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# Near-field/Far-field Interface of a Near-Surface Low-Level Radioactive Waste Site

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## ABSTRACT

Experimental and Modelling studies have been used to investigate the biogeochemical processes occurring at the interface zone between the near-field and far-field of the Drigg Low-Level radioactive Waste (LLW) trenches. These have led to a conceptual model of interface biogeochemistry, which has subsequently been modelled by the BNFL code known as the Generalised Repository Model (GRM). GRM simulations suggest that as organic rich leachate migrates into the far-field, iron III minerals such as iron hydroxide will dissolve, and reduced iron minerals such as siderite will precipitate due to microbial processes. Batch and column experimental studies have verified this conceptual understanding. Some unexpected processes, such as the presence of nitrate enhancing sulphate reduction, were also observed

## INTRODUCTION

The Drigg site is an operational facility for the near-surface disposal of Low-Level radioactive Waste (LLW). The site is located in north-west England and is owned and operated by British Nuclear Fuels plc (BNFL). Disposals are carried out under the terms of an authorisation granted by the UK Environment Agency. The authorisation is periodically subject to formal regulatory review. In September 2002 BNFL produced an updated post-closure safety case (PCSC) [1,2] supported by a post-closure radiological safety assessment (PCRSA) for the Drigg site.

The Drigg site includes two disposal systems: 1) An original system operated from 1959 to 1995 comprising a series of trenches excavated into glacial clays, back filled with LLW and covered with an interim water resistant cap. 2) Current disposal of compacted waste placed in steel ISO-freight containers, with void space filled with highly fluid cement based grout, and disposed of in a series of concrete vaults.

The objective of this paper is to outline the approach used in the PCRSA to assess the extent and influence of a near-field plume on the Drigg far-field. The paper will primarily consider the interface between the Drigg disposal trenches and the surrounding geosphere, however the PCRSA also considers the trench/vault and vault/geosphere interface. Experimental studies have been used to support conceptual model development, and key results are presented. The modelling results presented are focussed on establishing the extent of the interface region and the biogeochemical evolution over extended time periods that are not possible in experimental systems.

## DRIGG NEAR-FIELD / FARFIELD CONCEPTUAL MODEL

In order to demonstrate that all of the factors that could possibly affect the site have been evaluated, the PCRSA considers the Features, Events and Processes (FEPs) associated with the near-field/far-field interface in a systematic manner [2]. This systematic approach has led to the identification of key processes associated with the interface region, including changes to the chemistry of the interface due to: the addition of leachate and groundwater, microbial activity, geochemistry, and transport processes. In addition, evidence from monitoring of the near-field and far-field in the present day site has been essential in verifying that the processes postulated to occur on site are actively taking place.

In order to model the processes occurring at the interface it is essential to understand the properties and evolution of the near-field leachates that are ingressing into the far-field. Trench wastes comprise large quantities of cellulosic material (paper, cotton, and wood) and ferrous metals. The decomposition of these materials by microbial hydrolysis and corrosion [3] results in the development of anaerobic conditions within the waste.

Site specific aqueous and gaseous monitoring data and experimental studies simulating trench conditions [3] suggest that leachate will be elevated in substrates including cellulose hydrolysis products, such as acetate and volatile fatty acids (VFA). In the geosphere this organic material will be oxidised by a range of microbes including aerobic, denitrifying, fermentative, iron reducing, sulphate reducing and methanogenic bacteria depending on the presence of the relevant electron acceptors. These microbial reactions change the chemical environment at the near-field/ far-field interface, which in turn may lead to the dissolution or precipitation of various mineral phases [4].

## MATHEMATICAL MODELLING OF THE INTERFACE

It is important to understand the consequences of the conceptual processes presented above on radionuclide transport, as a part of the Drigg PCRSA. As near-field leachate compositions themselves change with time as the near-field evolves, the most effective way of analysing the complex interplay between leachate, geosphere materials and radionuclides is through modelling. In the case of the Drigg PCRSA this is done through the use of the General Repository Model (GRM).

The GRM was originally developed as a 2-dimensional finite difference biogeochemical transport code to simulate the evolving geochemistry of the Drigg near-field and in turn calculate the source term flux of radionuclides in groundwater. When configured to simulate the Drigg near-field the code is named DRINK (DRIgg Near-field Kinetic model) [5]. The results of DRINK modelling have been presented previously [6].

The code considers kinetically controlled steel corrosion, microbial induced cellulose degradation reactions and also the microbial mediated redox reactions between the product of these degradation reactions and species in groundwater (e.g. $SO_4$) and minerals in soils (e.g. $Fe(OH)_3$) [3]. The resulting pH and redox potential (pe) are used as a constraint for equilibrium speciation and mineral equilibrium calculations by a routine based on the geochemical code PHREEQE [7].

In the current work, the functionality within GRM has been used to model the biogeochemical evolution of the Drigg near-field/far-field interface as trench leachate leaves the Drigg near-field and interacts with the surrounding groundwater and geology (Figure 1).

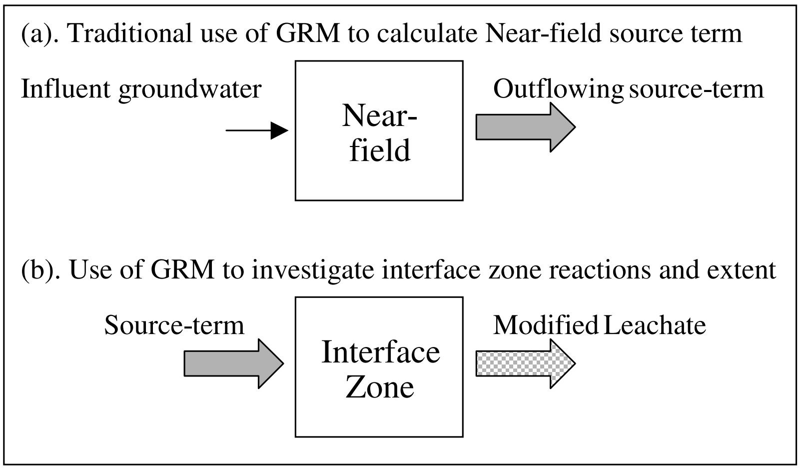

**Figure 1.** Schematic showing differing application of GRM to interface modelling

## Model Results

As the trench leachate enters into and interacts with the geosphere, the model results predict significant reaction to occur. Figure 2 shows a snap shot of acetate; $CO_2$ and immobile biomass concentrations throughout the model at 2030 years. At this time it can clearly be seen (Figure 2) that acetate is consumed close to the interface. Products of acetate utilisation include $CO_2$ which has increased from its initial level of pCO2 = 0.01 atm (Table 1) to a steady state value of $pCO_2 = 0.034$ atm, and immobile (solid) biomass, which is almost entirely located in the first few metres of the geosphere. Figure 3 shows the concentrations of mineral phases at 2030 years. Fe(OH)3A and calcite show moderate decreases in concentration from their initial inventory (Table 1), while siderite shows an increase. In addition, a new mineral phase pyrrhotite has precipitated in small quantity.

The results predict that biogeochemical reactions will not impact more than a few metres into the geosphere, however this prediction is due in part to the equilibrium nature of PHREEQE and the chemical module of GRM. In reality, reactions predicted to occur in the interface would to some extent be kinetically constrained. In turn this would lead to a broadening of the interface, for instance by allowing transport of acetate, and its utilisation in microbially mediated reactions to occur to a greater distance into the model. Conversely, addition of recharge to the model may narrow the interface due to the addition of reactive oxidising species e.g. $O_2$ and $NO_3$.

**Table 1.** Chemical input to interface simulation

| | Groundwater/ PCF concentration (mol/l) | TRENCH Leachate (mol/l) | | Groundwater/ PCF concentration (mol/l) | TRENCH leachate (mol/l) |
|---|---|---|---|---|---|
| pH | 7.35 | 5.931 | Fe+3 | 0.000E+00 | 0.000E+00 |
| Ca+2 | 2.012E-03 | 2.433E-03 | HS- | 0.000E+00 | 1.195E-04 |
| Mg+2 | 7.942E-04 | 6.057E-04 | NH4+ | 0.000E+00 | 1.240E-03 |
| Na+ | 1.271E-03 | 2.915E-03 | CH3COO- | 0.000E+00 | 4.205E-03 |
| Fe+2 | 1.185E-05 | 4.515E-04 | O2 | 0.000E+00 | 0.000E+00 |
| H4SiO4 | 1.608E-04 | 2.032E-04 | pCO2 | 1.00E-02 | - |
| Cl- | 1.340E-03 | 2.899E-03 | pN2 | 9.99E-01 | - |
| CO3-2 | 5.370E-03 | 4.091E-03 | CALCITE | 1.7346 | - |
| SO4-2 | 3.958E-04 | 1.475E-07 | SIDERITE | 0.85 | - |
| NO3- | 1.100E-04 | 1.000E-20 | FE(OH)3A | 0.4657 | - |

(NOTE: Na and K summed)

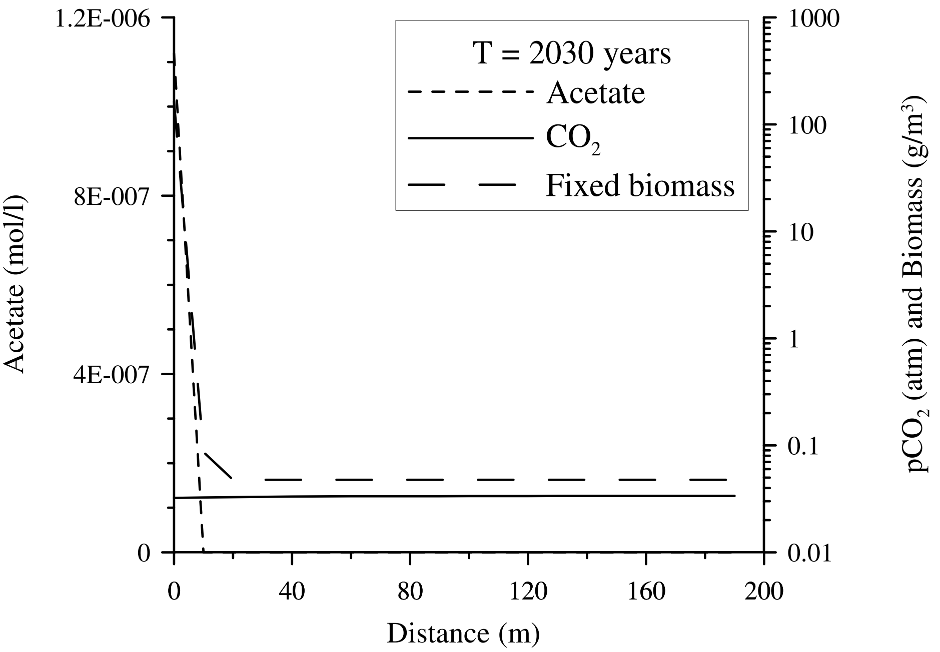

**Figure 2.** Concentration of Acetate; pCO2 and fixed (immobile) biomass in the model at 2030 years

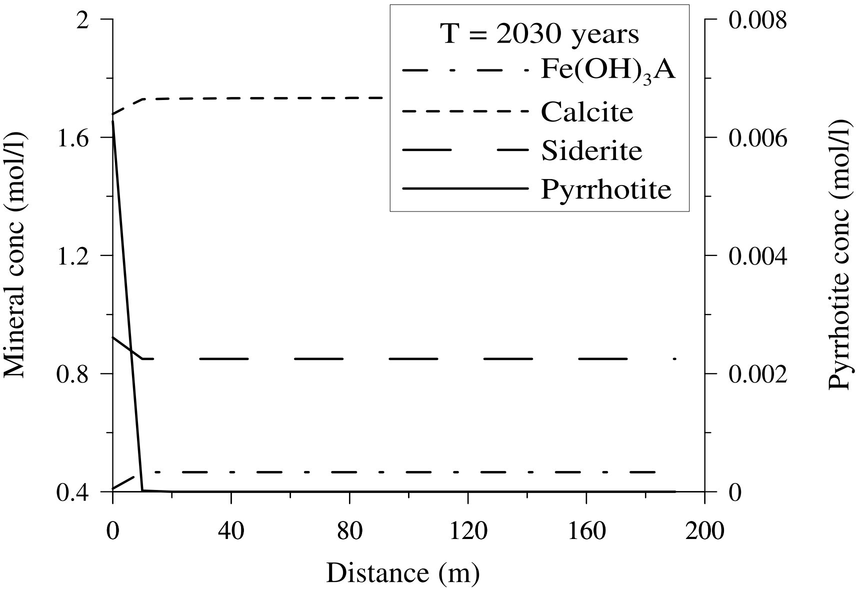

**Figure 3.** Concentration of mineral phases in the model at 2030 years

## EXPERIMENTAL VERIFICATION OF THESE PROCESSES

While modelling studies provide insights into the consequences of processes that could logically be assumed to operate at the interface, modelling is by its nature a simplification of the complex processes that occur in reality. In order to test that the model discussed above considers the salient features of the complex processes that can occur at the interface, BNFL has commissioned a series of experimental studies. These studies have been based on batch and column model systems containing sediments taken from the Drigg site, exposed to an aqueous phase of Drigg simulant groundwater or leachate.

On contact with sediments, both leachate and groundwater demonstrate an increase in pH and sulphate concentration suggesting that the sediments do influence the chemical environment of the aqueous phase. After prolonged incubation with sediment, leachate became depleted in organic acids with a concomitant increase in the pH. The aqueous phase electron acceptors nitrate and sulphate were utilised in succession, with nitrate being utilised before sulphate. Of significance, the presence of nitrate influenced sulphate reduction, with decreased sulphate reduction in the absence of nitrate. The precise mechanism for this process is not known.

A black deposit was observed in leachate columns containing non-sterilised sand. Prevention of precipitate formation by sterilisation or addition of Kathon, an inhibitor of microbial growth, indicated that the process was microbial. The blackening of the sediment was dependent on the presence of organic acids and sulphate, suggesting that the precipitate is a product of microbial sulphate reduction. The precipitate was identified as an iron sulphide, however attempts to identify its mineralogical form have so far been unsuccessful. Molecular microbiological tools including: Polymerase Chain Reaction (PCR) amplification; and probing for the DSR gene (encoding dissimilatory sulphite reductase: DSR) conserved amongst sulphate reducing bacteria; have shown that the blackened regions are enriched sulphate reducing bacteria, providing further evidence that the black precipitate is a biogenic sulphide.

Although it has been demonstrated that aqueous phase terminal electron acceptors, nitrate and sulphate are utilised as predicted in the conceptual model, the impact of iron (III) reduction is less well understood. Work is currently been funded by BNFL to characterise the mechanism of iron (III) reduction in Drigg sediments, and the resultant impact on radionuclide transport.

Preliminary studies to investigate the impact of changes to the established biogeochemical conditions on radionuclide transport utilised Cs and Eu as analogues of radioactive Cs and Eu. Both Cs and Eu were found to be more mobile in leachate than groundwater, in fact the Eu breakthrough in groundwater was so delayed, relative to the leachate result, that the experiment was terminated before breakthrough occurred. The enhanced mobilities cannot be accounted for solely in terms of chnages to speciation, because both Eu and Cs were affected despite being different species under the experimental conditions. The leachate cation concentration, due to $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$, exceeded the groundwater cation concentration by a factor of around 4. Therefore increased competition for sorption sites may have decreased retardation of Eu and Cs, as they progressed through the columns of sand in the leachate phase.

In addition to the chemical changes introduced by microbes, physical interactions may also impact upon radionuclide transport. The formation of microbial biofilm and the precipitation of minerals as a result of the biogeochemical environment may act to physically block pore spaces in the sediments, leading to a reduction in hydraulic conductivity. In GRM, microbial biomass is assumed to have a negligible volume and therefore the impact of clogging is not considered when modelling the interface. Studies using sediment columns equipped with pressure transducers suggested that microbial growth under denitrifying conditions has a negligible effect on the pressure drop across the column, and on examination with electron microscopy, microbial colonisation had not progressed to confluent microbial biofilms. This work is continuing and will consider the potential of blockage under a range of biogeochemical conditions, and will also assess the impact of microbial cells on radionuclide transport via the generation and blockage of sorption sites.

## CONCLUSIONS

In order to understand the consequences of an interface zone on radionuclide transport as part of the Drigg PCRSA, field data and experimental data have been used to derive a conceptual model of processes operating in the interface. The GRM code has been configured to model interface processes and indicates that some existing geosphere minerals could dissolve and new minerals precipitate in the interface zone due to microbial and chemical reactions.

Studies to verify these numerical simulations are broadly in line with GRM predictions. Some processes, such as nitrate enhancing sulphate reduction were not expected. Further studies are being conducted to investigate the impact of iron reductions within Drigg sediments and develop a model system for the investigation of metal/sediment under well-defined biogeochemical conditions. Most importantly studies will include investigations about the behaviour of radionuclides in the interface zone.

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