NAnet Project

WORK PACKAGE 1

Analogues for the near-field of a repository

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CONTENTS

1 INTRODUCTION

The fundamental objective of the geological disposal concept is to isolate radioactive wastes from the human environment for as long as is possible, allowing for radioactive decay to reduce the hazard posed by the waste. The designs of most repositories adopt the 'multi-barrier' principle, with the isolation capacity provided by a series of engineered barriers in the near-field and the host rock in the far-field (geosphere) as shown in Figure 1.

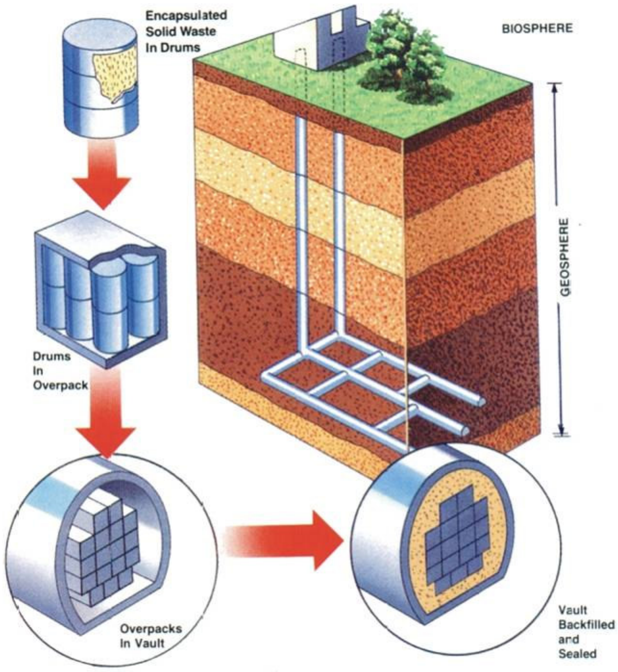

Figure 1: An example of the multi-barrier system for a repository.

The near-field itself generally comprises:

- the wasteform,
- the waste packaging, and
- various buffers, backfills and seals.

Some people also consider the engineered damaged zone (EDZ) and the chemically disturbed zone (CDZ) in the host rock that surrounds the repository excavations to be part of the near-field rather than the far-field.

In safety assessment models, the performance of the near-field can be evaluated by calculating the radionuclide release rate from the near-field to the geosphere. The release rate is a measure of progressive barrier failure over time, due to a combination of physical and chemical processes (and, in some cases, microbial processes) that act to:

- corrode and perforate the waste package or canister;
- dissolve or leach radionuclides from the wasteform; and

- transport (by advection or diffusion) radionuclides through the near-field barriers.

Other processes and their couplings can, however, affect near-field performance in complex ways, for example cement leachates can buffer the chemical conditions in the near-field reducing the solubility of many radionuclides. Nonetheless, the performance of the near-field barriers can be approximated most simply by quantifying the corrosion and degradation rates of appropriate materials.

The materials that are likely to be found in the near-field of a repository (either in the wasteform, packaging or buffer and backfill) include:

- silicate glass (vitrified waste),
- spent nuclear fuel,
- mineral and ceramic wasteforms,
- metals such as steel, copper and titanium,
- bentonite clay,
- cement and concrete, and
- organic materials (e.g. bitumen matrices and paper wastes).

A number of these materials exist in nature or have similar natural counterparts (e.g. copper and bitumen) but others are man-made technological developments (e.g. steel) which do not have natural equivalents but possibly may be found in the archaeological record. The essential alloying components contributing to steel's corrosion resistance (nickel and chromium) are, however, known to exist in natural formations.

Since their conception, natural analogues have been recognised as a useful means of ‘predicting’ barrier performance. Many tens of individual analogue studies have been performed in the last few decades on materials that can be found in natural or archaeological systems (such as glasses, iron, copper and clay) with the aim of ‘measuring’ corrosion and degradation rates. Some of these studies have provided quantitative information but the majority have provided only qualitative information that has, nonetheless, proved useful for conceptual model development. Work Package 1 of the NAnet project had the objectives of reviewing and assessing these analogue studies.

When investigating an analogue of a near-field material, ideally both the material itself and the environment in which it is located need to be similar to the repository system. So, for example, to investigate the long-term stability of glass it is not sufficient simply to find a natural glass that has a chemical composition which is similar to that of vitrified high-level waste, the natural glass must also be located in a physico-chemical environment which replicates the conditions to be found in a repository near-field (i.e. with respect to groundwater chemistry, Eh, pH, temperature etc). It is recognised, however, that there will never be an exact similarity between the analogue and repository systems and, therefore, it is the extent of the differences as well as the similarities which limits the value of the analogue study and of the information derived from it.

1.1 Approach

Overall, the NAnet project reviewed more than 70 separate analogue studies. As part of these reviews, those analogues that were considered to be relevant to the near-field were identified and assessed to determine whether they provide qualitative or quantitative information on specific near-field materials and processes. These studies were:

- Akrotiri (Santorini, Greece)
- Alligator Rivers (Australia)
- Bangombé (Gabon)
- BARRA project (Spain)
- Bézier Gallo-Roman Circus (France)
- Bitumens
- Boom Clay (Belgium)
- BORIS (Russia)
- Broubster (Scotland)
- Busachi (Sardinia, Italy)
- Caves and caverns: man-made
- Caves and caverns: natural
- Caves and caverns: preservation of materials
- Caves and caverns: seepage in man-made caverns
- Caves and caverns: seepage in natural caves
- Caves and caverns: stability of man-made caverns
- Cigar Lake (Canada)
- Col du Perthus (France)
- Disko Island (Greenland)
- Dunarobba Forest (Italy)
- El Berrocal (Spain)
- Gas migration: evaporites
- Geothermal and hydrothermal systems
- Glasses: archaeological and historical
- Glasses: natural
- Hadrian's Wall (Scotland)
- Hyrkkölä (Finland)
- Inchtuthil Roman fort (Scotland)
- Isle of Skye (Scotland)
- Josephenite
- Keweenaw Peninsula (USA)
- Khushaym Matruk (Jordan)
- Kinnekulle (Sweden)
- Krasnoyarsk (Russia)
- Kronan cannon (Sweden)
- Littleham Cove native copper (UK)
- Loch Lomond (Scotland)
- Maqarin (Jordan)
- Marysvale (USA)
- Menzenschwand (Germany)
- Mina Fe (Spain)
- Morro do Ferro (Poços de Caldas, Brazil)
- Oklo (Gabon)
- Orciatico Intrusion (Italy)
- Osamu Utsumi Mine (Poços de Caldas, Brazil)
- Peña Blanca (Mexico)

- Resins: natural
- Salt mines
- Scawt Hill (Northern Ireland)
- Seismic shaking
- Semail Ophiolite (Oman)
- Shinkolobwe (Zaire)
- Tono Mine (Japan)
- Zirconolite

In Work Package 4, it was recognised that there are many different potential audiences for analogue information. One primary audience is the safety assessment community because it has been widely recognised that they have made only limited use of analogue information in recent safety assessments. One explanation for this is that they simply are unaware of the extent of analogue information that exists and of its relevance. This may be because it is hard to find the information that meets their needs from the large body of technical reports and papers that have been published.

As a result of this conclusion from Work Package 4, it was decided that one of the most useful outcomes from this work package would be a simple referencing system that would enable safety assessors rapidly to find all those analogues that relate to specific near-field materials and processes, so that they could apply this information to the development and validation of safety assessment models.

The referencing system that was devised is based on a simple matrix of material-process couples, and this matrix is presented in Section 3.

2 SUMMARY OF ANALOGUE INFORMATION ON NEAR-FIELD MATERIALS

The following sections provide a summary of the available analogue information with respect to the main near-field materials derived from the reviews undertaken in the NAnet project.

2.1 Analogues of glass wasteforms

The liquid HLW from spent fuel reprocessing operations is solidified in a borosilicate glass matrix. Glass has been chosen as a suitable wasteform because of its apparent durability and relative ease of production. A number of glass compositions are used for several waste streams in different vitrification plants but a common characteristic is the inclusion in the mix of between 10 and 20 % B_2O_3 which reduces the melting temperature and, thus, waste losses by volatilisation during manufacture.

Analogues to borosilicate glasses exist in nature and in archaeology. Natural glasses have a volcanic origin and form when a lava or magma cools too quickly for crystallisation to take place. Natural glasses occur with a wide range of compositions. Typically it is the basaltic glasses which are considered to be most analogous to borosilicate glasses because they have similar SiO_2 contents of around 50 to 60 %. Nonetheless, no natural glasses exist with high boron or radionuclide contents. In chemical terms, therefore, basaltic glasses can be considered to be only partially analogous to the borosilicate glass wasteform.

Other differences between natural and waste glasses occur. Most significantly, natural glasses tend to occur in aggressive, oxidising conditions close to the land surface or in submarine environments where conditions are significantly different to those in a repository near-field. These differences mean that it is not appropriate, in most cases, directly to apply a degradation rate derived from a natural analogue glass to a waste glass. Having said this, comparison between glass degradation observed in nature on basaltic glasses and in the laboratory on borosilicate glasses qualitatively suggests that the two glass types degrade by the same mechanisms, if not at the same rates. As a consequence, natural analogue studies on basaltic glasses may provide useful qualitative information on glass degradation processes which could be used to constrain conceptual models for borosilicate glass evolution in a repository environment.

The most important glass degradation processes are devitrification, dissolution and hydrous alteration. In general, all glasses will devitrify (solid state recrystallisation) but the process is very slow and appears to be controlled, in part, by the presence of water, as highlighted by the fact that glasses from the Moon show very little sign of devitrification. On the Earth, it is uncommon to find glasses older than around 25 Ma, although much older glasses do occur at sites where groundwater access has been restricted. Qualitatively, this suggests that devitrification will not be a problem for borosilicate waste glass contained within an intact canister during the timescale of concern to safety assessment.

When in contact with water, glasses will dissolve. Since glass is a metastable solid, the dissolution rate is not solubility controlled, as is the case for most crystalline substances. Instead, dissolution rates are limited by the kinetics of the accompanying hydrous alteration processes (e.g. the supply of water) which result in the formation of an alteration layer comprising amorphous, gel-like phases which convert to more crystalline phases such as clays and zeolites: basaltic glass alteration is characterised by the formation of palagonite. Attempts to quantify basaltic glass dissolution rates in the presence of water have yielded values that range from 0.1 to around 5 µm/yr. In a repository, waste borosilicate glass cannot dissolve or hydrate until after the canister has failed, thereafter the alteration rate will be limited by the slow influx of water through the bentonite buffer. Thus, the alteration rates derived from analogue basaltic glasses are not appropriate for borosilicate waste glass but may be considered as highly conservative, upper bounding limits. This suggests that dissolution and alteration of the borosilicate waste glass will not be a problem during the timescale of concern to safety assessment.

Archaeological glasses may also be used as analogues to borosilicate waste glasses. Certain man-made glasses from the early 1800s were coloured by the incorporation of various metal oxides, including up to 5 % U in some examples (Figure 2). These glasses essentially provide a century long glass doping experiment, in which the effect of radiation damage on the glass and U migration through the glass may be measurable, although no such experiments are known to have been undertaken.

Figure 2: Examples of glassware coloured with uranium.

2.2 Analogues of spent fuel

Spent fuel has a basic composition of UO_2, with the exceptions of the metallic U fuel which is burnt in Magnox reactors and mixed U-Pu oxide (MOX) fuel which is burnt in some PWRs. Metallic U does not occur in nature and consequently there are no suitable natural analogues for it. Likewise, no naturally-occurring minerals contain Pu contents that approach the 5 % Pu found in MOX fuel and, thus, there are no appropriate analogues for this type of fuel.

The most appropriate natural analogue for spent UO_2 fuel is the naturally-occurring mineral uraninite which also has a nominal composition of UO_2 and the same cubic crystallographic structure. There are, however, important differences between uraninite and spent fuel, the most notable is that (with the exception of Oklo) natural uraninites have never experienced criticality and, thus, do not contain the high concentrations of fission products, actinides and actinide daughters found in spent fuel. At Oklo (Figure 3), uraninites contained within the natural fission reactors did experience criticality. The time elapsed since criticality is, however, so long that essentially all the transuranic nuclides and their active daughters formed during the criticality event have since decayed to stable nuclides.

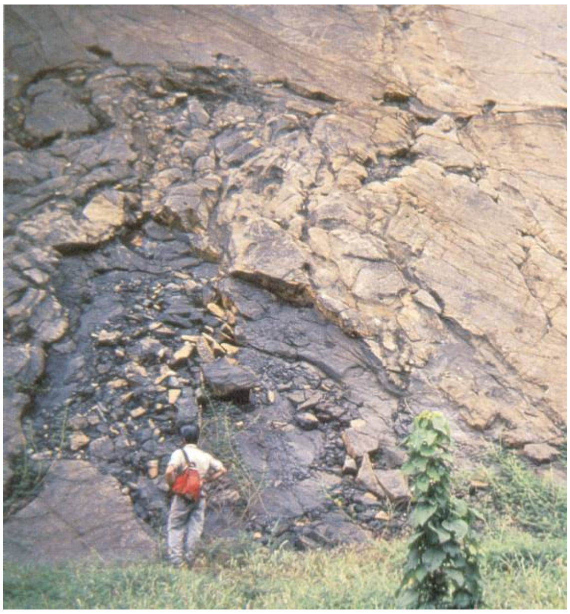

Figure 3: One of the natural fission reactors exposed in an outcrop at Oklo.

Natural uraninites are relatively widespread in many rock types. Many are hundreds of millions of years old, which provides qualitative evidence for their longevity and stability in certain geological environments. Uraninites from several analogue study sites have been investigated to understand and quantify these slow UO_2 dissolution and alteration processes. For the most part, the resulting information has been only qualitative but broadly these studies confirm laboratory results which show that in chemically reducing conditions uraninite is essential stable. In broad terms such conditions are found at repository depths in most rock types. This has been clearly demonstrated at Cigar Lake, for example, where uraninites some 1.3 billion years old have experienced only slight dissolution and alteration to coffinite during early hydrothermal conditions and no oxidative dissolution under present conditions.

Combined, the analogue information on uraninites from a range of subsurface environments indicates that their rate of dissolution is extremely slow when temperatures and groundwater fluxes are low, and when oxidation does not progress beyond U_3O_7. The majority of analogue studies can provide only qualitative evidence for the slow dissolution of uraninite, although methods to quantify dissolution rates are being developed.

In a spent fuel repository with limited Fe to buffer redox conditions (e.g. one using Cu canisters), it is possible that groundwater radiolysis may cause conditions to become locally oxidising inside a canister, in which case oxidative conversion of the UO_2 to U_3O_8 followed by more rapid dissolution is theoretically possible. As a consequence, a number of analogue studies have examined uraninite dissolution under oxidising conditions. These studies demonstrate that oxidation of uraninite can be extensive in conditions where there is a rapid turnover of water but it is not thought that such conditions are likely to occur in a repository.

Detailed investigation of uraninite dissolution processes under oxidising conditions have been undertaken at the Peña Blanca analogue site because this replicates the undersaturated groundwater conditions at the proposed US spent fuel repository at Yucca Mountain. Comparison of the analogue information from this site with laboratory studies on actual spent fuel indicates that both materials corrode by the same processes to form the same alteration products. Observations from Peña Blanca, together with the derived ages of the primary and secondary mineralisations, have been used to derive a quantitative radionuclide release rate which has been applied in a safety assessment for Yucca Mountain, to compare with an experimentally derived base case value.

Overall, natural analogue studies indicate that the kinetics of UO_2 dissolution is exceptionally slow under the reducing conditions expected in the near-fields of most spent fuel repositories. While dissolution rates cannot be quantified readily from natural analogue data, the abundance of naturally-occurring uraninite some 10^9 years old indicates its stability in the geological environment. Extrapolation of this apparent longevity to spent fuel in the repository environment should, however, be done cautiously, due to the uncertain long-term effects of the high levels of radioactivity and thermal history of spent fuel.

2.3 Analogues of mineral and ceramic wasteforms

Some wastes may be immobilised in mineral or ceramic wasteforms, such as SYNROC which is a synthetic mineral assemblage consisting of several oxides, including fluorites, perovskites, hollandites, reduced rutile and magnetoplumbite.

Natural zirconolites and pyrochlores are good analogue minerals for the synthetic component minerals in SYNROC because of their similar composition and structure. These natural minerals frequently exhibit very limited alteration suggesting they are stable in the geological environment, while leaching studies indicate that they may remain closed systems with respect to natural series radionuclides for tens of millions of years. This provides qualitative evidence to suggest that SYNROC should be a durable wasteform in a repository environment. Natural zirconolites and pyrochlores are, however, rare and generally found only as detrital grains in sedimentary formations. As a consequence, it is difficult to relate their observed stability to in situ geological conditions and to derive quantitative information which would be appropriate for input to a safety assessment. Laboratory studies will probably remain the best means of investigating the stability of these mineral phases.

2.4 Analogues of technical metals

Technical metals (i.e. fabricated alloys) will be used extensively in all repository designs for the fabrication of canisters and waste packages, and in engineered and support structures. In addition, some activated metals will form a component of certain ILW waste streams. Volumetrically, steel will be the most important metal in most repositories, although in some HLW or spent fuel repository designs other metals such as Cu, Ti or Pb may be used to fabricate canisters or used as a filler in canisters.

Analogues of some technological metals exist in nature and in archaeology. The natural analogue to steel is native Fe but this occurs in large amounts only rarely in a few locations where it has precipitated from an Fe-rich magma and has remained isolated from groundwater by a surrounding impermeable rock matrix. The fact that Fe rarely occurs in native form (it is usually incorporated into various oxide and silicate compounds) provides qualitative evidence that steel canisters will corrode in the repository, at least on a geological timescale. None of this information can be used, however, to derive a quantitative corrosion rate for use in a safety assessment. The rarity of native Fe means that archaeological analogues provide the best opportunity for estimating steel canister corrosion rates.

The world's largest native Fe occurrence in Disko Island, Greenland demonstrates the stability of the metal at low humidity and low temperature (periglacial conditions). Metallic iron in Disko formed about 30 million years ago but was exposed to the atmospheric conditions much later. Metallic iron is observed to be coated by magnetite and goethite layers at the micrometer scale, which seems to have protected the metal in dry arctic conditions.

The corrosion resistance and strength of steels is largely attributed to the alloying of iron by chromium, nickel and molybdenum in variable proportions. Also nickel-based alloys are sometimes used (e.g. Alloy 22). The occurrence of nickel-iron metal in josephinite, a rare mineral (and rock type) found in Oregon, has been studied as a natural analogue of the long-term behaviour of nickel-based metallic materials. Corrosion resistance of nickel-based alloys as well as that of stainless steel is mainly attributed to the formation of microscopic chromium oxide layer on the surface. Naturally occurring chromium oxide, chromite ($FeCr2O4$) is often associated with mafic and ultramafic rocks.

Several archaeological analogue studies have examined the corrosion of steel and Fe artefacts with a range of ages of up to a few thousand years. These show typical corrosion rate range of between 0.1 and 10 µm/yr. Unfortunately, such analogue studies have limited value because most archaeological materials are collected from aggressive, oxidising surface or near-surface environments which do not replicate near-field conditions. This is particularly important for Fe because this metal corrodes by quite different processes in anaerobic conditions (as expected in most repositories) than in aerobic conditions (as found in surface environments). As such, it is not appropriate, in most cases, directly to apply a corrosion rate derived from an archaeological Fe artefact to a steel canister in a safety assessment. The archaeological analogue data may be used, however, to provide upper bounding limits to long-term corrosion rates, given that aerobic corrosion of Fe is faster than anaerobic corrosion.

One archaeological study which has provided qualitative evidence of the durability of Fe in reducing environments is the hoard of Roman nails at Inchtuthil. The large mass of Fe nails buffered the redox conditions such that, at the centre of the hoard, conditions were reducing and nails located there exhibited only a thin oxidation layer after 2000 years of burial (Figure 4). The difference between Fe corrosion in oxidising and reducing conditions is well illustrated by the fact that some of these nails have corroded more rapidly since being exposed to the atmosphere in the 30 years since excavation than they did in 2000 years of burial in water saturated, reducing conditions.

The natural analogue of technical Cu is native Cu. Native Cu is quite widespread and can be found in aggressive, oxidising conditions, such as Cu nuggets in glacial rivers. Various analogue studies have examined native Cu from low-temperature geological environments and all have indicated that Cu is essentially inert under these conditions. Geological evidence does, however, indicate that Cu can be mobile under extreme hydrothermal conditions but these are not relevant to any repository environment. The difference between Fe corrosion in oxidising and reducing conditions is well illustrated by the fact that some of these nails have corroded more rapidly since being exposed to the atmosphere in the 30 years since excavation than they did in 2000 years of burial in water saturated, reducing conditions.

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Figure 4: One of the 2000 year old iron nails from Inchtuthil.

The native copper deposits at Keweenaw demonstrate the long-term stability of metallic copper. These deposits formed for more than 1 billion years ago, and boulders of metal have been exposed to the atmospheric conditions since at least post-glacial times but probably much longer. The native copper of Keweenaw was crystallized from hot chloride brines during cooling. Very saline waters (brines) are known to occur in the area even at present but the possible interactions between them and metallic copper are not known.

Archaeological analogues of Cu have also been examined in a number of studies. These indicate a typical corrosion rate range of between 0.025 and 1.27 µm/yr. A similar corrosion rate of 0.15 µm/year was recorded from the Kronan cannon analogue, although this was made from bronze (Figure 5).

Figure 5: One of the bronze cannon recovered from the wreck of the 300 year old Swedish warship Kronan.

Combining all the analogue information on metal corrosion, there are no quantitative data on corrosion rates for any metal that may be applied directly to a safety assessment because of differences in metal compositions and environmental conditions. There is, however, useful qualitative information on metal corrosion processes and semi-quantitative data that are useful for providing bounding upper limits to corrosion rates and to support laboratory data.

2.5 Analogues of bentonite clay buffer material

Bentonite will be used extensively in compacted form in HLW and spent fuel repositories as a buffer between waste canisters and the near-field rock. In the same repositories, bentonite may be mixed with sand or crushed rock and used as a backfill for access tunnels and shafts. Similarly, bentonite is used in some ILW repository designs as a buffer and backfill. The objective of using bentonite is to establish a very low permeability (diffusive) barrier to groundwater flow and radionuclide migration.

Bentonite is a relatively abundant natural material, usually formed by hydrothermal alteration of lavas and, thus, there are many potential analogue study sites. The characteristics of bentonite in a repository near-field (highly compressed, water saturated, in a chemically reducing environment with a thermal transient) are, however, significantly different to the near-surface conditions in which natural bentonite deposits are typically found. As a consequence, only a few natural bentonite deposits are appropriate as analogues, these tend to be:

– deposits which have been intruded by small igneous bodies to generate a thermal peak approximating the thermal transient from the waste;

– deposits in contact with deep, reducing groundwaters where groundwater-bentonite interactions can be studied;

– naturally compressed bentonite where its long-term hydraulic properties may be investigated; and

– deposits where bentonite is in contact with other materials which are analogues to components of the engineered barrier system to investigate possible interactions.

A number of analogue studies have been undertaken to investigate the mineralogical and physical transformations that may occur in bentonite as a consequence of ion-exchange with dissolved substances in groundwaters. Such transformations are potentially important because a change from bentonite to illite, for example, is accompanied by a loss in swelling pressure which, in the repository, may cause a possible decrease in its hydraulic barrier function. These natural analogue studies all indicate that these processes are limited kinetically and by the supply of exchange ions, and are unlikely to be a problem in a HLW or spent fuel repository over the timescales of interest to safety assessment. No appropriate analogue studies have, however, yet investigated the potential for mineralogical transformations in an ILW repository where high pH groundwaters may be in contact with bentonite.

The hydraulic barrier function of bentonite has been qualitatively investigated in a few natural and archaeological analogue studies, such as the preserved forest at Dunarobba (Figure 6). In this system, preservation of organic materials (wood) is ascribed to the hydraulic barrier provided by clay layers. The clays are neither mineralogically or physically identical to the compacted bentonite used in a repository but, nonetheless, this analogue provides qualitative evidence of the long-term stability of clays in a burial environment and the maintenance of low hydraulic conductivities.

Figure 6: The remnants of the one million year old 'fossil' trees at Dunarobba.

A few natural analogue studies have examined the impact of heating on bentonite. These studies have suffered from the problem that most igneous intrusions generate temperatures which are far-higher than those which would be experienced in a repository near-field. Likewise the pressure and chemical conditions are also dissimilar. Samples examined from some distance away from intrusions, where temperatures are lower, suggest that some mineralogical changes do occur, including crystallisation of K-feldspar and smectite causing cementation and fracturing of the bentonite mass. Nonetheless, insufficient studies in appropriate analogue situations have been undertaken to be able to determine whether the same effects would occur in the repository situation. If additional relevant analogue systems can be found, this issue would be worthy of further investigation.

One issue for compacted bentonite, yet to be resolved, is the possibility of a dense waste canister sinking through a water-saturated buffer acting as a viscous fluid over long periods of time. Laboratory and modelling experiments suggest that sinking would be limited but no appropriate analogue study has yet confirmed these results.

2.6 Analogues of technological concretes and cements

Technological concretes and cements (i.e. specially designed cementitious materials) will be used in most repository designs as rock supports and reinforcements, and plugs and seals. The largest volumes will be found, however, in ILW and LLW repositories where these cementitious materials are used as immobilisation matrices for certain waste streams and as a backfill between waste packages. In an ILW repository, these cementitious materials have a dual role: to provide physical immobilisation of the waste and to buffer the near-field chemistry to hyperalkaline conditions in which many radionuclides are poorly soluble. It is, thus, the durability of cement and the cement-groundwater interactions which are most important processes to understand, although other issues are also significant, such as the nature of interactions between high pH groundwaters and the far-field rock.

Analogues to cementitious materials exist in nature and in archaeology. Natural analogues to modern cements are naturally-occurring but rare cement minerals which can be found in a small number of unusual geological environment. Some of these minerals have been stable for tens of millions of years in locations where they are isolated from rapid influx of oxidising waters. The most comprehensively investigated natural analogue for cementitious materials and high pH environments is Maqarin where the pH of the groundwaters (up to pH 12.5) is controlled by the solubility of naturally-occurring portlandite, by exactly the same mechanism that would occur in an ILW repository. As a consequence, the Maqarin system has been used to undertake detailed testing and evaluation of the thermodynamic codes which will be used in safety assessments for ILW repositories to predict radionuclide solubilities. The hyperalkaline groundwaters at Maqarin interact with the host marls and this has caused the dissolution of some aluminosilicates and the precipitation a range of secondary calcium-silicate-hydrate compounds and zeolites. These processes have caused significant changes to the bulk porosity of the rock and modifications to the groundwater flow paths. Observations from these reactions have been used to develop conceptual models for the interactions between leachate plumes from a repository and the far-field rock.

Numerous historical cements and concretes have been investigated as archaeological analogues. Particular attention has been paid to pozzuolanic Roman cements, such as that found at Hadrian's Wall (Figure 7), and 20th century cements because these both contain the calcium-silicate-hydrate compounds that characterise modern Portland cements and, thus, mineralogically are the closest analogues to the cementitious materials which will be used in an ILW repository. Although no quantitative information on cement alteration rates can be derived from these archaeological analogues for direct use in safety assessment, they do provide convincing qualitative evidence for the potential longevity of cementitious materials for thousands of years. Geological analogues considerably extend the known longevity of cementitious materials to millions of years in some environments.

Figure 7: The remains of the 2000 year old Hadrian's Wall that includes cement mortars containing calcium-silicate-hydrate compounds.

2.7 Analogues of organic materials

A wide range of organic materials may be present in ILW and LLW, either as waste materials (e.g. ion-exchange resins and waste paper) or as an immobilisation matrix (e.g. bitumen). There may also be small volumes of organic material in HLW and spent fuel repositories (e.g. as cement additives). These different organic materials will decompose in the repository environment but at quite different rates, depending on their composition and physical structure. When organic materials degrade, they generate gases, and organic complexants and colloids which may act to increase radionuclide mobility.

Analogues of organic waste and wasteform materials exist in nature and in archaeology. Natural bitumens occur in certain parts of the world and are derived by natural distillation processes from crude oil. Some natural bitumens have been examined as analogues for the technical bitumens used in an ILW repository and these suggest that natural bitumens can remain stable for long periods of time, although microbial action and exposure to light can accelerate decomposition. Examination of bituminous materials at Oklo which envelope some uraninite grains, indicates that it can aid the retention of fission products, despite irradiation.

Archaeological artefacts made or water-proofed with bitumen are known up to 5000 years old and these have also been proposed as analogues for technological bitumen. Qualitatively, these geological and archaeological analogues point to the stability of bitumen under a wide range of physico-chemical conditions as well as their ability to isolate materials from water for long periods of time. The significance of these observations for the long-term behaviour of bitumen in a repository is, however, uncertain because of compositional differences between natural and technological bitumens (especially at Oklo) and, more importantly, because no natural bitumens are known from high pH environments which replicate the hyperalkaline conditions which would occur in a cementitious ILW near-field.

Natural analogues to cellulose-based organic wastes include the 2 Ma old preserved forest at Dunarobba. This analogue qualitatively demonstrates that cellulosic materials may degrade slowly in low-flow, reducing conditions. Dunarobba is, however, an inappropriate analogue for an ILW repository because the site does not replicate the hyperalkaline conditions of a repository. Relevant examples of cellulose degradation in high pH environments are necessary before firm conclusions can be drawn on cellulose degradation rates.

3 THE NEAR-FIELD ANALOGUE MATRIX

As discussed in the main report, it is evident that the explicit use of analogue information in safety assessments has been quite limited. One reason why this may be the case is that the potential users of analogue information are unaware of what information there is that could be relevant to their work.

It was recognised in Work Package 4 that the potential users of analogue information, particularly the safety assessors and the communications specialists, need easy access to analogue information that is relevant to the issues at hand.

In this work package, it was decided that the simplest way to provide access to analogue information relevant to the near-field was in the form of a matrix that had on one axis the range of near-field materials and on the other axis the range of processes that operate in the near-field. Intersections of the axes identify unique material-process combinations and analogue studies can be listed at the appropriate intersections. This is illustrated in the Figure 8 below which shows that the 'Kronan cannon' analogue study is relevant to the understanding of the corrosion of copper.

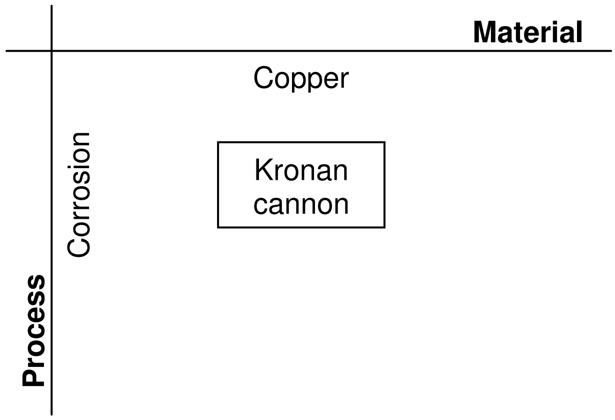

Figure 8: Example of the 'analogue matrix' for the near-field.

A generic near-field analogue matrix has been developed (Figure 9) that includes all of the analogue studies covered in NAnet that have near-field relevance, based on the outcome of the individual analogue reviews. It should be recognised that this matrix is for general reference use only and does not represent any particular repository design. Indeed, no actual repository near-field design would include all of the materials listed in Figure 9 and none would be subject to all of the processes listed. It should be noted also that on an analogue matrix, not all material-process interactions are possible in a repository. For example, radionuclide diffusion within the metal of a canister is not a relevant combination. In Figure 9, these 'invalid' combinations are shaded.

Figure 9 indicates, unsurprisingly, that there has been a preponderance of studies on materials that are widely found in nature, such as uraninite and bentonite, and processes that occur readily in different geological conditions, such as chemical corrosion and alteration. For these process-material combinations, there is a wealth of analogue information that provides substantial support for the development and testing of conceptual models, and some quantitative data to help constrain the rates of processes.

The matrix also indicates there are a number of gaps, where only a few or no analogue studies have examined particular process-material combinations. For example, analogue studies have only examined diffusion through bentonite clays but not through other near-field materials such as cement and concrete. Similarly, there is no available analogue information on some other transport processes through cement and concrete, including colloid transport and two-phase flow. Thus the matrix provides a useful means of identifying gaps where further analogue studies may be required.

It is recommended that repository specific matrices should be developed by analogue researchers and performance assessors to reflect their own particular repository designs and site characteristics. These matrices could then be populated to indicate how individual analogue studies have been or could be used to inform the development of their own safety assessment models for the near-field.

Figure 9: The generic analogue matrix for the near-field. The pink coloured squares represent 'invalid' process-material combinations that would not occur in a repository. The empty squares represent process-material combinations that can occur in a repository but no analogue study has investigated.

		Wasteform				**Waste package**				**Buffer**		**Near-field rock**
		Glass	**SF**	**Cement**	**Others**	**Copper**	**Steel**	**Titanium**	**Concrete**	**Bentonite**	**Concrete**	
Degradation of the engineered barriers	**Mechanical**	Glasses: archaeological Glasses: natural	Bangombe Cigar Lake Oklo Shinkolobwe	Hadrian's Wall	Bitumen studies Resin studies SYNROC studies	Hyrkkölä Keweenaw Kronan Cannon	Inchtuthil Disko Island	Josephinite	Beziers Hadrian's Wall	BARRA Boom Clay Busachi Col du Perthus Dunarobba Isle of Skye Kinnekulle	Beziers Hadrian's Wall	Asse Mine Borehole depths Caves and caverns Salt domes Salt mines Krasnoyarsk
	Chemical (corrosion, alteration and radionuclide release from wasteform)	Glasses: archaeological Glasses: natural	Alligator Rivers Bangombe Cigar Lake El Berrocal Mina Fe Oklo Tono Peña Blanca Shinkolobwe Marysvale	Hadrian's Wall Khushaym Matruk Maqarin Scawt Hill	Bitumen studies Resin studies SYNROC studies	Akrotiri Hyrkkölä Keweenaw Kronan Cannon Littleham Cove	Inchtuthil Disko Island	Josephinite	Hadrian's Wall Khushaym Matruk Maqarin Scawt Hill	BARRA Orciatico Busachi Col du Perthus Dunarobba Isle of Skye Kinnekulle Murakami	Hadrian's Wall Khushaym Matruk Maqarin Scawt Hill	Salt domes Salt mines Caves: seepage Khushaym Matruk
Radionuclide transport	**Advection (flow)**			Beziers Maqarin Khushaym Matruk Hadrian's Wall					Beziers Maqarin Khushaym Matruk Hadrian's Wall	Dunarobba	Beziers Maqarin Khushaym Matruk Hadrian's Wall	Björklund BORIS Caves: seepage Caves: preservation El Berrocal Geothermal systems Morro do Ferro Osamu Utsumi
	Diffusion									Loch Lomond Bangombe Boom Clay Cigar Lake Dunarobba Kinnekulle		Akrotiri Bangombe BORIS
	Colloid transport									Bangombe Cigar Lake		Alligator Rivers Bangombe BORIS El Berrocal Menzenschwand Morro do Ferro
	Two-phase flow									Gas studies		Gas studies Geothermal systems
Radionuclide retardation	**Sorption, precipitation and physical retardation**	Glasses: archaeological Glasses: natural	Bangombe Alligator Rivers Cigar Lake El Berrocal Mina Fe Oklo	Maqarin		Hyrkkölä Littleham Cove			Semail Ophiolite Maqarin Khushaym Matruk	Cigar Lake Boom Clay Bangombe	Semail Ophiolite Maqarin Khushaym Matruk	BORIS El Berrocal Morro do Ferro Oklo Alligator Rivers Osamu Utsumi

4 CONCLUSIONS

The NAnet project reviewed more than 70 individual analogue studies. Over half of these were found to be relevant to the materials or processes that may occur in a repository near-field.

These analogue studies have yielded a great deal of qualitative and some quantitative information and, on this basis, confidence in the stability and robustness of the near-field engineered barriers could be said to be increased.

Nonetheless, this analogue derived information has not made its way into many safety assessment reports and, thus, its true potential has not been realised. This situation is largely due to poor communication between the analogue researchers and the safety assessors and communications specialists.

It has been recognised that what is required is a simple method to allow relevant analogue studies to be quickly and easily identified from the large body of published information. This work package has developed a near-field analogue matrix that is intended to provide a generic introduction and reference system to the literature.

It is recommended that repository specific matrices are developed by analogue researchers to reflect the particular engineering designs and site characteristics for repositories under development or being planned in their own countries.