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The Harpur Hill Site: An assessment as an analogue to a cementitious GDF

Minerals and Waste Programme

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Foreword

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Abstract

This report provides a review of the Harpur Hill Site and whether or not it could be used to provide complementary information on understanding aspects of a cementitious geological disposal facility (GDF) for low and intermediate level radioactive waste (L/ILW) (hereafter simply referred to as 'GDF') and in a GDF for higher activity wastes where large amounts of structural concrete are utilized. The relevance to near surface disposal is not explicitly considered here, even though for some aspects the similarities between the site and such a facility may be greater. Leachate within and associated with an evolving GDF utilising cement based grouts/backfills for conditioning and backfilling of L/ILW will initially have a pH of more than 13 over the first 10^4 years post closure where sodium, potassium and calcium hydroxides (K-Na-Ca-OH) dominate the alkaline fluids derived from the cement. Demonstrated by on-site analysis, the alkalinity of the leachate at the Harpur Hill Site, which is derived from leaching of residual lime (CaO) in lime burning wastes, has a maximum pH of about 12.5. This is dominated by calcium hydroxide ($Ca(OH)_2$). As a result, the Harpur Hill Site is not a suitable analogue of the early stage of evolution of a cementitious GDF for L/ILW, where highly alkaline K-Na-Ca-OH (ca pH 13) dominates the geochemical interactions. The pH 12.5 $Ca(OH)_2$ dominated leachate present on parts of the site may, however, provide a suitable analogue for a more evolved (>10^5 years) cementitious GDF, and for the more distal parts of a leachate plume from a GDF, where K-Na-OH is no longer present, and help understand alkaline fluid interactions with clays.

While the deeper parts of the Harpur Hill Site are reducing, the near surface parts of the site are oxidizing. From soon after closure a GDF will be reducing and thus many of the processes known to be occurring at Harpur Hill, including metals corrosion and microbial degradation and resulting fate of cellulose degradation products, are not appropriate analogues for a cementitious GDF. This is because both the leachate chemistry and redox conditions are not relevant as they do not represent conditions within a GDF early post closure while the waste form evolves rapidly.

Because of these factors the site is unlikely to provide meaningful information on the expected evolution of a cementitious GDF that could be considered in a safety case and the site is not considered to be an adequate analogue for a cementitious GDF.

Executive summary

This report considers the features of, and the processes that are occurring at, the Harpur Hill Site, near Buxton, Derbyshire, and assesses their potential relevance to similar Features, Events and Processes that are predicted to occur in a cementitious geological disposal facility (GDF). The study was undertaken on behalf of the Radioactive Waste Management Limited (RWM), as part of a programme of work to assess the potential of the Harpur Hill Site as an analogue for understanding aspects of the long-term behaviour of repository materials in an alkaline environment, and the evolution of an alkaline disturbed zone (ADZ) around a cementitious GDF for low- and intermediate-level (L/ILW) radioactive waste and in a GDF for higher activity wastes where large amounts of structural concrete are utilized.

The site at Harpur Hill was exploited in the 1830's for the large scale production of lime, which continued until the early 1950's when production ended. The leaching of residual lime (CaO) within the lime waste deposited at the site, by percolating rainwater and shallow groundwater, has led to the development of alkaline, calcium hydroxide dominated leachate with a pH of about 12.5 and the formation of an alkaline 'lagoon' of calcium carbonate tufa precipitate.

A survey of the site identified that a range of materials, including metals, plastics, cellulose rich material (wood, grass, and other plant material) and alluvial clays, in contact with the high alkaline leachate (pH 12.5). This is similar to some materials in a cementitious GDF which, together with the pH 12.5 environment may be analogous to aspects of the evolution of a GDF system.

It should be emphasised that the Harpur Hill Site ***is not*** itself an analogue of a GDF, but rather that some of the features and processes occurring at the site may be analogous to some of the components of a cementitious GDF system. Of key importance in assessing the suitability of the Harpur Hill Site for analogue research was comparison of the processes and materials present in the site with the model understanding of how the geochemistry of a GDF and its associated ADZ will evolve in both time and spatially.

During the course of the work for this report a number of factors have become apparent that mean that the site is not an appropriate analogue for many aspects of an L/ILW GDF utilizing large quantities of cement based upon an Ordinary Portland Cement (OPC) composition. The main limitations are:

- Because the origin of the alkalinity of the site is derived from lime waste, it is at a pH of about 12.5 and dominantly calcium hydroxide - a cementitious OPC based GDF will be at a pH of about 13.5 with sodium/potassium hydroxide dominated leachate during the early stages of its evolution post closure (up to about 10^4 years) - limiting the applicability of the site to low pH cement analogue applications;
- Many of the materials observed at the site are in the surface environment where they are under oxidising conditions and experience fluctuating pH as a result of fresh water dilution from rain and surface water inputs, which are not analogous to GDF conditions; and,
- To date active microbes from deep in the tufa deposits where conditions are reducing and pH stable at >12 have been identified at the site, but the use of the site as an appropriate analogue has not yet been demonstrated.

In contrast, the site may provide a reasonable analogue for studying clay host rock or clay backfill interactions with $Ca(OH)_2$-dominated alkaline fluids at pH 12.5 in an evolved (ca10^5 years) cementitious GDF, or for the more distal parts of the ADZ and the diffusive alteration profile in a clay backfilled GDF. In this context the Harpur Hill Site represents the region of a GDF system that has interacted with an evolved $Ca(OH)_2$ cement leachate but beyond the region would be affected by interaction with a young K-Na-Ca-OH-dominated young cement leachate. The interactions observed at the Harpur Hill Site may also be relevant to GDF systems utilising low-K, low-pH cement based materials. Interactions between underlying clays on the site and the

alkaline fluids under reducing conditions over a ca 100 year timescale provide the most relevant opportunity for studying alkaline alteration, rates of penetration of the alkaline fluids and, perhaps, related microbial activity in the clays as alkalinity reduces with increasing distance into the clay. While practicality of hand sampling of this material has recently been demonstrated, uncertainty remains about the clay minerals present and no sterile sampling has been undertaken for microbial analysis.

Because the site is not a good analogue for many aspects of a cementitious GDF and that there is remaining uncertainty about some of the characteristics of the site, we do not currently think that the site offers enough potential to warrant undertaking a major programme of studies based on this site and do not recommend such studies here at this stage.

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1 Introduction

1.1 OBJECTIVES

The generic disposal system safety case (gDSSC) (NDA; 2010) considers the performance of a Geological Disposal Facility (GDF) in the period following its closure. The gDSSC also includes a suite of status reports, which presents the status of research and development on a number of topics relevant to the safety case. Using these assessments as a basis, Radioactive Waste Management Limited (RWM), the successor to the NDA-RWMD, has prepared a Science and Technology Plan (NDA, 2014) which identifies the need to consider potential analogues to support the understanding of coupled processes operating in the geosphere, in relation to the evolution of a UK GDF. Current concepts for a GDF for the disposal of low- and intermediate-level radioactive wastes (L/ILW) envisage the use of cement as a matrix for encapsulating wastes, backfilling and sealing the GDF. For these and high level wastes, cement is used for structural concrete and grout used in construction. To this end, the NDA-RWMD have previously participated in a number of natural analogue studies focussed on understanding the biogeochemical interactions of highly alkaline (pH >12) cement pore fluids within a cementitious GDF and its geosphere environment (e.g. Jordan (Maqarin) Natural Analogue Project Alexander, 1992; Linklater, 1998; Smellie, 1998; Pitty and Alexander, 2011), and more recently the Cyprus Natural Analogue Project (Alexander and Milodowski, 2013). As part of this programme of analogue research, NDA-RWMD commissioned the desk study, reported here, to assess the potential of an industrial highly alkaline leachate site at Harpur Hill, near Buxton, Derbyshire, to provide analogue information relevant to a GDF.

NDA-RWMD interests in this study are in understanding whether or not processes observed as occurring at the Harpur Hill Site could provide information to strengthen safety case arguments in the gDSSC, therefore providing enhanced confidence in demonstrating understanding of such processes relevant to the GDF Engineered Barrier System (EBS) and/or the host rock. The principal objective of this report is to provide an assessment of the Harpur Hill Site, with regard to its potential to provide useful analogue information on the processes and geochemical interactions that might occur during the biogeochemical evolution of a cementitious GDF. This report identifies the features and processes represented at the Harpur Hill Site and assesses their relevance and potential for further investigation as analogues in the context of the model understanding of the geochemical evolution of a cementitious GDF. It is not the intention of this report to provide a review of other cement analogue studies, nor to discuss other GDF-relevant processes (e.g. gas production) which cannot be addressed by reference to the Harpur Hill Site. This review was undertaken using existing information and the acquisition of new data was outside the scope of this study. Where appropriate, this study has considered data arising from unrelated research that is ongoing at the site.

A companion report provides details of the background geological, geomorphological, hydrological, and evolutionary history of the Harpur Hill Site and provides a catalogue of the materials found to be present (Milodowski et al., 2013).

1.2 APPLICATION OF ANALOGUE STUDIES

As noted by Alexander et al. (2014), argumentation by use of analogue systems is well established in many fields including philosophy, biology, linguistics and law. For the specific case of radioactive waste management, the term “natural analogue” has developed a particular meaning associated with supporting arguments for the long-term safety of repositories (see Chapman et al. 1984; Miller et al. 2000 and www.naturalanalogues.com for further discussion). Key factors here are the heterogeneity and complexity of natural systems and, in particular, the very long timescales over which safety must be assured.

The potential evolution of repositories, designed for specific types of waste and disposal sites, can be simulated by the use of mathematical models, but the extent to which such models can be validated by conventional approaches is inherently limited.

Here, analogue systems, natural, archaeological and industrial, which have similar properties to components of repositories, have a unique role to play in understanding the evolution of repository system components over timescales beyond the practical or realistic duration of laboratory experimental systems. The extent to which natural and other analogue system evolution in the past can be understood and modelled with existing tools and data gives an indication of the ability to determine future evolution of the repository. Analogue sites have the potential to link short term laboratory studies, medium term *in-situ* studies and geological time periods relevant to the repository safety assessment within realistic spatial scales and complexity/heterogeneity compared to laboratory experimentation/computer modelling.

The initial use of analogues focused on improving understanding of key processes and model/database testing (e.g. McKinley, 1989) and, indeed, this is still a major justification for some analogue projects. Arguments based on analogy complement more conventional safety assessment within a safety case and their additional roles include their use in public communication (e.g. West et al. 2002) and staff training. A recent focus has been the use of analogues to provide general support for the safety case (by studying the evolution of relevant systems over geological timescales); these can be utilised to provide examples of repository performance to opinion formers, politicians, concerned academics and the public and to increase confidence in extrapolating results from laboratory and field experiments to the repository.

Improving system understanding can range from examining global concepts (e.g. fundamental feasibility of preserving geochemical anomalies for millions of years – see discussions on Oklo and Cigar Lake in Miller et al. (2000)) to direct quantification of specific processes (e.g. matrix diffusion depths – see Smellie et al. 1985). Similarly, model testing can range from rather weak qualitative comparison of expectations with observations (e.g. relative retention of elements within Oklo reactor cores) to quantitative assessment of the relevance of laboratory databases (e.g. for material corrosion) to more formal assessment of the predictive capability of specific model and databases (e.g. blind predictive modelling of solubility limits).

1.3 ANALOGUE TYPES

Analogue systems can be divided into *anthropogenic* (i.e. industrial and archaeological, or the result of other past human activity) or *natural*.

When considering natural analogues there are a number of different definitions for radioactive waste technical applications, in addition to those not associated with radioactive waste disposal. Direct quotes with respect to radioactive waste disposal include:

- "…an occurrence of materials or processes which resemble those expected in a proposed geological radioactive waste repository." (Come and Chapman, 1986).
- "…the essence of a NA is the aspect of testing of models, whether conceptual or mathematical, and not a particular attribute of the system itself." (McKinley, 1989).
- "….NAs are defined more by the methodology used to study and assess them, than by any intrinsic physico-chemical properties they may possess." (IAEA, 1989).
- "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 or test models appropriate to performance assessment work." (Miller et al., 1994).

Where knowledge is currently lacking, analogues can provide additional data to reduce uncertainty and build confidence in safety assessments i.e. identify if processes are or are not likely to occur. Other supporting lines of evidence provided by natural or archaeological analogues are those where the analogue of choice shows a similar behaviour to sources in the repository and/or surrounding environment under the same conditions (e.g. Eh and pH) and across similar timescales.

Examples of the use of natural analogues include:

- Using artefacts from relevant archaeological settings to measure and compare corrosion rates to performance assessment model predictions, supporting evidence for the potential longevity of materials used in repositories (e.g. observations on the corrosion rate of iron in from Inchtuthil Roman nail hoard, (Miller et al., 1994; 2000; JAEA, 2005);
- Using material at analogue sites to assess their performance of waste forms and engineered barrier materials under *in-situ* repository relevant conditions (e.g. preservation of native copper isolated in geologically-old (Permian) mudrocks (Milodowski et al., 2000, 2002); analogues of high-level waste (HLW) glass waste forms (Havlova et al., 2007); interaction of bentonite with low-alkali cement pore fluids (Alexander at al., 2008; Alexander and Milodowski, 2013;));
- Using total geological analogues to confirm general understanding of processes which lead to the immobilisation of waste radionuclides (e.g. Poças de Caldos Natural Analogue Project (Chapman et al., 1992a; 1992b); the Maqarin Natural Analogue Project (Alexander, 1992; Linklater, 1998; Smellie, 1998; Pitty and Alexander, 2011)); and,
- Providing definitive positive or negative evidence to support radionuclide mobilisation/ immobilisation processes (e.g. mobility of uranium in clay host rocks (Havlova et al., 2006)).

It should be noted that the above list is not exhaustive. A more comprehensive summary of the application of natural analogue studies to a wide range of radioactive waste management issues are given in the detailed reviews by Miller et al. (1994; 2000). The recent review by Savage (2011) focuses on analogue systems applied specifically to understanding the long-term behaviour of a cementitious GDF.

There are, however, a number a problems associated with the use of analogues that should be recognised. Correct interpretation of natural analogues requires a good understanding of both the processes featured and the extent of applicability to a repository system. As a consequence, the lack of understanding surrounding the use and application of natural analogues has resulted in misapplication. This is by both data producers, because of a lack of understanding of radioactive waste applications, and by radioactive waste scientists (modellers), who do not understand the data source, leading to over interpretation.

In essence, when used correctly, analogues can be used to study and understand processes that may be occurring within a repository system. This knowledge can be used to improve system understanding. Arguments based on analogy can complement more conventional safety assessment within a safety case.

There are a number of industrial analogues that have been used previously to consider the effects within the near field and Alkaline Disturbed Zone (ADZ) of alkaline cement leachates from a cementitious GDF. These have been reviewed previously by Savage (2011), and include: cement-aggregate reactions, alkaline flooding of hydrocarbon reservoirs, and the interactions of cement-lining mudrock in the Tournemire Tunnel, in France. These have partially bridged understanding of the gap in time and space scales between laboratory and *in-situ* tests, and observations from natural analogues (e.g. highly alkaline spring systems at Maqarin in northern Jordan (Alexander, 1992; Linklater, 1998; Smellie, 1998; Pitty and Alexander, 2011) and Cyprus (Alexander and Milodowski, 2013a,b and references therein), saline alkaline lakes (Savage, 2011). The timescales of these previous industrial analogue studies are of the order of 100 years, with space-scales up to several hundreds of metres (Savage, 2013).

Harpur Hill-based research similarly has the potential to form a 100-200 year timescale bridge between information derived from short term laboratory experiments, medium term Underground Research Laboratory tests and natural geological analogue systems. In particular, the Harpur Hill Site is of direct relevance to processes occurring between $Ca(OH)_2$ dominated rock-water interaction within the distal ADZ predicted to influence the GDF after 10^4 -10^6 years.

1.4 THE HARPUR HILL SITE

The site at Harpur Hill, about 1.5 km southwest of Buxton, was exploited in the 1830’s for the large scale production of lime for the agricultural, building and chemical industries which continued until the early 1950’s. Lime production was an inefficient process leading to the creation of large amounts of waste in the form of under- and over-burnt limestone, lime fines, together with ash produced from the low quality local coal used to fuel the process. This waste has been deposited in tips at a number of locations at Harpur Hill, one of the larger tips being created by ‘tumble tipping’ over the side of the Brook Bottom valley. Because the waste is partly comprised of calcined limestone containing lime (CaO), it reacts with water to form a calcium hydroxide-dominated leachate with a pH of greater than 12. The leachate is migrating through the tip and emerging from its base into the Brook Bottom valley. Here, contact with atmospheric carbon dioxide and mixing with local bicarbonate water results in the precipitation of calcium carbonate. This has led to the development of an extensive tract of soft, fine-grained tufa deposits over a large area of the valley bottom downstream of the spoil tip. Figure 1 provides a summary of the features of the site. Where largely undiluted by fresh water, the fluid in the resulting lagoon in the vicinity of the tip base maintains a high pH (>12). Mixing with fresh water inflows and uptake of atmospheric carbon dioxide occurs as the surface water flows downstream, resulting in continued calcium carbonate deposition and pH reduction. Evaluation of the industrial archaeology of the site indicates that this process has probably been occurring since soon after waste tipping on the side of the valley commenced (over 100 years ago) and precipitation is continuing today. A more detailed summary of the Harpur Hill Site is provided by Milodowski et al. (2013).

A survey of the materials, both natural and anthropogenic, present at the Harpur Hill Site has identified the presence of a range materials from metals, plastics and rubbers to cellulose rich (wood and grass) matter, alluvial clays and various exogenic rocks (including sandstones, siltstones and shales). These are summarised in Table 1 and more detailed information is provided by Milodowski et al. (2013).

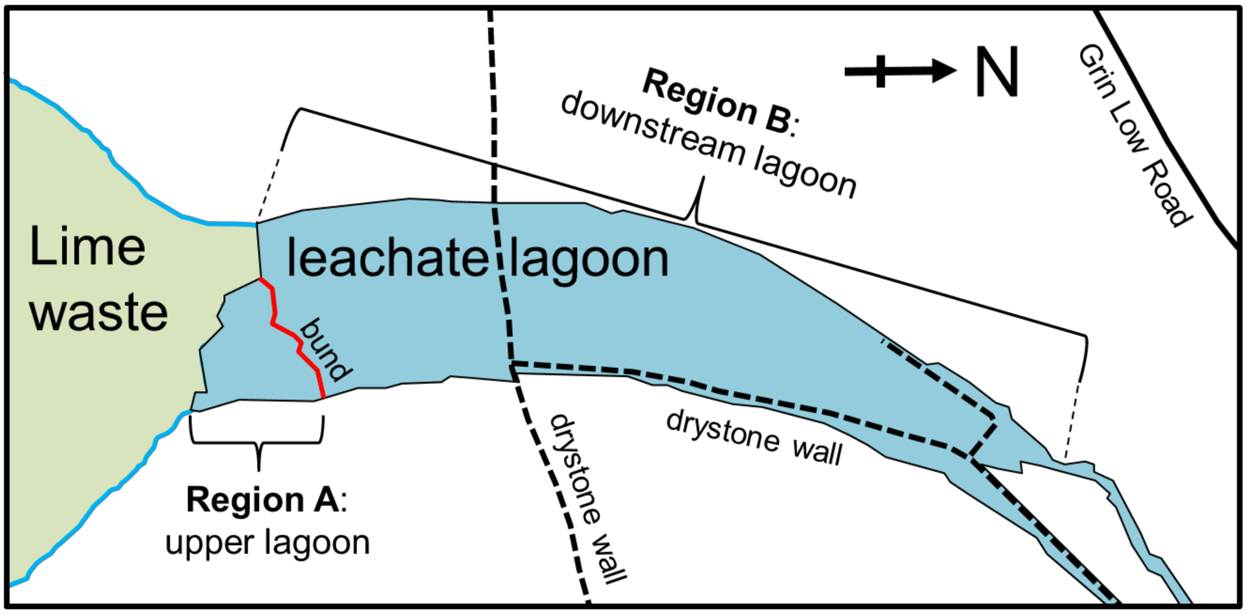

Figure 1: Schematic diagram of the Harpur Hill Site showing the main physical features.

Material Type	Materials Present	Environment	Relevance
Natural Organic Materials	Grass (cellulosic) Trees Herbaceous plants, horsetails, algae and mosses Wood Microbes	Most observed in near surface oxidizing conditions with fluctuating pH. Grass observed at base of tufa where stable reducing, pH 12.5 conditions present.	Most of these materials are in environments not relevant to a cementitious GDF utilizing large quantities of OPC at an early stage in its evolution.
Metals and metallic materials	Copper metal Lead metal Gold metal Aluminium alloy Various steels including galvanised steel Brass Plastic coated steel and copper metal	All observed under near surface oxidizing conditions with fluctuating pH. Steels and probably copper and brass present in stable reducing, pH 12.5 conditions.	
Industrial materials and waste products	Bricks Concrete Clinker (lime and silicate) Part burnt coke and coal Glass and various kiln glazes	All observed under near surface oxidizing conditions with fluctuating pH.	
Geological materials	Sandstone Clays, common rock forming silicates etc Limestone	Most observed in near surface oxidizing conditions with fluctuating pH. Clay observed at base of tufa where stable reducing, pH 12.5 conditions present and other materials likely to be present under these conditions.	
Plastics and rubber	Polythene Polystyrene Polyethylene Terephthalate Bitumen Rubber	All observed under near surface oxidizing conditions with fluctuating pH.	
Fluids	Shallow $Ca(OH)_2$ oxidising Deeper $Ca(OH)_2$ reducing Ephemeral highly localised pH 13 Fresh $Ca\text{-}HCO_3$ type pH 7-8 streamwater and localised springs		
Other	Newspaper	Observed under near surface oxidizing conditions with fluctuating pH.	

Table 1: Summary of the materials and pore fluid types present in the highly alkaline leachate and tufa deposits at the Harpur Hill Site.

Most of the materials listed in Table 1 are either not representative of materials within a cementitious GDF, or are not present in geochemical conditions relevant to those within the GDF environment or the ADZ in the surrounding host rock. The main exceptions to this are the alluvial clays, and also potentially some of the steel and cellulosic materials (if they can be appropriately located and sampled within reducing parts at the base of the highly alkaline lagoon). These materials all occur in abundance at Harpur Hill.

In contrast, other metals and materials may be of interest but they all occur in near surface oxidizing conditions, where pH shows extreme fluctuations from pH 7 to around pH 12 in response to rainfall/snow melting events. It is possible that some of these other metals and materials occur in more stable reducing and highly alkaline conditions at the base of the lagoon but their very low abundance render it impractical to locate, sample and study them in relevant environmental conditions on the site. This near surface environment with oxidising conditions and large pH fluctuations variations is irrelevant to a deep GDF environment. The context and appropriateness of analogue materials is discussed more fully in Section 2.

1.5 SITE ACCESSIBILITY

The majority of the lagoon at Harpur Hill is owned by Countess Cliff Farm. The farmer (Mr Poole) is amenable to allowing ongoing research activities using access across his land. A formal access arrangement would need to be agreed with him in the event that any large on-site research projects are initiated or for large scale sampling activities that may require machine access across his land (which would require demolition and reinstatement of dry stone walls) or significant disturbance to the site.

Ownership of the remainder of the site and the lime waste tips is uncertain and would need to be established to enable a formal approach to be made to the owners before major activities could be undertaken on these parts of the site.

2 The analogue context of Harpur Hill

This section focuses on features and processes at the Harpur Hill Site that could potentially contribute to providing enhanced confidence in demonstrating understanding of processes relevant to a UK GDF. It must be understood that Harpur Hill is ***not*** an analogue of an entire GDF. Nevertheless, some aspects of the geochemical environments and the associated processes influencing the behaviour of materials present within these environments may be analogous to particular components and processes within specific cementitious GDF systems in fractured crystalline rock ("higher strength rock" as defined in NDA, 2010) and clay host rock ("lower-strength sedimentary rock" as defined in NDA, 2010). The Harpur Hill Site is not relevant to halite or other evaporite host rocks ("evaporite" as defined by NDA, 2010). Thus, in considering the potential of the Harpur Hill Site to provide analogue insights into aspects of long term GDF performance, it is ***essential*** to consider the materials present, the geochemical environments, and the processes operating at Harpur Hill in the context of an evolutionary model of a GDF in both time and space.

The accepted, commonly used model for the evolution of pH within the near field of a cementitious GDF, as a function of time, is illustrated in Figure 2 assuming that an Ordinary Portland Cement (OPC) type cement composition will be used (based on Atkinson et al., 1985). It must be emphasised that the timescale assumes a simple mixing tank model of the near field and specific host rock characteristics. Figure 3 illustrates the evolution of the geochemistry within the ADZ in the host rock as a function of distance (based on Linklater, 1998), assuming very simple solute transport and rock/water interactions. In addition, some of the features, environments and processes operating at Harpur Hill, are compared with the timescale and regions of influence for major GDF relevant processes in Figure 2 and Figure 3. This provides a basis for the suitability of the Harpur Hill Site to be evaluated in the context as an analogue for the evolution of components of a cementitious GDF system.

2.1 MICROBIAL ACTIVITY

Microbial activity in the GDF and far-field will be closely linked after closure to the degradation of organic matter and the availability of carbon. The first ca 10^4 years within the near field and proximal ADZ (i.e. region of the ADZ immediately adjacent to the GDF) will be dominated by young cement leachate (YCL) (K-Na-Ca-OH) porewater with a pH >13. This will be followed by $Ca(OH)_2$ dominated porewater maintained at a pH 12.5 extending to at least 10^5 years (Figure 2). Some laboratory and natural system studies have suggested that the upper limit for significant microbial activity is around pH 11.5 (Sturr et al., 1994; Sorokin et al., 2001; Sorokin, 2005; Bassil et al., 2014). However, other research at natural hyperalkaline sites (e.g. Oman, Maqarin (Jordan), Cyprus) clearly demonstrates that alkaliphilic microorganisms can survive to above pH 12.5 (Bath, 1988; Alexander, 1992; Linklater, 1998; Smellie, 1998; Alexander and Milodowski, 2011; Rizoulis et al., in press). The principal factors governing microbial activity are the availability of energy and nutrient sources (Alexander, 1992; West et al., 1992; West and Chilton, 1997; Linklater, 1998). Above pH 11.5 the rate of microbial activity will be slower (pertinent to laboratory studies) but over GDF safety case timescales microbial activity may still contribute significantly to the geochemical evolution of the GDF, including the degradation of cellulose and other organic materials, and the corrosion of metals (e.g. steel).

In the context of the geochemical evolution of a GDF (Figure 2 and Figure 3), the early very high-pH stage (up to pH 13.5), associated with a YCL, is not represented at the Harpur Hill Site. The alkaline leachate at Harpur Hill is $Ca(OH)_2$ type leachate (pH up to 12.5) resulting from the dissolution of residual lime and portlandite in the lime clinker. Consequently, the Harpur Hill Site is not an appropriate analogue to study the biogeochemistry of the GDF, or the proximal ADZ, because the GDF evolution up to about 10^4 years post closure will be dominated by YCL fluids. The chemistry of the Harpur Hill Site is more analogous to the intermediate cement leachate (ICL) ($Ca(OH)_2$-dominated) stage.

With regard to understanding the degradation of cellulose and other organics within the GDF, it seems likely that much of this will have already taken place before the ICL stage (Figure 2) through a combination of microbial degradation and abiotic alkali degradation. Thus, although cellulosic materials are present at Harpur Hill (Milodowski et al., 2013), there may be only very limited relevance in studying the biodegradation of these materials in the $Ca(OH)_2$ leachate.

There may be some merit of the Harpur Hill Site as an analogue for understanding the impact of microbiological processes on the corrosion of metals. Microbial activity may have a significant influence on the corrosion of metals in the GDF. The corrosion is expected to occur during the YCL stage but may continue through the ICL stage. Harpur Hill may present an opportunity to investigate the impact of microbial activity on metal corrosion during this stage. Steel is the most likely metal that will have any application from Harpur Hill. However, its relevance depends entirely on proving that suitable samples of relevant metals can be found within the deeper, reducing parts of the site (i.e. at the interface between the highly alkaline lagoon sediments and the underlying alluvial clay). Locating, appropriate sampling and sample preservation of these materials is likely to be challenging.

Generic study of the microbiology of the highly alkaline leachate system at Harpur Hill could provide further useful insights into the pH tolerance of microbes. However, work to date on the site has focussed on the microbiology of the near surface sediments (e.g. Bassil et al; 2014), which are oxidizing and subject to large pH fluctuations in response to rainfall and snow-melt conditions. This is unrealistic for comparison with the environment within and around a deep GDF, where conditions will be stable and reducing soon after closure, and will change only very slowly over millennia. Although this might be relevant for near surface disposal, such as the UK Low Level Waste Repository, any useful analogue study of the geomicrobiology for application to a deep GDF would necessarily have to focus on the interface between the highly alkaline lagoon sediments and the underlying alluvial clay, where it has been demonstrated that conditions are reducing and maintain a constantly high pH (Burke et al., 2012; BGS unpublished data).

The Harpur Hill Site could also potentially provide a useful analogue insight into the microbiology of the distal ADZ, beyond the path-length scale influenced by the very high pH YCL (Figure 3). Here, the volumetrically smaller YCL fluid plume will have been depleted and "overstepped" by the much greater volume of $Ca(OH)_2$ dominated leachate. In the distal regions of the ADZ, microbes may potentially be active and utilising soluble isosaccharinic acid (ISA) and other organic degradation products leached from the GDF. The Harper Hill Site is analogous to this situation, in regard to the evolution of the GDF in time and space. However, research would again have to focus on the biogeochemistry of the deeper, reducing parts of the site.

2.2 CELLULOSE DEGRADATION

The key issue with regard to cellulose degradation is the influence of cellulose degradation products (CDPs), such as ISA and other smaller organic molecules, on radionuclide migration. These CPDs may form soluble complexes with radionuclide species and enhance the mobilization and migration of radionuclides from the GDF.

It seems likely that most of the cellulose and other organic materials will have broken down by about 10^4 years, as a result of microbial and abiotic decomposition during the very high pH YCL stage (pH >13). In this context, the decomposition of cellulosic materials (wood, grass) in the Harpur Hill Site in the $Ca(OH)_2$ leachate is not relevant to the early cellulose degradation influence by a YCL (K-Na-Ca-OH) chemistry in the GDF.

2.3 COLLOID FORMATION AND MIGRATION

Colloid formation and transport still represent a significant uncertainty in the safety case. To date there have been no studies on the nature of colloids or their behaviour in the highly alkaline leachate at Harpur Hill. The chemistry of the Harpur Hill leachate would only be relevant to either the chemistry of the intermediate cement leachate (ICL) and old cement leachate (OCL) stages in the fluid evolution around a GDF (Figure 2), or to the distal ADZ (Figure 3), where fluid chemistry is dominated by interactions with $Ca(OH)_2$. For practical reasons, it is likely that any colloid transport studies at Harpur Hill would only be feasible in the shallow surface drainage stream. Here conditions are oxidizing, and consequently, are unlikely to represent the behaviour of colloids under reducing conditions in a deep GDF, particularly with regard to redox-sensitive species.

2.4 RADIONUCLIDE BEHAVIOUR

Radionuclide solubility, speciation and transport are a major concern through the lifetime of a repository. The Harpur Hill Site can offer only limited potential as an analogue to study the long-term behaviour of radionuclides within the context of a cementitious GDF or the associated ADZ.

The background limestones are notably very pure; a factor determining why these rocks are currently worked in the area as a source of high-purity $CaCO_3$ for the chemical industry. The lime clinker spoil, which represents the “source-term” for the $Ca(OH)_2$ leachate contains other materials, such as part-burnt shale, impure coal and coal ash, within which analogue trace metals (such as U, Th, Se, Co, Ni) may occur in addition to lime clinker from the kilns. However, there are currently no data available on the chemistry of the lime waste to define its potential as a source term for these elements. The chemistry of the highly alkaline leachate at Harpur Hill has been analysed as part of the independent BGS research on the site. Determined by inductively-coupled plasma - mass spectrometry, these data show that the leachate contains extremely low concentrations of analogue elements such as U, Th, Ni, Co, Se and REEs; Cs, Sr and Ba are present as significant trace elements.

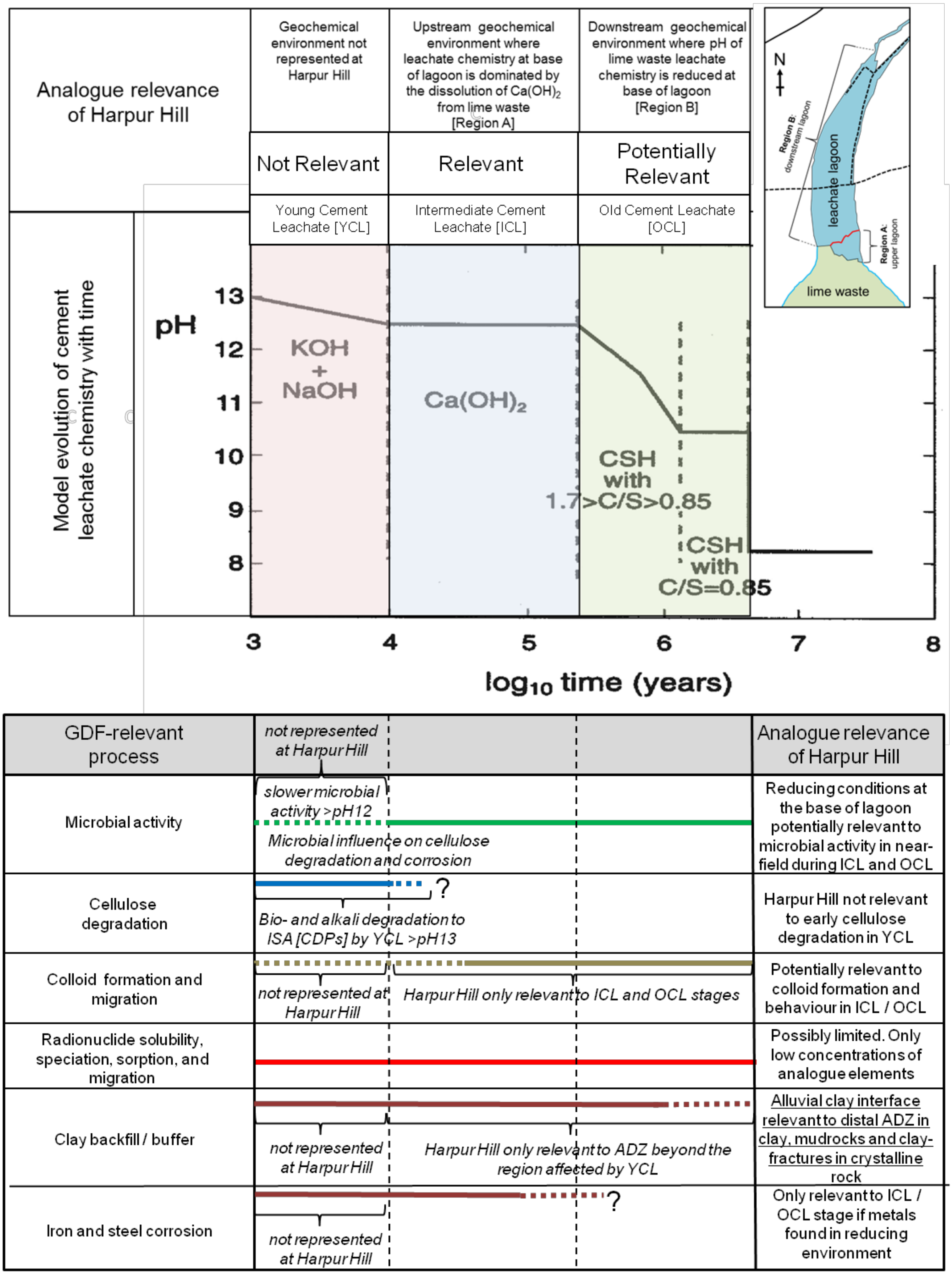

Figure 2: Model of the evolution of pH within the near field of a cementitious GDF as a function of time (based on Atkinson et al., 1985), compared with the timescale and regions of influence for major GDF relevant processes and features of the Harpur Hill Site.

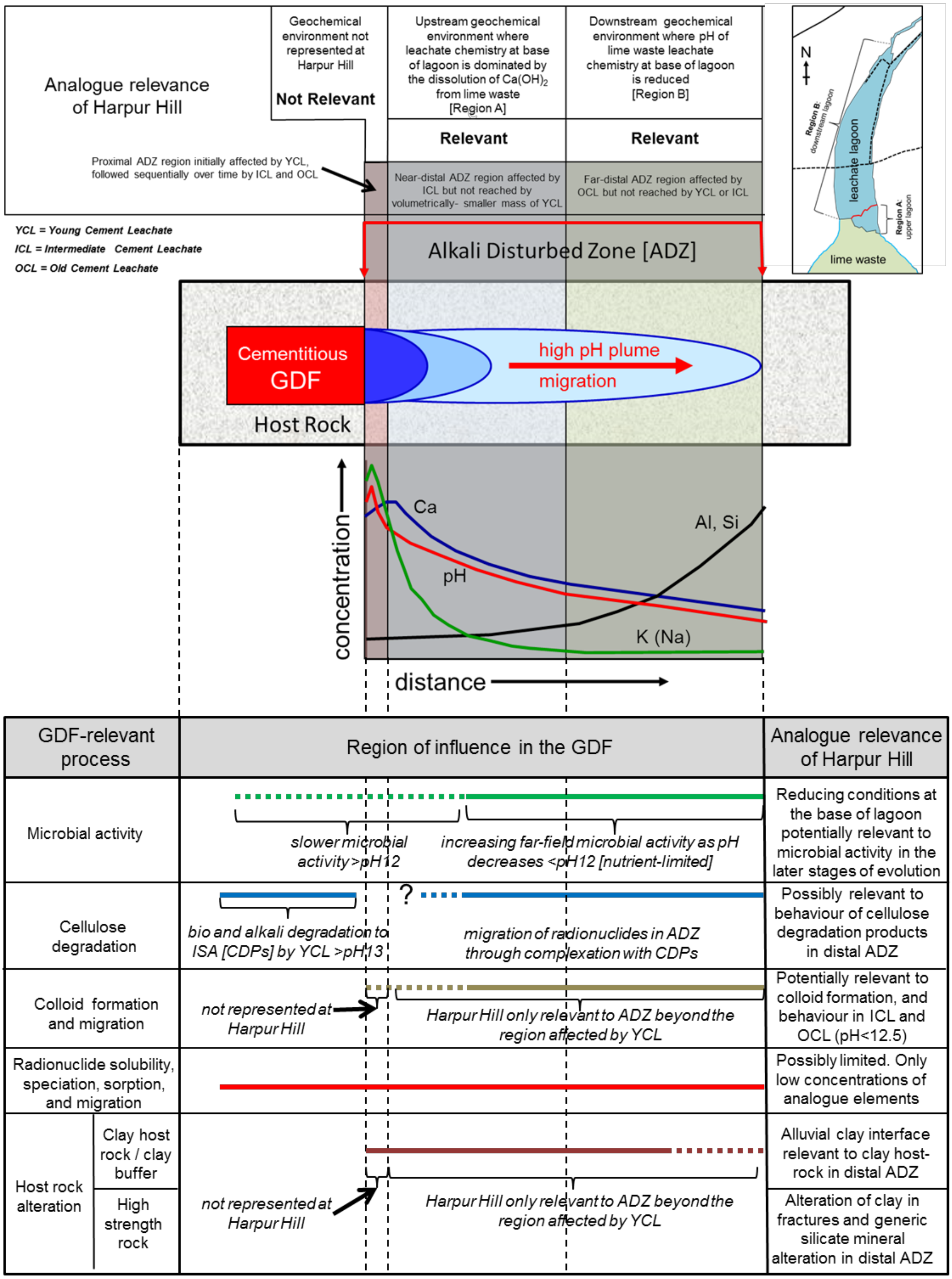

Figure 3: Model of the evolution of the geochemistry within the ADZ as a function of distance (based on Linklater, 1998), compared with the timescale and regions of influence for major GDF relevant processes and features of the Harpur Hill Site.

2.5 HOST-ROCK ALTERATION

As discussed earlier, the Harpur Hill Site represents the $Ca(OH)_2$-dominated ICL stage in the near field (Figure 2 and more distal regions of the ADZ (Figure 3). The earlier, YCL stage is not represented at Harpur Hill. In the proximal ADZ region, the host rocks for a GDF will be affected and “pre-conditioned” by interaction with the YCL *before* they “see” the ICL. This alteration is not represented at Harpur Hill. The Harper Hill Site is analogous to the more distal regions of the ADZ, where the volumetrically smaller YCL fluid will have been depleted and “overstepped” by the much greater volume of $Ca(OH)_2$ dominated leachate. Here, the intermediate cement leachate will interact directly with the host rock.

In this context, the interactions between the lime waste leachate at the interface between the highly alkaline lagoon (or at the base of the waste tip) and the underlying alluvial clays at Harper Hill could provide a potentially good analogue to study the mineralogical alteration of a clay host rock by cement pore fluids, or for the alteration of clay-filled (or clay-lined) fractures in fractured crystalline rock. This is relevant to the generic understanding of clay alteration by pH 12.5 $Ca(OH)_2$ fluids in more distal regions of an advective flow system in fractured crystalline or shale/mudstone host rocks, or the more distal parts of a diffusive alteration profile in plastic or indurated clay host rocks.

Clay mineral alteration by highly alkaline fluids is kinetically slow, and little alteration has been observed over the timescale of most laboratory experiments. Study of the alteration of clay by the pH 12.5 pore fluids at Harper Hill would extend understanding of the alteration of clay over timescales of up to 100 years. This is comparable to, or extends, our knowledge from other analogue studies, such as those looking at diffusion of cement pore fluids from cement-lined tunnel walls into the adjacent clay host rock in the Tournemire Tunnel (Savage, 2011).

The relevance of the Harpur Hill Site to alteration of crystalline fractured host rock by cement leachate from a GDF is limited. No appropriate rock types are present at Harpur Hill, other than loose blocks of exogenic Permo-Triassic sandstone, which could provide a quartz-feldspar-rich material. However, these blocks are only present in the shallow near surface environment that is not relevant to a GDF. Study of the mineral alteration in alluvial clays underlying the highly alkaline leachate lagoon could provide generic information of silicate-interaction with ICL. But again, this would represent the alteration anticipated within the distal ADZ rather than the proximal ADZ.

2.6 CLAY BUFFER – CLAY BACKFILL ALTERATION

The context of the Harpur Hill site as an analogue for investigating the alteration of clay backfill materials or clay buffer materials is broadly similar to that described for the alteration of clay host rocks (Section 2.5). In this regard, the Harpur Hill Site could furnish insights into the alteration behaviour of clay buffer materials in the more distal parts of an alkaline pore fluid diffusion profile, beyond the region influenced by interaction with the early YCL.

2.7 IRON AND STEEL CORROSION

Iron and steel materials are abundant within the Harpur Hill Site. Most of the materials were observed in the oxidizing near surface environment, where conditions are not relevant to those in a GDF. Most iron and steel corrosion in the GDF is expected to occur within 10^4 years but some metal may persist beyond this. During this time, the chemistry of the GDF will be strongly influenced by the YCL that is not represented at Harpur Hill (Figure 2). However, if the iron and steel canisters persist into the period when the groundwater in the repository is buffered by $Ca(OH)_2$, then Harpur Hill may potentially provide an analogue where by the corrosion of iron and steel under these conditions could be studied. In this regard, it would be essential to examine these metals from the reducing environment at the base of the highly alkaline lagoon. Although the assessment of the materials present on site only recorded near surface iron and steel artefacts (Milodowski et al., 2013), it is very likely that iron and steel can be found in parts of the site where the chemistry is more appropriate to those anticipated in a GDF though appropriate sampling and sample preservation may be challenging.

2.8 BENEFITS AND LIMITATIONS OF THE HARPUR HILL SITE

During this assessment the relevance of the Harpur Hill Site to a range of GDF evolution scenarios or 'stages' and cross cutting themes was considered. This consideration included aspects of the analogue source term, waste package and the EBS components, biogeochemical, microbiological and radionuclide behaviour of the ADZ and freshwater interaction zone. The Features, Events and Processes (FEPs) involved in each of the chosen stages of an evolving GDF ('Operational phase', 'Early emplacement', 'Early post closure' and 'Later post closure') are summarised in Table 2, together with an assessment of the relevance of the Harpur Hill Site to a cementitious GDF.

While the precise timing of specific events during the development and evolution of the Harpur Hill Site cannot be determined, most of them can be fixed to specific decades or better. The site could provide an opportunity to study highly alkaline environments at a timescale between laboratory based experiments and natural analogue studies with the potential to demonstrate processes over timescales of up to about 100 years.

The Harpur Hill Site is only partially characterised and is not yet fully understood. The redox complexity and pH distribution make understanding the Harpur Hill Site complex. This is particularly the case in the surface and near surface parts of the site where rain and surface water inflows result in fluctuating pH and varying degrees of dilution. Where measured at depth in the southern part of the site, conditions are consistently reducing and the pH stable at about 12.5. Appropriate sampling has not yet been undertaken and there is currently limited evidence for microbial activity at depth where conditions are stable so uncertainty remains about whether microbes are present and/or are dormant under these conditions. If microbial activity is confirmed at Harpur Hill under reducing conditions and pH >12, the site may be an appropriate analogue for aspects of a mudrock hosted GDF or one using clay based backfills to develop understanding of the impacts of microbial activity in areas more distant from emplaced cementitious wastes or using low pH cement based materials.

The site is not a suitable analogue of the stages of repository evolution for a GDF where OPC is used for grouts, backfills and structural concretes because the early stages (to ca 10^4 years) of GDF evolution in this case will be dominated by YCL with a pH of ca 13.5.

In a cementitious GDF it is likely that most organic material degradation will occur at an early stage (within the first few thousand years) when pH is >13 and conditions are reducing. The surface location of the Harpur Hill Site limits options and the site does not represent the biogeochemical conditions necessary to replicate this environment at this stage when pH >13 YCL dominate. Similarly, most steel corrosion is likely to occur during this stage of GDF evolution with reducing conditions and pH >13 which are not represented at the Harpur Hill Site.

Although steel and other artefacts are present in an alkaline environment, the materials observed to date are all located within the oxidising surface environments where pH fluctuates by several orders of magnitude. For studies to be relevant, the artefacts would need to be found within the constant highly alkaline and reducing environments at the base of the lagoon deposits or the lime waste spoil. While it is feasible that various materials will be present in this environment, this has not yet been demonstrated and there are likely to be practical difficulties locating these and carrying out appropriate sampling; preservation will be challenging.

GDF 'stage'	Timeframe post closure (y)	FEPs of interest that could be present at Harpur Hill	Areas of the Harpur Hill Site considered	Potential materials and processes present	What Harpur Hill or analogue research has been done/is available?	Relevance
Operational (surface storage or operating as an open repository (pre-backfill)	N/A	• Conditioned waste form (e.g. wet grouted steel boxes) • Oxidising environment (in air) • Temperature controlled? • Light? • Carbonation? • Corrosion (internal/external)? • Biodegradation? • Gas production and consumption • Humidity	Base of the waste heap to south of site	• Near surface interactions • Corrosion • Saturated – unsaturated interface (e.g. metals, cellulose degradation, plastics and rubbers, wood and glass).	Bartiera et al. (2013), Soler (2013), Lavielle et al. (2012), Tremosa et al. (2012), Gaboreau et al. (2011), Savage (2011).	Grouted waste in surface storage where oxidising conditions prevail may develop leachate with pH >13. Metals corrosion and cellulosic waste degradation will occur. During this stage a GDF is unsaturated or recently re-saturated and will be oxidising. While the oxidising conditions and some of the materials present at the site are relevant, the $Ca(OH)_2$ dominated alkaline fluid is different to the leachate in recently cement grouted waste or recently emplaced L/ILW in a GDF. High alkalinity will inhibit microbial activity. The Harpur Hill Site is not a suitable analogue for this stage.
Early emplacement - unsaturated (backfilled gallery with cement based material) Very high pH (c. 13)	$0\text{-}10^2$	• Grouted waste form • Reducing O_2 levels with time • Increasing groundwater saturation with time • Carbonation? • Corrosion (internal/external)? • Biodegradation? • Temperature effects? • Gas production and consumption	Base of the waste heap to south of site	• Interactions at depth • Corrosion • Saturated zone (e.g. metals, cellulose degradation, plastics and rubbers, wood, glass).	Bartiera et al. (2013), Soler (2013), Lavielle et al. (2012), Tremosa et al. (2012), Gaboreau et al. (2011), Savage (2011)	During this stage a GDF is re-saturating or recently re-saturated and reducing conditions will develop as all free oxygen is rapidly consumed by corrosion and biodegradation processes. The GDF will be dominated by YCL fluids (pH >13) for which the Harpur Hill Site is not an appropriate analogue because there are no areas with assured pH >13 (YCL dominated) and because most of the materials present at the site, e.g. for corrosion studies, are in an oxidising environment.

Table 2: Summary of GDF evolutionary 'stages', associated Features, Events and Processes, and relevance to a cementitious GDF.

GDF 'stage'	Timeframe post closure (y)	FEPs of interest that could be present at Harpur Hill	Areas of the Harpur Hill Site where FEPs may occur	Potential materials and processes present	What Harpur Hill or analogue research has been done/is available?	Relevance
Early post closure – re-saturated (Back filled gallery with cement based material) Very high pH (young cement leachate c. pH 13, 10^{2-4} y timescale)	10^2-10^4	• Grouted waste form • Anoxic (except immediately post closure) • Groundwater saturated (except immediately following closure) • Carbonation? • Corrosion? • Biodegradation? • Temperature effects? • Gas production and consumption	Base of the waste heap to south of site	• Interactions at depth • Corrosion • Saturated zone (e.g. metals, cellulose degradation, plastics and rubbers, wood, glass, geological materials).	Bartiera et al. (2013), Soler (2013), Lavielle et al. (2012), Tremosa et al. (2012), Gaboreau et al. (2011), Savage (2011), Khoury and Al-Zoubi (2014), Khoury (2012), Maqarin (Alexander 1992, Linklater 1998, Smellie 1998, Pitty and Alexander 2011)	During this stage a GDF has re-saturated and fully reducing conditions will developed. The GDF will be dominated by YCL fluids (pH >13) for which the Harpur Hill Site is not an appropriate analogue because there are no areas with assured pH >13 (YCL dominated) and because most of the materials present at the site, e.g. for corrosion studies, are in an oxidising environment.
Later post closure (Back filled gallery with cement based material) Reducing pH (intermediate cement leachate (portlandite buffered) pH12.5 10^{4-5} y timescale then evolved cement leachate (CSH buffered) c. pH 10, 10^{5-6} y timescale)	10^4-10^{5+}	• Grouted waste form • Anoxic groundwater • Carbonation? • Corrosion (internal/external)? • Constant *in-situ* temperature	Interface between high alkaline lagoon sediments/lime waste tip and underlying clay in the south-west end of the site	• Interactions between clays and alkali fluids in the deep reduced saturated zone, • Corrosion (e.g. metals, glass).	Savage (2011), Khoury and Al-Zoubi (2014), Khoury (2012 Maqarin (Alexander 1992, Linklater 1998, Smellie 1998, Pitty and Alexander 2011)	An evolved cementitious GDF and ADZ will be dominated by CaOH leachate with a pH ca12.5 under reducing conditions and aspects of the Harpur Hill Site are a potential analogue for this stage. The extent and nature of alteration of clay by the pH 12.5 fluids under reducing conditions may be applicable, particularly to a mudrock hosted GDF with large amounts of cement based materials. By this stage it is probable that all cellulosic waste and most metals within L/ILW will have degraded and the relevance of microbial processes, if any, at this stage are highly uncertain. The site is not an analogue for understanding microbial processes related to an evolved cementitious GDF (discussed in Section 2.1).

Table 2: Summary of GDF evolutionary 'stages', associated Features, Events and Processes, and relevance to a cementitious GDF. (cont.).

Once clay mineralogy is determined the site may be considered suitable for studying clay/pH 12.5 leachate interactions relevant to an evolved (10^4+ years) cementitious GDF or any GDF design using low pH concrete (e.g. for vault or tunnel linings).

2.9 THE POTENTIAL OF THE HARPUR HILL SITE FOR SELECTED STUDIES IN THE CONTEXT OF A CEMENTITIOUS GDF

The Harpur Hill Site has been assessed for its suitability for undertaking a programme of analogue studies in respect of some aspects of a cementitious GDF. These are summarised in Table 3, which also provides a critique of the suitability of the potential studies in relation to improving understanding of aspects of a cementitious GDF.

Possible studies	Possible applicable cementitious GDF system component/ process	What could we learn? What could this add to the knowledge base?	Suitability of the processes occurring at Harpur Hill Site as an analogue for the processes occurring in a cementitious GDF	
			FEPs of possible relevance	**Critique of Harpur Hill Site FEP's in cementitious GDF context**
Investigation of *in-situ* microbially mediated biogeochemical processes occurring in a high pH environment.	Several microbially mediated processes will occur in an L/ILW GDF near field. These include: • Gas generation/ consumption; • Corrosion of metals; and, • Biodegradation of organic waste.	What relevant microbial groups are active under conditions similar to those in a GDF and what factors constrain their level of activity. If autotrophic hydrogen metabolising bacteria can consume hydrogen at this pH, then potentially credit can be taken by this process for reducing the hydrogen issue. Understanding the role of micro niches in allowing microbial activity under high pH conditions.	It is believed that there have been 100+ years of microbial evolution with the highly alkaline fluid associated with the Harpur Hill Site. The microbes that have evolved to tolerate the alkaline fluids in the site may have properties similar to those that will persist in a GDF after closure.	Redox complexity and the pH distribution make understanding this site complex. Most of the recorded microbial activity is in the near surface (oxidizing) parts of the site in areas with fluctuating pH and varying degrees of dilution that intermittently provide conditions more conducive to microbial growth (pH <11.5). This could be of relevance to a cementitious near surface facility such as the UK Low Level Waste Repository in west Cumbria but not a GDF. There is some evidence at the site for microbial activity at depth where conditions are reducing and pH ca 12.5 (e.g. Burke et al., 2012). Because the site is not a suitable analogue of the stages of repository evolution for an OPC based GDF when these processes are significant, no further work is suggested. If the use of low pH cement based grouts, backfills or structural concretes are considered for L/ILW or HLW GDF development the site may merit reconsideration as a suitable analogue for the study of relevant microbiological processes.

Table 3: Critique of selected studies that could be undertaken at the Harpur Hill Site in the context of a cementitious GDF.

Possible studies	Possible applicable cementitious GDF system component/ process	What could we learn? What could this add to the knowledge base?	Suitability of the processes occurring at Harpur Hill Site as an analogue for the processes occurring in a cementitious GDF	
			FEPs of possible relevance	**Critique of Harpur Hill Site FEP's in cementitious GDF context**
Interaction of high-pH leachate with clays.	Alteration of the clays present by interaction with highly alkaline fluid is relevant to L/ILW with a cement based grout/backfill – or any GDF containing extensive structural concrete - in a mudstone or clay host rock. The pH and chemistry at Harpur Hill is relevant to an evolved cement buffered L/ILW GDF and interactions between low pH concretes and clay rich host rocks.	There have been 100+ years of interaction with a thick clay layer under near surface, reducing conditions. The clay alterations can be established with development of the alteration zone under highly alkaline cement fluid conditions.	Sampling has been demonstrated to be possible by research funded by the BGS and others. There is a significant thickness of clay across at least the upper part of the site that is under reducing conditions. The interaction period at Harpur Hill is longer than for any URL or laboratory based experiment carried out to date. Harpur Hill is comparable in timescale to the Tournemire analogue, but has a significantly greater amount of alkaline fluid present. Harpur Hill could represent alteration at greater distance in the distal ADZ of an evolving GDF system where the influence of the volumetrically smaller early high pH/high- YCL will be less significant than the $Ca(OH)_2$-dominated stage which is volumetrically greater, and consequently, where the host rock will not have been conditioned by prior interaction with YCL. May be applicable to cement grouted wastes in storage and cementitious LLW disposal in shallow/surface sites particularly if low pH cements are utilised.	For investigations into clay/alkaline interactions alone, sites other than Harpur Hill may be more suitable. Clay mineralogy not yet characterised. In the proximal near field, i.e. the rock volume closest to a GDF for a cementitious GDF, the host rock will have been affected by alteration resulting from the presence of early cement leachate (pH >13) and Harpur Hill is not an analogue for this. Once clay mineralogy is determined the site may be considered suitable for studying clay/pH 12.5 leachate interactions relevant to an evolved (10^4+ years) cementitious GDF or any GDF design using low pH concrete (e.g. for vault or tunnel linings).

Table 3: Critique of selected studies that could be undertaken at the Harpur Hill Site in the context of a cementitious GDF. (cont.).

Possible studies	Possible applicable cementitious GDF system component/ process	What could we learn? What could this add to the knowledge base?	Suitability of the processes occurring at Harpur Hill Site as an analogue for the processes occurring in a cementitious GDF	
			FEPs of possible relevance	**Critique of Harpur Hill Site FEP's in cementitious GDF context**
Interaction of high-pH cement leachate on geomicrobiology and biogeochemistry in clays.	The viability of microbial activity at pH >12 under reducing conditions can be determined which may affect mudrock host rocks and clay based backfills in galleries more remote from cementitious waste forms.	Does microbial activity constrain the interaction between clays and highly alkaline fluids, significantly changing the alteration rates or products?	If appropriate sampling at the site identifies evidence for microbial activity at depth where conditions are reducing and pH is ca 12.5 the site has the potential to be used to generically study the viability of microbiological activity at pH >12.	In a GDF most microbial activity and organic interaction will be in the near field, particularly that adjacent to the GDF. Harpur Hill does not represent the biogeochemical conditions necessary to replicate this environment at the stage when organic wastes etc are present (up to 10^4 years) when pH >13 YCL dominates. There is some evidence at the site for microbial activity at depth where conditions are reducing and pH ca 12.5 (e.g. Burke et al., 2012). Because the site is not a suitable analogue of the stages of repository evolution when these processes are significant no further work is suggested. If microbial activity is confirmed at Harpur Hill under reducing conditions and pH >12 the site may be an appropriate analogue for aspects of a mudrock hosted/clay based backfilled GDF to develop understanding of the impacts of microbial activity.

Table 3: Critique of selected studies that could be undertaken at the Harpur Hill Site in the context of a cementitious GDF. (cont.).

Possible studies	Possible applicable cementitious GDF system component/ process	What could we learn? What could this add to the knowledge base?	Suitability of the processes occurring at Harpur Hill Site as an analogue for the processes occurring in a cementitious GDF	
			FEPs of possible relevance	Critique of Harpur Hill Site FEP's in cementitious GDF context
Cellulose degradation in a highly alkaline environment.	Understanding of fate of cellulose degradation products (CDP) in an alkaline environment.	Above about pH 12, microbial activity is assumed to be limited. In the GDF cellulose can break down to ISA (a CDP) abiotically during the initial very high pH stage (pH 12-pH 13). ISA will then be solubilised and flushed out of the GDF fairly early-on. ISA can be utilised by microbes but this is likely to be in the ADZ region where the pH falls below about pH 11.5 permitting microbial activity.	There is grass (cellulose) at the interface where it is anoxic and wood in the site which may provide CDP in an environment representative of the distal near field of a cementitious GDF.	There is some evidence at the site for microbial activity at depth where conditions are reducing and pH ca 12.5 (e.g. Burke et al., 2012). In a GDF for L/ILW it is likely that all cellulose degradation will occur at an early stage (0 to 10^4 years) when pH is >13 and when conditions are reducing. The surface location of the Harpur Hill Site limits options. Because the site is not an appropriate analogue of the stages of repository evolution when these processes are significant no further work is suggested.

Table 3: Critique of selected studies that could be undertaken at the Harpur Hill Site in the context of a cementitious GDF. (cont.).

Possible studies	Possible applicable cementitious GDF system component/ process	What could we learn? What could this add to the knowledge base?	Suitability of the processes occurring at Harpur Hill Site as an analogue for the processes occurring in a cementitious GDF	
			FEPs of possible relevance	**Critique of Harpur Hill Site FEP's in cementitious GDF context**
Corrosion Studies.	The long term development of micro niches in which microbes are able to control their environment and the impact of these on corrosion process and hydrogen generation.	It is generally assumed that the corrosion rates of most metal wastes and containers will be very slow under highly alkaline, reducing conditions. Is there any indication that the presence of microbes could increase such corrosion – e.g. by production of lower pH micro niches.	Mild and other steels are present in the alkaline environments at Harpur Hill, and potentially relevant to some of the steel in a GDF.	There is uncertainty about how long materials have been in oxidising and reducing environments? While ferrous metals could be located in a reducing environment at Harpur Hill appropriate sampling and preservation will be challenging. Harpur Hill is not a saline site so is of limited relevance to a deep site in the UK. Although steel artefacts are present in an alkaline environment, the materials observed to date are within oxidising surface environments where pH fluctuates by several orders of magnitude. For corrosion studies to be relevant steel artefacts would need to be found within the constant highly alkaline and reducing environments at the base of the lagoon deposits or lime waste spoil. It is feasible that steel in this environment may potentially be present but has not been demonstrated. Because the site is not a suitable analogue of the stages of repository evolution when these processes are significant no further work is suggested.

Table 3: Critique of selected studies that could be undertaken at the Harpur Hill Site in the context of a cementitious GDF. (cont.).

Possible studies	Possible applicable cementitious GDF system component/ process	What could we learn? What could this add to the knowledge base?	Suitability of the processes occurring at Harpur Hill Site as an analogue for the processes occurring in a cementitious GDF	
			FEPs of possible relevance	**Critique of Harpur Hill Site FEP's in cementitious GDF context**
Modelling, Interpretation and Application of Harpur Hill Research.	Pre-study predictive modelling should be undertaken to derive conceptual models of process and expected outcomes. Experimental data can be utilised to enhance models and to derive process understanding of GDF evolution.	Appropriate predictive modelling should be carried out prior to any other studies to derive conceptual models of expected outcomes. This will be important in designing sampling/testing programme etc. Post experimental data can be utilised to test the model and to derive process understanding of GDF evolution.	Test programme can be focused on important uncertainties and undertaken in a way that maximises potential.	Unless further studies are initiated no further work is suggested. If any studies are considered appropriate focused pre- and post-study modelling should be undertaken.
Harpur Hill as a resource for laboratory studies to examine microbial impacts on transport properties.			Harpur Hill is a potential source of microbes that survive at pH 12 which may be useful in undertaking laboratory based experiments on specific aspects/components of a GDF.	Is the site a suitable source? Uncertainty remains about the microbial population at depth in the tufa deposits where pH is constant and conditions are reducing. They may only be present in the near surface parts of the site where pH fluctuates significantly and where conditions are oxidising when they can hibernate when conditions are too harsh (pH >11.5) for microbial activity. Because the site is not a suitable analogue of the stages of repository evolution when these processes are significant no further work is suggested.
Site characterisation.	Acquisition of background site information and sampling will be required if any studies are undertaken to underpin the research activities. These will be specifically designed and tailored to support the research activities and, specific project requirements. Unless further studies are defined in future no activities are needed.			

Table 3: Critique of selected studies that could be undertaken at the Harpur Hill Site in the context of a cementitious GDF**.** (cont.).

3 Conclusions

Initial studies of the Harpur Hill Site suggested that it might be a suitable site for studying interactions between highly alkaline (pH >12) fluids and components of a cementitious GDF. It contains a significant volume of tufa which is being deposited from $Ca(OH)_2$ rich fluid with a pH of about 12.5. The leachate lagoon and associate tufa deposits contain a significant amount of materials, including metals, plastics and cellulosic materials that have accumulated over the years, some of which were considered to have the potential to study their interactions with the leachate over decades. The site has been used for several years as a source of alkaliphilic microbes used to perform laboratory based experiments.

While not part of this study, additional field work has been undertaken at the site, including more systematic data collection, both *in-situ* and by sampling for laboratory analysis, and the successful hand coring of the clays beneath the tufa at the southern end of the site. This has allowed a better understanding of the site to be developed which in turn has enabled a more detailed assessment to be made of the suitability of the site for analogue studies.

It should be emphasised that the Harpur Hill Site is not itself an analogue of a GDF, but that some of the features and processes occurring at the site may be analogous to some components of a GDF system. Of key importance in assessing the suitability of the Harpur Hill Site for analogue research was to compare the processes operating on different materials present in the site, with the model understanding of how the geochemistry of the GDF and its associated ADZ evolves in both time and space.

During the course of the work for this report a number of factors have become apparent that mean that the site is not an appropriate analogue for many aspects of an L/ILW GDF utilizing large quantities of cement based upon an Ordinary Portland Cement (OPC) composition. The main limitations are:

- Because the origin of the alkalinity of the site is derived from lime waste, it is at a pH of about 12.5 and dominantly calcium hydroxide - a cementitious OPC based GDF will be at a pH of about 13.5 with sodium/potassium hydroxide dominated leachate during the early stages of its evolution post closure (up to about 10^4 years) - limiting the applicability of the site to low pH cement analogue applications;
- Many of the materials observed at the site are in the surface environment where they are under oxidising conditions and experience fluctuating pH as a result of fresh water dilution from rain and surface water inputs, which are not analogous to GDF conditions; and,
- To date active microbes from deep in the tufa deposits where conditions are reducing and pH stable at >12 have been identified at the site, but the use of the site as an appropriate analogue has not yet been demonstrated.

In contrast, the site may provide a reasonable analogue for studying clay host rock or clay backfill interactions with $Ca(OH)_2$-dominated alkaline fluids at pH 12.5 in an evolved (ca10^5 years) cementitious GDF, or for the more distal parts of the ADZ and the diffusive alteration profile in a clay backfilled GDF. In this context the Harpur Hill Site represents the region of a GDF system that has interacted with an evolved $Ca(OH)_2$ cement leachate but beyond the region would be affected by interaction with a young K-Na-Ca-OH-dominated young cement leachate. The interactions observed at the Harpur Hill Site may also be relevant to GDF systems utilising low-K, low-pH cement based materials. Interactions between underlying clays on the site and the alkaline fluids under reducing conditions over a ca 100 year timescale provide the most relevant opportunity for studying alkaline alteration, rates of penetration of the alkaline fluids and, perhaps, related microbial activity in the clays as alkalinity reduces with increasing distance into the clay. While practicality of hand sampling of this material has recently been demonstrated, uncertainty remains about the clay minerals present and no sterile sampling has been undertaken for microbial analysis.

Because the site is not a good analogue for many aspects of a cementitious GDF and that there is remaining uncertainty about some of the characteristics of the site, we do not currently think that the site offers enough potential to warrant undertaking a major programme of studies based on this site and do not recommend such studies here at this stage.

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