-brown as iron in the rock is oxidised). Dissolved elements then diffuse across the redox front;

- There is clear evidence for uranium precipitation and enrichment (1 cm nodules of pitchblende often with secondarily formed iron) on the reducing side of the redox front which occurred within the last 300,000 years;
- Any primary uranium left behind the front in the oxidising zone is associated with iron oxyhydroxides;
- The overall chemistry is of the redox fronts is very complex and involves microbial catalysis of many reactions involving iron, sulphur and uranium;
- The fronts move at a rate of 1 to 20 m in 1 million years, which is the same as the rate of erosion at the site;

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) as iron in the rock is oxidised).

Various geochemical model approaches and codes were developed and tested to describe the reactions across the redox fronts at the mine. These showed that main reactions (such as pitchblende redox reactions) could be simulated. However, none of the codes tested were able to model the mineralogy observed at the redox front and the rate of front movement.

Uncertainties and differences

- The development of redox fronts at the mine differs from those that might occur in a GDF near-field in that those at the mine are connected to and driven by the Earth's atmospheric system and near-surface groundwater flow, and those in a GDF are not;
- The formation and movement of the redox fronts could not be modelled which underlined the inadequacy of the coupled codes used. More code and thermodynamic database development is needed before such codes can be used in assessing long-term safety

performance. Additionally the complex geochemical systems meant that no clear understanding of radionuclide retardation processes emerged;

- Microbes play a key role in understanding the chemistry and kinetics of reactions across the redox front. However, their significance in a GDF will be dependent on the availability of nutrient and energy sources which will differ according to the GDF design concept.

Relevance – what we have learnt

- This study showed that redox front locations are controlled by a system of hydraulically active fractures and that elemental movement over the redox front was predominantly by diffusion. This will also be the case for radiolytically induced redox fronts migrating out of the near-fields of HLW, spent fuel and high activity ILW repositories, depending on the level of shielding associated with the waste package;
- The study is also relevant to the near- and far-field interface saturated zone (initiation, propagation and retardation potential of redox fronts);
- Geochemical models are used in assessing safety cases and the studies at Osamu Utsumi mine were able to rigorously test them, resulting in improvements to thermodynamic databases. Since this study was undertaken, further developments have been made;
- Most of the information from this study is semi-quantitative or qualitative and useful in scenario development and method development, particularly when studying the evolution of redox fronts and their role in radionuclide mobilisation;
- The time scale addressed by the study extends to over 1 million years (1 Ma) ago so falls within safety case assessment periods.

Further reading

BRUNO, J., DURO, L. AND MIREIA, G. 2002. The applicability and limitations of thermodynamic geochemical models to simulate trace element behaviour in natural waters. Lessons learned from natural analogue studies. *Chemical Geology* **190**, 371– 393.

CHAPMAN, N.A., MCKINLEY, I.G., SHEA, M. AND SMELLIE, J. A. T. (EDITORS) 1992. The Poços de Caldas project: Natural analogues of processes in a radioactive waste repository. *Journal of Geochemical Exploration (Special Edition)*. **Volume 45** (1-3).

CHAPMAN, N.A., MCKINLEY, I.G., SHEA, M. AND SMELLIE, J. A. T. (EDITORS) 1992. The Poços de Caldas project: Natural analogues of processes in a radioactive waste repository. *Journal of Geochemical Exploration (Special Edition)*. **Volume 46** (1).

CROSS, J.E., HAWORTH, A., LICHTNER, P.C., MACKENZIE, A.B., MORENO, L., NERETNIEKS, I., NORDSTROM, D.K., READ, D., ROMERO, L., SCOTT, R.D., SHARLAND, S. AND TWEED, C. 1990. Testing models of redox front migration and geochemistry at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *SKB Technical Report*, **TR90-21**, SKB, Stockholm, Sweden; *Nagra Technical Report*, **NTB90-30**, Nagra, Wettingen, Switzerland; *UK DoE Technical Report*, **WR 90-052**.

MILLER, W.M., ALEXANDER, W.R., CHAPMAN, N.A., MCKINLEY, I.G. AND SMELLIE, J.A.T.. 2000. *Geological Disposal of Radioactive Wastes and Natural Analogues*. Waste Management Series, Vol. 2, Pergamon, Amsterdam, The Netherlands.

NAGRA 1993 Poços de Caldas: Nature's Experiments. *Nagra Bulletin* **1/93**

SMELLIE, J. *Analogue evidence from uranium orebodies*, Report to Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2009.

WABER, N., SCHORSCHER, H.D., MACKENZIE, A.B., PETERS, T. 1990. Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. *SKB Technical Report*, **TR90-11**, SKB, Stockholm, Sweden; *Nagra Technical Report*, **NTB90-20**, Nagra, Wettingen, Switzerland; *UK DoE Technical Report* **WR 90-042**.

The El Berrocal Project: an analogue for uranium mobilisation and migration from a radioactive waste repository

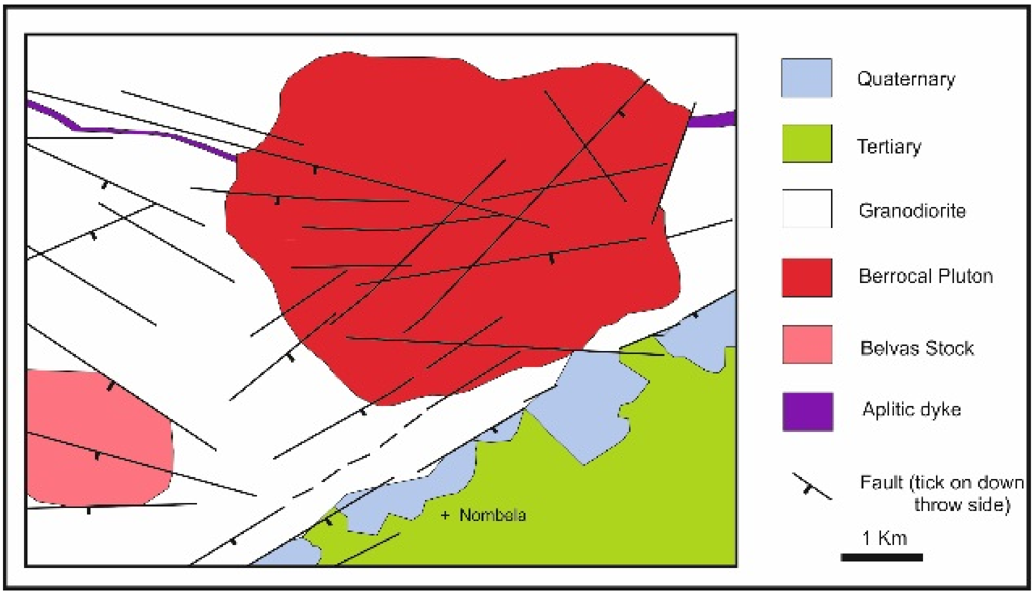
Overview

The El Berrocal project studied a vein occurrence of uranium minerals as an analogue for spent fuel evolution. The project was an FP2 Euratom (European Commission) funded project that was co-funded by ENRESA (Spain), CIEMAT (Spain) and Nirex (UK) with participants from Spain, Italy, France and the UK. The project ran from 1991 to 1995 and was an integrated project that examined a number of aspects of natural radionuclide migration associated with uranium mineralisation hosted in the El Berrocal Granite.

The key objective of the project was to develop an understanding of past and present processes that control the migration behaviour and distribution of naturally occurring radionuclides in a fractured granitic environment with a focus on those processes that are relevant to a GDF safety case.

Uranium mineralisation

The El Berrocal Mine is about 90km SW of Madrid and comprises a granitic intrusion that has an age of 289 Ma which in the El Berrocal area is faulted against Tertiary sediments.

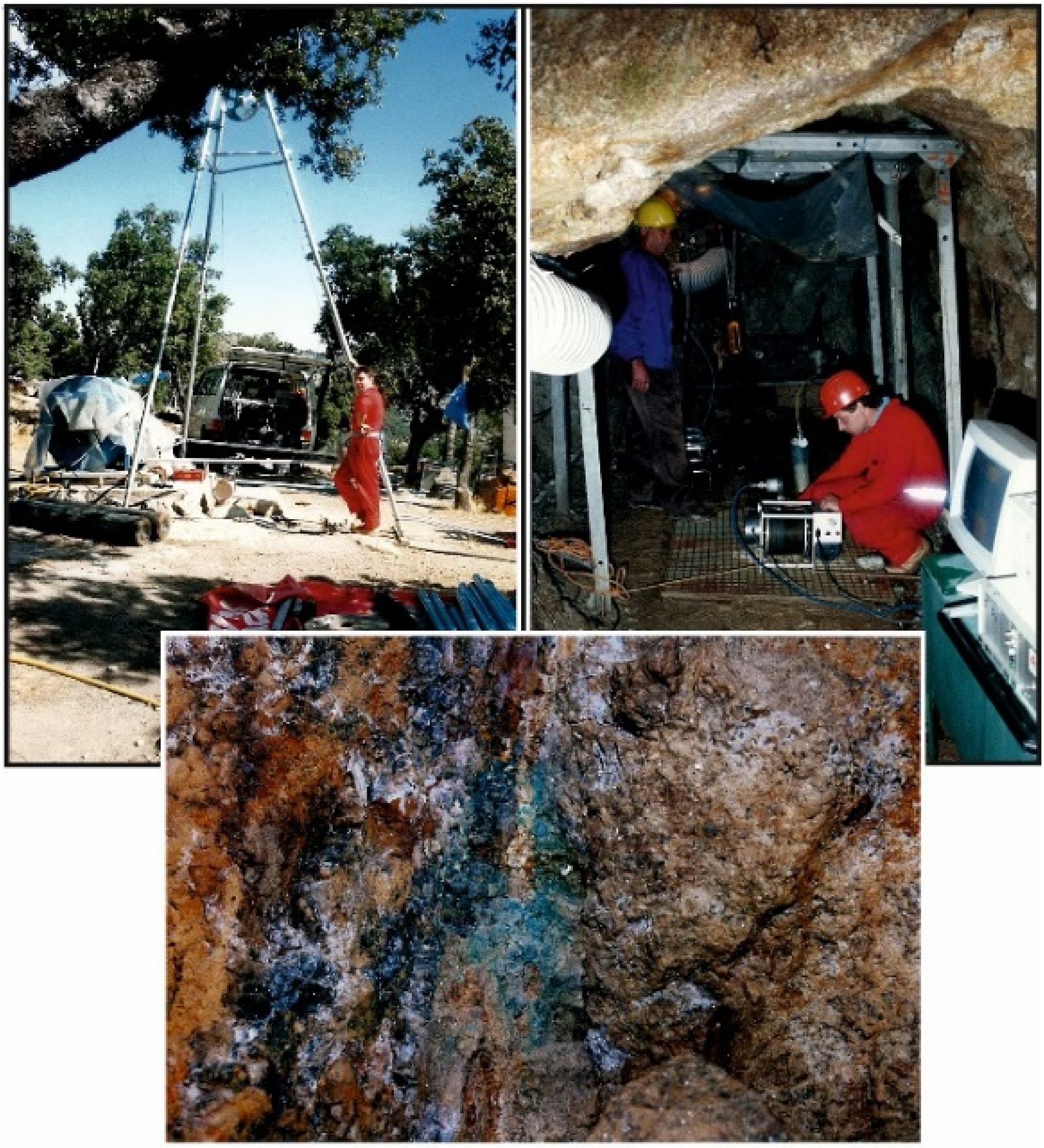


Geological map of El Berrocal

El Berrocal

- The granite hosts several uranium rich quartz veins, at least two of which were considered economic and were mined over a number of years prior to abandonment in the late 1960s;
- One of the larger veins, up to two metres wide, was the focus of the study. This vein had been mined by a series of adits (galleries) which exploited the vein over a distance of about 100 m. One accessible adit, about 70 m long was utilised for some of the studies undertaken by the project.

- The primary uranium mineral is uraninite (pitchblende) but uranium secondary minerals are common and sulphide minerals are present as accessories.



Borehole drilling and uraninite vein mineralisation at El Berrocal

Nineteen boreholes to a maximum depth of 609 m, with a combined total length of more than 2100 m, mainly fully cored, were drilled during the project, from both surface and underground sites, to evaluate the site. The focus of these boreholes was to:

- *Characterise the granite and mineralisation;*
- *Characterise fractures and discontinuities;*
- *Characterise groundwater chemistry and flows;*
- *Examine variation of physio-chemical characteristics with depth, and;*
- *Facilitate tracer testing.*

Uncertainties and limitations

- The disturbed nature of the El Berrocal mine site means that it was difficult to establish boundary conditions for the processes studied. In particular the near-surface oxidizing environment is different to the reducing environment that will be found in a geological disposal facility (GDF) for radioactive waste after closure. This means that uncertainty remains as to how directly relevant the results are to a GDF environment;
- There will be differences in the host rock mineralogy, chemistry and physical properties when compared to actual GDF environments;
- The geochemical modelling comparison exercise showed that the modelling codes had limited predictive success.

Relevance - What we have learnt

- Research at El Berrocal has provided information relevant to the safety case of a GDF for radioactive waste in a granitic host rock. The low temperature hydrothermal processes that have occurred at the site and subsequent chemical weathering are considered to be analogous to some of the geochemical processes that are expected in a GDF for high-level radioactive waste (HLW);
- The mineralisation in the uranium-quartz vein, including the sulphides, was deposited by low temperature hydrothermal circulation fluid associated with a phase of extensional brittle fracturing with the minerals being sourced from the granite. Following a phase of tectonisation further uranium mineralisation was deposited at lower temperatures (35 to 100°C);
- The accessory minerals and clay minerals play an important role in retaining heavy elements released during granite alteration and from the uranium-quartz mineralisation with uranium precipitated as U(IV) in phosphate minerals or retained by calcite;
- Comparison of calculated UO_2 dissolution fluxes for a normal uraninite, the primary uranium source at El Berrocal, with predictions from models for spent fuel dissolution show that the fundamental behaviour of the UO_2 is consistent;
- Uranium concentrations in groundwater at El Berrocal ranges from $4x10^{-9}$ to $8x10^{-6}$ M, dominated by carbonate complexes in the shallow oxic waters which are transformed to tricarbonate species in the deeper higher pH waters with U(IV) hydroxides dominating in reduced groundwater zones at depth;
- Colloid sampling of groundwater found populations between 108 and 1012 particles/litre, relatively low for ground waters. The colloids appear to sorb only a small proportion of the radionuclides present in the rock-water system.

Further reading

ENRESA; 1996; *El Berrocal Project – Characterization and validation of natural radionuclide migration processes under real conditions on the fissured granitic environment* – Topical Reports; *Volume I – Geological Studies* (596p); Volume II – *Hydrogeochemistry* (557p); Volume III - *Laboratory migration test and in situ tracer test* (224p); Volume IV – *Hydrogeological Modelling and Code Development* (680p); Enresa, Madrid.

RIVAS, P., HERNÁN, P., BRUNO, J., CARRERA, J., GÓMEZ, P., GUIMERÀ, J., MARÍN, C., AND PÉREZ DEL VILLAR, L.; 1997; *El Berrocal Project – Characterization and validation of natural radionuclide migration processes under real conditions on the fissured granitic environment – Final Report*; **EUR 17478**; European Commission Luxembourg Office for Official Publications of the European Communities; ISBN 92-827-9673-6; 522p.

RIVAS, P., HERNÁN, P., ASTUDILLO, J., BRUNO, J., CARRERA, J., DE LA CRUZ, B., GUIMERÀ, J., GÓMEZ, P., IVANOVICH, M., MARÍN, C., MILLER, W., AND PÉREZ DEL VILLAR, L.; 1998; *El Berrocal Project - Summary Report;* **EUR 17830**; European Commission Luxembourg Office for Official Publications of the European Communities; ISBN 92-828-2147-1; 70p.

SMELLIE, J. *Analogue evidence from uranium orebodies*, Report to Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2009.

Needle's Eye, Scotland: uranium mobilisation and migration

Overview

The multi-barrier system of a geological disposal facility (GDF) is designed to ensure long-term containment of radioactive waste. Were degradation in the functioning of a component of the barrier to occur, the design of the multi-barrier system could instead rely on very slow movement of radionuclides in the near- and far-field into the rock without adversely affecting the surface environment. The Needle's Eye study investigated some of the processes that influence the mobilisation, transport and retardation of uranium from a small uranium vein into organic rich sediments.

Radionuclide migration in a GDF

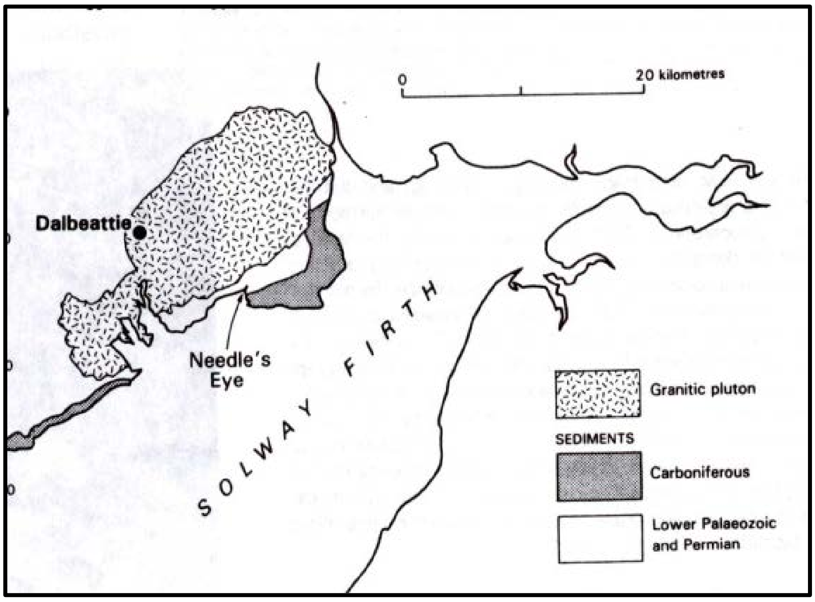
Over a long period of time the engineered barriers of a GDF will degrade and, eventually, the waste will be exposed to the groundwater. Some radionuclides will dissolve in very slow moving groundwater but their transport away from a GDF will be retarded by interactions with the rock and any corrosion products from the engineered barriers. Dilution of the radionuclides in the groundwater will also occur. Radionuclide mobility is threfore a key consideration in a safety case assessment for a GDF for radioactive waste.

The Needle's Eye Natural Analogue

The Criffel Granodiorite forms high, rounded heather-clad hills that rise above the flatter terrain comprising Silurian metasedimentary rocks, near Needle's Eye. ©A.E Milodowski, 2015

Geological setting

The Needle's Eye natural analogue site is located on the northern shore of the Solway Firth at Southwick, near Dalbeattie, in south-west Scotland. It takes its name from a natural rock arch known as Needle's Eye that was formed by coastal erosion of the cliff. The present day topography is controlled by a major SW-NE-trending fault, juxtaposing Carboniferous Limestone against the Silurian metasedimentary rocks, and is defined by the ancient post-glacial sea-cliff. The base of the cliff is fringed by a wave-cut platform and raised beach upon which post-glacial estuarine sediments and present day anoxic organic-rich peat bog and saltmarsh sediments have been deposited. These extend some 10 m towards the flood plain of marine silty sediments covered in salt resistant vegetation.

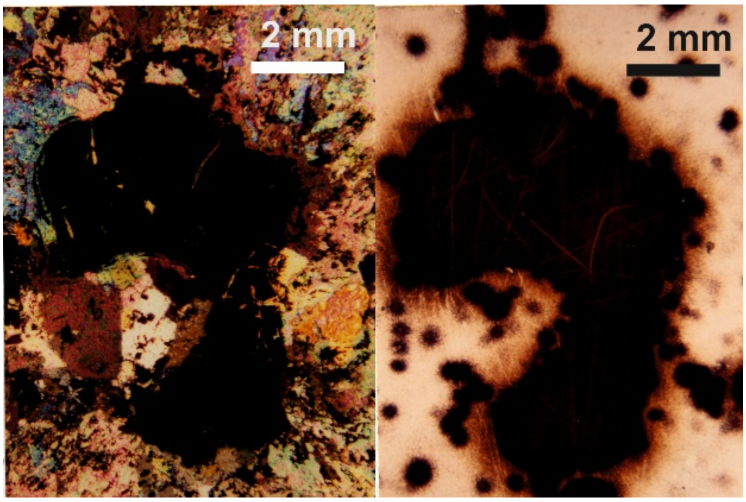


Geological map and location of the Needle's Eye natural analogue site © British Geological Survey

Mineralisation

The area contains a suite of metal-rich veins comprising mainly of ferroan dolomite and calcite with complex assemblages of hematite, chalcopyrite, pyrite, digenite, galena, cobalt-nickel-arsenides and sulphides and rare clausthalite and bismuth minerals. Uraninite (UO_2, variety pitchblende), secondary uranophane (Ca-U-silicate) and brittle hydrocarbon (bitumen) occur as coatings or enclosed within dolomite in the veins. The veins are hosted in hornfelsed Silurian metasedimentary strata within the contact aureole at the southern margin of the Caledonian Criffel Granodiorite. The veins radiate away from the granitic pluton, the largest of which reaches the shoreline. Pitchblende from one of the veins has been dated at 185±20 million years (Miller and Taylor, 1966).

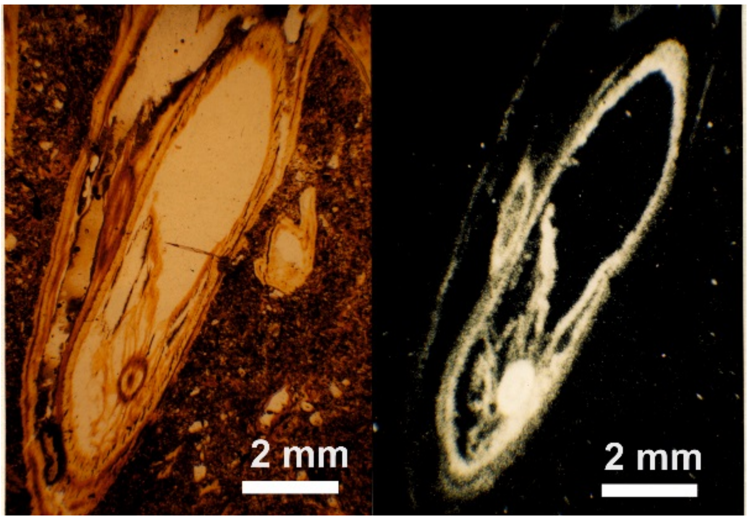
Calcite-dolomite vein breccia containing pitchblende and sulphide mineralisation is being leached by groundwater percolating through the cliffs at Needle's Eye. ©British Geological Survey.



LEFT: Transmitted light photomicrograph of thin section showing opaque uraninite (pitchblende) in a dolomite and calcite groundmass. RIGHT: Fission track print showing intense radioactivity from uranium distribution. ©British Geological Survey.

Ancient cliff line with saltmarsh at the base of the cliffs, Needle's Eye

Uranium leached from the vein mineralisation in the cliffs is accumulating in the organic-rich peat bog and salt marsh sediments at the base of the cliffs. ©A.E Milodowski, 2015.



LEFT: transmitted-light photomicrograph of thin section of peat showing plant root fabric. RIGHT: Autoradiograph of the same area showing that uranium is concentrated within the lignified tissue of the root. ©British Geological Survey

Uncertainties and limitations

- The study is limited to a near-surface / surface environment for uranium and thorium nuclide migration processes, in a temperate maritime climate. The redox conditions are oxidising in the fractured granodiorite cliff and reducing in some sections of the Merse sediments. The near-surface system at Needle's Eye does not make it a good analogue for a GDF near-field environment;
- Information from the study cannot be applied directly to a safety case because of gross differences between the Needle's Eye and a GDF environment in terms of chemistry and the mineralogical and physical characteristics of the materials. However it can be used to inform biosphere uptake and behaviour.

Relevance - What we have learnt

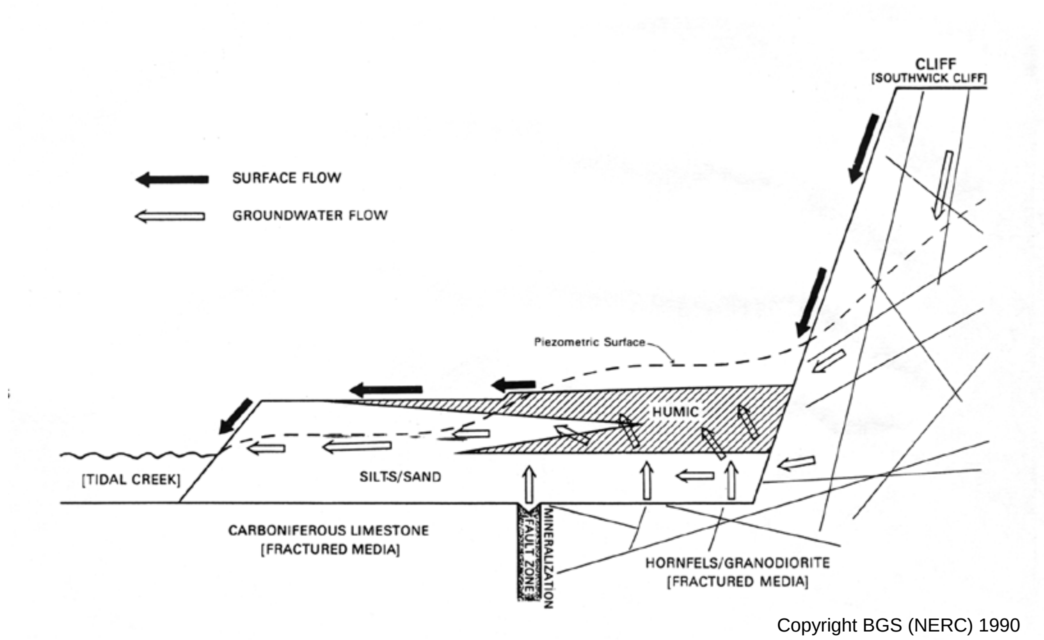
Meteoric groundwater percolating through fractured Silurian metasediments in the cliffs has mobilised uranium from the veins. The study showed that pitchblende has undergone dissolution by two processes:

- The first process involved slow leaching over a long time period, probably by reducing waters, resulting in the preferential dissolution of ^{234}U relative to ^{238}U;
- The second process involves rapid contemporary dissolution by oxidising waters;
- In contrast to uranium, dissolution and transport of thorium was negligible.

Some of the mobilised uranium has been re-deposited as stable oxidised (U(VI)) uranium minerals near the veins. However, mass balance calculations show that about 80-90% of the uranium has been transported by the shallow groundwater and has been redeposited in the anoxic soils in the peat bog at the base of the cliff, where it has been fixed by sorption onto organic (humic) material and iron oxyhydroxide minerals in the soil;

- Part of this uranium accumulation in the estuarine and peat bog sediments arises from groundwater discharging from the bedrock at the base of the sediments; and part of the uranium accumulation occurs at the surface of the peat from surface water flowing over the bog;
- Plants have also taken up significant uranium;

- Uranium is also concentrated by bacteria associated with the degradation of bituminous hydrocarbons in the weathering vein mineralisation. The site is easily accessible and has been well characterised, with quantitative hydraulic conductivity data for the different sediment types, and some data have been acquired for U sorption onto silty and organic-rich sediments;
- The site is relevant for understanding the processes of near-surface migration of U and its decay-series nuclides in shallow groundwater systems, and its fixation in organic-rich soils and sediments. Needle’s Eye is a good example of a geosphere-biosphere interface system involving peat;
- The analogue has proved valuable for testing geochemical speciation models and chemical transport research codes and are also relevant to biosphere studies;
- The time-scale of the analogue covers the period from the end of the last Ice Age to the present day, i.e. the past 12,000 years or so.
- The analogue demonstrates that solid humic organic materials in a GDF environment could act to retard uranium migration.



Schematic cross-section of the Needle’s Eye natural analogue site

Further reading

BASHAM, I.R., MILODOWSKI, A.E., HYSLOP, E.K. AND PEARCE, J.M. 1989. The location of uranium in source rocks and sites of secondary deposition at the Needle’s Eye natural analogue site, Dumfries and Galloway. *British Geological Survey Technical Report*, **WE/89/56**; also as *HMIP REPORT*, **DOE/HMIP/RW/89.091**

CRAWFORD, M.B. AND HOOKER, P.J. 1994. The geochemical behaviour of uranium in groundwaters from the Merse sediments at the Needle's Eye natural analogue site, southwest Scotland. *British Geological Survey Technical Report*, **WE/92/33**; also as *HMIP REPORT*, **DOE/HMIP/RR/94/008**.

FALCK, W.E. AND HOOKER, P.J. 1992. Uranium solubility and solubility controls in selected Needle's Eye groundwaters. *British Geological Survey Technical Report*, **WE/90/30**.

HIGGO, J.J.W., FALCK, W.E. AND HOOKER, P.J. 1989. Sorption studies of uranium in sediment-groundwater systems from the natural analogue sites of Needle’s Eye and Broubster. *British Geological Survey Technical Report*, **WE/89/40**.

HOOKER, P.J. 1991. The geology hydrogeology and geochemistry of the Needle's Eye natural analogue site. *t, Commission of the European Communities Nuclear Science and Technology Report*, **EUR 13434**, CEC, Luxembourg.

LEDOUX, E., JAMET, PH., HOOKER, P.J. AND ESCALIER DES ORRES, P. 1991. Hydrogeochemical modelling of the Needle's Eye, natural analogue (Scotland). In Source, Transport and Deposition of Metals, PAGEL, M. AND LEROY. J.L. (EDITORS). *Proceedings of the 25th Anniversary Meeting of the Society for Geology Applied to Mineral Deposits, Nancy, 30 August-3 September 1991*. Balkema, Rotterdam, pp. 65-68.

MILLER, J.M. AND TAYLOR, K. 1966. Uranium mineralisation near Dalbeattie, Kirkudbrightshire. *Bulletin of the Geological Survey of Great Britain*, **25**, 1-18.

MILODOWSKI, A.E., WEST, J.M., PEARCE, J.M., HYSLOP, E.K., BASHAM, I.R. AND HOOKER, P.J. 1990. Uranium mineralized micro-organisms associated with uraniferous hydrocarbons in southwest Scotland. *Natur*e, **347**, 465-467.

MACKENZIE, A.B., WHITTON, A.M., SHIMMIELD, T.M., JEMIELITA, R.A., SCOTT, R.D. AND HOOKER, P.J. 1991. Natural decay series radionuclide studies at the Needle's Eye natural analogue site, II,1989-91. *DOE Report* **DOE/HMIP/RR/91/044**; also *British Geological Survey Technical Report*, **WE/91/37**.

MACKENZIE, A.B., SCOTT, R.D., HOUSTON, C.M. AND HOOKER, P.J. 1991. Natural decay series radionuclide studies at the Needle's Eye natural analogue site. *Commission of the European Communities Nuclear Science and Technology Report*, **EUR 13126**, CEC, Luxembourg.

ROBERTS, P.D, BALL, T.K., HOOKER, P.J. AND MILODOWSKI, A.E 1989. A uranium geochemical study at the natural analogue site of Needle's Eye, SW Scotland. In: *The Scientific Basis for Nuclea*r Waste Management, Proceedings of the XII International Material Research Symposium, 10-13 Oct. 1988, Berlin. Materials Research Society Symposium Proceedings. **Vol.127**, 933-940.

SCOTT, R.D. MACKENZIE, A.B., BEN-SHABAN, Y.A., HOOKER, P.J. AND HOUSTON, C.M. 1991. Uranium transport and retardation at the Needle's Eye natural analogue site, south west Scotland. In Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere. Proceedings of the 'Migration '89' International Conference, Monterey, CA, USA, Nov. 6-10 1989. *Radiochimica Acta*, **52/53**, 357-365.

SMELLIE, J. *Analogue evidence from uranium orebodies*, Report to Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2009.

Broubster, Scotland: uranium mobilisation and migration

Overview

The multi-barrier system of a geological disposal facility (GDF) is designed to ensure long-term containment of radioactive waste. Were degradation in the functioning of a component of the barrier to occur, the design of the multi-barrier system could instead rely on very slow movement of radionuclides in the near- and far-field into the rock without adversely affecting the surface environment. The Broubster study investigated some of the processes that influence the mobilisation, transport and retardation of uranium from a small uranium vein into organic rich peat bog sediments.

Radionuclide migration in a GDF

- Over a long period of time, the engineered barriers of a GDF will degrade and, eventually, the waste will be exposed to the groundwater and will begin to degrade. Some radionuclides will dissolve in very slow moving groundwater, but their transport away from a GDF will be retarded by interactions with the rock and any corrosion products from the engineered barriers. Dilution of the radionuclides in the groundwater will also occur.
- The safety of a GDF is demonstrated using a safety case, which shows it complies with regulatory targets associated with radionuclide releases in the environment. So understanding and evaluating radionuclide migration and retardation is an important part of a safety case.

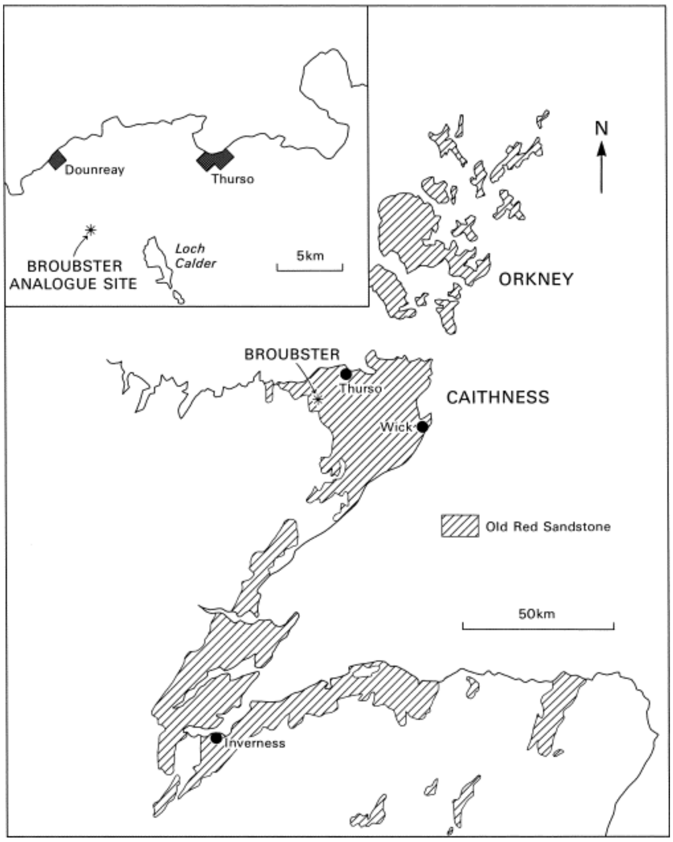
The Broubster Natural Analogue

Geological setting

The Broubster natural analogue site is located about 6 km southeast of the Dounreay nuclear site in north Caithness, Scotland. The detailed geology, hydrogeology and geochemistry of the Broubster site are described in Ball and Milodowski (1989) and Milodowski et al. (1989). The site consists of low-relief terrain, with marsh and peat-bog filling depressions and brown earth soils on higher ground, developed on a veneer of glaciogenic boulder clay deposited on gently northward-dipping bedrock belonging to the Lower Caithness Flagstone Group (Lybster Subgroup) of the Middle Old Red Sandstone. These strata comprise cyclical sequences of non-marine mudstones, siltstones, sandstones and limestones that were deposited in a predominantly lacustrine environment (with occasional fluviatile incursions) in the Devonian Period about 400 million years ago (Mykura, 1993).

Mineralisation

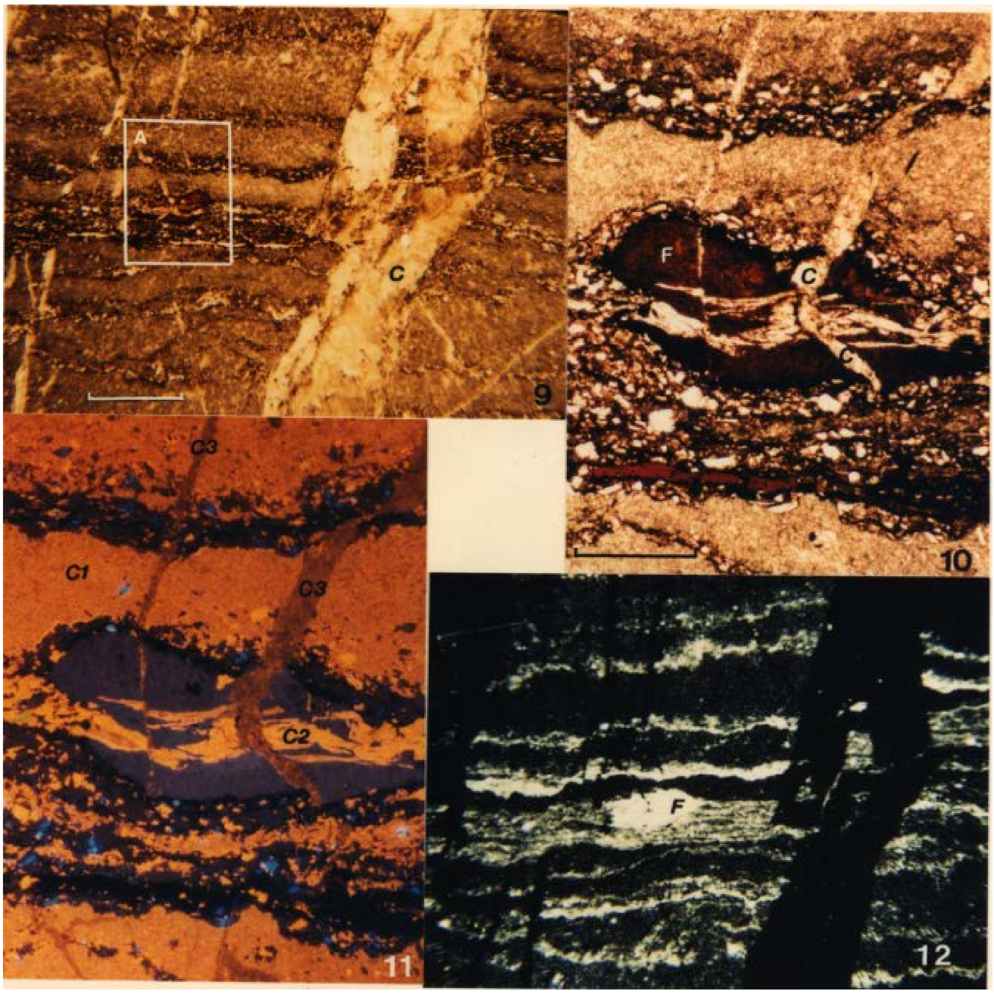
Radiometric and geochemical investigations by the BGS in the late 1960s revealed uranium, zinc, lead and molybdenum mobilisation, transport and dispersion downslope from a source in the bedrock close to the surface in the higher ground on the west side of the site into the peat-bog overlying boulder clay to the east of the site. These metals are derived from a mineralised northeast-trending fault cutting a 0.4 m thick bed of bituminous limestone. The fault-bounded vein mineralisation comprises predominantly calcite and dolomite with minor pyrite, chalcopyrite, sphalerite, galena, barite and globules of sticky uraniferous bituminous hydrocarbon containing inclusions of uranium silicate.



Location of the Broubster natural analogue site. (from Milodowski et al., 1989. ©British Geological Survey)

Sampling undisturbed soils and sediments at the Broubster natural analogue site using Kubiena soil tins (from Milodowski et al., 1989. ©British Geological Survey).

Shallow oxidising groundwater percolates through fractures and the mineralised fault, leaching uranium and other metals, which have then been redeposited down-gradient in the organic-rich peat-bog sediments. The bituminous limestone is also strongly uraniferous, with over 100 ppm U, and probably also represents a significant source of uranium. The uranium in the limestone resides within detrital and authigenic apatite, dispersed authigenic brannerite-like U-Si-Ti oxide phases, monazite and xenotime, often associated with pyrite, and within organic-rich lamellae and replacive bituminous hydrocarbon globules. Phosphatic fossil fish fragments are also highly enriched in uranium as a result of diagenetic alteration



Photomicrographs of thin sections of limestone with corresponding fission track prints, showing the distribution of uranium within organic-rich laminae and fossil fish fragments (from Milodowski et al., 1989. ©British Geological Survey).

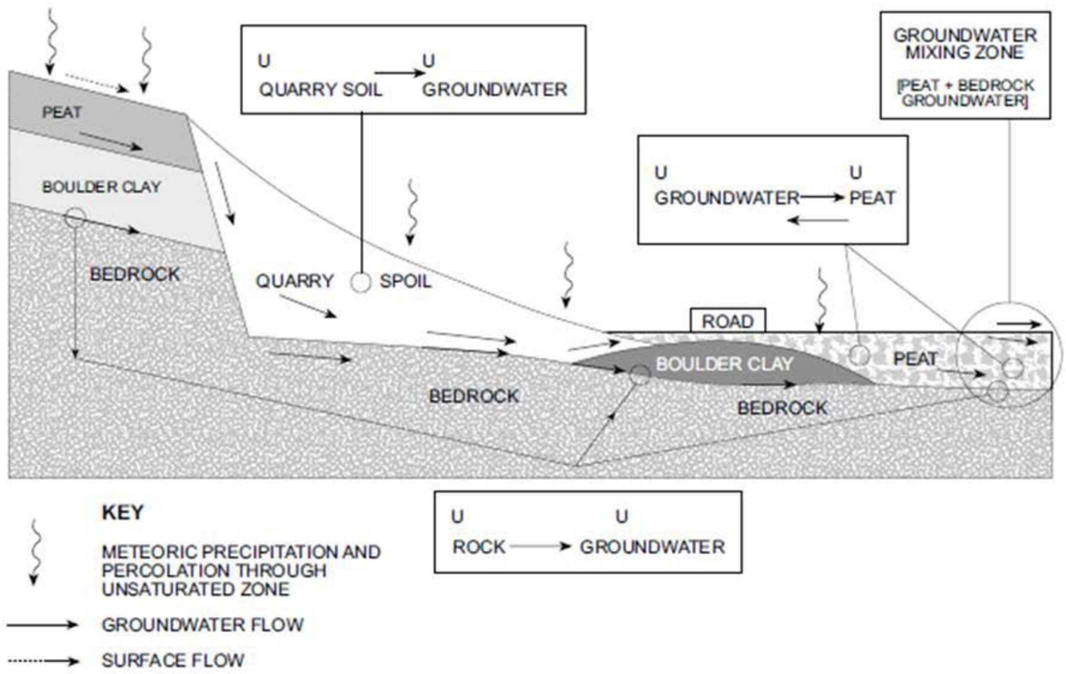
Uncertainties and limitations

- The study is limited to a near-surface / surface environment for uranium nuclide migration processes, in a temperate maritime climate. The near-surface system at Broubster is relatively oxidising and does not reflect the reducing conditions that will be found in a GDF near-field environment after closure;
- Information from the study cannot be applied directly to a safety case because of gross differences between Broubster and a GDF environment in terms of chemistry and the mineralogical and physical characteristics of the materials, however, it can be used to inform biosphere uptake and behaviour;
- There are some uncertainties associated with the past flow rates and compositions of the groundwater, particularly in regard to groundwater discharging from the fault zone;

- The site has been chemically disturbed by changes in land use during the 1970's. Liming to improve grazing on the land on the west of the site resulted in changes in pH and remobilisation of uranium and other elements. Consequently, the geochemistry of sediments and water sampled during the analogue investigations (between 1986 and 1991) may not totally reflect the lower pH values that probably prevailed originally during the accumulation of the bulk of the uranium anomaly in the peat.

Relevance - What we have learnt

Meteoric groundwater percolating through uranium-bearing fault mineralisation in Devonian limestone has mobilised uranium from the fault into an adjacent peat bog downstream.



Schematic illustrating groundwater movement, and uranium mobilisation, transport and accumulation across the Broubster natural analogue site (from Ball and Milodowski, 1989 ©British Geological Survey)

The study showed that the uranium mobilisation and redeposition has involved the following processes:

- Weathering and groundwater leaching has mobilised uranium and other metals from the fault mineralisation and limestone host rock;
- Uranium has migrated via groundwater transport and dispersion over a distance of more than 100 m and has been re-concentrated downstream in anoxic organic-rich peat-bog sediments, reaching concentrations up to 0.1 weight % U in parts of the bog;
- The bulk of the uranium has been transported as soluble U(VI) fulvic acid complexes;
- The uranium has been fixed in the peat by interaction with carboxylic acid functional groups on humic substances;
- The secondary dispersion pattern closely followed the local drainage pattern of the site, with the uranium anomaly following a surface drainage channel flowing to the northeast;
- Radium was also observed to be preferentially concentrated within manganese oxyhydroxide horizons ("wad") within the brown soils developed over the fault and weathered limestone;

- Radiocarbon dating has shown that the base of the peat is over 4,000 years old.
- The site is easily accessible and has been well characterised, with quantitative hydraulic conductivity data for the different sediment types;
- The site is relevant for understanding the processes of near-surface migration of uranium (and its decay-series nuclides) in shallow groundwater systems, and its uptake and fixation in organic-rich soils and sediments. Broubster is a good example of a geosphere-biosphere interface system involving peat;
- The study indicates that fulvic acid colloids play a key role in the aqueous transport of uranium at this site;
- The analogue has proved valuable for testing uranium speciation models and chemical transport research codes;
- The time-scale of the analogue covers the Holocene period for approximately the past 5,000 years.
- The analogue demonstrates that solid humic organic materials in a GDF environment could act to retard uranium migration.

Further reading

BALL, T.K. AND MILODOWSKI, A.E. 1989. The geological, geochemical, topographical and hydrogeological characteristics of the Broubster natural analogue site, Caithness. *British Geological Survey, Technical Report,* **WE/89/37**.

BOWIE. S.H.U., OSTLE, D. AND GALLAGHER, M.J. 1970. Uranium reconnaissance in northern Scotland. Transactions of the *Institution of Mining and Metallurgy,* **B79**, 180-182.

GALLAGHER, M.J., MICHIE U.MCL., SMITH R.T. AND HAYNES L. 1971. New evidence of uranium and other mineralisation in Scotland. *Transactions of the Institution of Mining and Metallurgy,* **80**, 150-173.

HIGGO, J.J.W., FALCK, W.E. AND HOOKER, P.J. 1989. Sorption studies of uranium in sediment-groundwater systems from the natural analogue sites of Needle's Eye and Broubster. *British Geological Survey, Technical Report,* **WE/89/40**.

LONGWORTH G., IVANOVICH M. AND WILKINS, M.A. 1989. Uranium series disequilibrium studies at the Broubster analogue site. *AEA Technology Report,* **AERE R 13609**.

MILODOWSKI, A.E., BASHAM, I.R., HYSLOP, E.K. AND PEARCE, J.M. 1989. The uranium source-term mineralogy and geochemistry at the Broubster natural analogue site, Caithness. *British Geological Survey, Technical Report,* **WE/89/50**.

MYKURA, W. 1983. Old Red Sandstone. In: *Geology of Scotland. 2nd edition*. GY Craig (Editor) Chapter 8, 205-251. Scottish Academic Press, Edinburgh.

READ, D. AND HOOKER, P.J. 1992. Using data from natural environments to improve models of uranium speciation in groundwaters. *Journal of Geochemical Exploration*, **46**, 63-81.

READ, D., BENNETT, D.G., HOOKER, P.J., IVANOVICH, M., LONGWORTH, G., MILODOWSKI, A.E. AND NOY, D.J. 1993. The migration of uranium into peat-rich soils at Broubster, Caithness, Scotland, *U.K. Journal of Contaminant Hydrology*, **13**, 291-308.

SMELLIE, J. *Analogue evidence from uranium orebodies*, Report to Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2009.

SMITH, B., STUART, M.E., VICKERS, B.P. AND PEACHEY, D. 1990. The characterisation of organics from the natural analogue site at Broubster, Caithness, Scotland. *British Geological Survey Technical Report*, **WE/89/33**.

South Terras Mine: uranium mobilisation and migration

Overview

The multi-barrier system of a geological disposal facility (GDF) is designed to ensure long-term containment of radioactive waste. Were degradation in the functioning of a component of the barrier to occur, the design of the multi-barrier system could instead rely on very slow movement of radionuclides in the near- and far-field into the rock without adversely affecting the surface environment. This study was carried out to investigate some of the geochemical controls on the mobilisation of uranium from uranium-bearing mine spoil and its fixation in surrounding clay-rich soils and alluvial sediments.

Radionuclide migration in a GDF

- Over a long period of time, the engineered barriers of a GDF will degrade and, eventually, the waste will be exposed to the groundwater and will begin to degrade. Some radionuclides will dissolve in very slow moving groundwater, but their transport away from a GDF will be retarded by interactions with the rock and any corrosion products from the engineered barriers. Dilution of the radionuclides in the groundwater will also occur.
- The safety of a GDF is demonstrated using a safety case, which shows it complies with regulatory targets associated with radionuclide releases in the environment. So understanding and evaluating radionuclide migration and retardation is an important part of a safety case.

The South Terras Analogue

Geological setting

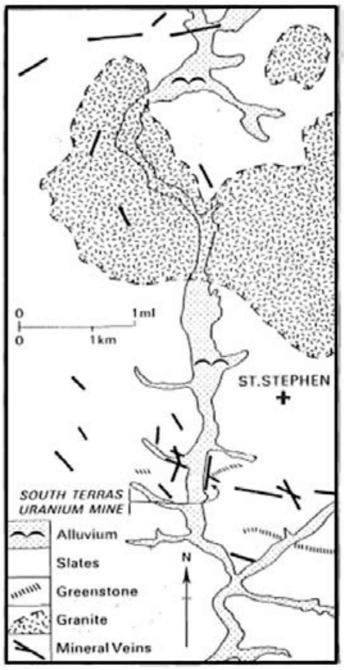
The disused South Terras Mine is located near the village of St. Stephen in Cornwall, England. It was formerly known as Union Mine and was initially worked for ochre (iron ore) until uranium was discovered in 1873. The uranium lode was up to 1.2 m wide and was one of a number of similar veins that occur to the south of the St. Austell granite. The mine was the largest and most important producer of uranium in the region before closing in 1929. The uranium was produced mainly for use in glass making (i.e. to produce green glass), and a total of a total of 736 tons of ore was produced up to 1910, including 286 tons from the dumps (Dines, 1956). Mining waste containing significant uranium was dumped directly onto the surface of clay-rich alluvial sediments and soils originally covering the sites. Some of this dumped material has subsequently been reworked and disturbed: both for further extraction of uranium ore, but also by the local farmer for use as aggregate in local trackways.

Mineralisation

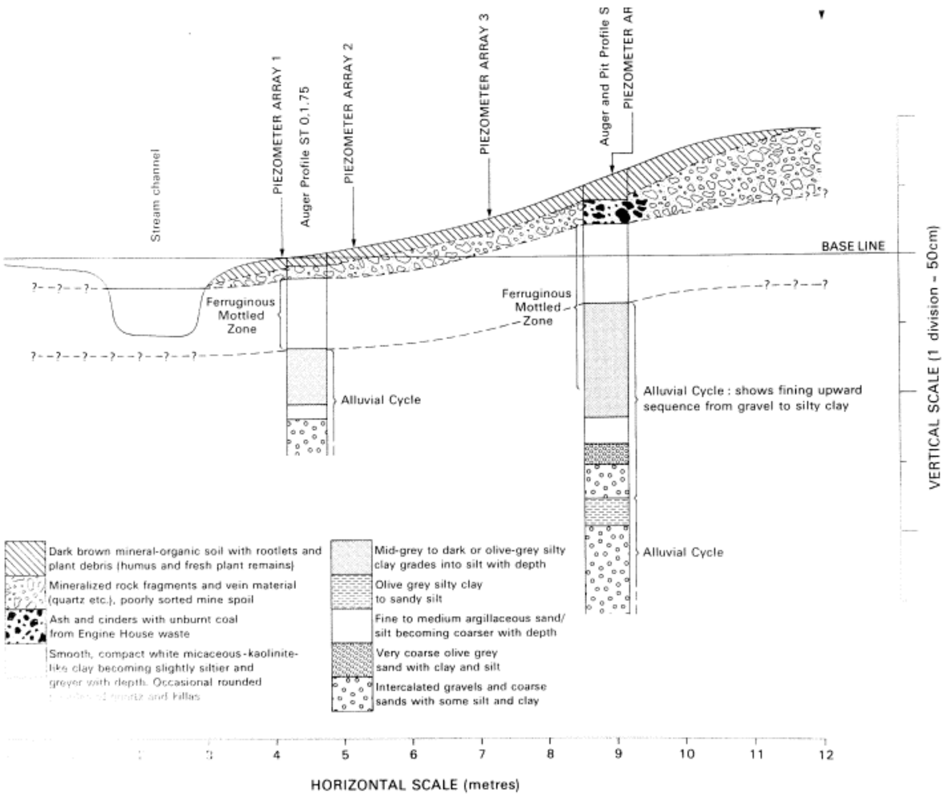
The primary uranium phase excavated was pitchblende, but secondary minerals such as zippeite, torbernite and autunite were also common. Although the main lode is no longer accessible, all of these minerals are still present in the dumps now seen on the surface.

Uranium migration

The British Geological Survey studied the migration of uranium-series radionuclides from the spoil heaps. This was the focus of The South Terras analogue study that was carried out between 1986 and 1990. Rain water percolation through the waste dumps leaches uranium from the spoil heap minerals, and the leachate is infiltrating into the underlying and adjacent alluvial deposits. Near-surface groundwater is transporting the mobilised uranium through these clay-rich sediments towards a small tributary stream of the nearby River Fal.



Geological map of the South Terras site
(from Dines, 1956. ©British Geological Survey)



Cross-section through the South Terras analogue site showing the details of the alluvial sediment sequence
(from Hooker et al., 1989. © British Geological Survey)

Uncertainties and limitations

- The 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;

- The study was limited to uranium and some of the U-series nuclides. Other trace elements occur in the spoil heap minerals (e.g. Co, Ni, Cu, As), but these were not analysed in sufficient detail to provide any generic value as an analytical database for geochemical modelling of contaminant migration in alluvial sediments;
- The study is limited to a near-surface / surface environment for uranium and thorium nuclide migration processes. The mine dumps are unsaturated, although the groundwater table is near-surface in the underlying alluvial sediments. Uranium sorption can be highly dependent on the presence of organic coatings on mineral surfaces and small changes in pH and Eh, and there is some uncertainty in the measurement of *in situ* redox conditions. The redox conditions are likely to be oxidising in the mine waste, which does not make it a good analogue for studying uranium a post-closure GDF near-field environment. Although, the diffusion of uranium into the underlying alluvial sediments, where conditions may be anoxic are potentially more relevant;
- There are gross differences between the mine waste materials and a GDF environment in terms of chemistry and the mineralogical and physical characteristics of the materials.

Relevance - What we have learnt

- The pitchblende and secondary uranium minerals in the mine wastes are providing the source of uranium and thorium in the underlying alluvial sediments. The uranium leached by rainwater percolating through the mine dumps is being transported into the underlying clay-rich alluvial sediments;
- Solubility modelling of the groundwaters showed that the groundwaters in the alluvial sediments beneath the mine dumps were under-saturated with respect to pitchblende and secondary uranium minerals, which implies that sorption was the principal mechanism for retardation and fixation of uranium;
- Sorption had minimised the contribution of uranium-series elements to the uranium in the stream, where it was difficult to distinguish any spoil-derived uranium from any background uranium. At a depth of about 1.2 m within this sediment section, the groundwater uranium concentration decreased from 214 ppb U near the heaps to a much lower value of 0.77 ppb U nearest the stream. The $^{230}Th/^{234}U$ activity ratios for the sediments were less than unity, explained by the addition of U from solution (Hooker et al., 1989). Read et al. (1991) modelled the sorption behaviour of U using surface-complexation theory to describe the interaction of aqueous U-species (mainly uranylphosphate anions) with the sediment minerals. They provided a more fundamental description of the uranium sorption process than a simple K_d approach.
- The site is relevant for understanding the processes of near-surface migration of uranium and thorium in shallow groundwater systems, and its fixation in near-surface clay-rich soils and sediments. Therefore, it is perhaps most relevant for near-surface low-level radioactive waste repositories associated with similar sedimentary environments (e.g. Drigg);
- The analogue has proved valuable for testing research codes for modelling geochemical speciation and transport of uranium and thorium, in particular using the CHEMTARD code (Read et al., 1991);
- The time-scale of the analogue is short, covering 0-100 years, with approximately 80 years of uranium leaching from the mine dumps and migration into the shallow alluvial sediments.

Further reading

DINES, H.G. 1956. The metalliferous mining region of South-West England. *Memoirs of the Geological Survey of Great Britain*, **2**, 541-543.

HOOKER, P.J., IVANOVICH, M., MILODOWSKI, A.E., BALL, T.K., DAWES, A. AND READ, D. 1989. Uranium migration at the South Terras mine, Cornwall. *British Geological Survey Technical Rep*ort, **WE/89/13** and *UK DOE Report*. **DOE/RW/89.068**.

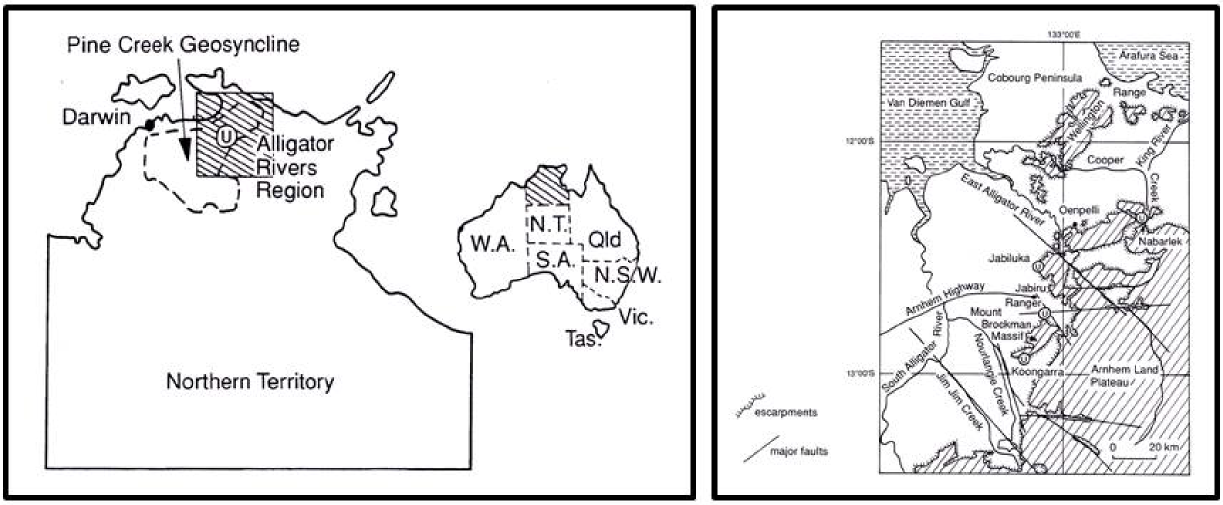
READ, D., HOOKER, P.J., IVANOVICH, M. AND MILODOWSKI, A.E. 1991. A natural analogue study of an abandoned uranium mine in Cornwall, England. *Radiochimica Acta*, **52/53**, 349-356.

SMELLIE, J. *Analogue evidence from uranium orebodies*, Report to Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2009.

Alligator River, Australia: uranium mobilisation and migration

Overview

The Koongarra uranium ore body is one of four large uranium deposits which are located in the Alligator Rivers Region in the Northern Territory of Australia. The uranium deposit was discovered in the early 1970s by airborne geophysical measurements and over forty boreholes were drilled to characterise the 1,600 million year old orebody. The deposit has never been exploited because of restrictions imposed by the Australian government and the area has subsequently been granted protected status in 2013. Consequently the area is relatively undisturbed. The site was studied to further understanding of the factors controlling uranium mobilisation and retardation.

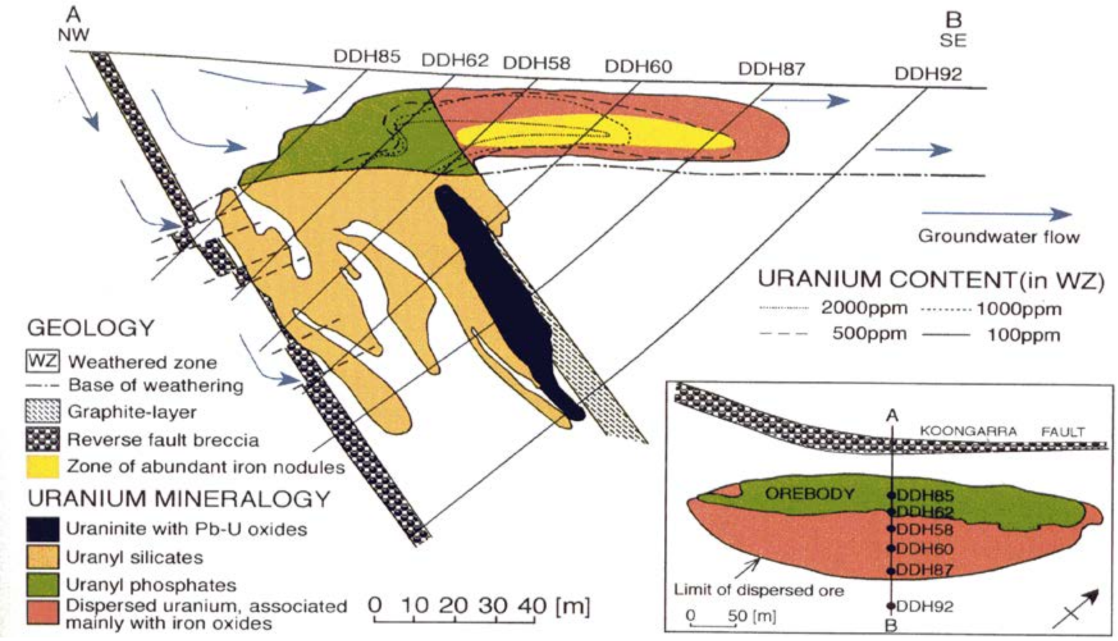


The Koongarra uranium ore body lies in the Alligator Rivers region of northern Australia

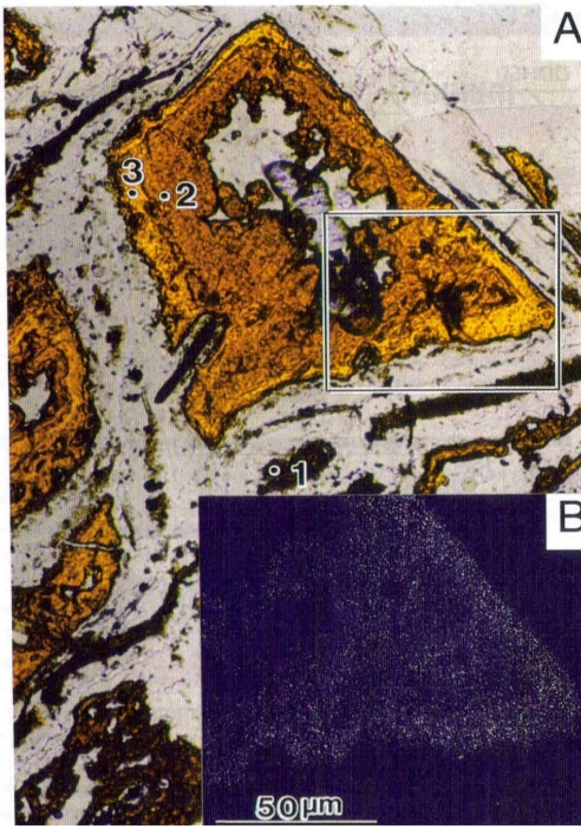
The analogue

The site has been investigated as an analogue for the geological disposal of radioactive wastes since 1981. The investigations have comprised detailed studies of the geology, geomorphology, mineralogy, hydrology, geochemistry and climate. With regard to the behaviour of radionuclides in the host rock, the main emphasis was placed on the characterisation of uranium in the different mineral phases, the identification of mobilisation and retardation processes and the application of geochemical and radionuclide transport models.

The main ore body goes down to some 100 m deep and the top 25-30 m has experienced near-surface weathering for the last 1-6 million years. For most of the year, the shallow part of the ore body is above the water table, but in the rainy season, the area experiences intense floods. This has led to mobilisation and transport of the uranium released from the ore by weathering, forming a downstream plume of dispersed uranium extending about 100 m in a south-easterly direction.



Cross section of the Koongarra orebody showing the rock types, uranium distribution, zone of abundant iron nodules and uranium content in sediment samples (Duerden et a. 1992).



Iron nodules: some of the uranium trapping phases at the Koongarra ore body (Sato et al., 1997).

A: 1 – amorphous iron oxide, 2 – mixture of amorphous iron oxide and geothite (crystalline iron oxide), 3 – geothite. Light grey material is the clay. Kaolinite. The highest uranium content was found in the geothite, the lowest in the clay.

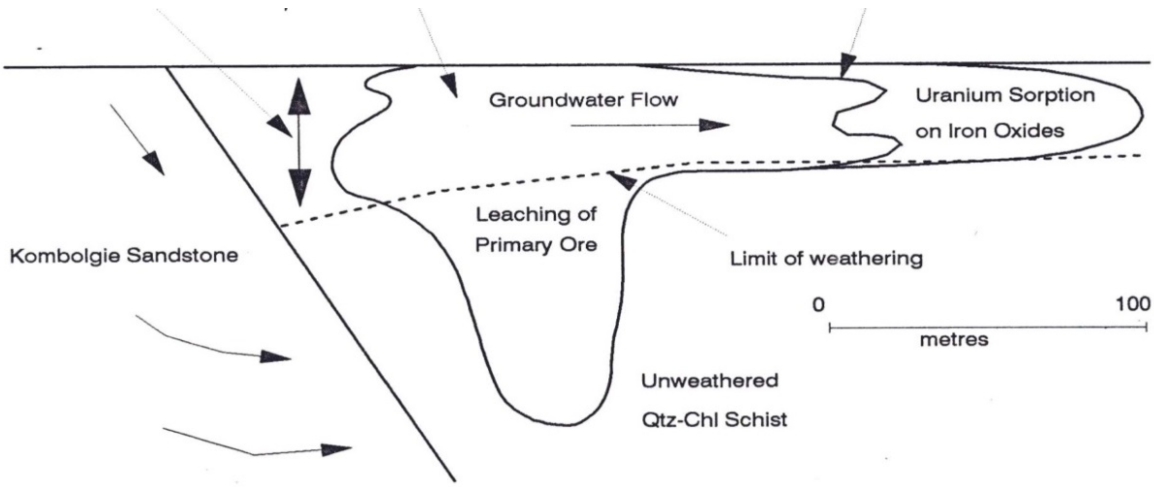
B: Scanning Electron Microscope analysis of the box in A shows the uranium distribution (white dots).

Uncertainties and limitations

- A significant amount of effort went into understanding why uranium was released from the primary ore body and then trapped in the near-surface dispersion plume. However, the site and these mechanisms are of little relevance to deep GDF designs;
- The uranium was released from the ore body by surface groundwaters which are unlike those found at GDF depths (high dissolved oxygen, carbonate and organics) and the groundwater transport rates are much higher than at depth;
- Further, the fixation of uranium in the downstream dispersion plume is by mechanisms which have little in common with a deep GDF. Much of the uranium is trapped on rust-like iron oxides which will be rare in a deep GDF environment;
- It was later proposed that the near-surface nature of the site is analogous to a shallow, low-level waste GDF and that the retardation processes in the dispersion plume are similar to those around such a shallow GDF. However, this does not hold up to detailed investigation because the uranium minerals in the primary ore body are more similar to the material found in spent fuel, which would not be disposed of near surface;
- Further, the intense tropical weathering at this site (to produce the rust-like iron phases) means the uranium uptake mechanisms are of little relevance to a UK GDF site;

Relevance – what we have learnt

- Even though this is a much more active environment (both physically and chemically) than that of a GDF host rock, the fact that uranium has only migrated about 100 m in 1-6 million years increases confidence in the barrier properties of GDF host rocks;
- Despite the weak analogy between the site and a GDF for radioactive waste, much valuable academic work on uranium immobilisation in the near-surface environment was carried out within the Alligator Rivers Analogue Project;
- Of some relevance to waste disposal was the extensive testing of radionuclide transport codes – 13 different transport models of different complexity were examined, including:
    - 1D and 2D models;
    - Retardation processes: sorption, precipitation; phase transition and α-recoil effects. These considered processes ranging from an advection dispersion model (with K_d-concept for radionuclide retardation) to a 1D transport model coupled with a groundwater geochemistry model;
- The modelling turned out to be more difficult than expected due to the complexity of the site including changes to the groundwater flow paths with time and general uncertainties about past hydrogeological conditions, etc. Nevertheless, different models were able to describe different aspects of the system, in particular the present day uranium distribution across the site.



Conceptual transport model of the Koongarra uranium deposit (Duerden et al., 1992).

Further reading

DUERDEN, P. LEVER, D.A., SVERJENSKY, D.A .AND TOWNLEY, L.R. 1992. *Alligator Rivers Analogue Project: Final Report, Volume 1 Summary of findings*. OECD/NEA, Paris, France. The project is reported in its entirety in volumes 2-16 of the same OECD/NEA series.

LOWSON, R.T AND MCINTYRE, M.G. 2013. (234)U/(238)U signatures associated with uranium ore bodies: part 1 Ranger 3. *Journal of Environmental Radioactivity*, **118**, 150-156.

LOWSON, R.T. 2013. 234)U/(238)U signatures associated with uranium ore bodies: part 3 Koongarra. *Journal of Environmental Radioactivity*, **118**, 163-168.

SATO, T., MURAKAMI, T., YANASE, N., ISOBE, H., PAYNE, T.E. AND AIREY, P.L. 1997 Iron nodules scavenging uranium from groundwater. *Environmental Science and Technology*, **31**, 2854-285.

SMELLIE, J. *Analogue evidence from uranium orebodies*, Report to Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2009.

URANIUM INFORMATION CENTRE 2001. *Geology of Uranium Deposits, Nuclear Issues Briefing Paper # 34, November 2001*, Uranium Information Centre, Melbourne, Australia (www.uic.com.au/nip34.htm)

Loch Lomond, Scotland: a study of halogen migration

Overview

The multi-barrier system of a geological disposal facility (GDF) is designed to ensure long-term containment of radioactive waste. If the engineered barrier system were to fail the safety of the system could instead rely on very slow movement of radionuclides in the host rock without adversely affecting the surface environment.

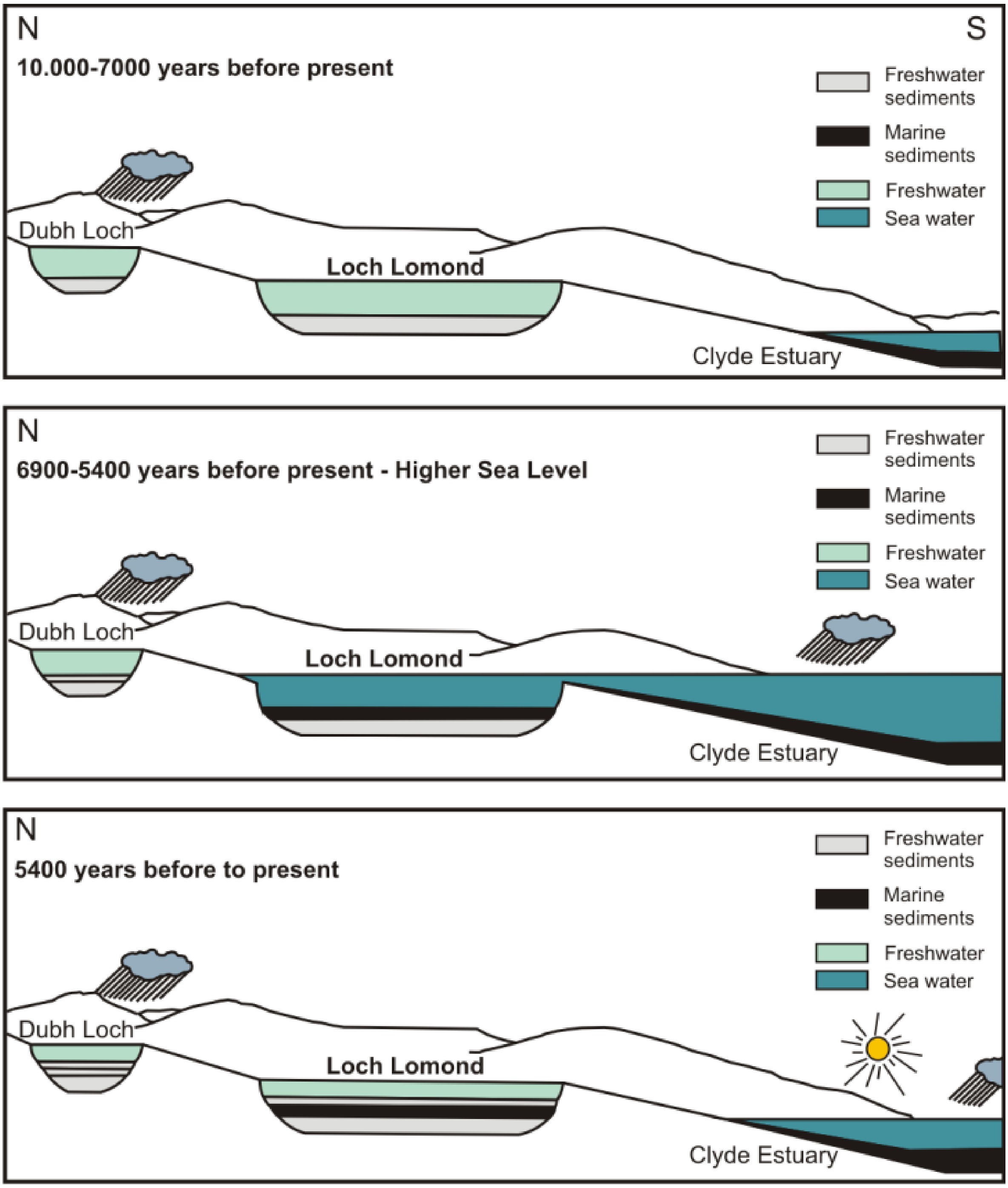
Over a long period of time, the engineered barriers of a GDF will degrade and, eventually, the waste will be exposed to the groundwater and will begin to degrade. Some radionuclides will dissolve in very slow moving groundwater, but their transport away from a GDF will be retarded by interactions with the rock and any degradation products from the engineered barriers. Dilution of the radionuclides in the groundwater will also occur. So understanding and evaluating radionuclide migration and retardation is an important part of a safety case for a GDF. The anionic radionuclides ^{36}Cl and ^{129}I present as fission and activation products in spent fuel and low- and intermediate-level radioactive waste (L/ILW) are of potential concern because of their relatively long half-lives (e.g. 302,000 years for ^{36}Cl) and their high mobility, and will potentially be released relatively early post-closure of a GDF (Grambow, 2008).

Loch Lomond Natural Analogue

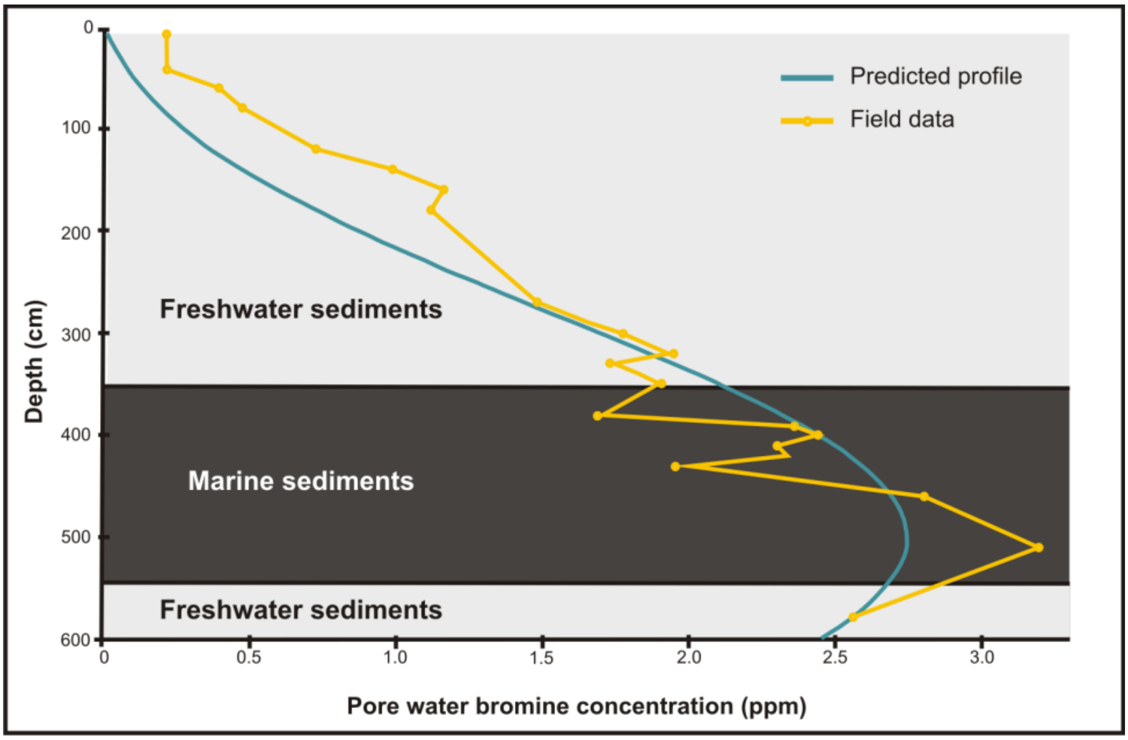
Loch Lomond in the southern Highlands of Scotland is presently freshwater and landlocked. However the loch (lake) had an incursion of seawater during a marine (Flandrian) transgression from the Firth of Clyde which occurred from 6900 to 5400 years ago. This event is clearly recorded in the loch sediments by a one metre band of marine deposits, which has subsequently been covered with further freshwater sediments giving a geochemical variation.

- All the sediments are clay-rich (up to 80% in some horizons). The marine sediments can be identified as they have higher concentrations of chloride, bromide and iodide (halogens), as found in seawaters. However, these halogens have migrated into the adjacent freshwater sediments and porewaters recording a history of diffusive transport;
- Fixation of iodine, bromine, uranium and radium-226 in the marine layer was associated with organic carbon, and porewater concentrations of bromine and iodine also decrease with distance from the marine sediments;
- The study demonstrated that the loch sediments have provided an effective sink for bromine and iodine for thousands of years with only slow releases into the porewaters and slow diffusion towards the sediment surface and the lake waters above;
- The measured bromine concentration profile is very similar to model diffusion profile calculations based on simple diffusion, assuming an initial concentration of 60 ppm (with

reversible sorption and no advective transport) with a diffusivity coefficient of 10^{-11} m^2/s^{-1}. Experimental work showed that sorption of several radionuclides was irreversible.



Conceptual model of the evolution of Loch Lomond (based on McKinley, 1989).



Comparison of actual measured profile for bromine in the Loch Lomond sediments compared to the modelled diffusion profile.

Uncertainties and limitations

- Currently, information from Loch Lomond provides only very limited information for clay-rich environments or a bentonite buffer;
- Information from the study cannot be applied directly to a PA transport code because of gross differences between the Loch Lomond sediments and a GDF environment in terms of chemistry and the mineralogical and physical characteristics of the materials.

Relevance – What we have learnt

- The analogue provides good illustrative evidence for demonstrating the slow diffusive movement of radionuclides such as ^{36}Cl and ^{129}I through saturated low permeability clay barriers;
- It shows that simple diffusion may account for element migration in these environments, providing a diffusion coefficient for bromine;
- Many models of radionuclide migration assume that radionuclide sorption is instantaneous and reversible, but this analogue suggests that this assumption may be inaccurate and that the underlying kinetics of radionuclide migration in any clay environment may need further investigation.
- This study is useful when applied to diffusion-dominated clay GDF environments and also to transport within bentonite buffer material. Comparison of the analogue observations with numerical model predictions showed that the models can replicate the main features of the diffusion profile. This provides confidence that the models can adequately represent the main release, transport and retardation processes.

Further reading

GRAMBOW, B. 2008. Mobile fission and activation products in nuclear waste disposal. *Journal of Contaminant Hydrology*, **102**, 180-186.

HOOKER, P.J., MACKENZIE, A.B., SCOTT, R.D., RIDGWAY, I.G., MCKINLEY, I.G. AND WEST, J.M. 1985. A study of long term (103-104 y) elemental migration in saturated clays and sediments (Part III). *British Geological Survey Technical Report*, **FLPU 85-9**; *CEC Radioactive Waste Management Series*, **EUR 10788/2**, CEC, Luxembourg.

MACKENZIE, A.B., SCOTT, R.D., MCKINLEY, I.G. AND WEST, J.M. 1983. A study of long term (103-104 y) elemental migration in saturated clays and sediments. *British Geological Survey Technical Repor*t, FLPU 83-6.

MACKENZIE, A.B., SCOTT, R.D., RIDGWAY, I.G., MCKINLEY, I.G. AND WEST, J.M. 1984. A study of long term (103-104 y) elemental migration in saturated clays and sediments (Part II). *British Geological Survey Technical Report,* **FLPU 84-11**. *CEC Radioactive Waste Management Series,* **EUR 10788/1**, CEC, Luxembourg.

MACKENZIE, A.B., SHIMMIELD, T.M., SCOTT, R.D. AND HOUSTON, C. M. 1989. Development of an analytical method for the analysis of I and Br concentrations in lacustrine sediment interstitial water. *British Geological Survey Technical Report,* **WE/89/65**.

MCKINLEY, I.G. 1989. Applying natural analogues in predictive performance assessment. *Nagra Internal Repor*t, Nagra, Wettingen, Switzerland.

MACKENZIE, A.B., SHIMMIELD, T.M., SCOTT, R.D., DAVIDSOM, C. M. AND HOOKER, P. J. 1990. Chloride, bromide and iodide distributions in Loch Lomond sediment interstitial water. *British Geological Survey Technical Report*, **WE/90/2**.

FALCK, W.E. and Hooker, P. J. 1990. Quantitative interpretation of Cl, Br and I porewater concentration profiles in lake sediments of Loch Lomond, Scotland. *British Geological Survey Technical Report,* **WE/90/3**.

4.2 COLLOID MIGRATION IN NATURAL SYSTEMS

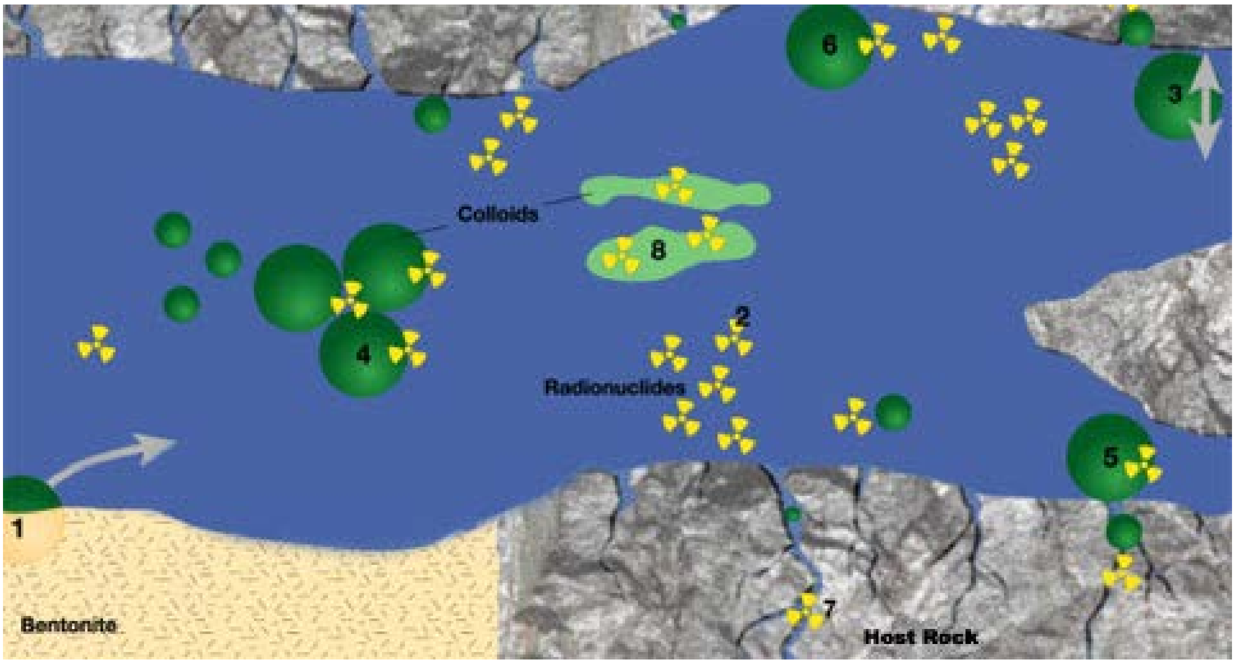
Poços de Caldas, Morro do Ferro, Brazil – colloid transport

Poços de Caldas, Morro do Ferro, Brazil – colloid transport

Overview

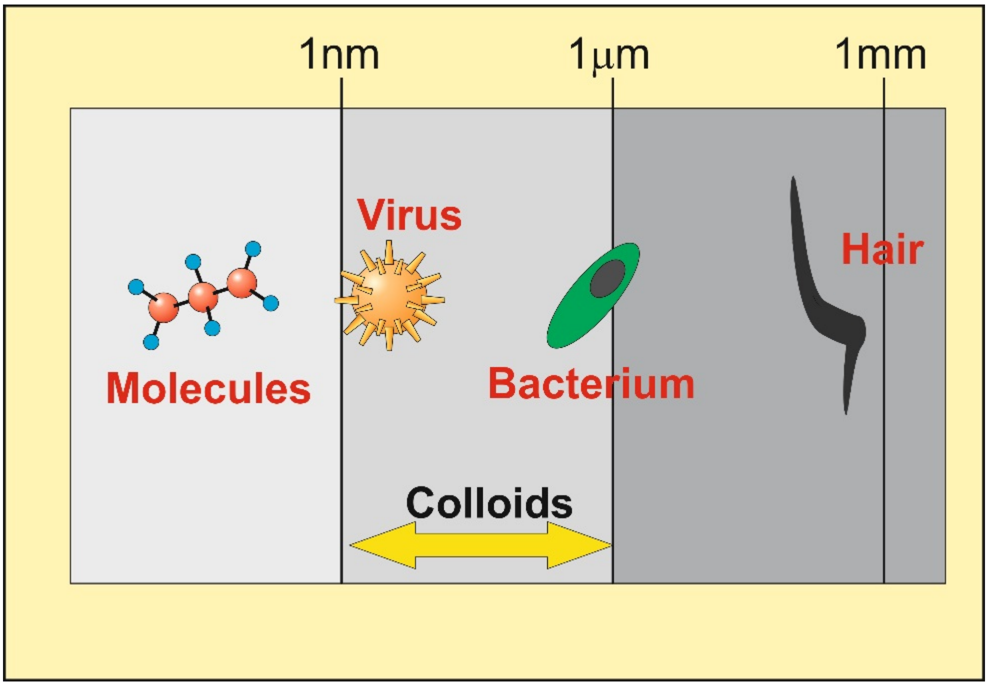
Why are colloids of such interest?

Models of radionuclide transport in the geosphere are generally based on the assumption that the radionuclides are transported only as dissolved species in the groundwater. This may be over-simplistic because of the fact that they neglect the potential effect of advective transport of radionuclides bound to colloids (or nano-particles). Colloids comprise material suspended in groundwater in the size range 1 µm to 1 nm (or roughly in the size range of viruses and bacteria).



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 (courtesy of Nagra). ***(1) Generation of GDF-derived colloids (in this case, from the bentonite barrier); (2) Dissolved radionuclides (from the waste) in ground water; (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; and (8) Sorption of radionuclides onto organic colloids or incorporation of radionuclides into organic colloids***.

Colloids can affect the transport of radionuclides in the groundwater in several ways (above), some of which (e.g. sorption on colloids) could increase transport speeds 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.

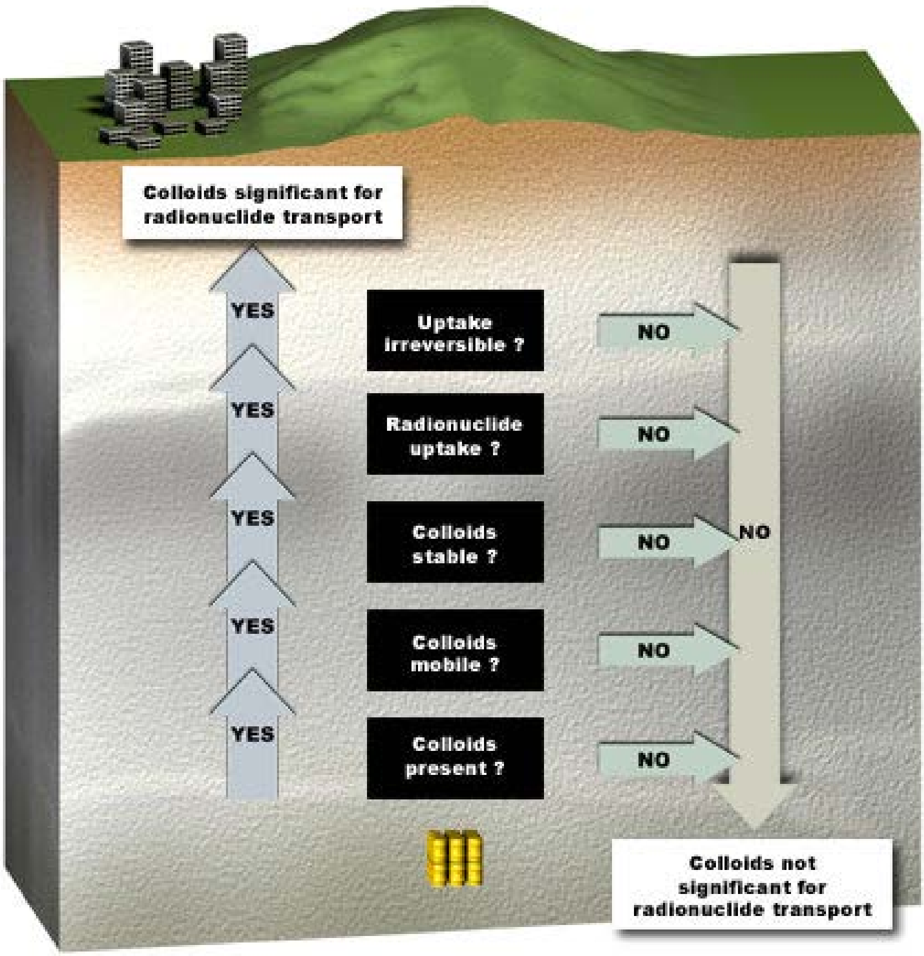


Comparison of the size of colloids with other particulate matter in groundwater

The Morro do Ferro natural analogue study

Morro do Ferro, Brazil (courtesy of Nagra).

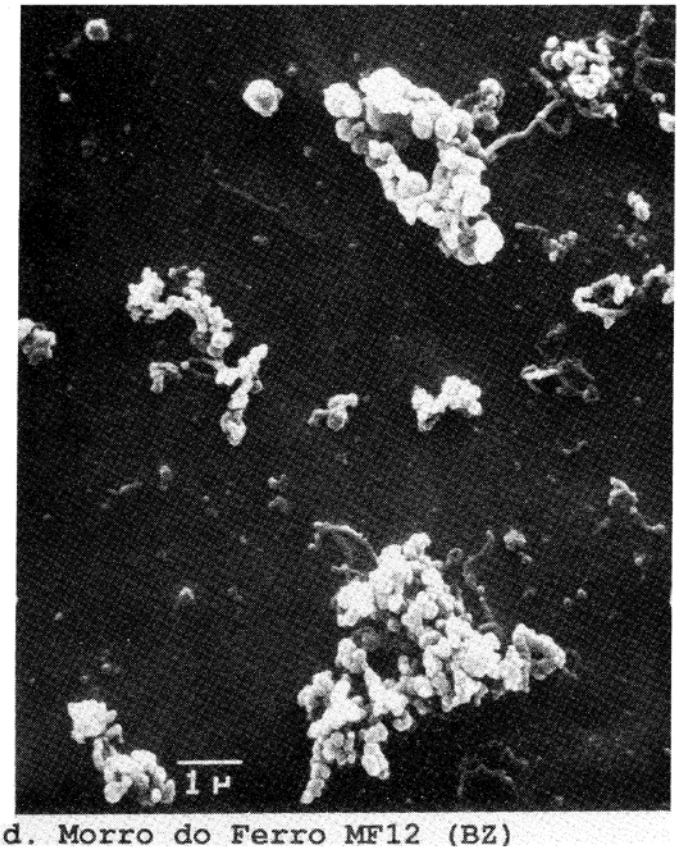
In an attempt to break this deadlock, one of the areas of focus in the Poços de Caldas NA project was the study of colloids. In particular, the site at Morro do Ferro (the 'Hill of Iron') was chosen for extensive study. Before work began, however, the task of defining the significance of colloid-associated radionuclide transport was broken down into a 'colloid ladder of significance'. Basically, before colloids could possibly lead to significant radionuclide migration from a deep GDF to the surface biosphere, a number of barriers would have to be overcome. If the chain of events could be broken at any one of these steps on the ladder, then colloid-associated radionuclide transport could be consigned to the 'insignificant mechanism' pile at the bottom of the ladder, in a system akin to the snakes and ladders game.



The colloid ladder of significance (from Chapman et al., 1993).

At Morro do Ferro, a near-surface ore body (containing large inventories of Th and REE - rare-earth elements) at the top of the hill provides a 'source term' for colloid-associated radionuclides. The topography means that the structure of the groundwater flow was easy to define and so samples could be collected at several points downhill, moving away from the ore body towards the groundwater release point into surface waters in the stream at the bottom of the hill.

Measurements clearly showed that colloids containing significant concentrations of Th and other safety-relevant elements were present in the vicinity of the ore body but that, at locations down-flow from this point, colloid signatures reflected the local rock, rather than the ore-influenced source water. Additionally, no colloids from the ore body were found in the lower boreholes nor in the stream at the base of the hill. Despite being observed in the groundwaters sampled in the upper boreholes, no clay colloids were observed in the lowest borehole. These data provide qualitative evidence that, despite the presence of colloid-associated radionuclides, the colloids do not act as a transport 'short-circuit'.



Photomicrograph of colloids from Morro do Ferro (magnification x15,000). From Meikeley et al. (1991).

Uncertainties and limitations

- The near-surface nature of the site means that direct relevance to a deep GGDF is difficult to show. For example, many of the colloids are organic, something which is unlikely in deep GDF groundwaters and the site shows significant seasonal variation in the groundwater levels;
- While colloids do not appear to transport radionuclides here (because of either of their low mobility or instability), no data are available on the precise mechanisms involved in the radionuclide immobility;
- A lack of speciation measurements for the radionuclides present also makes a mechanistic understanding of the radionuclide and colloid retardation difficult.

Relevance – what we have learnt

- Morro do Ferro is an unique site where, for the first time, researchers were able to follow colloid-associated REEs and radionuclides from the ore body point source along the entire flow system to the surface;
- In this GDF-analogous system, the data provide strong evidence that, despite the presence of safety-relevant elements such as Th associated with colloids, they do not appear to act as a transport short-circuit, bypassing the normal geosphere retardation mechanisms;
- Although a mechanistic understanding is missing, the data indicate the presence of rather large colloids and/or agglomerates of these large colloids, which are irregular/angular shaped. Both observations imply little transport of colloids in the groundwater system;

- The study also showed that the approach is fundamentally sound and that it only requires a more appropriate natural analogue site to provide quantitative data – and several potential sites exist in the UK.

Further reading

CHAPMAN, N.A., MCKINLEY, I.G., SHEA, M.E. AND SMELLIE, J.A.T. (EDITORS). 1993. *The Poços de Caldas project: natural analogues of processes in a radioactive waste repository*. Elsevier, Amsterdam, NL.

MCCARTHY, J. AND DEGUELDRE, C. 1991. Sampling and characterisation of colloids and particles in groundwater for studying their role in contaminant transport. In: VAN LEEUWEN, H.P. AND BUFFLE, J. (EDITORS) *Environmental Particles*. IUPAC Environmental Analytical and Physical Chemistry, Series II.

MIEKELEY, N., DE JESUS, H.C., DA SILVEIRA, C.L.P. AND DEGUELDRE, C. 1991. Poços de Caldas Report No. 9: Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *SKB Technical Report*, **TR 90-18**, SKB, Stockholm, Sweden.

SWANTON, S. BERRY, J.A. KELLY, M.J. AND ALEXANDER, W.R. 2010. Review of colloids in the geosphere and their treatment in performance assessment. *NDA Technical Report*, **2010-XY**, NDA, Moor Row, UK.

4.3 WHOLE SYSTEM PERFORMANCE

Oklo - a natural analogue for the long-term behaviour of a GDF

Cigar Lake, Canada – a natural analogue for an entire GDF?

Oklo - a natural analogue for the long-term behaviour of a GDF

Overview

Oklo: a unique uranium orebody

It is important to stress that no natural system represents an entire design of a geological disposal facility (GDF) for radioactive waste However at Oklo, by virtue of a series of 16 fossil natural reactors which achieved criticality (when the rate of neutron production and loss are equal).some 2,000 million years ago, the site provides an unique opportunity. Here it can be assessed whether the radioactive waste remaining after the reactors shut themselves down have remained in the vicinity of the reactor zone following nuclear fission and subsequently over geological timescales much greater than the expected lifespan of a deep GDF.

The Oklo natural reactors lie in southeast Gabon

The Oklo reactors were discovered in 1972 when an anomalous uranium isotope signature was detected in a French laboratory during routine analysis of miscellaneous uranium ore samples from several world localities. Subsequently this sample was traced to the Gabon and eventually the presence of natural fission reactors was confirmed.

Criticality in individual reactors lasted anything from 150,000 to 1 million years and temperatures ranged from 160-350°C during the reactions, meaning that the reactions involved in trapping the radionuclides in the rock have little to do with those expected in and around a GDF (no criticality in expected to occur in a GDF as temperatures to the order of100°C are anticipated) but the fission products are similar to those from a nuclear power station.

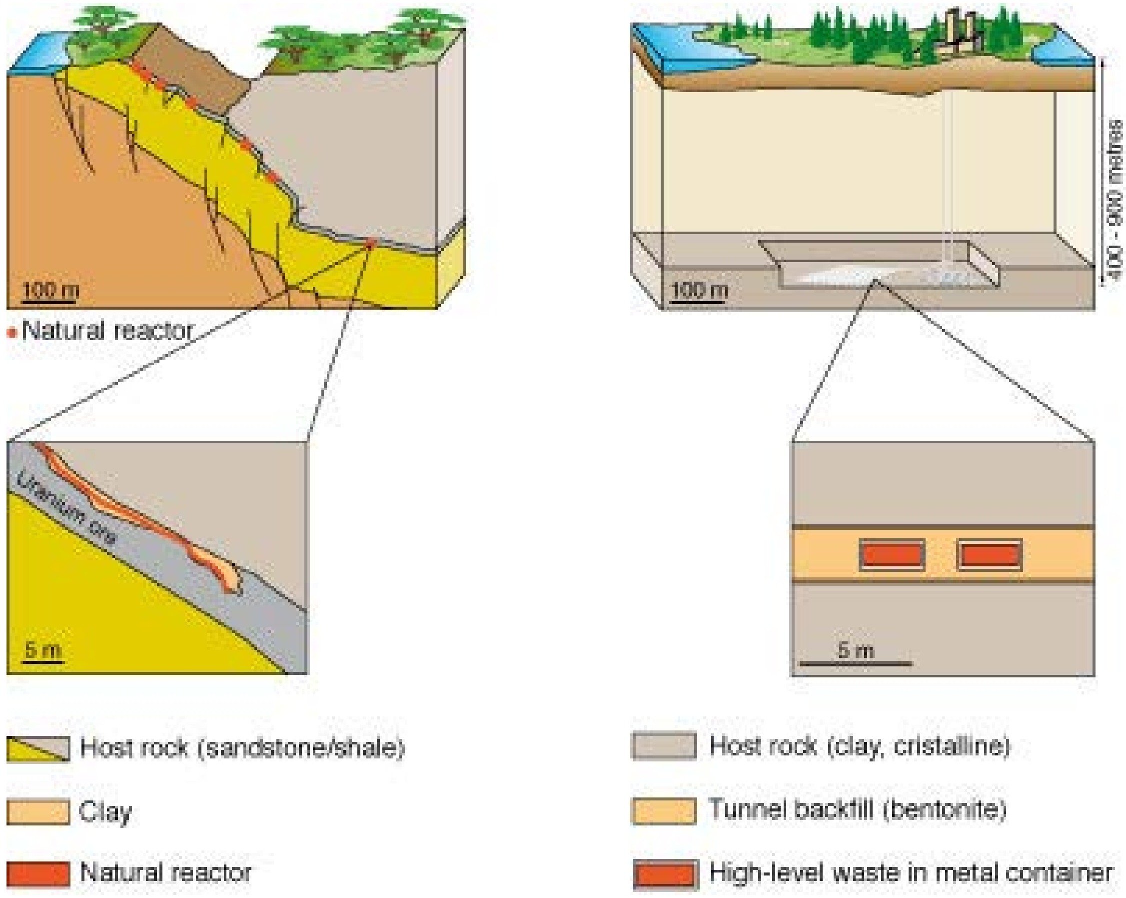
The site also has a complex geological history, with the area subsiding to several kilometres deep after the reactors closed down, only to be uplifted again to the near surface where they were discovered (at a few 10s of metres below the surface). Several of the reactors suffered significant fracturing several hundred million years ago, further complicating any interpretation of the uranium ore longevity and radionuclide retardation in the host rock.

A view of the open cast mine at Oklo (Francois Gauthier-Lafaye)

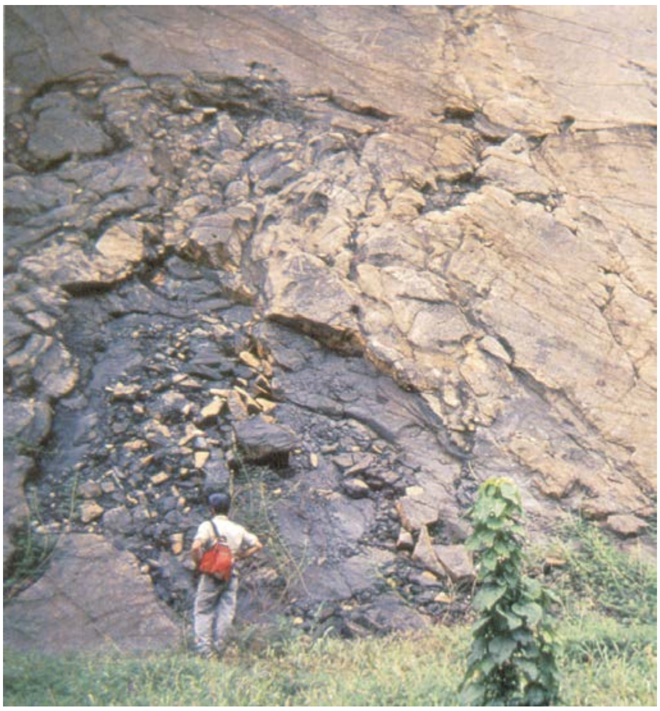
The analogue

Oklo would seem to be an ideal natural analogue for assessing the performance of a GDF for radioactive waste through geological time, a location where predictions about rates of movement of various radionuclides could be rigorously tested. Radionuclide migration can be traced from a well-defined source term (i.e. the reactor zone, which is a spent fuel analogy), out through the surrounding clay (bentonite buffer analogy) and into the far-field environs 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). However, 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 spent fuel, quantitative analysis of this system is extremely difficult because of the highly complex geochemical and hydrothermal history of the region. And the fact that the environment around the reactors must have changed numerous times in the 2,000 million years since criticality means that it is difficult to draw meaningful conclusions from the data.

With respect to radionuclide uptake on the clays surrounding the reactor zones, it is difficult to differentiate between high temperature (during criticality) and low temperature (ambient groundwater interaction) dispersion patterns. In general, radionuclide transportation and retardation of the waste products in the fossil reactor zones appears equivocal; the heavy actinide elements were retained, as would be expected, but it is unclear if the lack of any movement is due to entrapment in the uranium ore or because of the host rock. More mobile radionuclides either underwent local redistribution within the reactor zones or migrated completely out of the reactor zones by relative amounts roughly in accordance with modelling expectations. But not enough is known about the groundwater chemistry and temperature over 2,000 million years to make any quantitative statements possible.



Some commentators note the similarities between the Oklo site and a GDF design with the multiple engineered barrier system (EBS) and the host rock (Nagra).



Imprint of the core of a natural reactor on the pit wall at Oklo (Miller et al., 2000).

Current status – could we go back?

It is tempting to think that we could return to such an unique site and re-examine it with safety case aims in mind, but 15 of the 16 reactors have now been mined out, the last is protected (for the time being) by a concrete sarcophagus. As such, there is little value in returning to Oklo.

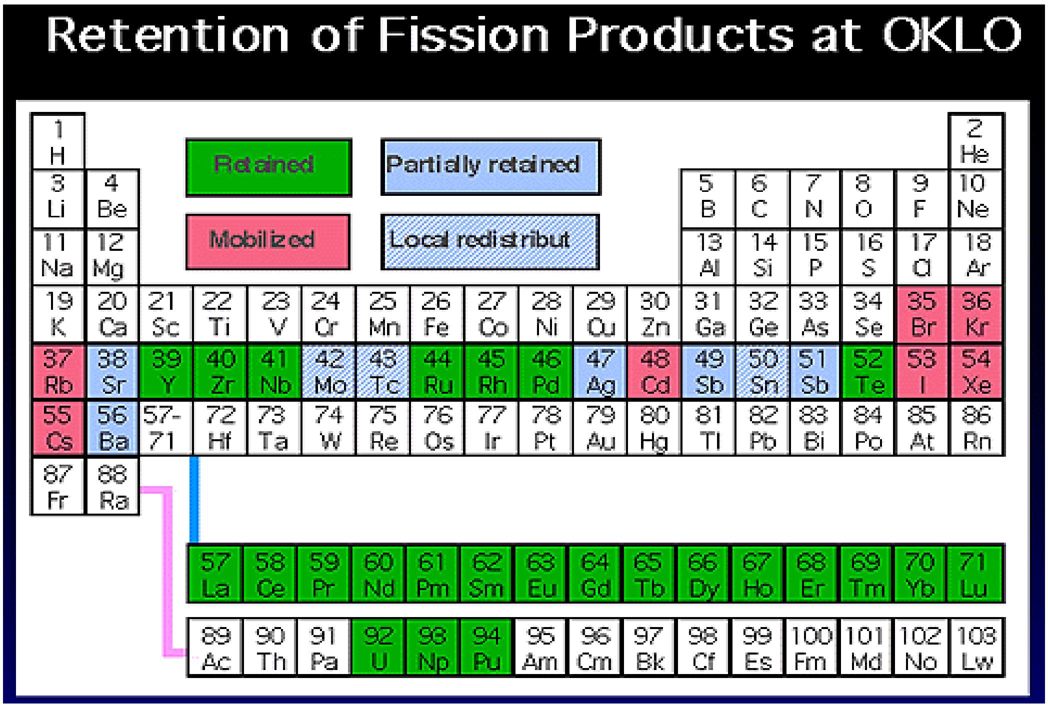
The concrete sarcophagus over the last surviving Oklo reactor zone (John Smellie, Conterra).

Uncertainties and limitations

- 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, it is simply not possible to estimate how the site groundwaters have changed over the 2,000 million years since reactor criticality and so little can be shown quantitatively about radionuclide retention at the site;
- In the early stages of the 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.
- A direct comparison of spent fuel and the reactor zone uranium ore was not possible because of important physico-chemical differences between the two types of uranium allied to a lack of information on the initial high temperature and later low temperature behaviour of the reactor zones;
- The Oklo analogy is often taken further than the science can support it. For example, in 1991, the British Nuclear Forum wrote:

"The Oklo reactors ran gently at the kilowatt-power level for millions of years. They never blew up. The radiation and waste from them did not deter surrounding life forms......";

Because the only life forms present on the earth at the time were early micro-bacteria, this is hardly surprising and has absolutely no relevance to a GDF safety case. It is also important to note that Oklo reactors could only work 2 billion years ago as the enrichment of Uranium-235 than was so much higher.



Many radionuclides were trapped in or around the reactors, but a lack of information on the boundary conditions means that no quantitative data have been produced for SA (John Smellie, Conterra)

Relevance – what we have learnt

Despite an incredibly long history of repeated, regional and local perturbations at the Oklo site, the 16 reactor zones were still present after some 2,000 million years, clearly showing that a multiple barrier EBS and protecting host rock can still guarantee the longevity and performance of a GDF.

Oklo demonstrates that man-made fission products from the nuclear fuel cycle can also occur naturally. As such this may be of use when communicating to non-technical audiences, emphasising the point that such isotopes are not "completely new, man-made hazards".

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."

Further reading

BRITISH NUCLEAR FORUM 1991. Mother earth's natural reactors. *Nuclear Forum, September 1991 Issue*, London, U.K.

CURTIN UNIVERSITY OF TECHNOLOGY web site: http://oklo.curtin.edu.au

Gauthier-Lafaye, F. Holliger, P.H. and Blanc, P-L. 1996. Natural fission reactors in the Franceville Basin, Gabon: A review of the conditions and results of a critical event in a geological system. *Geochimica et Cosmochimica Acta,* **60**, 23, 4831-4852.

Hickes, T.W. and T.D. Baldwin, 2014. The Likelihood of Criticality Synthesis Report. NDA RWM commissioned report RWMD/003/001.

SMELLIE, J.A.T. 1995. The natural analogue at Oklo, Gabon. *Radwaste Magazine*, **2**, No. 2, 18-27.

J. SMELLIE. *Analogue evidence for naturally occurring criticalities*, Report to United Kingdon Nirex Limited, 2005.

SMELLIE, J. *Analogue evidence from uranium orebodies*, Report to Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2009.

TROTIGNON, L., MICHAUD V., AND LOUVAT, D. 2000. Application of the Oklo natural analogue project to nuclear waste disposal model, testing and development, pp 401-407 In: LOUVAT, D., MICHAUD, V. AND VON MARAVIC, H. (EDITORS), *Proceedings of the 2nd. EC-CEA Oklo Phase II Workshop, May 20/21, 1999, Cadarache, France*. **EUR Report Series 19137 EN**, Luxemburg.

Cigar Lake, Canada – a natural analogue for an entire GDF?

Overview

A geological analogy of an entire geological disposal facility (GDF) for radioactive waste would provide extremely valuable long-term information for understanding its behaviour and performance into the far future.

An analogue for an entire GDF

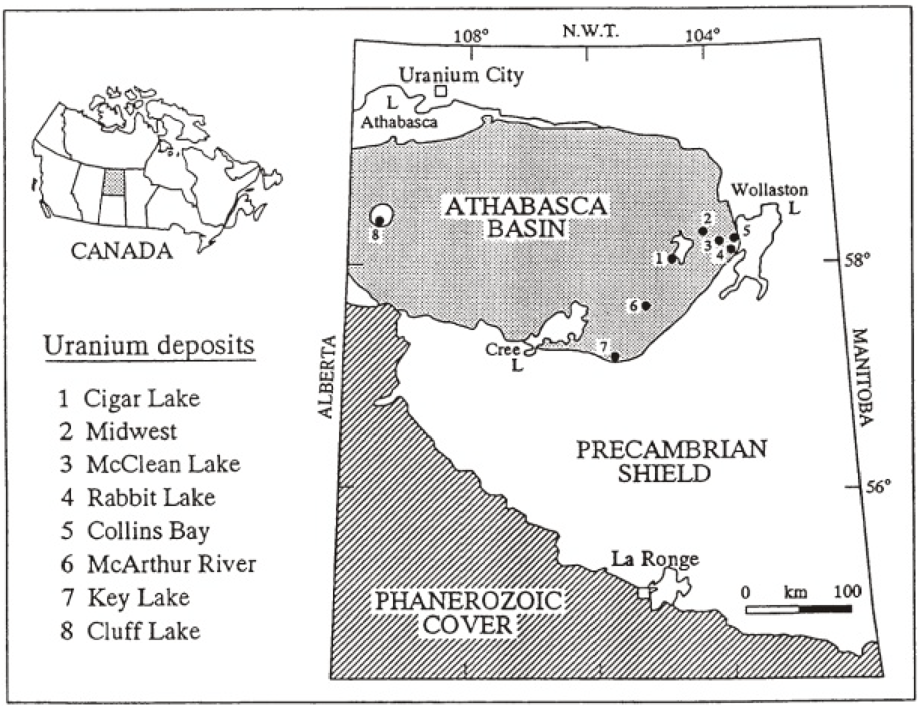
In early analogue studies, there was often the temptation to take the information and try to apply it to a complete GDF design. This was reflected to some extent in the approaches taken in the early studies of the Oklo and Poços de Caldas sites and even the Maqarin area more recently.

Generally, this approach has been of limited success because most analogue studies are focussed on particular processes or mechanisms, indeed often looking at just one specific aspect of a GDF system. Even in the larger 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 a particular GDF design.

However, perhaps one analogue study has come closer than most to being an analogy for an entire GDF, namely Cigar Lake in Canada.

The Cigar Lake uranium ore body

This uranium ore body is one of the largest in the world, with proven reserves of 87,000 tonnes of uranium (U). The ore is also unusually rich in uranium, with an average ore grade of 21% and a maximum of 60%. Rather surprisingly, although the ore body is only about 450 m below surface and located within a rather permeable sandstone, there is no reported radiological indication of its presence on the surface.



Cigar Lake is one of a number of significant uranium deposits in the Athabasca Basin, Canada (Cramer and Smellie, 1994).

The Cigar Lake 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, uranium mineralisation occurs at the base of the Athabasca Sandstone, where it unconformably overlies crystalline metamorphic basement rocks. The deposit is one of the richest uranium ore bodies in the world, yet this exhibits no traces of radioactivity at the surface.

Cigar Lake, Canada. At the surface, there are no traces of one of the richest uranium ore bodies in the world.

Natural analogue studies at Cigar Lake

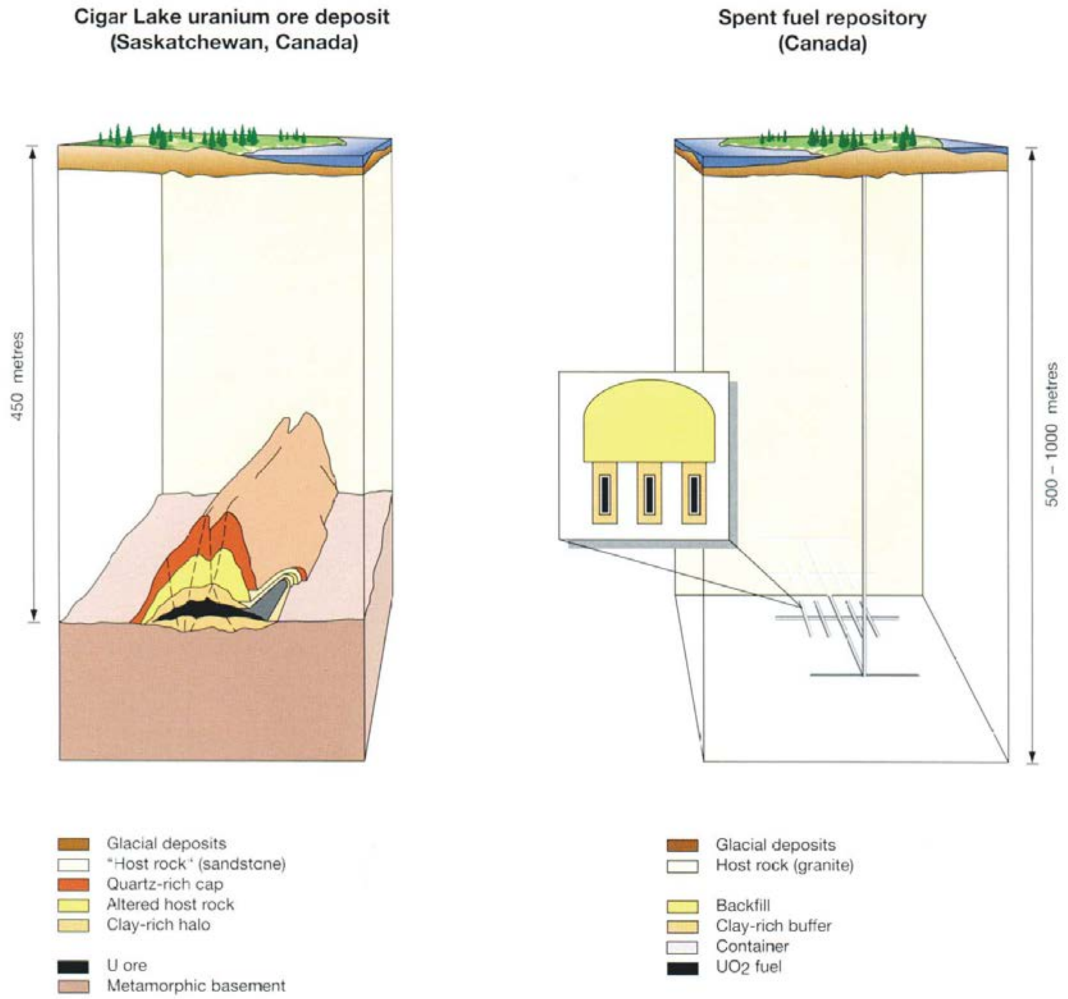
Natural analogue studies were initiated by Atomic Energy Canada Ltd. (AECL) in the early ‘80s, while preliminary ore exploration was ongoing. This work was related to their studies of CANDU (natural uranium) spent fuel disposal, as the ore body was considered a good analogue of this particular type of waste. Early studies focused on uranium mineralogy and were fairly qualitative. During this period, the presence of a change in chemical conditions (redox halo around the uranium ore and the isolating role of a surrounding altered zone with a high clay content (mainly illite) were identified. These allowed the analogue to be presented as representing aspects of the engineered barrier system (EBS) for many spent fuel disposal concepts along with the host rock.

In collaboration with Svensk Kärnbränslehantering AB (SKB), work became more quantitative during the late ‘80s and early ‘90s, examining the processes influencing the mobilisation, migration and transport of uranium from the ore and through the surrounding clay barrier.

The Cigar Lake site and many of the associated analogue applications are extensively reported in the literature and, in terms of geological disposal, the key characteristics of the site are:

- Qualitative/general evidence of the very long term (about 1,300 million years) chemical stability of an extremely rich ore body (containing high concentrations of U and a range of other safety relevant elements including Ni, Co, Mo and Pb);
- Highly effective containment of radionuclides under present conditions with no significant surface radiological signature of the ore, despite the relatively high permeability of the host sandstone formation;
- No evidence of criticality, but extensive radiolysis (molecular disruption by radiation) of water (radiolysis) was shown within this rich ore body, as would be expected in a GDF for high-level waste and spent fuel;

- The role of the clay-rich layer surrounding the uranium ore appears to be to protect the ore from degradation, despite the presence of microbes, dissolved organics and colloids in the ore pore-waters;
- For high-level waste (even more relevant for spent fuel), semi-quantitative confirmation of the effectiveness of UO_2 as a waste matrix and proposed secondary phases that were shown to form during waste leaching.



The basis of the analogy: comparison of the Cigar Lake ore body (left) with the multiple EBS for a GDF for HLW or SF (right) (from Miller et al., 2003).

Uncertainties and limitations

- The great age (1,300 million years) of the Cigar Lake ore body makes definition of boundary conditions for the greater part of its history difficult. This is an inherent limitation to natural analogues in general, which is acknowledged and accounted for .As such, the analogy with a GDF should not be overplayed;
- The analogy is much better for CANDU fuel (natural U, which has a relatively low burn-up) than light water reactor or high burn-up enriched-UO_2 fuels;
- Further studies would be constrained by the fact that mining has commenced and this will have already considerably perturbed the natural system (excavation by freezing/water-jet boring).

Relevance – what we have learnt

- It provides a good argument for the potential of disposal in stable host rocks. This stability allows the altered zone around the ore body to shield the uranium from the effects of relatively high water flow through the host sandstone – and for periods far beyond those required for the hazard from radioactive waste to decay to insignificance;
- Although the site is now disturbed, there is still the possibility of direct measurement of concentrations of spontaneous fission products (particularly plutonium) in the rich ore body. This may be of use when communicating to non-technical audiences, emphasising the point that such isotopes are not "completely new, man-made hazards", but actually exist already in nature.

Further reading

CÔME, B. AND CHAPMAN, N.A. (EDITORS). 1986. Natural analogue working group, first meeting, Brussels, November 1985. *CEC Nuclear Science and Technology Report*, **EUR 10315**, CEC, Luxembourg.

CRAMERS, J.J. AND SMELLIE, J.A.T. 1994 (Editors) Final report of the AECL/SKB Cigar Lake Analog Study. *AECL Technical Report*, **AECL-10851**, Whiteshell, Canada and *SKB Technical Report*, **TR 94-04**, Stockholm, Sweden.

MILLER, W., HOOKER, P., SMELLIE, J., DALTON, J., DEGNAN, P., KNIGHT, L., NOSEK, U., AHONEN, L., LACIOK, A., TROTIGNON, L., WOUTERS, L., HERNAN, P. AND VELA, A. 2003. Network to review natural analogue studies and their applications to repository safety assessment and public communication (NAnet). *Synthesis Report*, NAnet Project, Funded by the European Community under the "Competitive and Sustainable Growth" Programme (1998-2002). Contract No. FIKW-CT-2002-20204.

SMELLIE, J.A.T. AND KARLSSON, F. 1996. A re-appraisal of some Cigar Lake issues of importance to PA. *SKB Technical Report*, **TR 96-08**, SKB, Stockholm, Sweden.

SMELLIE, J. *Analogue evidence from uranium orebodies*, Report to Nuclear Decommissioning Authority Radioactive Waste Management Directorate, 2009.

5 Glossary

ADZ	Alkali disturbed zone
BGS	British Geological Survey
CASH	Calcium aluminosilicate hydrate
CSH	Calcium silicate hydrate
GDF	Geological disposal facility
EBS	Engineered barrier system
HLW	High level waste
ILW	Intermediate level waste
LLW	Low level waste
L/ILW	Low and intermediate level waste
RWM	Radioactive Waste Management
SF	Spent fuel