

**Coupling Diffusive Transport and Chemical Reaction in the
Generalised Repository Model (GRM) – 10047**

S. Kwong and J.S. Small
National Nuclear Laboratory
Chadwick House, Warrington,
UK. WA3 6AE.

ABSTRACT

Recent updates have been made to the GRM code to include the implementation of a diffusive solute transport process model to extend the use of code from that for LLW near-surface disposal to deep geological disposal of ILW/HLW. The present work demonstrates the use of the GRM code to modelling the combined hydrogeological (diffusion and advection) and chemical effects in geological systems with low groundwater flows that are typical of deep geological disposal facilities.

The high accuracy of the updated GRM code in modelling diffusive solute transport is established via comparing the model results with the analytical solutions of an idealised diffusion test case and a through diffusion experiment. An illustrative reactive transport model is also presented to demonstrate the use of the code in environments typical of deep geological disposals, and which examine the interplay of kinetic controlled biogeochemical processes with advective and diffusive transport.

The illustrative reactive transport model results are encouraging and show that the disposal system evolves in a physically realistic manner. The results presented highlight the combined physical and chemical containment properties of geological disposal systems. The GRM code thus provides a suitable tool for modelling diffusive reactive transport in conditions typical of deep geological disposal systems.

INTRODUCTION

Deep geological disposal is increasingly being recognised as the preferred option for the long-term management and eventual disposal of high activity and long-lived radioactive waste. The deep geological disposal approach is favoured by many countries, including Finland, Sweden, France, Belgium, Switzerland, Canada and Japan, where suitable water saturated formations occur in both hard rock and clay formations. In the UK a programme has started to identify a suitable geological site for the management of high- and intermediate-level radioactive wastes.

A geological disposal system or repository involves isolating radioactive waste deep inside a suitable rock formation to ensure that no harmful quantities of radioactivity reaching the biosphere. The system is generally based on a multi-barrier design that involves placement of wastes deep underground, protected from potential disruptions by man-made and/or natural events. A typical deep repository is likely to be hundreds of metres below ground, with the waste sealed in durable containers that are surrounded by low-permeability rock (or clay) barrier to prevent radioactive material leakage into the environment.

One of the main requirements for a suitable deep repository site is that the geological formation surrounding the repository would ensure slow groundwater transport from the repository to the surface. In addition, conditions that would favour geochemical and mineralogical processes to prevent and delay radionuclide transport of dissolved species are also desirable. The chemically reactive processes that occur in disposal facilities may be mediated by microbial processes that metabolise the variety of chemical compounds present in transuranic and intermediate level wastes (TRU/ILW), together with organic carbon and hydrogen present in the geological and engineered systems. When groundwater flow is very slow, radionuclide transport is largely influenced by diffusion and sorption, with the additional effects due to the diffusive transport of reactive species that also leads to chemical zonation around waste packages which could provide additional containment of radionuclides.

Repository performance needs to be assessed over an extended period of time to assess its safety implications. Numerical models of groundwater flow, solute transport and chemical processes offer a viable and cost effective means to predict the long term evolution of site condition, and provide a more detailed understanding of the effects on the mobility of contaminants.

The Generalised Repository Model (GRM) [1] was originally developed to model the biogeochemical, microbially mediated processes occurring in low level waste, but has recently been successfully applied to deeper geological disposal repositories including the VLJ repository, Finland, where its ability to model biogeochemical processes including gas generation have been tested against long term, large scale experiments [2].

Recent updates have been made to GRM to include the implementation of a diffusive solute transport process model that is important in geological systems with low groundwater flows. The updated code will thus extend the use of GRM from that for LLW near-surface disposal to deep geological disposal of ILW/HLW.

The work presented here demonstrates the use of the GRM code to modelling the combined hydrogeological (diffusion dominant) and microbially mediated chemical effects in geological systems with low groundwater flows that are typical of deep geological disposals.

OVERVIEW OF THE GRM CODE

The GRM (Generalised Repository Model) is a computer code [1] that was originally developed by the Research and Technology department of BNFL (now National Nuclear Laboratory) to model the long term chemical evolution of near surface disposal sites, such as the UK Low Level Waste Repository (LLWR). GRM is a biogeochemical reactive-transport model that considers kinetic controlled corrosion¹ and microbiological reactions together with equilibrium chemical speciation and mineral reaction (Figure 1). GRM includes a comprehensive set of microbial mediated aerobic and anaerobic kinetic controlled processes that utilise commonly occurring substrates and electron donors and acceptors. The following microbial processes are included, represented by a Michaelis –Menton kinetic formulation [3];

- aerobic metabolism;
- denitrification;
- fermentation;
- iron reduction;
- sulphate reduction;
- acetogenesis;
- methanogenesis;

The extent of these microbial processes is determined by input kinetic constants and the concentration of the metabolic substrates. The current microbial data set has been compiled for studies of low level waste [2]. Both organic carbon and hydrogen (H₂) can be utilised as electron donors for the above processes. The corrosion module can consider processes of aerobic and anaerobic corrosion. The later anaerobic process is of prime relevance to geological disposal, where it contributes H₂ electron donor for the above microbial processes. Iron corrosion products also have the potential to control redox potential. Based on the extent of the microbial processes the GRM selects and calculates redox potential (Eh) for the following redox couples [2];

- oxygen, O₂ / H₂O
- nitrate NO₃⁻ / N₂
- iron Fe(III)/Fe(II)
- sulphur SO₄²⁻ / HS⁻
- methane CO₂ / CH₄
- fermentation CH₂O / CH₃COOH + H₂

¹ The primary degradation processes considered in the GRM include cellulose hydrolysis and steel corrosion, although cellulose hydrolysis and the associated gas generation often relates to near surface repository rather than deep geological disposals

Using the determined Eh calculated by the kinetic module (Figure 1) the chemical module performs an equilibrium speciation calculation that considers the dissolution and precipitation reactions of minerals and radionuclides and determines pH by charge balance.

The GRM computer code utilises a two-dimensional finite difference approach to consider transport in saturated groundwater. The GRM model also allows species transport from the unsaturated zone to the saturated zone via a release coefficient model, although this is less relevant for deep geological disposal applications.

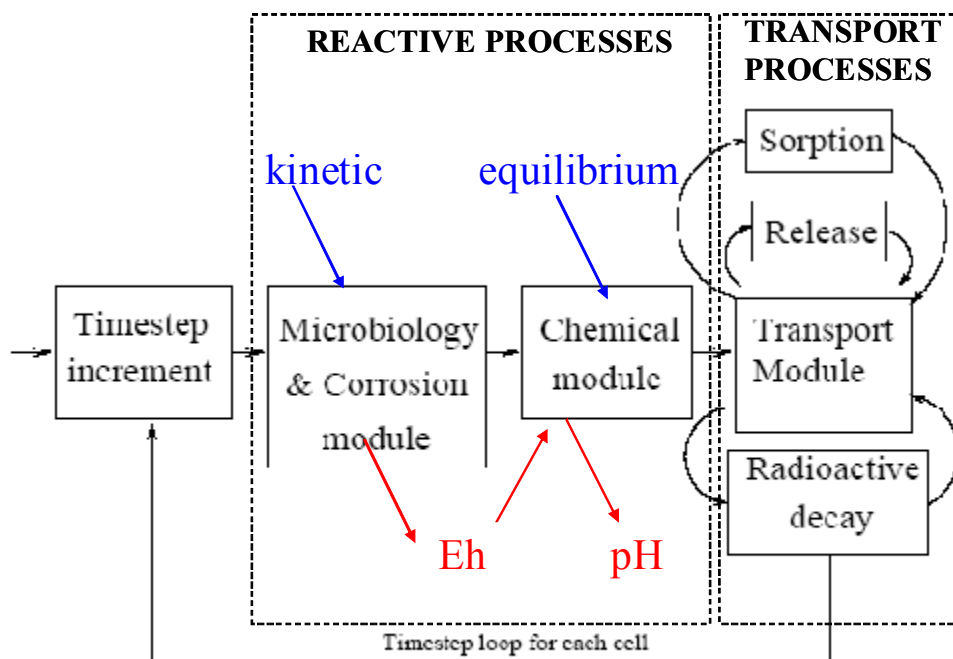


Figure 1. Schematic of the reactive-transport process modules within GRM [1].

GRM uses a finite difference approach, evolving the system through a sequence of time steps. Given the very different processes modelled, the time evolution of different aspects of the system is likely to proceed at very different rates. It could be computationally inefficient to evolve all aspects of the system at the rate of the most rapid process, due to the large time scale ranges of the processes involved. Recognition of this point has led to the development of three main computational sequence modules, each being characterised by a separate timescale. The modules are:

1. Microbial module. The kinetic approach to microbiology implies that a short time step is required for the microbial calculations (typically less than 1 day).
2. The transport module that examines the movement of chemicals in the groundwater. The timescale for these calculations will depend on the system size, the groundwater advection velocities and diffusion rates if appropriate.
3. The chemistry module, which determines the current chemistry within the saturated zone. PHREEQE/C is used in GRM, which assumes equilibrium chemistry. Timescales for the chemical evolution of a site are likely to be highly situation specific.

GRM uses a two-step approach (Figure 1) for solving the coupled chemistry and transport problem. In the first step, an explicit finite difference method solves the transport equation that includes the effects of sorption and radioactive decay. Reactive chemistry is dealt with separately in the second step, where the chemical equilibrium submodel is

called to calculate the distribution of the chemical species under thermodynamic (partial) equilibrium conditions. By splitting the transport and reaction aspects in this way, it is assumed that:

- the transportation of species in the system is not sufficient to cause significant local deviations from chemical equilibrium; and,
- the chemistry in the system evolves sufficiently slow so that the concentration of each species over the course of a transport time step is approximated adequately by its concentration at the start of the time step.

The full suite of microbiological processes, chemical speciation, mineral reaction, including radionuclide solubility and sorption are restricted to the saturated zone. Gas solubility, and hence the composition of gas in the unsaturated zone, is also determined with reference to water present in the saturated zone. Reference [4] documents details of a wide range of program test cases which have been designed to test the extensive capabilities of the GRM program.

DIFFUSIVE SOLUTE TRANSPORT MODELLING

The performance of the GRM code on diffusive solute transport modelling for slow flowing groundwater relevant to environments typical of deep geological disposals is assessed. The implementation of diffusive transport in the GRM is verified using one-dimensional test cases against analytical solutions, and measurements from a through diffusion experiment [5].

Diffusion is the process by which matter is transported from one part of a system to another as a result of random molecular motion [6]. Fick's law describes the rate of diffusive mass transport. Combining Fick's law with the law of mass conservation produces a parabolic partial differential equation for diffusive mass transport under transient conditions.

The equation describing solute diffusion (in 1-dimension) in groundwater can be written as

$$\frac{\partial C}{\partial t} = D_E \frac{\partial^2 C}{\partial x^2} \quad (\text{Eq. 1})$$

where $C=C(x,t)$ is the concentration of the solute in groundwater at position x and time t , and D_E is effective diffusion coefficient of a solute in groundwater. For cases with no adsorption, the effective diffusion coefficient of a solute in a soil system can be estimated from the solute's diffusion coefficient in water, soil porosity, and soil water content using the so-called MQ model [7]

$$D_E = D_o \frac{\theta_v^{10}}{\theta^2} \quad (\text{Eq. 2})$$

where D_o is the solute diffusion coefficient in water, θ_v is the volumetric water content² of the soil medium, and θ is the porosity of the soil. In saturated conditions $\theta_v=\theta$, Eq. 2 reduces to

$$D_E = D_o \theta^{\frac{4}{3}}, \quad (\text{Eq. 3})$$

² **Volumetric water content**, θ_v , is the portion of volume of a soil sample that is occupied by water, expressed as fraction by volume. Mathematically, $\theta_v = V_w / V_T$ where V_w is the volume of water and $V_T = V_s + V_v = V_s + V_w + V_a$ is the total volume (that is Soil Volume + Water Volume + Void Space). In saturated conditions, $V_a=0$ and $V_w=V_v$, giving $\theta_v=\theta$.

Analytical diffusive transport test case (Case A)

The first diffusive transport test case (Case A) concerns the one-dimensional spreading of a chemical plume to represent a scenario where the diffusing substance has an initial concentration C_0 in soil water from position zero to position h (called the mixing depth in this model). The diffusing substance has an initial concentration of zero at other positions. At times greater than zero, the material diffuses through the soil, but none of the material diffuses out of the soil at position zero. Mathematically, this can be represented as

$$C(x,0)=C_0 \quad \text{for } 0 < x < h$$

$$C(x,0)=0 \quad \text{for } x \geq h$$

And

$$\frac{\partial C}{\partial t} = 0 \quad \text{For } x=0 \text{ and } t \geq 0$$

The solution to the partial differential equation with this set of initial and boundary conditions is

$$C(x,t) = \frac{1}{2} C_0 \left\{ \operatorname{erf} \left[\frac{h-x}{2\sqrt{(D_E/\theta)t}} \right] + \operatorname{erf} \left[\frac{h+x}{2\sqrt{(D_E/\theta)t}} \right] \right\} \quad (\text{Eq. 4})$$

where $\operatorname{erf}(\cdot)$ is the error function.

Through diffusion experiment test case (Case B)

The second diffusive transport test case (Case B) is based on a through diffusion experiment [5] using a sedimentary rock sample taken from a research site in Japan. A disk-shaped specimen of diameter 64 mm and thickness 10 mm sealed in an acrylic holder was set between two identical-sized reservoirs (each of volume 44 ml) which are used as source and measurement cells. The initial Cl concentration of the NaCl solution in the source and measurement cells were set to 40.00 mol/l and 0.0 mol/l respectively. Cl ion as a non-sorbing tracer was then allowed to diffuse through the rock specimen from the source cell to the measurement cell, with its concentrations measured over time using Ion Chromatography. The tracer concentration measurements (Figure 4) taken at both the source and measurement cells over a period of 71 days are used for model comparison.

DIFFUSIVE REACTIVE TRANSPORT MODELLING APPLICATION

An illustrative two-dimensional reactive transport model has been developed to explore the coupled effects that result between;

- diffusive and advective transport;
- kinetic controlled microbial processes; and
- equilibrium chemical speciation, mineral and radionuclide dissolution and precipitation.

The GRM model considers a generic case relevant to geological disposal of TRU/ILW where a disposal waste package containing contaminants (uranium) and other multivalent reactive species (iron, sulphate, nitrate) are enclosed in a highly impermeable but reactive medium and where diffusion is the main transport mechanism. Iron is in the form of Fe(II) and represents corrosion products present in waste and containers used. The effect of a sealed waste package container (which to physically isolate the waste) is not considered in this scenario. The present model therefore examines the effects that may develop after any such containment is breached. The model examines how

the evolving chemical conditions of the repository and diffusive properties of the waste and surrounding medium may affect the containment/mobility of the uranium. The enclosing medium has neutral pH and may represent a clay host rock, or low permeability clay or rock backfill. Along a boundary of the model is an advective transport pathway, which might represent features such as fractures in rock, or void spaces amongst waste packages. Groundwater that saturates the waste package contains organic matter, and it is assumed that the host rock of the disposal facility and other engineering maintain reducing conditions external to the waste package. These strongly reducing conditions are represented by the partial pressure of hydrogen (0.99 atm H₂) in the model.

The model is configured in a 2-dimensional array of 20 x 20 cells (Figure 2) where a single row of 20 cells represents an advective region and 19 adjacent rows of 20 cells represent the diffusive zone (no advective flow) including an area of waste source with kinetic release over time. The model considers an area of 5m by 0.48m. The advective row has a width of 0.1m while the remaining 19 rows representing the diffusive regions are of 0.02m width.

The main diffusive region of interest is within the 19 rows over a width of 0.38m (38cm). Note that the width (or breadth) of the diffusive region is exaggerated in the figures. A groundwater flow rates of 10 ml/day was considered in the advective region. In the diffusive region of the waste and enclosing medium an effective diffusion coefficient of 1.0E-11 m²/s and a porosity of 0.15 were considered. Other modelling studies of diffusion in the clay host rocks have considered similar diffusion coefficient values [8].

The waste region (shaded red/purple in Figure 2) contains uranium at a concentration of 1.0E-03 mol/l of pore fluid. The presence of Fe(II) corrosion products in the form of FeCO₃ are considered in the waste. The model also considers that reactive chemical species nitrate and sulphate are present in the TRU/ILW waste in the two regions: region 1 (shaded purple) has concentration of 5.0E-3 mol/l NO₃⁻ while region 2 (shaded red) has a lower concentration of 1.0E-3 mol/l. The sulphate concentration in both regions is 1.0E-3 mol/l. Chloride is also present in the waste at a concentration of 1.1E-1 mol/l in region 1 or 1.5E-1 mol/l in region 2 (to balance the nitrate) to provide charge balance to compensate for the additional nitrate in region 1. Chloride is not reactive in the model.

The enclosing diffusive medium (clay) is represented by the calcium and iron containing carbonates (calcite, siderite), which is defined by a partial pressure of carbon dioxide (1.45E-2 atm CO₂) that buffers pH to near neutral conditions. Sulphate minerals present in the clay (gypsum, celestite) similarly control the sulphate concentration in groundwater that saturates the clay. The groundwater that saturates the waste and enclosing clay also contains dissolved organic matter, which in the GRM is represented by an acetate concentration of 9.2E-5 mol/l.

The GRM model was run to simulate a period of 100 years of reaction and diffusion.

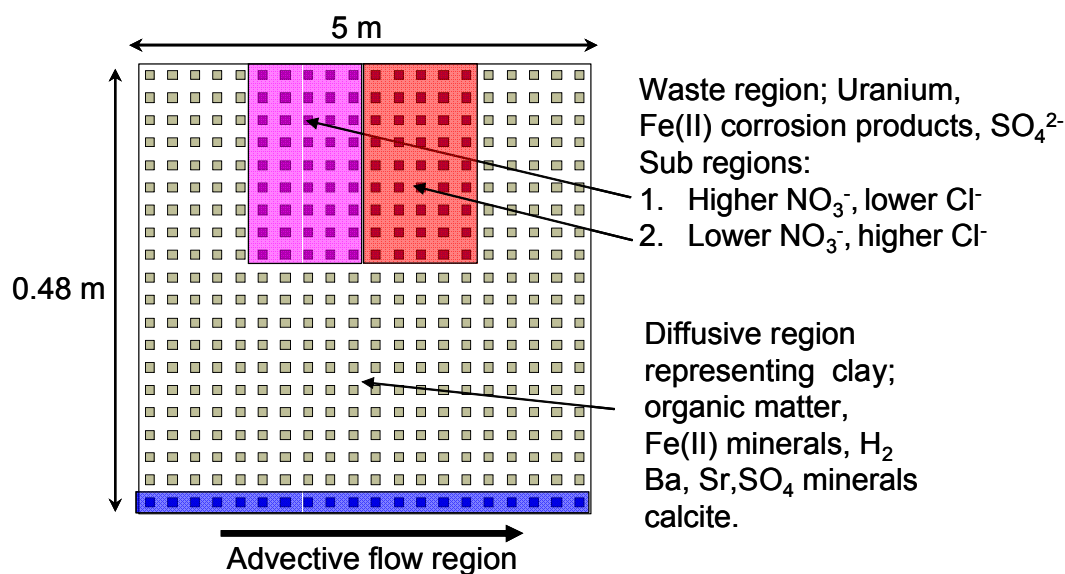


Figure 2. Schematic illustration of the GRM reactive transport (advection and diffusion) application model.

RESULTS AND DISCUSSIONS

The GRM code was initially used to model the above two diffusion solute transport tests cases to assess the performance of the code in modelling diffusive transport. This is followed by illustrative reactive transport models to demonstrate the use of the code to examine the coupling between kinetic controlled biogeochemical processes with advective and diffusive transport in environments typical of deep geological disposals.

Analytical diffusive transport test case (Case A)

With $D_E=1E-10$ m²/s, $h=0.1$ m and $C_0=1$ mol/m, a 1 m long soil media was modelled at different porosity values ($\theta=1.0$ and 0.3) using a 'coarse grid' model with 10 cells (i.e. uniform cell size 0.1m), and a 'fine grid' model with 14 cells (i.e. 0.5m cell size for $X=0$ m to 0.4m, and 0.1m cell size between $X=0.4$ m to 1m). Figure 3 shows the comparison between the analytical solution (Eq. 3) and modelled results for Case A. The modelled results show excellent agreement with the analytical solution, except for the coarse grid model result where discrepancies increase slightly in regions of high concentration gradient during the initial phase of the diffusing plume. The use of the localised refined grid (i.e. using finer grid from $X=0$ m to 0.4 m) in the fine grid model leads to noticeable improvements in the model results in the regions of high concentration gradients. The difference between the coarse-grid and fine-grid model results is seen to diminish over time and become insignificant after 10 years, this highlights the issue on the use of appropriate grid size required to adequately resolve the high concentration gradient particularly when an accurate prediction of the concentration is required. The results presented above show fairly good agreement between the model results and the theory can be obtained using a relatively coarse grid (i.e. 0.1 m cell size), but noticeable improvement can be obtained using refined grid in localised region where high concentration gradients occur.

It is worth noting the lower porosity case (i.e. $\theta=0.3$) shows faster solute migration than the case with $\theta=1$. This may seem counter intuitive initially, but can be readily realised from equation (2). Such that for a given value of D_E , a reduction in porosity would lead to a proportionally larger increase in D_o due to the non-linear relationship. For example, under saturated conditions Equation (2) reduces to $D_E = D_o \theta^{\frac{4}{3}}$, for $D_E = 1.0E-10$ m²/s, $D_o = 1.0E-10$ m²/s for $\theta=1$ and $D_o = 4.98E-10$ m²/s for $\theta=0.3$, hence a 70% reduction in porosity leads to an increase of ~400% in the value of solute diffusion coefficient D_o . In practical situations, it is more likely that a working fluid is considered (hence a given solute diffusion coefficient D_o), with the effective diffusion coefficient D_E to increase with porosity, amid in a non-linear manner (Eq. 2).

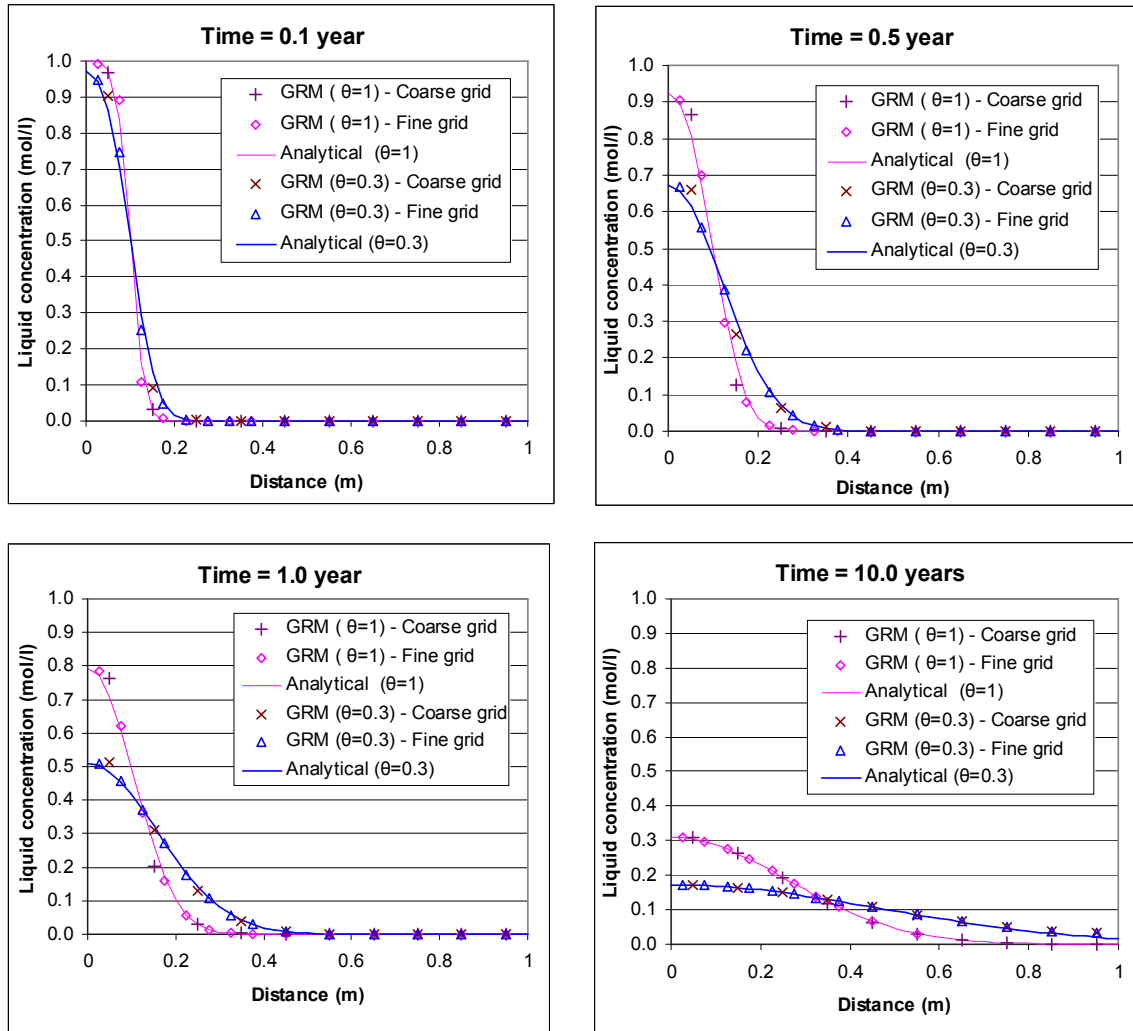


Figure 3. Comparison of concentration evolution for Case A (due to diffusive transport) between the modelled and analytical solutions for a 1.0 m long medium over 10 years.

Through diffusion experiment [5] test case (Case B)

The through diffusion experimental setup (Case B) is represented in the GRM model using a row of 35 cells of constant height 3.22E-3 m (i.e. representing the cross-sectional area of the 64 mm diameter specimen). The 10 mm thick specimen is represented by 9 cells of length 1.11E-2 m, while both the source and measurement cells are discretised using 12 cells of length 1.14E-03 m (i.e. representing a volume of 44 ml). An additional cell of very low diffusivity is added to both (outer) ends of the diffusion test cell to represent the non-diffusive flow condition. Three GRM model runs (namely RUN1, RUN2 and RUN3³) are performed using the derived sets of effective diffusion coefficient D_E and rock capacity factor α^4 (equals to porosity θ for non-sorbing species as the sorption coefficient K_d becomes zero) values from the through diffusion experiment [5]. The parameter values for the through diffusion experiment and its representation in the GRM model are summarised in Table I.

Table I. Parameter values for the through diffusion experiment and its model representation.

Features	Description	Model representation (with cell height=3.22E-3 m)		
		Total length	No. of cells (cell length)	Transport properties
Rock specimen	Diameter = 6.4E-2 m Equivalent cross sectional area = 3.22E-3 m ² Length = 1.0E-2 m	1.0E-2 m	9 (1.11E-3 m)	RUN1: $D_E = 1.80E-11$ m ² /s; $\theta=0.38$ RUN2: $D_E = 2.03E-11$ m ² /s; $\theta=0.30$ RUN3: $D_E = 1.980E-11$ m ² /s; $\theta=0.34$
Source cell	Volume = 4.4E-5 m ³	1.37E-2 m	12 (1.14E-3 m)	$D_E = 1.80E-8$ m ² /s; $\theta=1$
Measurement cell	Volume = 4.4E-5 m ³	1.37E-2 m	12 (1.14E-3 m)	$D_E = 1.80E-8$ m ² /s; $\theta=1$
Added 'wall' cell in the model representation of the source and measurement cells	Non-diffusive wall of the source and measurement cells	1.14E-3 m	1 (1.14E-3 m)	$D_E = 1.80E-14$ m ² /s; $\theta=1$

Figure 4 shows the comparison between the measured and modelled concentration changes in the source and measurement cells of the through diffusion experiment [5]. This shows the concentration decrease in the source cell and the concentration increase in the measurement cell over a period of ~80 days as *Cl* solution diffuses through the rock specimen. To minimise changes in solution volumes in the source and measurement cells, only 20 micro-litres of solution was taken for each sampling [5]. The concentration values presented below are normalised to the initial source concentration.

³ Reference [5] shows that similar and consistent sets of transport properties (i.e. D_E and θ) can be derived using the measurements based on i) concentration decrease in the source cell only, ii) the concentration increase in the measurement cell only, and iii) the differential concentration between the two cells, of which values are used for RUN1, RUN2 and RUN3 respectively.

⁴ The rock capacity factor $\alpha = \theta + K_d \cdot \rho$ where θ is the porosity; K_d is the sorption coefficient; and ρ is the density of the test media.

The modelled results agree well with the measurements (Figure 4), with only minor differences between the results from the three runs (i.e. RUN1, RUN2 and RUN3). In particular very good agreement between the modelled results and measurements are obtained for the source cell over the whole 80-day period, and for the measurement cell over the first half of the 80 days. Amongst the three model runs, it is noted that RUN3 (with transport properties derived using the differential concentration between the source cell and measurement cell) agrees best with the measurements. This demonstrates the GRM code as a suitable basis for modelling diffusive transport in conditions typical to deep geological disposal applications.

Discrepancies between the model prediction and measurement become more apparent for the measurement cell towards the end of the period (i.e. 71 days), where the measured concentration is notably higher than the model prediction. The discrepancies (between model and measurement) in the measurement cell can be partly explained by the effect of taking solution sampling, such that the solute diffused through the specimen is to mix in a diminishing volume of liquid, thus leading to a higher concentration than that would achieve by mixing in the original (larger) volume. Despite caution was taken in the experiment by taking a small sample volume (e.g. 20 micro-litres), the cumulative sample volume taken over a longer period is likely to have an increasingly significant effect. The effect of sampling seems to be less significant for the source cell.

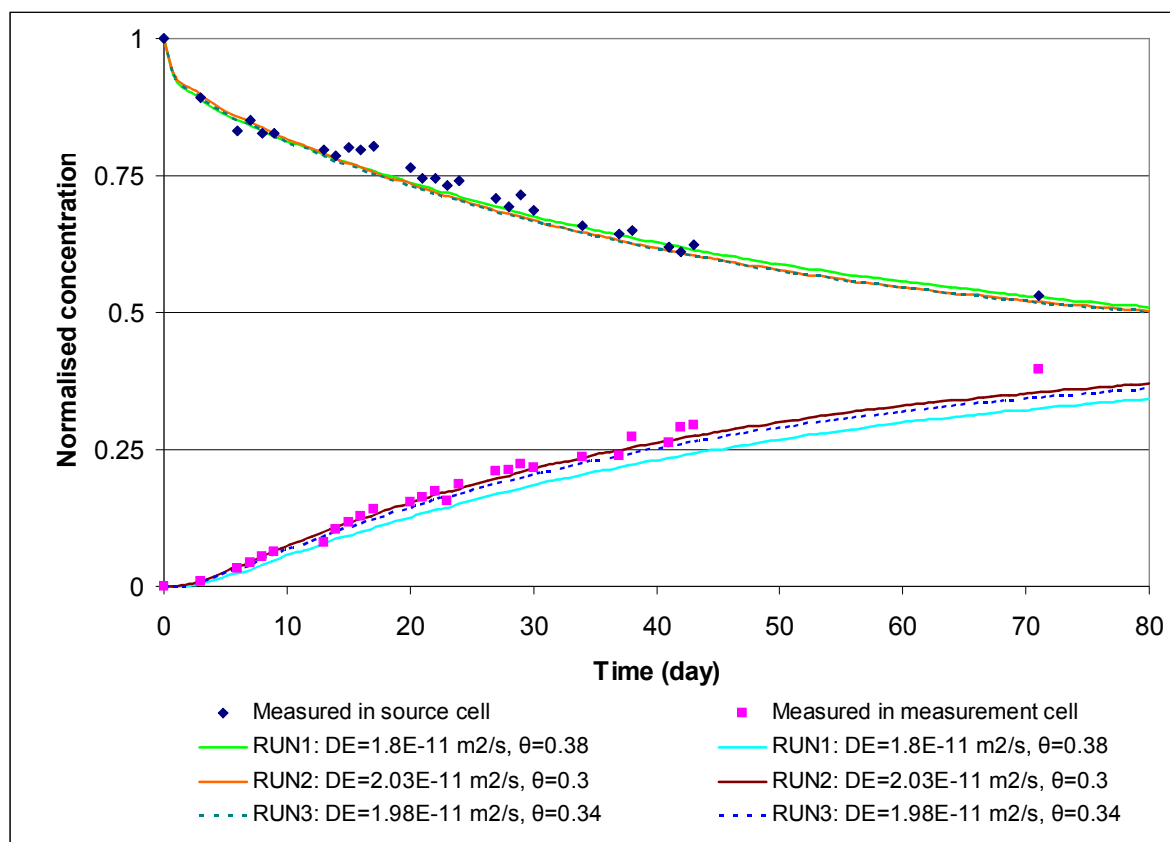


Figure 4. Comparison between the measured and modelled concentration changes in the source and measurement cells of a through diffusion experiment [5].

RESULTS OF THE GRM APPLICATION MODEL TO GEOLOGICAL DISPOSAL

With the initial conditions described above, the system representing a TRU/ILW waste package was modelled for a period of 100 years. Figure 5 presents summary outputs at the end of the simulation period. Figure 5a illustrates the diffusive behaviour of chloride, which is both non reactive and non-sorbing. Chloride presents in the waste region (purple region in the figure) diffuses away from the source and moves towards the advective region, such that at the exit of the advective zone attains a concentration of 4×10^{-2} mol/l, which is about 0.88 that of the maximum concentration in the waste region. The remaining figures illustrate the biogeochemical reactions occurring mediated by microbial processes. The presence of nitrate in the waste results in its rapid reaction by denitrifying bacteria, which utilise organic carbon, H_2 and Fe(II) as electron donors. The oxidation of Fe(II) corrosion products results in the formation of $Fe(OH)_3$ (Figure 5b), with the amount of $Fe(OH)_3$ formed proportional to the nitrate content of the waste.

The redox potential (Eh) determined by the kinetic routine is illustrated in Figure 5c, which shows that the oxidation of Fe(II) to Fe(III) in the waste to maintain a higher Eh at around -0.1 volts. It is observed that this oxidised zone extends into the adjacent clay by diffusion of species and the precipitation of $Fe(OH)_3$, (Figure 5b). In the majority of the clay zone sulphate reduction occurs due to the dissolved organic matter input from groundwater passing through the advective region that diffuses through the clay zone. Hydrogen present also acts as an electron donor for sulphate reduction. More strongly reducing conditions are established at the inlet of the advective fracture, where sulphate becomes totally reduced by the inflowing organic carbon. The microbial biomass that results from these main reactions of the electron acceptors and donors present is illustrated in Figure 5d. Most microbial activity is seen to occur in the waste region and at the interface with the clay zone. A further region of microbial activity occurs near the inlet of the advective region.

The resulting diffusive and chemical effect on uranium is illustrated in Figure 5e and Figure 5f. In the waste region uranium is in the U(VI) oxidation state and has high solubility. Aqueous uranium becomes mobile and readily diffuses from the waste. Under the sulphate reducing conditions established in the clay, uranium precipitates as $UO_2(am)$ and thus the concentration of dissolved uranium falls significantly compared to that of the non-reactive chloride species (Figure 5a). The migration of uranium from the waste region is affected to a small extent by the different nitrate contents of the waste in region 1 and region 2 (Figure 2). Uranium is also precipitated in the advective zone, where the very strongly reducing conditions are developed. The uranium concentration exiting the advective zone is 1.63×10^{-6} mol/l and is a factor of 0.03 lower than that of the maximum concentration in the waste region. As a result of the chemical processes occurring the concentration gradient of uranium across the diffusion zone is about 30 times that of the non-reactive Cl species. This illustrates the potential significance of chemical effect on diffusive transport of radionuclides which needs to be taken into account to gain an improved understanding of the long-term behaviour of the geological disposal system.

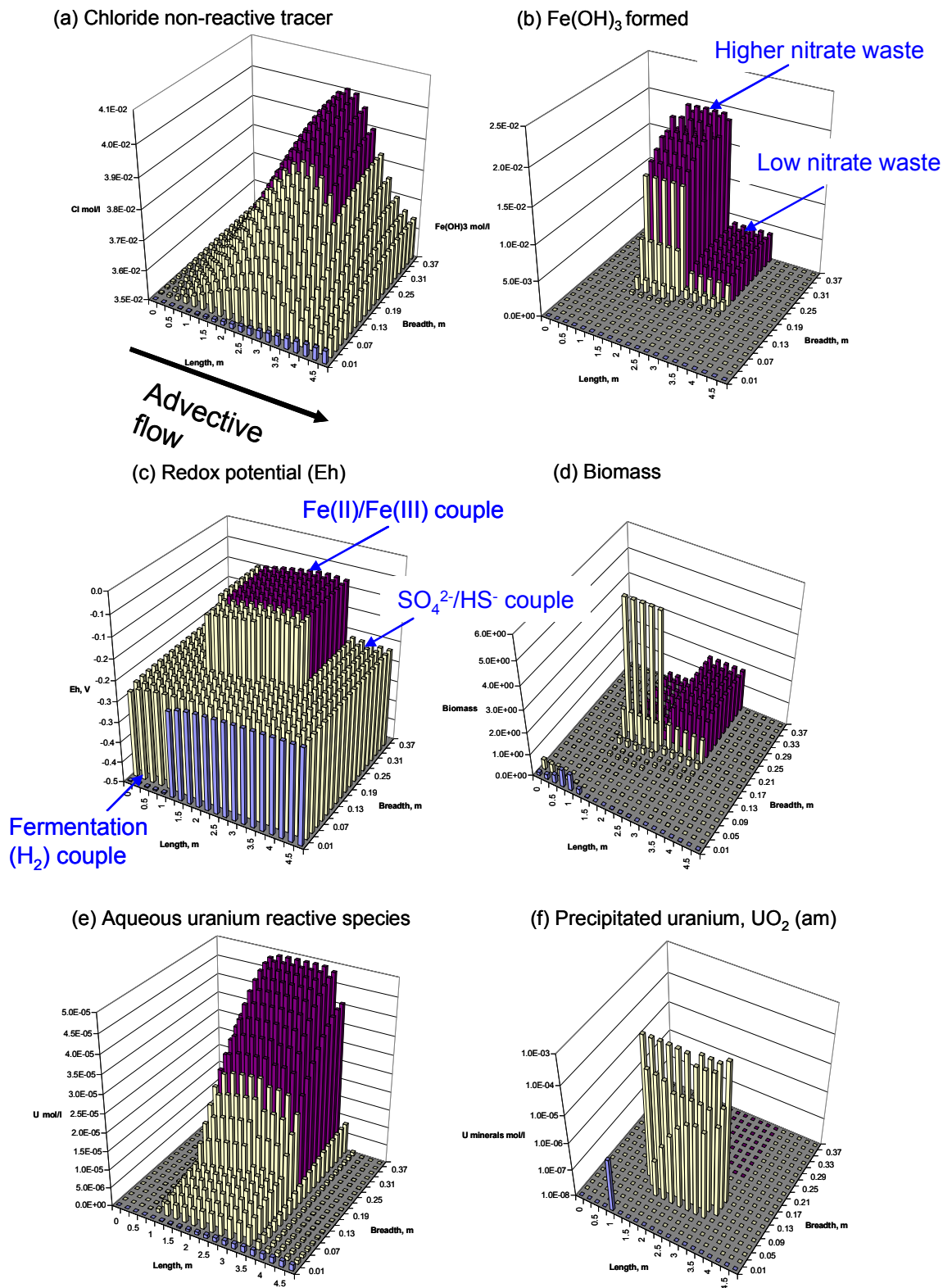


Figure 5.. Outputs from the GRM example application to TRU/ILW waste disposal in a geological repository after 100 years.

CONCLUSIONS

The recently updated GRM code is applied to model the combined hydrogeological (diffusion and advection) and chemical effects in geological systems with low groundwater flows that are typical of deep geological disposals.

The accuracy of the diffusive transport model of the GRM code is assessed in two diffusion solute transport tests cases, firstly via comparing the model results against the analytical solution of an idealised diffusion test case, and secondly against a through diffusion experiment. Very good agreements are obtained in both cases.

An illustrative reactive transport modelling application demonstrates the use of the code to examine the interplay of kinetic controlled biogeochemical reactive processes with advective and diffusive transport. In the example presented the reactive-transport coupling develops chemically reducing zones, which limit the transport of uranium. These results thus highlight the combined physical and chemical containment properties of geological disposal systems. The model results are encouraging which show the disposal system to evolve in a physically realistic manner.

This supports the GRM code as a suitable tool for modelling diffusive reactive transport in conditions typical of deep geological disposal designs.

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REFERENCES

1. S. Kwong, Program User's Guide for the code GRM, Version 6.1. NNL Report (2009a).
2. J. Small, M. Nykyri, M. Helin, U. Hovi, T. Sarlin and M. Itävaara, M. "Experimental and modelling investigations of the biogeochemistry of gas production from low and intermediate level radioactive waste". Applied Geochemistry Vol 23, pp.1383-1418 (2008).
3. P. L. McCarty and F. E. Mosey, Modelling of Anaerobic Digestion Processes (A Discussion of Concepts), Water Sci. Technol. 24 No.8, pp.17-33 (1991).
4. S. Kwong, Program Verification Report for the code GRM, Version 6.1. NNL Report (2009b).
5. M. Zhang, M. Takeda and H. Nakajima, "Determining the Transport Properties of Rock Specimens using an Improved Laboratory Through Diffusion Technique", Scientific Basis for Nuclear Waste Management XXIX, Materials Research Society Symposium Proceedings Vol. 932, pp.135-142 (2006).
6. J. Crank, "The mathematics of diffusion". Oxford University Press, New York, p. 12-15 (1956).
7. R.J. Millington and J. M. Quirk, "Permeability of porous solids". Trans. Faraday Soc. 57:1200-1207 (1961).
8. E.C. Gaucher, P. Blanc, J.M. Matray and N. Michau, "Modeling diffusion of an alkaline plume in a clay barrier". Applied Geochemistry Vol 19, pp.1505-1515 (2004).