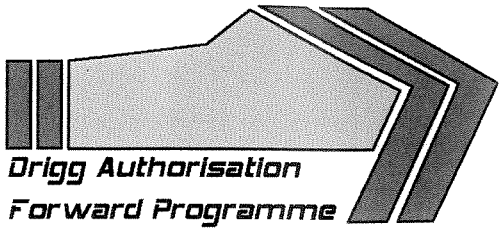

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Program User's Guide for the Code GRM, Version 4.1

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Summary

This document provides a guide to the capabilities, application and running of the code GRM[a] version 4.1 GRM is designed to model radionuclide and gaseous releases from LLW disposal sites.

[a] Generalised Repository Model

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1 Introduction

Radionuclide migration from low level waste (LLW) disposal sites is of interest to all parties involved in LLW management. The complexity of the relevant interactions, coupled with timescales on the order of thousands of years, makes the prediction of radionuclide behaviour difficult. Mathematical modelling provides a practical option for investigating this behaviour and providing insight into radionuclide release.

GRM[1] is a computer code which can be used to model the long term evolution of near surface, LLW disposal sites with significant groundwater flow. The GRM deals with the interaction of a range of processes including: radioactive decay, precipitation/dissolution reactions, sorption onto either the waste matrix or colloidal particles. Radionuclide speciation is determined by the prevailing geochemistry, with changes to ambient pH and pe being determined through interactions between microbial activity and the site chemistry.

1.1 Background

The GRM code was originally developed as a generalization and expansion of the now obsolete DRINK (Drigg Near-field Kinetic model) code. The name DRINK has been retained to describe GRM when configured to simulate the Drigg site. GRM version 4.1 can model many different physical processes, which can be switched on or off according to flags in the input deck. Justifications of the settings used for these flags in modelling a particular site often raise important issues for the GRM user. By using different flag settings, the user is able to examine the impact of modelling assumptions through sensitivity runs.

The processes included in the code are those considered, at the present time, to be likely to have a significant impact on the chemical evolution of a LLW site and therefore on the source term. Consequently, GRM has been designed to be highly adaptive, initially making use of standard process descriptions which can then be replaced as better quality data becomes available and the fundamental understanding of the underlying phenomena improves. The code development has attempted to marry the complexity and detail to which processes are modelled with the level of information that is likely to be available to the user.

The purpose of this document, the Program User's Guide (PUG), is to provide a comprehensive description of the capabilities, application and running of the code GRM version 4.1. It discusses the various processes which can be modelled using the code and

[1] Generalised Repository Model

includes a detailed specification of the input files required. The document forms one of a set of three reports which are produced to meet the software QA requirements. The other two are the Program Programmer's Guide (PPG) [1] which gives details of the actual coding of the model, and the Program Verification Report (PVR) [2], which describes a programme of code testing.

A brief outline of the components and capabilities of the code can be found in this introduction, with a more indepth discussion available in the following sections. This PUG has been compiled using various supporting documents and relevant reference will be made where appropriate.

1.2 Applications to Disposal Sites

The GRM is a biogeochemical transport code, which can be used to model radionuclide, liquid and gaseous arisings from the near field, and as such may be useful in LLW disposal site performance assessments. The lack of codes to provide such performance assessment data has been highlighted previously [3, 4]. More generally, the flexibility of the GRM code makes it a useful tool with which to develop an understanding of the processes that may be important in LLW sites. The code could also be used to model the long–term development of domestic waste disposal sites such as landfills. Although most applicable to near surface sites, cementitious monoliths can be considered from the point at which all barriers have degraded.

1.3 Introduction to Processes Modelled

The transport aspects within GRM are handled with a finite difference solver, which is interfaced with the PHREEQE [5] or PHREEQC [6] [2] geochemical speciation codes. The resulting geochemical transport is further interfaced with various functional groups. These groups describe:

- sorption;
- corrosion;
- microbiology;

[2] GRM v4.1 is the first version to include the PHREEQC speciation code. PHREEQC provides a method to investigate surface complexation and ion exchange sorption processes. Currently there are limitations to the interfaces with other functional modules, most notably radioactive decay, corrosion, and microbiology (See Appendix. O)

- radionuclide decay;
- colloidal migration;
- mineral precipitation/dissolution; and,
- gaseous release.

Regions within GRM are represented as homogeneous, finite–difference cells. Each cell is subdivided vertically into a saturated and an unsaturated zone. The horizontal 2D transport of dissolved species and colloidal particulates in the saturated zone is modelled using standard advection and dispersion equations. Material in the unsaturated zone is assumed not to be transported horizontally. Vertical transport in the model is represented by means of the transfer of material from the unsaturated to the saturated zone. The unsaturated zone of each cell is assigned a value of porosity and therefore the cell is provided with a head space.

Geochemical calculations including pH determinations are carried out by a modified version of the PHREEQE/C speciation code. Mineral precipitation and dissolution is determined by a fully automated reaction path model. Mineral equilibration can either be instantaneous and mediated by PHREEQE/C, or kinetically controlled. Redox reactions involving oxygen, nitrate, ferric iron, sulphate and organic molecules are not mediated by PHREEQE/C and are predominantly controlled by microbial reactions. The redox status of these species is taken out of the control of PHREEQE/C by separating the relevant redox states (eg, Fe(III) and Fe(II)) within the thermodynamic database. GRM calculates the pe of a cell from the most oxidising redox couple, using standard pe functions [9, 10]. Step changes from one couple to the next occur through microbial action removing the most oxidising couple.

The microbial module of GRM is based on the landfill model of Young [64] in conjunction with a number of other models [11, 12]. Currently nine microbial groups carrying out a range of processes are included within the code. The processes considered can be roughly classified as:

1. aerobic metabolism;
2. denitrification;
3. fermentation;
4. iron reduction;

5. sulphate reduction;
6. acetogenesis;
7. methanogenesis;
8. reoxidation (using oxygen); and,
9. reoxidation (using nitrate).

The primary electron donors considered are hydrogen and dissolved organic carbon. The latter is generated through the hydrolysis of polymeric organic carbon present as either cellulose, proteins or fats. Hydrogen is produced both by anaerobic corrosion of iron and by microbial fermentation. Bacterial substrate removal and biomass growth are described using Monod kinetics as described by McCarty and Mosey [13], with the addition of a pH control factor.

Corrosion of iron is modelled within GRM to represent the degradation of items such as steel drums, which typically form part of the LLW inventory. Corrosion is treated separately within the unsaturated and saturated zones. In both cases aerobic and anaerobic corrosion are included, but the resulting products are different. Corrosion in the unsaturated zone is a three phase process where iron oxidation is followed by oxide depletion and then by anaerobic magnetite production. Aerobic corrosion in the saturated zone produces ferric oxyhydroxides. The user may choose either ferric or ferrous iron as the corrosion product. Both products are accompanied by the evolution of hydrogen. Provided that the pH is less than a specified value [3], saturated zone corrosion may produce colloidal ferric oxyhydroxides.

The corrosion and microbial processes modelled in GRM, are able to generate six gases, namely hydrogen, carbon dioxide, hydrogen sulphide, nitrogen, ammonia and methane. Three other gases are considered in GRM. These are:

- oxygen;
- radon; and,
- water vapour.

Radon is produced by the decay of radium. Water vapour is included to model the release of tritium. Molecular oxygen can be consumed within the model but is not produced.

[3] This value is specified by the user in `grm.cor` (although it is usually set at around 9.0).

Colloidal–facilitated nuclide transport is simulated by allowing up to three types of colloidal particles to be included. Interaction between the colloid types is limited to the coupled partitioning between adsorbed and dissolved contaminant species. It is assumed that colloids are not sorbed, have the same advective and dispersive properties as other transported species and that filtration is not significant.

Radionuclide sorption onto the non-mobile geomatrix may either occur at a specified rate or be coupled to the nuclide speciation while sorption onto colloids is taken to be instantaneous. Sorption distribution coefficients may either be specified as constants at the species level or at the elemental level as explicit functions of pH. Note that, since speciation is dependent on solution composition, even the species–dependent distribution coefficients must implicitly be functions of the leachate chemistry, including pH. Four distribution coefficients can be used for each species. One of these describes the partition between the solute and the geomatrix, whilst the others are relevant to the different colloid types.

Accounting for radionuclide decay is complicated by the presence of solute, sorbed and solid phases of the nuclides. Once a nuclide has decayed, the daughter product will be redistributed between its solute, sorbed and mineral phases according to the ambient bulk chemistry.

2 Timescales and the Modular Approach

Material present within the model is assigned by GRM into one of the following states:

- unsaturated material, including geological and waste material above the water table;
- saturated material, including geological and waste material below the water table;
- liquids, including any dissolved material; and,
- adsorbed material.

The adsorbed material covers those contaminants that have been removed from their original position within the system and have become attached to another region through the process of either precipitation or sorption. Such material includes mobile and immobile components.

The processes involved in the transfer of material between cells, zones within cells and between the above states are time dependent. As stated previously, 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 very wasteful to evolve all aspects of the system at the rate of the most rapid process[4]. Recognition of this point has led to the development of three main calculational sequence modules, each being characterised by a separate timescale. The modules are:

1. Microbial module. The kinetic approach to microbiology implies that a short timestep is required for the microbial calculations (typically less than 1 day).
2. The transport module, which examines the movement of chemicals in the groundwater. The timescale for these calculations will depend on the system size and the groundwater velocities, but is likely to be several days at the very least.
3. The chemistry module, which determines the current chemistry within the saturated zone. PHREEQE/C is used, which assumes equilibrium chemistry. Timescales for the chemical evolution of a site are likely to be highly situation specific. However, it is clear that the re-application of PHREEQE/C is only worthwhile when the conditions in a cell have been sufficiently perturbed through the action of the other processes.

[4]In addition, such an approach could lead to stability problems. For example, if too small a time step is used in a finite-difference solution to the transport (advection-diffusion) equation, numerical noise may not be attenuated [14].

Indeed, the overall philosophy of the code is based on a modular approach to the processes modelled. However because of the central role played by the transport and geochemistry modules, these two form the framework into which the other processes are interfaced. The main modules exhibit a definite hierachy of timescales. This is an extremely helpful observation from a coding perspective, as it allows one to construct a simple timestepping loop. The time loop used in GRM is illustrated in the figure below.

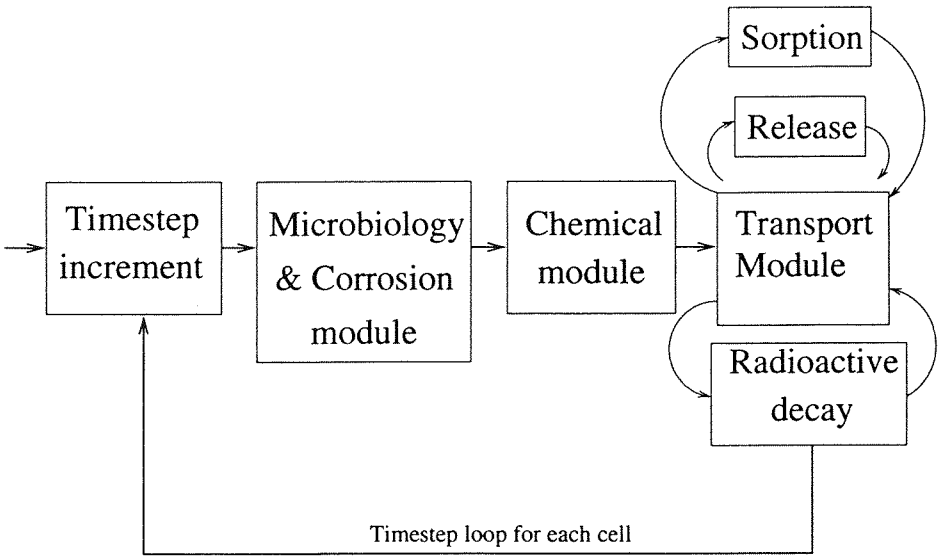

Figure 1: Time loop for several modules in GRM.

After each increment of the transport time, the microbiology module is called. This implements its own time loop, using the shorter microbial timestep. After the microbial calculations have been performed, a check is made to see whether or not the next speciation time has been reached. If so then the chemical module is called. The transport module is then called, after which the simulation time is incremented by the transport timestep and the loop is repeated. Note that the looping requires that the speciation timestep be at least as long as the transport step and that the microbial timestep be no longer than the transport step.

The following processes are allowed to evolve according to the transport timestep:

- The flow of material between cells and zones. Both the groundwater and any mobile

particles within it will move, according to the direction and speed of groundwater movement.

- Sorption and desorption. A contaminant can be interchanged between the groundwater and the surface of the material it is in contact with. This model assumes that this is a kinetic process: thus it takes time for the relative concentrations in the groundwater and those on the surrounding material to reach an equilibrium condition.
- Release from the unsaturated zone. As infiltration water passes through the unsaturated zone it removes material. Three release processes are identified:
  1. Loose material of a large size fraction can be washed down into the saturated zone where it remains.
  2. Material dissolves in the infiltrating water and is carried down to mix with the groundwater below the water table.
  3. Material of small size fraction is washed down into the saturated zone where it is held in suspension and is consequently able to migrate horizontally.

2.1 Coupling of Chemistry and Transport

Neglecting adsorption and radioactive decay for the moment, the general system of partial differential equations describing interactive transport for a system of n species has the form:

$$\frac{\partial c_i}{\partial t} = -\underline{\nabla}.(\underline{q}c_i) + \underline{\nabla}.(\underline{\underline{D}}.\underline{\nabla}c_i) + \sum_{j=1}^{n} S_{ij}[\{c\}] \qquad (1)$$

where:

- c_i is the solute concentration for species i;
- the first term on the right-hand side (RHS) describes advection, $\underline{q}$ being the Darcy velocity (this is related to the pore velocity by $\underline{q} = \phi\underline{v}$, where ϕ is the porosity and $\underline{v}$ the pore velocity);
- the second term on the RHS describes dispersion, $\underline{\underline{D}}$ being the hydrodynamic dispersion tensor; and,

- the third term on the RHS represents the reactive chemistry, using the notation[5] of a coupling matrix, S, which will be a functional of all the species concentrations.

There are many strategies for solving this coupled system although some are likely to remain computationally intractable for the foreseeable future (see for example, Ref. [16]). Since the GRM code computes many model processes in order to determine the S matrix, a simple approach to the solution of Eq. 1 is highly desirable so that the CPU and storage requirements can be kept to manageable levels. One of the simpler approaches, and indeed the one that is adopted within the GRM code, is to follow a two-step approach. In the first step, the S matrix is set to zero and the transport equation is solved by an explicit finite difference method. 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, we assume 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 slowly enough that the concentration of each species over the course of a transport time step is well approximated by its concentration at the start of the time step.

Obviously, these two assumptions are strongly related to each other and to the assumption of defining a hierarchy of timescales in the problem.

[5] as in Ref. [15] for example.

3 Transport Model

This section deals principally with the geochemical transport model, outlining its theoretical basis. An indication of the simplifying techniques which have been found necessary and their supporting assumptions are given.

3.1 Groundwater Flow

GRM does not contain a groundwater flow solver and hence the flowfield, $\underline{v}(\underline{r}, t)$, must be supplied externally. The user is supplied with two methods of doing this:

1. The flowfield may be specified explicitly within the input file `grm.flw`. For simple one-dimensional test cases, one could write this file manually but this is unlikely to suffice for real site simulations where the flowfield will be of a complex two-dimensional nature. In such situations, a `grm.flw` file could be constructed from interpretation of the results of the BNFL groundwater flow solver GRWOLF [17]. Note that if the option of using a `grm.flw` file is chosen, then the finite–difference grid on which calculations are to be performed must also be supplied manually (in file `grm.grd`).
2. The groundwater flow package MODFLOW [18] may be used. GRM has the ability to read data directly from the (unformatted) output files produced by MODFLOW. Note that these files must have the stem `modf.` to be recognised by GRM. If this option is chosen, then the finite–difference grid (together with various hydraulic properties) is specified using the MODFLOW pre-processor package MODELCAD [19] via the MODELCAD grid (`.grd`) output file. This grid file must be named `modf.grd` for use by GRM.

Within version 4.1 of GRM there is a facility for defining a variable flowfield. In order to do so, one must use the `grm.flw` option described above. The user can specify flowfield parameters for a number of distinct flowfield periods (up to 10 periods may be defined in the current version of the code). The parameters are assumed to remain constant throughout each such period.

3.2 Species Transport

The pure transport processes in GRM are described by making a simple modification to Eq. 1 to yield:

$$\frac{\partial c_i}{\partial t} = -\underline{\nabla}.\underline{q}c_i + \underline{\nabla}(\underline{\underline{D}}.\underline{\nabla}c_i) - Pc_i + Rc_{iR} \tag{2}$$

The penultimate term represents the removal of groundwater from the system due to a pumping well on the boundary. The final term represents the addition of water due to a boundary well (c_{iR} is the species concentration at the boundary). These two new terms account for the effect of incoming and outgoing groundwater flux in the model domain.

The species transport in GRM is modelled by solving the above equation for each transport timestep, using an explicit–differencing scheme. Further discussion of differencing methods is available in many numerical texts (see for example Ref. [20]). The explicit–differencing scheme used by the current version of the code is based on the following representation of Eq. 2.

$$V_{i,j}\frac{\Delta c_{i,j}}{\Delta t} = F^x_{i-1,j} - F^x_{i,j} + F^y_{i,j-1} - F^y_{i,j} - p_{i,j}c_{i,j} + \sum_n r^n_{i,j}c^n_{i,j} \tag{3}$$

In the above equation:

- i and j label the finite difference cell;
- $V_{i,j}$ is the porevolume of the saturated zone of the cell;
- $F^a_{i,j}$ denotes the flux to/from the i,j th cell in the a-direction;
- $p_{i,j}$ is the rate of water extraction to the external environment; and,
- $r^n_{i,j}$ is the rate of water influx from the n th external source, at which the species concentration is c^n.

Should the cell $(i-1,j)$ or $(i,j-1)$ not exist then clearly the corresponding flux is set to zero. The fluxes F have their origin in the advective and dispersive terms of Eq. 2,

$$F^x_{i,j} = A^x_{i,j}v^x_{i,j}c^x_{i+\frac{1}{2},j} + 2A^x_{i,j}D^{xx}_{i,j}\frac{c^x_{i,j} - c^x_{i+1,j}}{x_{i+1} - x_{i-1}} + 2A^y_{i,j}D^{xy}_{i,j}\frac{c^x_{i,j} - c^x_{i,j+1}}{y_{j+1} - y_{j-1}} \tag{4}$$

and similarly for $F^y_{i,j}$. In Eq. 4 we have introduced $A^x_{i,j}$ and $A^y_{i,j}$ to represent the saturated area of the right and front faces respectively of cell (i,j).

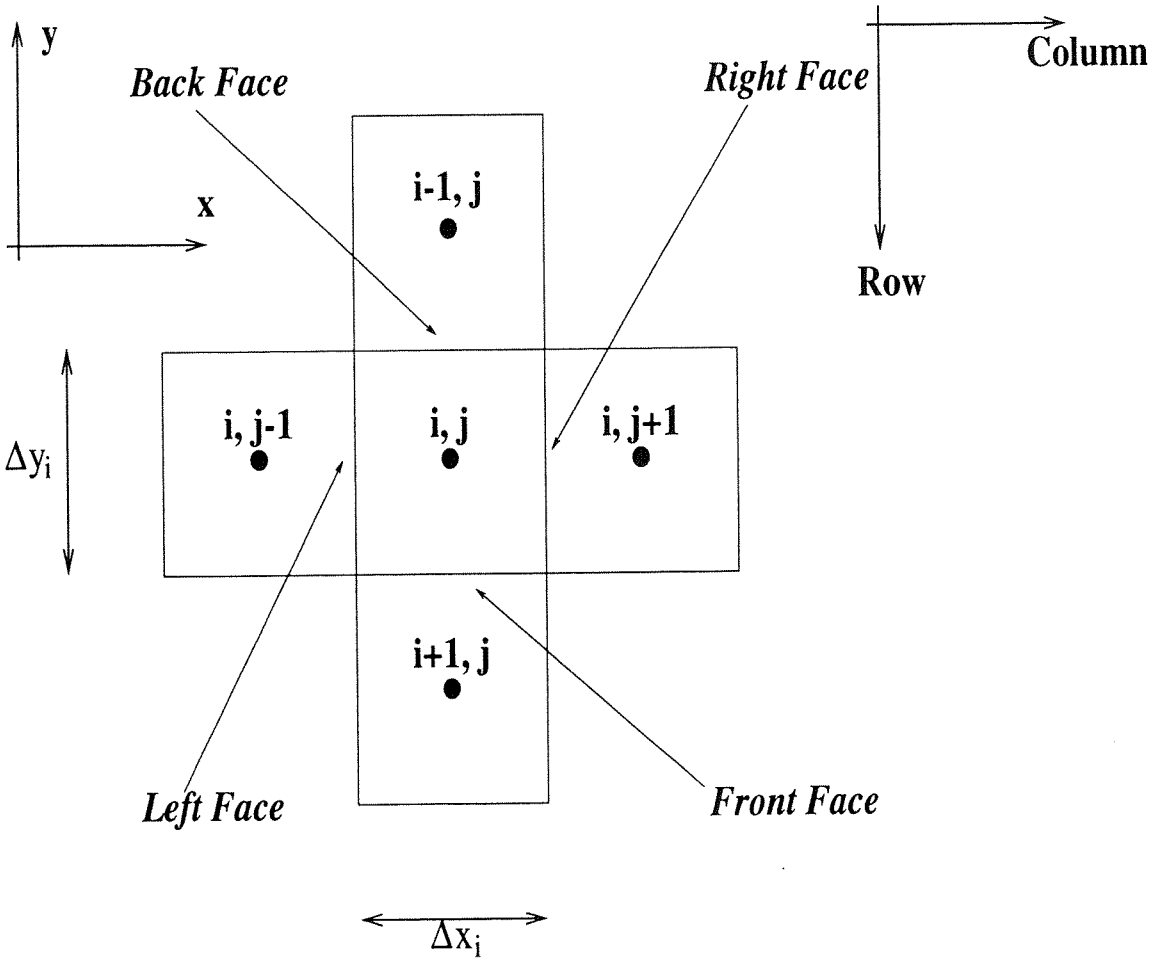

Figure 2: Definition of the cell faces.

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As illustrated in Fig. 2, the 'right face' of cell (i,j) is the boundary between cell (i,j) and cell $(i+1,j)$, while the 'front face' is the boundary between cell (i,j) and cell $(i,j+1)$.

The concentration $c^x_{i+\frac{1}{2},j}$ is defined according to the sign of the flux across the right face of the cell,

$$c^x_{i+\frac{1}{2},j} = \begin{cases} c^x_{i,j} & v^x_{i,j} \geq 0 \\ c^x_{i+1,j} & v^x_{i,j} < 0 \end{cases} \tag{5}$$

3.3 Dispersion

Following Refs. [14, 21], in GRM the dispersion tensor is decomposed into a contribution that is due to molecular diffusion, plus longitudinal and transverse components of mechanical dispersion. The strengths of these are described by parameters α_M, α_L and α_T respectively, defined by:

$$D_{ij} = \alpha_M \delta_{ij} + \alpha_T v \left(\delta_{ij} - \frac{v_i v_j}{v^2} \right) + \alpha_L \frac{v_i v_j}{v} \tag{6}$$

(Note that in this subsection, the indices i and j label spatial components i.e.directions, rather than cell positions.)

In practice, although α_M appears in the GRM code, its value is thought likely to be small and subject to large uncertainties. Thus, it has been hardwired to zero in the current version.

In the approximation of the first–order derivatives in Sec. 3.2, errors proportional to the second–order derivatives were introduced. This phenomenon is known as numerical dispersion and depends on the coarseness of the finite–difference grid, and also on the size of the transport/computational timestep. It is straightforward to show (see Appendix B of Ref. [2] for example) that the approximations result in an effective dispersion of [6]:

$$\widetilde{D}_{ij} = D_{ij} + \frac{1}{2} v_i v_j \delta t - \frac{1}{2} \delta_{ij} v_i \delta x_j. \tag{7}$$

In one dimensional simulations, it is possible for the user to attempt a correction of inaccuracies due to numerical dispersion by using Eq. 7 to adjust α_L. One should bear in mind, however, that Eq. 7 neglects terms of higher order which could be significant in some situations. The objective of this discussion of numerical dispersion is to highlight

[6] This equation is only a first-order approximation

the point that care must be taken when choosing the coarseness of the finite difference grid.

3.4 Checks

Whilst transporting the individual species concentrations, a test is made to determine if the concentration remaining in any one cell is negative. If the concentration does become negative, the amount transported is adjusted so that the amount remaining is zero.

The transport solver described above is contained within the transport module of the GRM. This transport module also updates concentrations due to radioactive decay, leaching and sorption. The transport module is in a time loop which is performed for each cell of the model (see Fig. 1).

Within the transport module of GRM version 4.1, there is an option which allows radionuclide mass balance calculations to be performed. This option is switched on using the flag IMSBAL in the main input file grm.dat. Within these calculations, no distinction is made between different isotopes, or the decay chains to which they belong. The check considers the total quantity of the element in the initial inventory, the amount entering the modelled domain from external sources, the amount leaving the modelled domain and the amount remaining in the modelled domain. Changes due to radioactive ingrowth and decay are also tracked. The results of these calculations are written to the output file grm.bal.

3.5 Boundary Conditions

Boundary conditions within GRM fall into two categories:

1. groundwater flowfield boundary conditions; and,
2. chemical speciation boundary conditions.

Like the internal groundwater flowfield, conditions falling into the first of these categories are either set in the input file grm.flw or within MODFLOW and are simply picked up by GRM at the data initialisation stage. Following the terminology of MODFLOW, there are three possible types of flowfield boundary condition:

1. constant head;
2. wells; and,

3. recharge.

For each type, positive values represent flows into the model domain and negative values represent flows out of the domain. Recharge flows into the modelled domain are used to represent infiltration from above and may be used in determining the rate of leaching from the unsaturated to the saturated zone of a cell (see Sec. 3.6). There is no physical distinction between well flows and constant head flows in the code, other than to provide two more types of external flow. In many GRM applications, it has become the practice to use constant head flows to describe seepage through the base of the modelled region and to use well flows to describe flows through all other external boundaries (apart from the top boundary).

In models where one or more constant head cells have been specified (and where MODFLOW is used), an extra block of data appears in the `.cbb` file. This block contains the flows within such cells. If one or more well cells are specified, a `.cbw` unformatted file is created. This file contains flows at every cell in the model. However, only those specified with non-zero well flows will have non-zero values. Recharge cells are handled similarly to well cells, the appropriate MODFLOW file having the suffix `.crc`.

Conditions in the second of the above categories, i.e., chemical speciation boundary conditions, are defined by the user in the input file `grm.bcs`. This file contains species concentrations and pH/pe data on a cell by cell basis for each type of external flow. Either constant or time–dependent boundary concentrations may be specified. Note, however, that if constant boundary concentrations are used then the influent streams are assumed to be nuclide free so that only macrospecies (and colloid) concentrations are specified in `grm.bcs`.

Only advective boundary fluxes are considered: i.e., dispersion through the external walls of the model domain is not considered.

3.6 Release from the Unsaturated Zone

Release of material from the unsaturated zone is performed on an elemental level: i.e., the rate of release of a particular microelement[7] is the same for all isotopes and species of that element. There are two different release models available within GRM and the user is able to choose which of the models is to be applied to each microelement in each cell of the grid.

[7] Microchemistry and macrochemistry are defined in Sec. 4.2.

The first model simply assumes first–order release: i.e., that the release rate for a particular element is proportional to the mass of that element in the unsaturated region. The release rate L is given by:

$$L = \frac{Q}{V_u \phi} mr, \tag{8}$$

where:

- Q is the water flux infiltrating through the unsaturated region (the recharge flow);
- V_u is the volume of the unsaturated region;
- ϕ is the bulk porosity of the unsaturated region;
- r is a user–supplied release coefficient; and,
- m is the mass of the element present in the unsaturated region.

The second model is more mechanistic and attempts to account for the effects of sorption and solubility on release. Neglecting solubility for the moment, the total element mass in the unsaturated region which is in the liquid phase (and therefore available for release) is:

$$\frac{m}{1 + \frac{\rho K_d}{\phi}}, \tag{9}$$

where ρ is the bulk density of the sorbing medium and K_d is a distribution coefficient. Accounting for solubility limitations, the maximum mass released over a single timestep is:

$$R_{\max} = c_s Q \Delta t, \tag{10}$$

where c_s is an effective solubility limit and Δt is the transport timestep. Thus, a mass $R_{\max}$ is released every timestep until:

$$\frac{m}{1 + \frac{\rho K_d}{\phi}} < c_s Q \Delta t. \tag{11}$$

After this time it is assumed that the remaining microelement mass is distributed uniformly over the volume $Q\Delta t$, so that the mass released over one timestep becomes:

$$R = \frac{m}{1 + \frac{\rho K_d}{\phi}}. \tag{12}$$

The second model described above is sometimes referred to as the two parameter release model (the parameters being c_s and K_d). A more complex approach to release was at one time investigated, using a one dimensional simulation of the vertical direction to derive the radioelement release function, which was then used to supply time dependent nuclide boundary concentrations to the GRM. Comparisons of the two parameter release model with the more complex treatment have been very favourable [22].

The parameter c_s was described above as an *effective* solubility limit. Although the concentration in the unsaturated zone could indeed be solubility limited due to mineral formation, the user may wish to set a value of c_s based on other considerations. For example, consider a radioelement that is not sorbed and does not form minerals. If it is evenly distributed in an unsaturated zone where the infiltration rate is modest, then the release rate will be constant during the time taken for the radioelement to be transported through the unsaturated zone. Such behaviour could be modelled through an appropriate choice of the effective solubility limit.

3.7 Waste Settling

GRM is principally concerned with modelling the saturated region within a waste repository. The role of the unsaturated region is mainly to provide a headspace for gases. As the waste in the saturated region is degraded, particularly due to hydrolysis of proteins, fats and cellulose, there will be a reduction in the total solids volume within this region. As this happens, solids within the unsaturated region will be able to drop beneath the water table. The solids which are able to drop are cellulose, proteins, fats, minerals, iron and corrosion products. In addition, nuclides (whether in the solid phase or sorbed onto other solid phases) are also allowed to drop.

The following simplifying assumptions regarding settling have been made:

1. the change in the solid volume within the saturated zone is due solely to the hydrolysis of cellulose, proteins and fats;
2. nuclides do not contribute to the waste volume (either in the saturated or the unsaturated zones);
3. the porosity of all solid phases is equal, i.e. there are no porosity changes due to settling;
4. the active fraction of ^{14}C in the unsaturated region is the same as in the saturated region for each carbon species at the start of the simulation and is not recalculated.

The active fractions of ^{14}C within the saturated region are recalculated using these constant active fractions of the unsaturated region. Thus, it is assumed that for ^{14}C, settling is an important process for a limited time, which is significantly less than the ^{14}C half life (5730 yr);

5. solids drop down in proportion to their volume fraction in the unsaturated zone;
6. there are no headspace volume changes in the unsaturated zone due to settling; and,
7. all mineral phases in the unsaturated zone have the same bulk density.

From assumption 1 above, the total change in the volume of solids within the saturated zone over a single time period is:

$$\Delta V_{\text{sat}} = \sum_{i=1}^{3} \left(\frac{\Delta M_{\text{cell}_i}}{\rho_{\text{cell}_i}} + \frac{\Delta M_{\text{prot}_i}}{\rho_{\text{prot}_i}} + \frac{\Delta M_{\text{fat}_i}}{\rho_{\text{fat}_i}} \right), \tag{13}$$

where ΔM_{cell_i} is the mass of type i cellulose[8] hydrolysed over a microbial timestep and ρ_{cell_i} is the bulk density of type i cellulose. Similarly, 'prot' and 'fat' are used to label proteins and fats respectively.

Recalling, from assumption 5, that solids drop in proportion to their volume fraction in the unsaturated zone we must construct the total volume of "droppable" solids in the unsaturated zone. This is given by:

$$\begin{aligned} \text{DV} = & \sum_{i=1}^{3} \left(\frac{M_{\text{cell}_i}}{\rho_{\text{cell}_i}} + \frac{M_{\text{prot}_i}}{\rho_{\text{prot}_i}} + \frac{M_{\text{fat}_i}}{\rho_{\text{fat}_i}} \right) \\ & + \sum_{j} \frac{M_{\text{min}_j}}{\rho_{\text{min}_j}} + \frac{M_{\text{iron}}}{\rho_{\text{iron}}} + \sum_{l} \frac{M_{\text{cp}_l}}{\rho_{\text{cp}_l}} \end{aligned} \tag{14}$$

where M and ρ denote mass and bulk density in the unsaturated zone respectively, min_j is the j th macromineral (not formed via corrosion), 'iron' is uncorroded iron and cp_l is the l th corrosion product.

The drop down of each individual "droppable" solid is now considered in turn.

1. Cellulose
   In line with assumption 5 above, the volume of type i cellulose which drops from the

[8] The different types of cellulose, fat and protein will be discussed later.

unsaturated to the saturated zone in a single timestep is:

$$V_{\text{cell}_i}^{\text{drop}} = \frac{\Delta V_{\text{sat}}}{\text{DV}} \frac{M_{\text{cell}_i}}{\rho_{\text{cell}_i}}, \tag{15}$$

so that the mass of type i cellulose which drops is:

$$M_{\text{cell}_i}^{\text{drop}} = \Delta V_{\text{sat}} \frac{M_{\text{cell}_i}}{\text{DV}}. \tag{16}$$

2. Proteins
   Proteins are handled similarly to cellulose.

3. Fats
   Fats are also handled similarly to cellulose.

4. Macrominerals (not formed via corrosion)
   The situation with minerals is simplified by assumption 7 above. This states that they all have the same bulk density, and so ρ_{min_j} in Eq. 15 has the same value for each j. This avoids the need to specify a different value for each mineral in the PHREEQE database. Thus the volume of mineral j which drops from the unsaturated zone is:

$$V_{\text{min}_j}^{\text{drop}} = \frac{\Delta V_{\text{sat}}}{\text{DV}} \frac{M_{\text{min}_j}}{\rho_{\text{min}}}. \tag{17}$$

   This leads to a dropped mass of:

$$M_{\text{min}_j}^{\text{drop}} = \Delta V_{\text{sat}} \frac{M_{\text{min}_j}}{\text{DV}}. \tag{18}$$

5. Uncorroded Iron
   Iron which remains uncorroded in the unsaturated zone is again similar to cellulose, the dropped mass being given by:

$$M_{\text{iron}}^{\text{drop}} = \Delta V_{\text{sat}} \frac{M_{\text{iron}}}{\text{DV}}. \tag{19}$$

   Although not physical, the iron which drops down to the saturated region is assumed to increase the dimensions of the iron plates, spheres and rods[9] in the saturated region and decrease them in the unsaturated region. This is done in order to allow subsequent corrosion of the dropped-down iron in the saturated region.

[9] These different geometries for iron are discussed in Sec. 9.

- Rods
  The number of rods in each region is assumed to remain unchanged. Hence, if the mass of the rods in the saturated region is M_{sat}, the density of mild steel is ρ and the number of rods is N, then:

$$M_{\text{sat}} = N\rho\pi r^2 l, \tag{20}$$

  where r is the average radius and l is the average length of the rods. If the mass of iron rods which drops down is ΔM, then:

$$M_{\text{sat}} + \Delta M = N\rho\pi R^2 L, \tag{21}$$

  where R and L are the new radius and length of the rods respectively. Assuming the same ratio of radius to length before and after the drop down, the new radius becomes:

$$R = \left[\frac{r}{l}\left(\frac{M_{\text{sat}} + \Delta M}{\rho N\pi}\right)\right]^{1/3}, \tag{22}$$

  and the new rod length is:

$$L = \frac{M_{\text{sat}} + \Delta M}{\rho N\pi R^2}. \tag{23}$$

  The new average rod radius and length in the unsaturated region are calculated in a very similar manner.

- Spheres
  If the mass of the spheres in the saturated region is M_{sat} and their average radius is r then:

$$M_{\text{sat}} = \frac{4}{3}\pi r^3 N\rho, \tag{24}$$

  where N is the number of spheres in the cell. Taking the mass of dropped–down spheres to be ΔM, the new mass is then:

$$M_{\text{sat}} + \Delta M = \frac{4}{3}\pi R^3 N\rho, \tag{25}$$

  R being the increased radius due to drop down, which is given by:

$$R = \left[3\left(\frac{M_{\text{sat}} + \Delta M}{4\pi N\rho}\right)\right]^{1/3} \tag{26}$$

  The average sphere radius in the unsaturated region is calculated in a very similar manner.

- Plates
  Taking the weight of the plates in the saturated region to be M_{sat}, their thickness to be t, total surface area (top and bottom) to be A and the density of steel to be ρ then:

$$M_{sat} = \frac{A}{2} t\rho. \tag{27}$$

  Assuming the ratio of surface area and thickness to be the same before and after the mass of iron has dropped down, then the new surface area (SA) can be written as:

$$SA = 2\left[\frac{A}{2}\left(\frac{M_{sat} + \Delta M}{\rho t}\right)\right]^{1/2}, \tag{28}$$

  where ΔM is the mass of iron plates which have dropped down. A new thickness is easily calculated. Similar expressions hold for the new surface area and thickness in the unsaturated region of the cell.

6. Corrosion Products
   Iron corrosion in the unsaturated zone gives rise to two possible solid products: Fe_2O_3 and Fe_3O_4. On dropping down into the saturated zone, these solids are assumed to instantaneously dissolve, giving appropriate quantities of liquid Fe^{2+} and Fe^{3+} ions. In the case of Fe_2O_3, one mole of solid gives two moles of Fe^{3+} ions. Fe_3O_4, however, is a mixed oxide so that one mole of solid gives one mole of Fe^{2+} and two moles of Fe^{3+}. Thus, over a single timestep, the masses of Fe_2O_3 and Fe_3O_4 which drop from the unsaturated zone are given by:

$$M^{drop}_{Fe_2O_3} = \Delta V_{sat} \frac{M_{Fe_2O_3}}{DV} \tag{29}$$

$$M^{drop}_{Fe_3O_4} = \Delta V_{sat} \frac{M_{Fe_3O_4}}{DV}. \tag{30}$$

   The corresponding increases in the liquid masses (kmol) of Fe^{2+} and Fe^{3+} are given by:

$$\Delta^{sat}_{Fe_2} = \Delta V_{sat} \frac{M_{Fe_3O_4}}{DV} \frac{1}{MW_{Fe_3O_4}} \tag{31}$$

$$\Delta^{sat}_{Fe_3} = 2\left[\Delta V_{sat} \frac{M_{Fe_2O_3}}{DV} \frac{1}{MW_{Fe_2O_3}} + \Delta V_{sat} \frac{M_{Fe_3O_4}}{DV} \frac{1}{MW_{Fe_3O_4}}\right]. \tag{32}$$

   where MW_X is the molecular weight of X.

7. Nuclides
   As was stated above, it is assumed that nuclides do not contribute to the waste volume. It is also assumed that, within the unsaturated zone, each nuclide is distributed evenly (on a volume basis) throughout the entire unsaturated volume. Thus, over each timestep, the proportion of the total mass of each nuclide which drops from the unsaturated zone is equal to the fraction of the total unsaturated volume which drops down. Thus:

$$\Delta M_{\mathrm{nuc}_i} = M_{\mathrm{nuc}_i} \frac{\Delta V_{\mathrm{sat}}}{V_{\mathrm{unsat}}} \tag{33}$$

   where M_{nuc_i} is the mass of nuclide i in the unsaturated zone and V_{unsat} is the total volume of the unsaturated zone (which is assumed to remain unchanged despite the settling).

   Nuclides dropping from the unsaturated zone are initially added to the liquid phase on entering the saturated zone and any necessary precipitation or sorption is handled subsequently by the appropriate section of code. Note that nuclide drop down occurs in addition to the existing release mechanism. The two effects are simply additive in general. However, this combination of mechanisms may potentially result in a greater amount of nuclide transfer within a timestep than the amount which was originally present in the unsaturated zone. Should this occur then the rates of the two processes are reduced on a pro rata basis such that the amount remaining in the unsaturated zone is zero.

The option for settling calculations to be included is switched on by the `IDROP` flag in the file `grm.dat`. The densities which are used to calculate the amount of mass which settles down to the saturated region are defined in the input file `grm.bug`. The `grm.bug` file also contains flags that enable settling to be switched on or off on a cell by cell basis.

3.8 Colloidal–Particle Facilitated Transport

3.8.1 Background

Traditionally contaminants that migrate under saturated or unsaturated conditions have been simulated assuming the existence of one or more mobile dissolved phases and an immobile solid phase associated with the soil matrix. Recently though, there is evidence that colloidal sized particles can transport radionuclides some distance away from the radionuclide source area [23]. However, this is dependent on a number of factors, such as [24]:

- are colloids present?
- are they present in large enough quantities to be significant?
- are they transportable [25]?
- do radionuclides associate with the colloids [26]?
- is uptake reversible or irreversible?

A major problem with modelling of colloidal transport is that the composition and properties of colloids will be very site specific. For instance, in the Kristallin-1 safety assessment [27], NAGRA, while not denying that colloids could be generated by the degradation of waste and canisters in their near field concept, have reasoned that the sequence of events that would have to happen to allow colloidal transport through their highly impermeable bentonite backfill "cannot happen, and the scenario is excluded from quantitative assessment".

Therefore, the most rigorous approach to the modelling of colloidal transport would involve:

- the chemical and physical properties of specific colloidal material found at a site;
- the interaction of this material with radionuclides;
- the interaction of the combined radionuclide–colloidal particle with matrix materials encountered in the flow path; and,
- an understanding of the impact that the physico-chemical evolution of the site will have on the above features.

Clearly, a great deal of site–specific information would have to be obtained in order to follow such a rigorous approach. The generated model would also be specific to a particular conceptual model of site behaviour. Colloidal migration is a relatively new, developing field of study in which the majority of published studies do not address all of the above issues. For this reason, the implementation of colloidal–facilitated transport in GRM uses a simple empirical association model. Its parameters can be obtained either generically or by empirical calibration. The GRM approach has the advantage of allowing an exploration of the sensitivity of model results to various colloidal assumptions based on conceptual and parameter uncertainty.

3.8.2 Model Implementation

The approach taken allows up to three types of colloid to be modelled. These may be defined in grm.bcs for influent/effluent streams, in grm.inv for the initial inventory composition, and in grm.kds for the distibution coefficients of microelements on the colloids. Colloid Type 1 is "hardwired" to the corrosion routines (i.e. linked to Fe^{3+} via COLPER). If the corrosion facility is not utilised, yet Colloid Type 1 is still defined in the inventory, then it will disappear at the first timestep (see 9.1). If other(non-corrosion related)colloid types are to be considered, these should be defined as Colloid Type 2 or 3. Multiple colloidal types are expected in natural porous media, owing to such factors as size distribution considerations, and potential inorganic and organic colloidal sources. In the GRM implementation, interactions among colloidal types are limited to adsorption kinetics between dissolved and adsorbed contaminant species.

The movement of colloids is assumed not to influence the flowfields in either the saturated or unsaturated zones. Under the further assumption that the colloidal particles are not sorbed and have the same advective and dispersive properties as the other transported species, one can incorporate the colloidal transport by making some simple modifications to the pure transport equation (Eq. 2):

- the colloid transport is treated by using Eq. 2 for each colloidal type (j), replacing the species concentration c_i by the colloidal particle density, $p^j(\underline{r}, t)$;
- transport of non-colloids is treated by using Eq. 2 as before, but replacing the species concentration c_i thus:

$$c_i \rightarrow c_i + \sum_j s_i^j p^j \tag{34}$$

  where $s_i^j(\underline{r}, t)$ represents the amount of species i that is adsorbed onto the mobile colloid species j.

The modelling of sorption of species onto the colloidal particles is described in Sec. 5. The GRM colloidal model is a simple one. Certainly it would be possible to go further. For instance, the sorption coefficient could be allowed to vary with the particle size and chemical nature. However, any such refinements would slow the code's operation and will only be included if data becomes available or if sensitivity studies indicate the value of the modifications.

4 PHREEQE/C Geochemical Model

The second step of the two–step approach described in Sec. 2.1 is undertaken by PHREEQE [5] or PHREEQC [6]. These are public domain packages, of which the former has been in industrial and academic usage for two decades. PHREEQE/C's most common uses are as stand–alone packages for geochemical speciation studies.

PHREEQC is derived from PHREEQE but has been rewritten eliminating many of the deficiencies and limitations of PHREEQE and gaining many new capabilities. These new capabilities are described in full within [6], however one feature of particular relevance is surface complexation which is described briefly within this document (Sec. 4.9). The compatibility of PHREEQC with other GRM options is described in Appendix O.

In GRM PHREEQE and PHREEQC have been adapted to perform integrated chemical thermodynamic equilibrations. These adaptations have required significant changes to the way in which PHREEQE and PHREEQC are used. While PHREEQC is superior in many ways, there are circumstances in which use of PHREEQE is advantageous (Sec. 4.2). In the following section, the equilibrium equations solved and the changes made to the packages are described. For simplicity only PHREEQE is referenced, however all descriptions apply equally to PHREEQC unless specified otherwise.

4.1 Chemical Equilibrium Relations

For an aqueous system which contains J dissolved chemical species, it is always possible to choose a set of I linearly independent primary variables ($I \leq J$) such that the formation of all chemical species can be expressed in terms of the primary variables. The primary variables represent I chemical components of the species, and from them secondary variables (representing all other chemical components) are determined through mass action equations.

To solve a system with I primary variables, obviously I equations are required. The equations are constructed here by applying the mass balance principle to each component except for hydrogen, oxygen and water. The mass balance equation for hydrogen is replaced by a charge balance equation. Conservation of electrons accounts for the mass balance of oxygen. The mass of water is assumed constant, since chemical reactions in groundwater involve only a small mass transfer of water [28]. If the aqueous system is in equilibrium with P mineral phases then an additional set of P unknowns is introduced in order to describe the amounts of the P mineral phases precipitated or dissolved. The additional equations required for the mineral phases are provided by solubility constants

which relate the minerals to the solution via mass action equations. The additional unknowns will appear in the mass balance equations for each component in the solid phase. Note that the number of mineral phases which can be in equilibrium with the aqueous phase cannot violate the Gibbs phase rule.

For a system in thermodynamic equilibrium containing I primary variables for J chemical species, and P mineral phases, mass balance equations for each of the I components (excepting those that describe H and O) can be written as:

$$\sum_{j=1}^{J} h_{ij} C_j = C_i^T + \sum_{p=1}^{P} b_{ip} \alpha_p, \tag{35}$$

where:

- h_{ij} is the stoichiometric coefficient of the i th component in the j th aqueous chemical species;
- C_j is the concentration of the j th species;
- C_i^T is the sum of the initial aqueous concentrations of component i;
- b_{ip} is the stoichiometric coefficient of the i th component in the p th mineral; and,
- α_p is the net mass transfer of the p th mineral (positive for dissolution, negative for precipitation).

The above equation simply states that the sum of the aqueous concentrations of chemical species J which contain the i th chemical component must equal the initial total aqueous concentration of the i th component plus the mass exchange between aqueous and solid phases of the i th component.

The mass balance equation for hydrogen is replaced by the charge balance equation, which states that there is no net charge in the solution:

$$\sum_{j=1}^{J} z_j C_j = 0, \tag{36}$$

z_j being the charge on the j th aqueous chemical species.

As stated earlier, mass conservation of oxygen is replaced by conservation of electrons. In order to formulate this, we define a redox state (RS) of the solution as a means of

keeping track of electron transfer during redox reactions. Following Ref. [5]:

$$\mathrm{RS} = \sum_{j=1}^{J} \nu_j C_j, \tag{37}$$

where ν_j is the "operational valence" which is assigned to the j th chemical species. By analogy to the mass balance equation, the conservation of operational valence can be written as:

$$\sum_{j=1}^{J} \nu_j C_j = \mathrm{RS}^T + \sum_{p=1}^{P} \mu_p \alpha_p, \tag{38}$$

where RS^T is the redox state of the initial solution and μ_p is the operational valence of the p th mineral. The number of electrons transferred between phases is a function of the concentrations of the reactants and products and the oxidation state of each chemical species in the reactants and products.

Finally, we turn to the additional equation required for each mineral phase in order to solve the system of equations for the equilibrium calculation. This is provided by the solubility product K_p of the mineral that describes the reaction by which a precipitate dissolves in pure water to form its constituent ions:

$$\prod_{i=1}^{I} a_i^{b_{ip}} = K_p. \tag{39}$$

Here, we have introduced a_i to denote the thermodynamic activity of the i th component (which is given by the product of C_i and the activity coefficient γ_i).

This completes the set of equations needed to solve the system. They constitute a set of $I + P$ non-linear equations in the P unknowns α_p and I of $\{C_i\}$. This system could be tackled by a variety of numerical methods. In practice, a Newton–Raphson iteration method is used in `PHREEQE` [5] and has been carried through into `GRM`. Once the solution has been established, activities or concentrations of the $I - J$ chemical components that are not represented by the primary variables are simply evaluated from the mass action equations:

$$a_j = \gamma_j C_j = K_j \prod_{i=1}^{I} a_i^{h_{ij}}, \tag{40}$$

where K_j is the equilibrium constant of the j th chemical species and γ_j is its activity coefficient.

4.2 Species Decoupling Methodology

The chemical modelling in PHREEQE can be simplified to good advantage by splitting the elements into two groups, which constitute the macrochemistry and microchemistry.

- Macrochemistry: This covers the chemistry of elements which exist in sufficiently large concentrations to affect each other. Thus, if one chemical in this group were removed it would alter the concentrations not only of species involving itself but also of other species.
- Microchemistry: this covers the chemistry of elements which exist in quantities so small that their presence only alters the concentrations of species of which they are a constituent.

The GRM code first considers the macrochemistry, which generally means those elements and species not involving a radioactive component. These calculations are carried out directly by PHREEQE. Subsequently the microchemistry is considered. Although these calculations use information supplied in the PHREEQE database, they do not use the PHREEQE code. Instead they rely on independent linearized equilibrium equations. This approach was chosen since the CPU time spent in the PHREEQE component of the GRM could otherwise have been about an order of magnitude greater than that devoted to all other modules. By separating the calculations in this manner, the number of species analysed by PHREEQE can be significantly reduced.

For example, it is expected that the user will be able to treat radioelements as belonging to the latter category since their concentrations should be small enough to have no significant chemical effect on the amount of any other element in solution. Radioelements are therefore categorized as microelements. A change in, say, the calcium concentration however could influence the amount of several other elements in solution and therefore it is treated as a macroelement. Experience has shown that this split in the elements can considerably reduce the computing time spent doing iterative PHREEQE calculations and that it entails only a very small loss in accuracy.

NOTE: In PHREEQC, the addition of new features, such as surface complexation, means that the species decoupling feature is no longer applicable. In PHREEQC the distinction between micro/macroelements is no longer made, and thus all elements are included in the mass-action and speciation calculations for the system.

4.3 Macrochemistry Determination

The macrochemistry is determined by applying PHREEQE in each finite–difference cell. Note, however, that speciation is not necessarily performed after every transport timestep (see Sec. 2). The transport and speciation timesteps are set separately, the only requirement being that the speciation calculations cannot be more frequent than the transport calculations.

Because of its original design as a stand–alone package with considerable input and output, the PHREEQE coding is relatively inefficient. Even after separation of the microchemistry and macrochemistry, a large proportion of the CPU time for a GRM run is spent in evaluating the macrochemistry. Various modifications have therefore been made in order to speed up the PHREEQE operations.

In its original form, PHREEQE reads in a large database of thermodynamic information, which consumes a significant amount of CPU time for each PHREEQE run. Thus, a useful modification was to do this only for the first, initializing PHREEQE run.

Normally PHREEQE takes a guess at the equilibrium speciation and then uses a Newton–Raphson iterative procedure to move towards the true solution. However, if the GRM timesteps have been chosen correctly then the macrochemical situation prior to the PHREEQE call should be reasonably close to that found after it. Thus, in the GRM code, the current macrochemistry is used as a first estimate, which should reduce the number of iterations required to update it. Because of this starting point, PHREEQE may be able to converge on the updated equilibrium speciation very quickly and so the PHREEQE requirement for at least five iterations has been removed.

The stand–alone PHREEQE code contains a number of numerical parameters which determine when a solution can be said to have converged. Most of these have been hardwired into the GRM code: robust values, suitable for the GRM context, having been chosen after a good deal of experimentation. Only one tolerance parameter has been left to the discretion of the GRM user, since the accuracy of the PHREEQE solution within GRM can occasionally be a little sensitive to it. This is ECLOSE, which controls the admissible deviation in the electrical balance equation. The user who wishes to experiment with this parameter should note that its value will affect the code run time. The number of iterations required[10] by PHREEQE scales like log ECLOSE.

During a GRM simulation, macrochemistry modelling is only performed at times less than a predefined time (TENDCHEM). Thus, there is a facility to switch off macrochemistry

[10]This statement follows from the following property of the Newton–Raphson method [29]: that, in a convergent scheme, the error in the $k+1$ th iteration is proportional to the square of the error in the k th.

modelling during a GRM simulation. After the time TENDCHEM the macrochemistry is frozen but microspecies modelling continues. The option to switch off macrochemistry modelling during a GRM simulation is included to enable the user to switch off the CPU intensive macrospecies modelling routines in situations where a steady–state bulk chemistry has arisen. This facility is useful during long-term simulations where steady–state situations arise and permits the execution of GRM runs which would otherwise be prohibitive due to runtime considerations.

For the PHREEQC option, speciation calculations are performed in exactly the same manner as in the stand alone PHREEQC code.

4.4 Macromineral Dissolution and Precipitation

In PHREEQE all solid phase materials are called minerals and this definition is carried through into the GRM methodology. PHREEQE was written so that precipitation and dissolution could be handled by the user in an interactive manner. Thus, PHREEQE examines the speciation it has predicted and gives an indication as to whether any minerals are supersaturated. However, without specific instructions it will not allow any of these to precipitate. The user must examine the saturation indices and then rerun the code indicating which of the minerals are to be allowed to precipitate. This procedure has been automated within GRM. Up to two minerals can be picked out at a time: the most supersaturated mineral (which is likely to precipitate) and the most undersaturated mineral which is present.

The automation means that within GRM, all minerals in the PHREEQE database can potentially be precipitated. Hence, the GRM user should take care to include in the database only those minerals which are likely to precipitate in practice, taking into account their precipitation/dissolution kinetics and their occurrence in low–temperature environments.

Precipitation or dissolution of a mineral from an aqueous solution is determined by its solubility product. The dissociation of a mineral $M_p^{a+}X_q^{b-}$ in solution is expressed as:

$$M_p^{a+}X_q^{b-} \rightleftharpoons pM_{(aq)}^{a+} + qX_{(aq)}^{b-}. \tag{41}$$

The product of the activities of the species involved in forming the solid phase is called the Ion Activity Product (IAP):

$$\text{IAP} = \{M^{a+}\}^p\{X^{b-}\}^q. \tag{42}$$

The value of the IAP when the solid phase is in equilibrium with the aqueous phase is called the equilibrium solubility product, K_{sp}. A saturation index, SI, for a mineral can

now be defined by:

$$\mathrm{SI} = \log \frac{\mathrm{IAP}}{K_{sp}}. \tag{43}$$

This index indicates whether the mineral is supersaturated, undersaturated or in equilibrium with the aqueous phase.

1. If SI is zero, the mineral is in equilibrium with the aqueous solution, so nothing will happen.
2. If SI is positive, the mineral is supersaturated and so to reach equilibrium, precipitation will occur.
3. If SI is negative, the mineral is undersaturated. If the mineral is in contact with the aqueous phase then dissolution will occur. However if none of the mineral is present then nothing will happen.

The larger the modulus of SI, the further from equilibration is the mineral. In practice, `GRM` selects minerals using a modified SI value [7], [8], dividing by the number of aqueous species that make up the mineral, excluding water and hydrogen ions. This scale factor is applied so that minerals containing large molecular assemblages (e.g., $MgCa(CO_3)_2$) can be compared with simple minerals (e.g., $CaCO_3$).

For the `PHREEQC` option, changes in mineral concentration results for dissolution and precipitation are calculated by the `PHREEQC` subroutines in exactly the same manner as in the stand alone `PHREEQC` code.

4.5 Microchemistry Determination

A separate `GRM` module is used to calculate the speciation of the microelements. It uses the results previously calculated by `PHREEQE` for the speciation of the major elements present in the solution.

Neglecting mineral formation and sorption for the moment, the total amount of microelement X in solution must be conserved during microelement speciation. Thus:

$$[\mathrm{X}] = [\mathrm{X_{free}}] + \sum_i [\mathrm{X}_i], \tag{44}$$

where $\mathrm{X_{free}}$ denotes the free X ion and the summation extends over the complex ions that are formed by association reactions of the free X ion with other macrochemical species in

solution (examples might be $ThCO_3^{2+}$, $Th(OH)_3^+$ and $Th(OH)_4$). Equilibrium constants for each i are given by mass action equations:

$$K_{X_i} = \frac{\{X_i\}}{\{X_{free}\}^{f_i}\{M_i\}^{s_i}}, \tag{45}$$

where $\{...\}$ denotes activity, M_i is the macrospecies which forms X_i along with X_{free}, and s_i and f_i are stoichiometric coefficients.

The activity coefficient relates concentration to activity by:

$$\gamma = \frac{\{a\}}{[a]}, \tag{46}$$

for any species, a. For an ionic species, the activity coefficient depends on the charge of the species, Z, and on the ionic strength of the solution, μ. There are several formulations for evaluating activity coefficients [5], but for microelements where $Z \neq 0$, the Davies equation has been judged [30] the most appropriate [11]:

$$\log\gamma = -AZ^2\left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - \frac{3\mu}{10}\right) \tag{47}$$

where A depends on temperature and solvent permittivity, and is evaluated within PHREEQE. Where $Z = 0$, the WATEQ DEBYE-HUCKEL equation is used, which in this case reduces to:

$$\log\gamma = b\mu \tag{48}$$

where b is a constant, assumed to be 0.1. Now, the concentration of X_i can be expressed using Eqs. 45 and 46 as:

$$[X_i] = \frac{K_{X_i}}{\gamma_{X_i}}\{X_{free}\}^{f_i}\{M_i\}^{s_i}. \tag{49}$$

Apart from the activity of the free X ion, all of the quantities on the right–hand side of the above equation are known. The activity coefficient is calculated as described above; $\{M_i\}$ was determined from the PHREEQE macrochemistry speciation and the equilibrium constants, K, are known from the PHREEQE database (they are corrected for temperature dependence by using the Van't Hoff expression and the enthalpy of reaction). Substituting

[11] This type of aqueous model is adequate at low ionic strengths but may break down at higher ionic strengths (in the range of seawater and above) [6]. These concentrations may be exceeded during modelling of fluid chemistries in LLW sites

into the conservation equation (Eq. 44), one derives a polynomial equation for free X ion activity:

$$[\mathrm{X}] = \gamma_{\mathrm{X_{free}}}^{-1}\{\mathrm{X_{free}}\} + \sum_i \frac{K_{\mathrm{X}_i}}{\gamma_{\mathrm{X}_i}}\{\mathrm{X_{free}}\}^{f_i}\{\mathrm{M}_i\}^{s_i}. \tag{50}$$

It is assumed within GRM that f_i is never larger than three. The resulting cubic equation is solved by using the Newton–Raphson method, based on a starting value obtained by neglecting the quadratic and cubic terms in Eq. 50. In most cases, however, the iterative method is not really needed since the correction terms to the initial estimate are generally negligible unless equilibrium constants for dimers and trimers are larger than those for monomers.

Once the microelement free ion species activity has been calculated then activities for the derived species are straightforward to evaluate using the above equations. Note, however, that calculation of the free ion species activity must be modified if solid species of the microelement are precipitated or redissolved (see Sec. 4.6).

For PHREEQC users see note in section 4.2. The user is also referred to the PHREEQC user guide for the treatment of activity correction [6].

4.6 Micromineral Dissolution and Precipitation

Using Eq. 43 and a generalization of Eq. 42, the saturation index can be written as:

$$\mathrm{SI} = -\log(K_{sp}) + \sum_n s_n \log\{A_n\}, \tag{51}$$

where the mineral is composed of master species A_n with stoichiometric coefficients s_n. In the case of microminerals, a simplification can be made, under the assumption that the limiting factor in precipitation and dissolution is the concentration (activity) of the microelement master species rather than that of any of the macrospecies with which it is reacting. To put the saturation indices of microminerals on a comparable basis with respect to the microelement, the relevant variable is the micro–saturation index (MSI):

$$\mathrm{MSI} = \frac{\mathrm{SI}}{s_m}, \tag{52}$$

s_m being the stoichiometric coefficient of the microelement. It is the MSI value that is used to determine the most supersaturated and undersaturated microminerals.

Equilibrating a micromineral leaves MSI= 0 and so results in a microelement activity that is given by:

$$\log A_m = s_m^{-1} \left(\log K_{sp} - \sum_{n \neq m} s_n \log A_n \right). \tag{53}$$

In the presence of microminerals, Eq. 50 is not solved for $\{X_{free}\}$ but the above solubility–limited value for the activity of the free microelement ion is used instead. Eq. 50 is then used to determine $[X]$, the total amount of microelement left in solution. After that, MSI values can be re-calculated to check whether any microminerals are still undersaturated or supersaturated. If not then the speciation of the aqueous species can be calculated from Eq. 45.

For PHREEQC users see note in section 4.2.

4.7 Cement Dissolution

The dissolution of the calcium hydrogen silicate (CSH) components of cements is difficult to model because of their variable composition and non-crystalline amorphous nature which give rise to an incogruent dissolution. One method has been suggested by Berner [31], in which CSH is represented by a non-ideal mixture of congruent components, the identity and nature of which are determined by the Ca to Si ratio. In GRM, this model for the CSH phase can be switched on by using the ICEM switch in the grm.dat input file. With this option, CSH is modelled with two macrominerals, CaH_2SiO_4 and SiO_2. In order to simulate the dependence of the dissolution on the Ca:Si ratio (r), the solubility products of these mineral phases are altered as the ratio changes. New solubility equilibrium constants, K_{sp}, are calculated by the code and are passed to the PHREEQE module.

Taking data from Ref. [32], if the amount of CaH_2SiO_4 present is zero, the $\log K_{sp}$ for SiO_2 is set at -2.71. Should the amount be greater than zero, then the following equations are used:

$$logK_{\mathrm{CSH}} = -7.12 + \left(1 - \frac{1}{r}\right)\left(0.79 + \frac{0.861}{(r - 1.2)}\right) \tag{54}$$

$$logK_{\mathrm{SiO_2}} = -1.994 + \left(\frac{0.861}{r - 1.2}\right). \tag{55}$$

The above equations are valid for $0 < r < 1$.

4.8 Kinetically–Controlled Mineral Precipitation and Dissolution

Macromineral dissolution is one of many non-equilibrium geochemical processes which occur in the environment. Chemical processes modelled in the majority of chemistry/transport coupled codes are simulated using equilibrium thermodynamics. Doing so significantly reduces the complexity of such models. This can often be justified on the grounds that the timescales involved are such that assuming that equilibrium has been established does not introduce significant uncertainty.

Nevertheless, kinetics may prove to be an important consideration in some geochemical and environmental simulations. For example, the dissolution of minerals such as calcite and ferric oxyhydroxides can be important as they are both pH buffers. It does not seem unreasonable to suppose that flow rates in a LLW environment may be of the order of a few metres per day. Since the dissolution of minerals such as calcite may take several days to reach equilibrium, it is plausible that dissolution kinetics could be important. A facility for the modelling of dissolution kinetics has therefore been included in the GRM.

4.8.1 Modelling Dissolution Kinetics

Mathematical details of dissolution kinetics are omitted here, but are available in many references. A good review can be found in Ref. [33].

Recognition of the fact that equilibrium thermodynamics may not be appropriate for chemical modelling of some environmental situations has led to much investigation of the kinetics of mineral dissolution[12]. Such work indicates that the following key features of mineral dissolution should be modelled:

- the total dissolution rate depends upon whether the dissolution of the solid phase or the transfer of dissolved species from near the solid surface to the bulk solution is the rate determining step;
- no matter what the type of solid, the rate of dissolution is strongly related to how far the bulk aqueous solution is from mineral saturation (the closer to mineral saturation, the slower the rate); and,
- the rate 'constant' is a function of the aqueous pH (particularly for silicates) and also depends on factors such as crystal size and morphology [34].

[12] A good deal of this work applies to the kinetics of silicate weathering, which involves long term (thousands of years) reactions that need not concern us here. Calcite dissolution has also been extensively studied. Its reaction rates are quite fast and so lend themselves to study on a laboratory scale.

For particular systems, some studies have modelled dissolution successfully by fitting dissolution rates to empirical polynomials. However, these are specific to the experimental conditions under consideration. No mechanistic information has as yet been gained which could lead to predictions outside laboratory conditions.

More fundamental chemical studies have given rise to a Transition State theory, outlined by Helgeson et al [35], as the generally–accepted model[13] of mineral dissolution–precipitation kinetics. This is based upon a derivation from "first principles" of how molecules associate and dissociate to form and dissolve solids. The theory has been particularly successful in deriving the pH dependence of rate constants for silicate dissolution. Similar models have also been used in modelling the dissolution of nuclear–vitrified glass, even though this is not a thermodynamically stable material [36].

A transition state model should really be derived from first principles for each mineral separately since it requires a great deal of fundamental understanding of the molecular level reactions for the mineral under consideration. Fortunately, the derivations have tended to be similar in general format and suggest a general empirical rate law [37]:

$$\text{Rate} = Ak(\Omega^m - 1)^n, \tag{56}$$

where m and n are constants, k is the rate constant, A is the surface area and Ω is the saturation state of the mineral. The parameters A, k, m and n are measurable in principle, but are rarely known. Thus, in the GRM code, the following generalized rate equation is employed, with the user supplying constants for the minerals of interest:

$$\text{Rate} = k_1 \left((10^{\text{SI}})^{k_2} - 1\right)^{k_3}. \tag{57}$$

The saturation index, SI($= \log \Omega$), appears instead of Ω. This quantity is easily accessible from the PHREEQE calculations (see Sec. 4.4).

A similar equation applies to the kinetics of mineral precipitation. We note that such an equation has been used in the coupled transport and chemistry code PRECIP developed by BGS in conjunction with the AEA [38]. Within PRECIP the transport and dissolution steps are combined in a unified set of equations which are then directly solved. This is a more rigorous approach than GRM which has a sequential modelling methodology. The intimate coupling of transport and dissolution in PRECIP means that in situations where dissolution kinetics are not appropriate, the code must still deal with such kinetics. The modular nature of GRM means that kinetic dissolution calculations are optional.

[13] It should be noted, however, that the same results have been obtained within other models.

4.9 Surface Complexation

The PHREEQC chemical speciation module permits modelling of sorption processes by consideration of surface sorbed species in the equilibrium thermodynamic model. This approach is distinct from the cation exchange process described in section Sec. 5.3 and considers the electrostatic effects present at mineral surfaces. The double diffuse layer model of electrostatic interaction (Dzombak and Morel) is included in the PHREEQC code. PHREEQC allows multiple surface complexers , termed a "surface assemblage", to exist in equilibrium with the aqueous phase. This phenomena is modelled by introducing a dummy component $\frac{F\psi}{2RT}$(F = Faraday's constant, ψ = potential at the surface, R = gas constant, and T = temperature in Kelvin), into the mass action equation for each surface species to represent electrostatic interaction in the surface double diffuse layer. A non-electrostatic model is also included for surface complexation. In this model, the electrostatic term is ignored in the mass-action expressions for surface complexes. In addition, no surface charge balance or surface charge verses potential relation is used; only a mole-balance equation is included for each surface site.

It should be noted that in PHREEQC, the distinction between micro/macroelements is no longer made. All elements are included in the mass-action and speciation calculations for the system including those involved in surface complexation. (For more details of surface complexation modelling see the PHREEQC user guide [6] and references therein).

5 Sorption

In an ideal, homogeneous, isotropic, saturated, porous medium, the transport of a non-interacting solute is described by Eq. 2. Real media, however, are not inert and most solutes will interact with the solid phase to some extent. These interactions will tend to decrease the rate of solute transport relative to bulk water, giving rise to an observed retardation. The mechanisms involved in such retardation are complex and will depend not only on the chemistry of the solute and solid phase but also on the macro- and micro-scale structure of the flow path. Such mechanisms include:

- diffusion into "dead–end" pores;
- molecular filtration;
- physical sorption;
- ion-exchange;
- mineralisation; and,
- precipitation.

In particular circumstances, only a few of these retardation processes may be significant. For example, in a porous medium with large pores, and with a solute well below saturation, only the physical sorption processes may need to be considered.

Two methods of modelling sorption are available within GRM. Firstly, one can introduce kinetic terms for sorption and desorption into the transport module. This kinetic case can be represented by:

$$\frac{\partial S}{\partial t} = \alpha(K_d C - S), \tag{58}$$

where S and C represent the sorbed and solute concentrations respectively and α is a rate constant. Alternatively, if these reactions are relatively fast, then one has:

$$S = K_d C. \tag{59}$$

If this instantaneous relationship is specified by the GRM user then sorption can be accommodated into the microelement speciation module described in Sec. 4.5.

While for simple systems (e.g., ion-exchange resins) K_d values may be thermodynamically based, the values used in transport models are generally a more empirical representation of kinetically fast (see Sec. 5.3), concentration–independent, reversible sorption.

Most radionuclide transport codes currently available are based on the K_d concept. Many of the numeric codes can incorporate K_d as a function of other parameters such as radionuclide concentration, pH, pe, and concentrations of major complexing ions. Within GRM, K_d values may be specified in either of two ways.

1. A different K_d may be assigned to each transported species. Default sorption data is provided for all the species of a given element. These values can then be overwritten with specific data on a species by species basis.
2. A different K_d may be assigned to each transported element as an explicit function of pH. The particular form of the pH dependence used within GRM version 4.1 is known as the "Empirical Rise Function" model. It results in a K_d of the form:

$$K_d = \frac{f}{1-f}, \tag{60}$$

where:

$$f = \frac{a-d}{1+(-\mathrm{pH}/c)^b} + d \tag{61}$$

and a, b, c and d are parameters specified in the sorption input file `grm.kds`.

In both cases the rate constants α are defined for each transported species for which a K_d is given. The GRM user is able to specify up to six different sets of sorption parameters for each species. Within each finite difference cell, the user sets a flag in order to select the parameter set used. This feature allows one to vary the sorption properties over the modelled domain in order to reflect, for example, variations in the properties of the sorbing media. A major assumption made in the sorption calculations is that the processes of physical sorption, ion-exchange, surface complexation and mineralisation, are capable of being characterized by a K_d value whilst the precipitation of a new phase is an independent event.

5.1 Instantaneous Sorption

If this option is chosen then radionuclide sorption is accounted for by modifying the microelement speciation calculations of Sec. 4.5. Consider first the effect of microelement sorption onto the geomatrix. From Eq. 59, the sorption coefficient controls the ratio of sorbed to dissolved material:

$$\frac{[Y_{\mathrm{sorb}}]}{[Y_{\mathrm{aq}}]} = \frac{\rho K_d}{\phi}, \tag{62}$$

where ρ and ϕ are the waste density and porosity respectively. One therefore has that:

$$[Y_{\text{total}}] = [Y_{\text{sorb}}] + [Y_{\text{aq}}] = \left(1 + \frac{\rho K_d}{\phi}\right)[Y_{\text{aq}}]. \tag{63}$$

Sorption onto colloidal material is treated similarly, the above equation being extended to:

$$[Y_{\text{total}}] = \left(1 + \frac{\rho K_d}{\phi} + \sum_t R_t\right)[Y_{\text{aq}}], \tag{64}$$

where the sorption ratio for the t th type of colloid is given (analogously to Eq. 63) by:

$$R_t = \frac{K_{dt} M_t}{V_{\text{sat}} \phi}. \tag{65}$$

In the above equation:

- K_{dt} is the sorption coefficient for the colloidal type;
- M_t is the mass of the colloidal type; and,
- V_{sat} is the saturated volume of the waste in the region that contains the mass M_t.

In order to account for sorption in determining microelement speciation, it is necessary simply to make the following identification in Eqs. 44 to 50:

$$[\text{X}] \equiv [\text{X}_{\text{total}}]. \tag{66}$$

5.2 Kinetic Sorption

If this option is chosen then sorption is decoupled from microelement speciation and treated as a separate process. Species may be sorbed onto the geomatrix/waste, static Fe(III) hydroxide or onto each of the three colloidal types. Sorption onto the geomatrix is kinetically controlled while that onto the colloids and Fe(III) hydroxide is assumed to be instantaneous.

Sorption onto the geomatrix/waste is simulated using the following equation:

$$\frac{dm_s}{dt} = K_d^g \alpha \frac{\rho}{\phi} m_l - \alpha m_s, \tag{67}$$

where:

- m_s is the mass of the species under consideration that is sorbed onto the geomatrix/waste;
- K_d^g is a species–dependent distribution coefficient;
- α is a rate constant;
- ρ is the geomatrix/waste bulk density;
- ϕ is the porosity; and,
- m_l is the species mass in the liquid phase.

Sorption onto the i th colloidal type is given by:

$$m_i = K_d^i \frac{c_i}{V_w} m_l, \tag{68}$$

where:

- m_i is the mass of species sorbed onto colloids of type i;
- K_d^i is the distribution coefficient for sorption onto colloids of type i;
- c_i is the mass of colloids of type i; and,
- V_w is the total solute volume.

Sorption onto Fe(III) hydroxide is similar to that for colloids, being given by:

$$m_{fe} = K_d^{fe} \frac{M_{fe}}{V_w} m_l, \tag{69}$$

where:

- m_{fe} is the mass of the species sorbed onto Fe(III) hydroxide;
- K_d^{fe} is the distribution coefficient for sorption onto Fe(III) hydroxide[14]; and,
- M_{fe} is the total mass of Fe(III) hydroxide produced by corrosion.

[14] Note that in the current version of the code this is assumed to be the same as the distribution coefficient for sorption onto the first colloidal type.

The total species mass in the liquid and sorbed phases,

$$M_{\text{tot}} = m_l + m_s + \sum_{i=1}^{3} m_i + m_{fe}, \tag{70}$$

is taken to be constant. Combining Eqs. 68, 69 and 70 gives:

$$m_l = (M_{\text{tot}} - m_s)\left[1 + K_d^{fe}\frac{M_{fe}}{V_w} + \sum_{i=1}^{3} K_d^i \frac{c_i}{V_w}\right]^{-1} \equiv (M_{\text{tot}} - m_s)r^{-1}. \tag{71}$$

Using this relation in Eq. 67 gives a differential equation for m_s only:

$$\frac{dm_s}{dt} = \frac{K_d^g \alpha \rho}{r\phi}(M_{\text{tot}} - m_s) - \alpha m_s, \tag{72}$$

which has solution:

$$m_s(t) = m_s(0)\exp\left[-\left(\frac{K_d^g \alpha\rho}{r\phi} + \alpha\right)t\right] + \frac{K_d^g M_{\text{tot}}\rho}{r\phi}\left[1 + \frac{K_d^g \rho}{r\phi}\right]^{-1}\left(1 - \exp\left[-\left(\frac{K_d^g \alpha\rho}{r\phi} + \alpha\right)t\right]\right) \tag{73}$$

The quantities m_l, m_i and m_{fe} can then be calculated from Eqs. 71, 68 and 69 respectively.

Note that kinetic sorption is modelled as a two step process, the first step occurring just before the transport calculations during each transport timestep and the second step occurring just afterwards. Thus the sorption timestep is set to half of the transport timestep.

Both the PHREEQE and PHREEQC speciation models can be used to consider equilibrium between aqueous species and ion-exchange sites on a solid surface/mineral.

5.3 Cation Exchange

As an alternative to the K_d approach, GRM has the ability to model cation exchange processes using a thermodynamic treatment. Use of this method ensures that the cation exchange reactions within GRM are mass balanced.

In the following description, we consider the example:

$$\text{Na}^+ + \frac{1}{2}\text{CaX}_2 \rightleftharpoons \text{NaX} + \frac{1}{2}\text{Ca}^{2+}, \tag{74}$$

where X is the ion-exchanger. The above equation is written in the Gaines–Thomas convention and represents the exchange of Na^+ and Ca^{2+} on an ion-exchange site. This

is a very common groundwater/soil/rock interaction reaction. In PHREEQE the equation would have to be written as two half reactions:

$$Na^+ + X^- \rightleftharpoons NaX \tag{75}$$

$$Ca^{2+} + 2X^- \rightleftharpoons CaX_2, \tag{76}$$

with association constants:

$$K_1 = \frac{\{NaX\}}{\{Na^+\}\{X^-\}} \tag{77}$$

$$K_2 = \frac{\{CaX_2\}}{\{Ca^{2+}\}\{X^-\}^2}. \tag{78}$$

The problem with the representations in Eqs. 75 and 76 is that PHREEQE will poorly evaluate the activity of the exchanged phases[15] (such as {NaX}).

The most popular treatment of exchange species activities uses the Gaines–Thomas convention of Eq. 74 and assumes that the activity of the exchanger phases is equal to their equivalent fractions. The equivalent fraction for a cation i is defined by:

$$\beta_i = \frac{\text{meq}_{i\text{X}}}{\sum_j^n \text{meq}_{j\text{X}}} \equiv \frac{\text{meq}_{i\text{X}}}{\text{CEC}} \tag{79}$$

where there are n ion-exchanged cations. Note that the second part of the above equation defines the cation exchange capacity (CEC). The Gaines–Thomas version of Eq. 77 is therefore:

$$K_{1,\text{GT}} = \frac{\beta_{\text{NaX}}}{\{Na^+\}\{X^-\}}. \tag{80}$$

The equivalent fraction is clearly dimensionless. However, PHREEQE expresses the activity of the exchanger species in concentration units. The conversion is made from the following relation:

$$\{NaX\} = \beta_{\text{NaX}}\text{CEC}\frac{\rho}{\phi Z_{\text{Na}}}, \tag{81}$$

where:

- ρ is the solid phase density;
- ϕ is the porosity; and,

[15] This is because PHREEQE calculates the activity of neutral species based on the assumption that these species are in solution, which ion-exchangers clearly are not.

- Z_{Na} is the charge on the cation, equal to 1 for Na^+.

Most data on ion-exchange is presented for the Gaines–Thomas convention. Using the above relation in Eq. 80, however, we can define a PHREEQE–usable constant:

$$\log K_{1,\mathrm{phq}} = \log K_{1,\mathrm{GT}} + \log\left(\frac{\mathrm{CEC}\rho}{\phi Z_{\mathrm{Na}}}\right) = \log \frac{\{\mathrm{NaX}\}}{\{\mathrm{Na^+}\}\{\mathrm{X^-}\}} \tag{82}$$

A similar manipulation could be performed for the CaX_2 half reaction. More generally, for a cation i, we have:

$$\log K_{i,\mathrm{phq}} = Z_i \log K_{i,\mathrm{GT}} + \log\left(\frac{\mathrm{CEC}\rho}{\phi Z_i}\right) = \log \frac{\{i\mathrm{X}_{Z_i}\}}{\{i^{Z_i+}\}\{\mathrm{X^-}\}^{Z_i}}, \tag{83}$$

where Z_i is the charge of the cation i.

5.3.1 Practical Input into PHREEQE

The most common application of ion-exchange is the simulation of a process whereby an initial solution at equilibrium with respect to the ion-exchange phase is perturbed by mixing with another solution. PHREEQE can be used to simulate the mixing with the ingressing water. The presence of ion-exchange species in the total system solution will mean that the full impact of cation exchange on the chemistry of the mixed solution will be modelled.

The following steps are required in order to perform such a simulation:

1. formulate the ion-exchange half reactions of interest;
2. convert the Gaines–Thomas data to match the PHREEQE half cells, according to Eq. 83;
3. place the data into the PHREEQE database;
4. determine the amount of cations in the ion-exchange phases;
5. perform an initial PHREEQE run with the ion-exchanged cations initially released into solution (this calculates the correct distribution of exchanged to free cations in the equilibrium solution); and,
6. mix this solution with the ingressing solution as required.

Formulate Reactions

Experimental ion-exchange data is predominantly presented in the Gaines–Thomas convention format with the reactions expressed similarly to Eq. 74. There is never any explicit reference to the exchanger X^-. The reason for this is simply that the amount of free X^- tends to be so small as to be unmeasurable in practical terms.

Appelo and Postma [33] outline the general resolution of this problem, as adopted by most modellers. They suggest making the association constant for one of the half-cells, say that for NaX, arbitrarily high ($K = 1 \times 10^{20}$ for instance). This results in an insignificantly small amount of X^- present in solution at equilibrium. It also has the advantage that the X^- species concentration is so small that the ionic strength calculation in PHREEQE is not affected. All the available Gaines–Thomas reactions can be manipulated with respect to the arbitrary NaX half reaction to give the half reaction constants of each of the other ion-exchanged cations. The effective Gaines–Thomas exchange constants remain unchanged. All that is assumed is that the amount of free X^- is very small. This seems practical as all exchange sites will in reality be covered by cations at all times.

Initial Exchanger Distribution

To run a problem where a system at equilibrium with respect to the ion-exchange phase is perturbed by changing chemistry, we need to determine the initial amount of all cations in the exchanged phases. This is necessary because when the incoming solution mixes with the initial solution, unless we have explicitly represented the mass of ion-exchange phases, the buffering caused by ion-exchange will not be taken into account. Thus, we require a description of the initial state of the total system of solution and exchanger phases. This could be attained through either of the following methods.

1. Appelo and Postma [33] explain how to formulate an exact analytical solution for the amounts of cations on exchange sites, in their *Example 5.4*. This uses the fact that all of the ion-exchange constants are known by this stage, and that all the exchange reactions may be expressed as a function of one reaction only (in our example NaX). A quadratic equation is solved for NaX and the results can then be back–substituted to determine the amounts of other cations on exchanger sites.

   The total system cation concentrations are then calculated from:

$$\{i\}_{\text{total}} = \{i\text{X}\}_{\text{exchange}} + \{i\}_{\text{solution}}. \tag{84}$$

PHREEQE is then run with these system cation concentrations, and with the CEC represented by the value of X^- through the relation:

$$\{X^-\}_{\text{real}} = \frac{\rho \text{CEC}}{\phi}. \tag{85}$$

The run will produce a total system description, with aqueous phase species and ion-exchanged phases present as "apparent" solution species[16].

2. In this method, PHREEQE is run (with the calculated exchange constants in the database) simply to calculate speciation of the equilibrated water, but with a very small quantity of exchanger ion X^- added to the solution. This quantity should be so small that it does not affect the chemistry of the solution.

   The results will have very small predicted quantities of the exchangers present in solution, such as NaX and CaX_2. What is wanted is not so much the absolute values of the exchanged species, but the relative amounts present. Hence, the molarity of each exchanged species can be scaled up to:

$$\{i\text{X}\}_{\text{real}} = \frac{\{\text{X}^-_{\text{real}}\}}{\{\text{X}^-_{\text{nom}}\}} \{i\text{X}\}_{\text{nom}}, \tag{86}$$

   where:

   - $\{i\text{X}\}_{\text{real}}$ is the required solution concentration of the exchanger;
   - $\{i\text{X}\}_{\text{nom}}$ is the nominal concentration in the PHREEQE run with very low X^-;
   - $\{X^-\}_{\text{nom}}$ is the very low value of X^- used in this PHREEQE run; and,
   - $\{X^-\}_{\text{real}}$ is the total amount of exchangeable sites.

   From this point onwards, the second method is identical to the first.

The second method is actually used in the PHREEQM program [33] and is the method used in GRM.

NOTE: For calculation of ion exchange speciation via PHREEQC, the user is referred to the PHREEQC user guide [6].

[16] As a check, the resulting solution should have the same species aqueous concentrations as the initial solution, only with added ion-exchange species.

6 Gaseous Physico-chemical Processes

6.1 Overview of Gas Transport

Gas production from waste repositories can be separated into two distinct processes: generation by the wasteform and gas migration to the surface. These processes are clearly dependent on the depth of the repository. Deeper structures are characterized by a greater degree of gas tightness, either by engineering design or natural impermeability of the host media or both. In general this leads to larger overpressures in the deep repositories (typically 10 to 100 bar) whilst shallow or surface burial gives rise to overpressures of only a few millibar.

Gases may be formed in LLW sites owing to radioactive decay (e.g., of radium to radon), the corrosion of metals, the microbial degradation of organic materials and the radiolytic decomposition of water and organic materials. Radiolytic gas production is considered to be negligible in LLW sites [39] and is therefore not modelled. Production of ^{14}C and ^{3}H labelled gases is simply estimated from the ^{14}C:C and ^{3}H:H ratios of the waste. The gases evolved will depend on the initial substrates but are typically: water vapour, radon, oxygen, nitrogen, carbon dioxide, hydrogen, hydrogen sulphide, methane and ammonia.

Although gas transport models employing the advective–diffusion equation have given good agreement with observations [11, 40], the complexity of such models and the requirements for high–quality, site–specific data makes them unsuitable for use in the GRM. Simpler gas transport models are also available in the literature (see for example Refs. [42, 43, 44]) and aspects of some of these have been incorporated into the GRM approach.

6.2 Gas Migration to the Surface

The procedure for handling gas migration within GRM is limited to conditions of incompressible gas flow. The gases produced are assumed not to be significantly transported with the groundwater and to make their escape to the atmosphere within the vicinity of their point of production. Thus, the gas generated within a particular cell escapes to the atmosphere from that same cell.

A three–reservoir model is used to represent the saturated zone of a cell, the cell headspace and the atmosphere. The unsaturated zone porevolume provides the cell headspace. Rates of exchange between the saturated zone and the headspace reservoir are

assumed to be fast with respect to the generation rates. Waste in the saturated zone is assumed to dominate gas production, with evolution and consumption along the transport pathways being taken to be negligible. Following Ref. [39], the displacement of porewater through ebulition (bubble flow) is assumed to be the dominant gas transport process in the saturated zone. Thus, gas flows between the saturated zone and the headspace reservoir are likely to be vertical owing to buoyancy and therefore the sweeping along of gases by the groundwater is likely to have only a small effect.

Gas transport in the unsaturated region of a shallow burial site is simplified in the GRM to a one-dimensional vertical flow through the headspace. A meaningful three-dimensional flow model would require detailed modelling of the horizontal resistances, necessitating a good deal of site data. Such information is unlikely to be available, and any pathway modelling is liable to be site specific. Therefore, in the general purpose GRM code, a one-dimensional model is appropriate. The approach should at least be sufficient to track the gross in– and out–flows.

Within the GRM approach, the atmospheric and headspace reservoirs are separated by a cap through which the gas can flow. In reality of course, a network of transport pathways will exist, both engineered (drains, soakaways, standpipes etc.) and intrinsic (soil fissures, root penetrations, geotextile ruptures etc.). Under some conditions, another significant influence could be atmospheric pumping (site breathing) [43]. Central to the modelling of atmospheric release is the concept of a cap permeability. At its simplest the cap permeability coefficient, K_1, can be defined by the Darcy flow equation:

$$\frac{V}{p}\frac{dp}{dt} = -\frac{KA(p-p_a)}{\mu L} = -K_1(p-p_a), \tag{87}$$

where:

- p is the headspace gas pressure;
- p_a is the local atmospheric pressure;
- V is the cell void volume (the headspace);
- K is the permeability;
- μ is the viscosity coefficient;
- A is the effective cross-sectional area; and,
- L is the effective thickness of the cover.

The parameter K_1 is more readily determined in the field than K (data was published, for example, in Ref. [44]).

Taking account of the gas production rate in the saturated zone, the headspace pressure is described by making a simple modification to Eq. 87:

$$\frac{V}{p}\frac{dp}{dt} = -K_1(p - p_a) + Q. \tag{88}$$

Assuming the production rate, Q, to be constant over the course of a microbial timestep, then Eq. 88 is easily integrated to give:

$$p = p_0\left(p_a + \frac{Q}{K}\right)\left[p_0 + \left(p_a - p_0 + \frac{Q}{K}\right)\exp\left(-\frac{(p_aK + Q)}{V}t\right)\right]^{-1}, \tag{89}$$

where p_0 is the headspace pressure at the start of the microbial timestep. Once the gas pressure has been found, the number of moles of gas supportable at the calculated pressure is determined from the ideal gas equation. Should the number of moles of gas exceed the supportable number then the excess is vented to the atmosphere in such a way that the proportions of each component gas in the headspace are maintained. On the other hand, if the number of moles of gas present is too small for the headspace pressure then the appropriate quantity of air is drawn in from the atmosphere[17]. In doing so, the carbon 14 fraction in CO_2 is updated under the assumption that atmospheric CO_2 does not contain this isotope.

6.3 Optional Treatment for Hydrogen

Large volumes of hydrogen may be produced in a LLW site due to metal corrosion. These large volumes are not always measured in the field. Thus, if the migration of H_2 is treated identically to that of other gases, it is possible that the large volumes evolved in the code may purge the other gases out of the system. If headspace CO_2 levels become negligible for this reason then the pH levels could be distorted. On the basis that H_2 is a light gas with high diffusivity, an option is provided for any gaseous H_2 produced to be short–circuited out of the model, therefore having no further impact on physico- or bio-chemical processes.

[17]The atmospheric composition is defined by the GRM user through data in the grm.bug file.

6.4 Solubility of Gases

The bulk gases considered within GRM (CO_2, O_2, CH_4, N_2, NH_3, H_2S, H_2) are split into three groups according to their solubilities and chemistries[18]. CO_2, NH_3 and H_2S are treated as soluble in the groundwater; O_2, CH_4 and N_2 are optionally soluble and H_2 is treated as totally insoluble.

The solubility of CO_2, NH_3 and H_2S in groundwater is important as these gases actually form a variety of species in the groundwater. Henry's law is used to partition the CO_2,NH_3 and H_2S between the gaseous and aqueous phases. O_2 is less soluble in water and does not form chemical species. It is used up by corrosion of iron and by aerobic bacteria, but is only available from the atmosphere and is not evolved from the groundwater. Since O_2 diffuses more slowly from the gas into the liquid phases than CO_2 and H_2S under non-turbulent conditions, the equilibration of O_2 between the gas and liquid phases has been made optional in the GRM code (it is controlled by the O2SW flag in the grm.bug file). CH_4 and N_2 may also be considered soluble if the switches CH4SW and N2SW are set in grm.bug. H_2 is a relatively insoluble gas and is always considered to be totally insoluble within GRM.

The above classification is supported by the data in the following table, which lists example equilibrium constants for use in the code. Data for CO_2, H_2S, O_2 and H_2 was obtained from the NEA12 thermodynamic database [10] whereas data for CH_4 was derived from [9]. N_2 and $NH_{3(g)}$ data was derived from a combination of both of these data sources. Data in the following table was calculated for standard temperature and pressure.

Gas	Gas Solubility Constant $\log K$	Enthalpy of Formation ΔH (kcalmol^{-1})	Equilibrium equation
CO_2	-18.15	0.79	$H_2O + CO_{2(g)} \rightleftharpoons CO_3^{2-} + 2H^+$
H_2S	-7.98	20.76	$H_2S_{(g)} \rightleftharpoons HS^- + H^+$
NH_3	11.01	-20.64	$NH_{3(g)} + H^+ \rightleftharpoons NH_4^+{}_{(aq)}$
O_2	-2.96	-1.84	$O_{2(g)} \rightleftharpoons O_{2(aq)}$
H_2	-3.15	-1.76	$H_{2(g)} \rightleftharpoons H_{2(aq)}$
CH_4	-2.86	-3.40	$CH_{4(g)} \rightleftharpoons CH_{4(aq)}$
N_2	-3.08	-1.54	$N_{2(g)} \rightleftharpoons N_{2(aq)}$

Table 1: Gas solubilities in water.

[18] Tritiated water vapour and ^{222}Rn gas are also included in the code.

6.5 Partitioning of Soluble Gases

The partitioning of soluble gases between the groundwater and the headspace is performed by the GRM code as a distinct procedure, independently of the chemical speciation. Indeed, the partitioning of each soluble gas is treated as being independent of the partitioning of all other soluble gases. The procedure followed is outlined below, the calculations being performed each microbial timestep. The procedure is subject to the following assumptions:

1. the aqueous phase is in equilibrium with the headspace gases;
2. there is perfect mixing between the gases;
3. perfect mixing occurs in the aqueous phase;
4. the headspace gas has constant pressure during the partitioning process;
5. the pH is constant and is not immediately affected by the partitioning process (see Sec. 6.7 however);
6. other gases are assumed to be constant over the calculation, even other soluble gases;
7. the soluble species used in the partitioning calculation for carbon dioxide are CO_3^{2-}, HCO_3^- and H_2CO_3;
8. the soluble species used in the partitioning calculation for hydrogen sulphide are H_2S, S^{2-} and HS^-; and
9. the soluble species used in the partitioning calculation for ammonia are NH_4^+, NH_4Cl,NH_4NO_3, $NH_4SO_4^-$.

Of course, much of the credibility of the above assumptions rests on the claim that there are small changes in the number of moles of each gas in each phase over the course of a single microbial timestep.

Consider for example the partitioning of carbon dioxide. From Dalton's law of partial pressure:

$$\{CO_{2(g)}\} = \frac{P_{CO_2}}{RT}, \tag{90}$$

where P denotes partial pressure, R is the gas constant and T is the absolute temperature. The following thermodynamic equation applies to the equilibrium of carbon dioxide:

$$H_2O + CO_{2(g)} \rightleftharpoons CO_3^{2-} + 2H^+, \quad \log K = -18.15 + P_{CO_2}. \tag{91}$$

The corresponding equilibrium constant[19] is:

$$K_{CO_2} = \frac{\{CO_3^{2-}\}\{H^+\}^2}{\{H_2O\}\{CO_{2(g)}\}}, \tag{92}$$

where $\{H_2O\}$ is the activity of water, which is determined within PHREEQE. It is equal to 1 for dilute aqueous solutions. Using Dalton's law, Eq. 92 can be rewritten as:

$$\frac{K_{CO_2}P_{CO_2}}{RT} = \frac{\{CO_3^{2-}\}\{H^+\}^2}{\{H_2O\}}. \tag{93}$$

The activities are related to the concentrations through activity coefficients, as in Eq. 46. Now, letting the total number of moles of CO_2 be T_{CO_2}, the number of moles of CO_2 gas be G_{CO_2} and the number of moles of all other gases be $\overline{G}_{CO_2}$ then Eq. 93 can be expressed as:

$$\frac{cG_{CO_2}}{G_{CO_2} + \overline{G}_{CO_2}} = T_{CO_2} - G_{CO_2}, \tag{94}$$

where c is a known constant. Rearranging leads to:

$$G_{CO_2}^2 + G_{CO_2}(c + \overline{G}_{CO_2} + T_{CO_2}) - T_{CO_2}\overline{G}_{CO_2} = 0. \tag{95}$$

This is a quadratic for G_{CO_2}, with one positive and one negative root. Taking the former, one can determine the updated partial pressure for carbon dioxide and then, from Eq. 93, the activity for the aqueous ion is deduced.

Other important dissolved species of carbon dioxide are HCO_3^- and H_2CO_3. The thermodynamic equations associated with each of these species are:

$$H_2O + CO_{2(g)} \rightleftharpoons H_2CO_3, \quad \log K = -1.47 + P_{CO_2} \tag{96}$$

$$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-, \quad \log K = 10.33 \tag{97}$$

$$2H^+ + CO_3^{2-} \rightleftharpoons H_2CO_3, \quad \log K = 16.68, \tag{98}$$

where Eq. 98 follows from Eqs. 91 and 96. By definition, equilibrium constants for Eqs. 97 and 98 are given by:

$$K_{HCO_3^-} = \frac{\{HCO_3^-\}}{\{H^+\}\{CO_3^{2-}\}} \tag{99}$$

$$K_{H_2CO_3} = \frac{\{H_2CO_3\}}{\{H^+\}^2\{CO_3^{2-}\}}, \tag{100}$$

[19] which is temperature corrected in the code.

and from these equations, the activities of the other dissolved species can be evaluated.

It should be noted that the solubility products for the dissolved bulk gases CO_2, O_2, H_2S, N_2, NH_3 and CH_4 are temperature corrected using the Van't Hoff equation:

$$\log K(T = 298) - \log K(T) = \frac{-\Delta H_r^o}{2.303R}\left(\frac{1}{298} - \frac{1}{T}\right), \tag{101}$$

where:

- temperatures are expressed on the Kelvin scale;
- $K(T)$ is the solubility product/equilibrium constant at temperature T;
- ΔH_r^o is the reaction enthalpy constant; and,
- R is the gas constant.

Relevant values for ΔH_r^o and $\log K(T = 298)$ are taken either from the `PHREEQE` database or else from data supplied in the input file `grm.bug`.

6.6 Partitioning of Radioactive Gases

These gases are partitioned using slightly different methods to that of the previous section. Ref. [41] states that the mole fraction solubility (MFS, the number of moles per mole of water) of ^{222}Rn is given by the following expression:

$$\text{MFS} = \exp\left[-90.5481 + \frac{13002.6}{T} + 35.0047 \ln\left(\frac{T}{100}\right)\right], \tag{102}$$

at a ^{222}Rn gas partial pressure of 1 atm. From this, the number of moles of ^{222}Rn in the liquid phase is:

$$\begin{aligned} T_{^{222}\text{Rn}} - G_{^{222}\text{Rn}} &= NV_l(\text{MFS})P_{^{222}\text{Rn}} \\ &= NV_l(\text{MFS})\left(\frac{G_{^{222}\text{Rn}}}{G_{^{222}\text{Rn}} + \overline{G}_{^{222}\text{Rn}}}\right), \end{aligned} \tag{103}$$

where N is the number of moles of water per unit volume (55.556 per litre) and V_l is the liquid volume. Apart from the specification of the constant, the above equation is of the same form as Eq. 94.

In the case of Tritium, it is assumed that in a tritiated water molecule only one of the hydrogen atoms is tritium. Assuming f (the fraction of tritiated water molecules)is the same in both the saturated and the unsaturated zones, then f is given by:

$$f = T_{^3\mathrm{H}} \left[NV_l + \frac{273.15 V_g}{T N_g} P_{\mathrm{H_2O}} \right]^{-1}, \tag{104}$$

where $P_{\mathrm{H_2O}}$ is the partial pressure of water vapour, V_g is the headspace volume and N_g is the volume occupied by 1 mole of gas at 0°C (0.022414 m^3). The first term in square brackets considers the water in the saturated phase and the second term takes the headspace water vapour into account.

The number of tritium moles in the gaseous phase is then just:

$$G_{^3\mathrm{H}} = T_{^3\mathrm{H}} - fNV_l. \tag{105}$$

6.7 Equilibrating Gases at Chemical Speciation

The methods described above are used to partition the gases between the liquid and gaseous phases at each microbial timestep. A constant pH was assumed in performing the partitioning calculations. However, the pH will in fact depend on the partitioning of gases that are chemically active when dissolved; in particular on carbon dioxide and hydrogen sulphide. This may result in problems if the frequency of speciation calculations is much slower than that of microbial calculations[20]. To avoid such problems, the speciation calculations performed by PHREEQE have been modified.

Pseudo species for the chemically active gases CO_2,NH_3 and H_2S are introduced into the PHREEQE database. When modelling the equilibration of gases with water, the standard PHREEQE assumes an open system with a constant gaseous partial pressure. Gases are dealt with in the 'mineral' part of the calculations since they are in a different phase to the liquid. The logarithm of the partial pressure replaces the equilibrium saturation index in defining an equilibrium with the liquid. In the case of CO_2 Eq. 91 is used within the 'mineral' part of PHREEQE. From Eq. 93, one can define a corresponding equilibrium constant K_{dis} as:

$$K_{\mathrm{dis}} = \frac{K_{\mathrm{CO_2}}}{RT} = \frac{\{CO_3^{2-}\}\{H^+\}^2}{\{H_2O\}P_{CO2}}. \tag{106}$$

[20] In particular, in some situations it was found that the variation of pH from speciation to speciation fluctuated greatly because of the disconnect between the equilibrium of carbon dioxide and the pH of the solution.

If the atmosphere were to be pure CO_2 gas then K_{dis} would equal to the ion activity product (cf. Sec. 4.4). In the GRM however, each cell of the model domain represents a system where the partial pressure of a headspace gas can change in response to gaseous evolution and dissolution. To reflect this point a known number of moles of soluble gas is equilibrated with the saturated zone during the PHREEQE speciation. This is achieved by adjusting the equilibrium constant used by PHREEQE, as explained below. Advantages of the method are that the partial pressure of the gas can be varied during equilibration and that other soluble gases (such as H_2S) can be coupled in the same manner. The main assumption is that the total number of moles of gas in the headspace is constant during equilibration, which is approximately true if:

- the headspace volume is very much greater than the liquid volume within a zone; and/or,
- the gas is very near to equilibrium in the first place.

The pseudo species CO2GAS is added into the PHREEQE database via its association equation (the reverse of Eq. 91), which has an equilibrium constant:

$$K_{\text{ass}} = \frac{1}{K_{\text{dis}}} = \frac{\{H_2O\}P_{CO_2}}{\{CO_3^{2-}\}\{H^+\}^2}. \tag{107}$$

Thus:

$$\frac{K_{\text{ass}}}{V_l}(G_{CO_2} + \overline{G}_{CO_2}) = \frac{\{H_2O\}}{\{CO_3^{2-}\}\{H^+\}^2}\left(\frac{G_{CO_2}}{V_l}\right). \tag{108}$$

The above equation is used to define the equilibrium constant for the pseudo species CO2GAS:

$$\log K_{\text{CO2GAS}} = \log K_{\text{ass}} + \log(G_{CO_2} + \overline{G}_{CO_2}) - \log V_l. \tag{109}$$

The equilibrium constant is therefore adjusted to take account of the total number of moles of gas in the headspace and the liquid volume in the cell being modelled.

A simple change had to be made to the PHREEQE code to take account of these gas pseudo species. The activity of water is determined as a function of the sum of all the species concentrations in solution. The pseudo species must not be included in this calculation as they represent the gaseous phase and are not really present in the water.

NOTE: With the PHREEQC option gas composition can be set by mineral phases, but this cannot be coupled to gas production, or consumption by corrosion or microbiological processes.

7 Modelling of Redox processes

Redox reactions as a whole are important to hydrogeochemical processes. A plot of the redox status, pe (or Eh) and the pH (Pourbaix diagram) can realistically portray the solubility of many mineral phases and the occurrence of geochemical species in groundwater under thermodynamic equilibrium.

Although the theoretical redox behaviour of inorganic groundwater constituents is well defined, the measurements and estimates of redox conditions in natural systems often reflect disequilibrium conditions. A good example of this is demonstrated by the pe values measured between a platinum and reference electrode for the Borden aquifer by Nicholson et al. [45] and the corresponding analytic values calculated from the measured concentrations of various redox couples.

In general, therefore, the use of a unique pe in a groundwater system would not be realistic. However, the speciations within GRM (see Sec. 4) require a definite pe to be specified in order to determine the microelement oxidation states. The imposition of a fixed pe throughout a model run is not acceptable, since this would not represent the cycle of oxidising, reducing and oxidising conditions likely to be encountered in LLW disposal sites.

This problem is resolved within GRM by identifying the major redox active elements, and taking the redox reactions of these elements out of the control of PHREEQE. The redox active elements identified within GRM and the species that have been separated within the PHREEQE database are listed in Table 2 below, the individual species representing the two halves of the redox couple for that element(NOTE: There is an option to disable the first and/or second redox couples).

Element	Species	
	Oxidised	Reduced
Oxygen	O_2	H_2O
Nitrogen	NO_3^-	N_2
Iron	Fe^{3+}	Fe^{2+}
Sulphur	SO_4^{2-}	H_2S
Carbon	CO_2	CH_4

Table 2: Redox active elements and species.

The pe within each cell is calculated during each speciation step from the relative pro-

portions of these two halves of the most oxidising redox couple present. For this purpose the corresponding Nernst equation for the couple is used. The relative proportions of each couple will change due to factors such as groundwater ingress, microbial metabolism and chemical reactions. The pe thus determined is effectively not used for the macrospecies since their member elements with multiple oxidation states are prevented from taking part in redox reactions by defining them as master species. However, the dominant pe is explicitly used to determine the relevant oxidation state of microspecies, which are assumed to be in equilibrium with the dominant redox couple.

7.1 Microbial Mediation of Redox Reactions

Microorganisms can play an important role in determining the redox status of an environment by acting as catalysts in oxidation–reduction reactions. In this role, microorganisms take advantage of thermodynamic disequilibria, which result in oxidised and reduced species being present simultaneously. By catalysing the transfer of electrons from reduced to oxidised compounds, microorganisms generate the energy to support their growth. Such processes usually involve the oxidation of organic compounds, such as glucose, and the reduction of inorganic compounds, such as molecular oxygen and nitrate. However, both the electron donor and acceptor can be inorganic, the oxidation of elemental sulphur and sulphide to sulphate using molecular oxygen being a classic example.

The amount of energy available from the transfer of an electron depends on the oxidation states of the electron donor and acceptor involved. The more oxidised the donor and the more reduced the acceptor, the greater the energy yield per transfer. In an environment where more than one electron acceptor is present, thermodynamics dictates that an electron donor will always preferentially donate to the most oxidised acceptor present. Once the most energetically favourable acceptor has been exhausted, the next most favourable acceptor will then be utilised. In reality, environments where all the required bacteria and all the range of electron acceptors are present are rare, if they exist at all, but the sequential use of electron acceptors (and the associated changes in ambient pe) has been observed, some of the best examples being gradients within aquatic sediments.

There are a large number of biologically–mediated redox reactions which could occur in the environment [46]. Only a subset of these are included within the GRM. The redox reaction pathways incorporated are listed below in order of their strengths as oxidants.

1. $O_2 \rightarrow H_2O$
2. $NO_3^- \rightarrow N_2(g)$

3. Fe(III) $\rightarrow$ Fe(II)
4. $SO_4^{2-} \rightarrow HS^-$
5. $CO_2 \rightarrow CH_4$ (methane production)
6. Reduction of organic matter (fermentation)

Note that the couples Mn(IV)oxide $\rightarrow$ Mn(II) and $NO_3^- \rightarrow NH_4^+$ are not included at present and are assumed to be insignificant.

7.2 Calculation of the Ambient pe

It is assumed that the most oxidising couple present defines the pe of the solution. This is calculated from the appropriate Nernst equation, the equations used being outlined below. Equilibrium constants (K) for the equations were calculated for a temperature of 10°C.

1. $O_2 \rightarrow H_2O$:
   Under aerobic conditions the amount of oxygen dissolved in solution is 2.3×10^{-4} moll^{-1}. Oxygen is definitely limited when it is more than 1000 times less than the aerobic value. Therefore, the oxygen couple is considered dominant if the dissolved oxygen concentration is greater than 1×10^{-7} moll^{-1}.

   When $O_2 \rightarrow H_2O$ is the dominant couple, the pe is derived from the equations:

$$\frac{1}{4}O_2(g) + H^+ + e^- \rightleftharpoons \frac{1}{2}H_2O \tag{110}$$

$$K_{O_2} = \frac{[H_2O]^{\frac{1}{2}}}{[O_2]^{\frac{1}{4}}[H^+][e^-]}. \tag{111}$$

   Taking $[H_2O] \approx 1.0$ then:

$$\mathrm{pe} = \log K_{O_2} - \mathrm{pH} + \frac{1}{4}\log[O_2], \tag{112}$$

   where $\log K_{O_2} = 22.81$ from Ref. [10].

2. $NO_3^- \rightarrow N_2(g)$:
Nitrate becomes the dominant couple when oxygen is limited and the NO_3^- concentration is greater than 1×10^{-6} moll^{-1}. This value has been chosen because sulphate reducing microbes are inhibited [47] above this concentration.

When $NO_3^- \rightarrow N_2(g)$ is the dominant couple, the equations used to calculate the pe are:

$$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- \rightarrow \frac{1}{10}N_2(g) + \frac{3}{5}H_2O \quad (113)$$

$$\Rightarrow \text{pe} = \log K_{NO_3^-/N_2} - \frac{6}{5}\text{pH} + \frac{1}{5}\log[NO_3^-], \quad (114)$$

where $\log K_{NO_3^-/N_2} = 22.22$, using data from Refs. [9, 10]. In writing Eq. 114 it is assumed that the partial pressure of nitrogen is 1.0. This is likely to be a good approximation under most circumstances, but the partial pressure may be lowered if large quantities of other gases are produced by waste degradation.

3. Fe(III)/Fe(II):
Iron(III) is likely to be present mainly in the form of solid $Fe(OH)_3$. The iron couple is used as the dominant couple when the nitrate couple cannot be used and the total amount of iron(III) present, including $Fe(OH)_3$, is greater than 1×10^{-6} moll^{-1} of porewater. The limiting concentration has been set arbitrarily.

There is a choice of equation to determine the pe depending on whether $FeCO_3$ solid is present or not. If the $FeCO_3$ solid concentration is less than 1×10^{-6} moll^{-1}, then the pe is determined from:

$$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O \quad (115)$$

$$\Rightarrow \text{pe} = 19.75 - \log[Fe^{2+}] - 3\text{pH}. \quad (116)$$

Otherwise, the pe is determined from:

$$Fe(OH)_3 + 2H^+ + HCO_3^- + e^- \rightarrow FeCO_3(s) + 3H_2O \quad (117)$$

$$\Rightarrow \text{pe} = 19.93 - 2\text{pH} + \log[HCO_3^-]. \quad (118)$$

The $\log K$ values for both of these cases have been determined from data in Refs. [10, 48].

4. SO_4^{2-}/H_2S:
The next couple to be considered is the sulphate/sulphide couple which becomes important when any iron(III) present has been fully reduced to iron(II) and sulphate is present in reasonable quantities (greater than 1×10^{-6} moll^{-1}).

The equations used to calculate the pe are:

$$SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S(aq) + 4H_2O \tag{119}$$

$$\Rightarrow \text{pe} = \frac{1}{8}\log K + \frac{1}{8}\log\frac{[SO_4^{2-}]}{[H_2S]} - \frac{10}{8}\text{pH}, \tag{120}$$

where $\frac{1}{8}\log K = 5.39$ from Ref. [10].

5. Methane production:
This couple can be used if the level of methane produced within the last timestep is above 1×10^{-6} moll^{-1}. Methane is formed from organotrophic or H_2-consuming reactions. The H_2-consuming reaction is:

$$\frac{1}{8}CO_2(g) + H^+ + e^- \rightarrow \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O, \tag{121}$$

while the organotrophic reaction is made up from the following two half-reactions:

$$CH_3COOH + 2H_2O \rightarrow 2CO_2(g) + 8H^+ + 8e^- \tag{122}$$

$$CO_2(g) + 8e^- + 8H^+ \rightarrow CH_4(g) + 2H_2O, \tag{123}$$

giving:

$$CH_3COOH \rightarrow CH_4(g) + CO_2(g). \tag{124}$$

Thus the equation used to calculate pe from methane production is:

$$\text{pe} = 3.16 - \text{pH}, \tag{125}$$

the $\log K$ value coming from data given in Ref. [10]. Note that in writing Eq. 125, the partial pressures of carbon dioxide and methane have been ignored. This is equivalent to the case where the partial pressures of these gases are identical and should be a good approximation if the pressures are similar whenever this couple is dominant. Thus, for this couple the pe is totally dependent on the pH of the solution. Since methanogens are really only active in near–neutral conditions the pe should be between about -3.13 and -5.13.

6. Fermentation:
   The fermentation of glucose to acetic acid is here taken to be representative of all fermentation reactions within GRM. This is because cellulose, which is a polymer of glucose, is likely to be the dominant, degradable organic material in LLW disposal sites. The equation for this fermentation is:

$$C_6H_{12}O_6 + 4H_2O \rightarrow CH_3COOH + 8H_2 + 4CO_2. \quad (126)$$

   In this incomplete oxidation reaction only two thirds of the glucose is used in the oxidation step of CO_2 production, the other third being used in the production of acetic acid. Thus, the reaction to define pe is:

$$\frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}H_2O \rightarrow \frac{1}{4}CO_2(g) + H^+ + e^- \quad (127)$$

$$\Rightarrow \text{pe} = -\log K - \text{pH}, \quad (128)$$

   where $\log K = 0.2$ from Ref. [9]. This couple has a very low pe value (about -7.2 at neutral pH), much lower than that predicted for the methanogenesis couple. However, observations have indeed been made [49, 50] where pe dips down to about -8.0 as acid fermentation builds up and then when methanogenesis sets in the pe rises to about -4.0.

   In writing the Eq. 128, the partial pressure of carbon dioxide and the concentration of glucose have been ignored. Thus, it is assumed that the following quantity is small:

$$\frac{1}{4}\log P_{CO_2} - \frac{1}{24}\log[C_6H_{12}O_6]. \quad (129)$$

   Lowering the partial pressure of carbon dioxide would result in an even lower pe, whilst a reduction in the glucose concentration would produce higher pe values. The assumption is convenient since it is unclear how the glucose concentration would be defined and because the implementation of Eq. 128 provides a useful representation of highly reduced conditions. From the Ref. [9] data, the couple as given in Eq. 128 is a little below the stability limit of water. An alternative would be to use that stability limit as the lowest redox couple. This would lead to similar results to those currently obtained with the fermentation couple.

7. No dominant couple:
   The fermentation couple is only used if the acetic acid concentration is at least

1×10^{-6} moll^{-1}. Should this not be the case, and no dominant pe has been identified then the pe is left unaltered from its previous value.

Note that if the microbial pe determination route is not selected for use, but pe calculations are still required, then these can be performed through PHREEQE. To improve the speed at which PHREEQE converges on a pe, a starting value is provided by considering the $O_2 \rightarrow H_2O$, Fe(III)/Fe(II) and SO_4^{2-}/H_2S couples.

8 Microbiology

8.1 Introduction

Microorganisms are ubiquitous in all natural environments and are involved in a wide variety of processes which may impact on radionuclide migration from LLW disposal sites. These include:

- the reduction of waste volume, which may have a detrimental effect on cap integrity;
- the production or degradation of organic complexants, which enhance the mobility of radionuclides;
- changes to the ambient pH and pe through the degradation of organic and inorganic compounds and the production of acidic by-products;
- the production of gaseous end products including CO_2, CH_4, H_2 and H_2S, which may be labelled with radioactive isotopes;
- the methylation of radionuclides to gaseous products;
- the generation of particulate material which may act as a host to contaminant transport;
- the direct uptake and transport of radionuclides;
- the clogging of drains and blocking-off of pores in engineered barriers; and,
- microbial induced corrosion of metallic waste and engineered components.

In the GRM model, the main impact of microorganisms is through the effects of microbial metabolism on site chemistry, in particular on the ambient pe and pH. Including microbiology also enables modelling of CO_2, CH_4, H_2 and H_2S generation, which can be converted into values for radiolabelled gases through knowledge of the relevant ^3H and ^{14}C inventories. In addition, GRM models the removal of organic LLW components, which causes volume reduction of the waste. The omission from the code of the other processes outlined above is not intended to imply that these do not occur in LLW sites. Rather, there is considered to be insufficient data on their impact to warrant their inclusion at this time.

8.2 Fundamental Assumptions Regarding Microbiology

There are a number of fundamental assumptions inherent in the manner microbiology is represented in GRM. These are outlined below.

- Microbial activity is only modelled in the saturated zone; no microbial activity (except hydrolysis) is modelled in the unsaturated zone. Note however, that the inclusion of unsaturated zone microbial activity can be factored in by including data from microbially–active lysimeter studies.
- The transport of microbes by groundwater flow is not modelled.
- The major mode of microbial growth is in the form of attached biomass.
- Heat generation by microbial activity is neglected.
- No bacterial population ever completely dies out. (This allows all microbial pathways to be active in the code whenever the correct conditions apply.)

8.3 Microbial Populations and Pathways

Eight microbial groups, carrying out a range of processes, are currently represented within GRM. The processes are not intended to be an exhaustive list of microbial metabolism within LLW disposal sites, but are intended to represent the major significant pathways. The groups included are approximately the same as those included in the GAMMON model [51, 52] with the addition of iron reducing bacteria. The processes modelled only occur if the relevant electron acceptors and electron donors are present. Simplifications are also introduced into GRM by considering only one bacterial "population" to be responsible for each process. This population is split into a neutraphilic and a alkaliphilic[21] component, the latter describing microbes which are optimally active under extreme alkaline conditions at pH values larger than about 8 [53]. In reality, of course, a whole spectrum of bacterial species would be competing for each substrate. The GRM user is able to switch off any microbial pathway by setting the relevant substrate removal rate to zero. The groups are outlined below.

1. Aerobic metabolism
   These microbes consume oxygen as the terminal electron acceptor and organic compounds as electron donors. The range of possible electron donors includes:

[21] The term alkaliphilic can sometimes be found spelt as alkalophilic. In this report, we have followed the convention of Ref. [53].

- cellulose hydrolysis products;
- volatile fatty acids;
- free fatty acids;
- acetic acid;
- peptides; and,
- glycerol.

2. Denitrification
   Two groups of denitrifying bacteria can be modelled. These bacteria consume nitrate as the electron acceptor and organic compounds or hydrogen as the electron donors. The user is able to choose whether these bacteria are able to consume hydrolysis products, or whether they consume fermentation products only.

3. Fermentation
   These bacteria can consume glucose, peptides and glycerol. Fermentation of glucose generates short–chain carboxylic acid, carbon dioxide and hydrogen. Peptide and glycerol fermentation are treated similarly, except that a mixture of acetic acid and short–chain carboxylic acids is produced, the exact proportions being determined by the GRM user.

4. Iron Reduction
   These bacteria consume ferric iron as a terminal electron acceptor and fermentation end products and hydrogen as electron donors.

5. Sulphate Reduction
   Two types of sulphate reducing bacteria are modelled. Sulphate is consumed as an electron acceptor. Fermentation end products are consumed as electron donors by one type of bacteria, while the other type utilises hydrogen.

6. Acetogenesis
   These bacteria oxidise long–chain volatile fatty acids to acetic acids and hydrogen.

7. Methanogenesis
   Two types of methanogens are modelled. The first produces methane from the metabolism of acetic acid. The second consumes hydrogen and carbon dioxide in order to generate methane.

8. Reoxidation
   These bacteria oxidise inorganic substrates (iron (II), sulphides and pyrite), using nitrate and oxygen as the electron acceptors. Another type oxidise dissolved ammonia species using oxygen only.

The two primary substrates for GRM microbiology are organic polymeric substrates and hydrogen. The former are assumed to be part of the original inventory and to be dominated by cellulose. Proteins are an exception since they may act as a substrate and yet may be produced as a result of recycling of dead biomass. Hydrogen is produced by the anaerobic corrosion of metallic waste components and from the fermentation of organic compounds. The polymeric organics are subdivided into three rough groups: cellulose, proteins and fats. These are hydrolysed to soluble products which are then metabolised through aerobic respiration, denitrification or fermentation. The bacterial populations metabolising these routes are assumed to be the only populations capable of hydrolysis.

End products of fermentation are preferentially further degraded through iron reduction, sulphate reduction, acetogenesis and methanogenesis. They can also be degraded by aerobic metabolism and denitrification. GRM is therefore able to model situations where the products from anaerobic cells are washed into neighbouring aerobic or anoxic[22] cells.

All of the microbial populations present in GRM have alkaliphilic sub-populations which become active under alkaline conditions. This implies an alkaline route for the hydrolysis of cellulose. The product of this microbial hydrolysis is referred to in the code as ISA. In the current version of GRM, ISA is treated in the same manner as glucose. Hence, references to ISA in the code should not be confused with isosaccharinic acid, which can be produced as a result of chemical cellulose hydrolysis. The name ISA has been used in anticipation of future code developments, in which the alkaline chemical route will be modelled by linking the cellulose hydrolysis product under alkaline conditions to the PHREEQE speciation calculations.

8.4 Microbiological Process Modelling

All microbial groups modelled in GRM are subject to growth and decay. Growth is modelled via energy–generating and biomass–generating reactions. The former describe oxidation of electron donors; the latter involve the conversion of carbon–containing substrates into microbial biomass. An idealised formula, $C_5H_7O_2N$ [54], is used for the microbial biomass. Growth can be limited by the availability of nitrogen, in the form of ammonia and/or

[22] Anoxic is a term for an environment under denitrifying conditions.

nitrate. On death, cells are split into non-degradable and degradable fractions, the latter being recycled through the polymeric substrates. Note that in the modelling of all of the microbial processes, the active fraction of ^{14}C (see Sec. 10.2) is tracked for each carbon–containing species.

During a GRM simulation, microbiological process modelling is only performed at times less than a user–defined time TENDBUG. This facility allows the user to switch off microbiological calculations during a GRM simulation. After the time TENDBUG no further microbial calculations are performed. This facility is useful during simulations where steady–state situations arise or where microbial processes are thought to no longer influence the biogeochemical evolution of the system (as, for example, in situations where all microbial substrates have been exhausted).

8.5 Kinetic Relationships

Two general kinetic relationships are employed in the microbial modules of GRM. It should be noted that the resulting kinetic equations, and all other differential equations used within the microbial module, are solved in the GRM code to leading order in the microbial timestep, Δt_{bug}. This will be a good approximation if all of the changes over the course of each microbial timestep are small.

1. Hydrolysis of Polymeric Substrates.
   A first order rate equation is used to model the hydrolysis of the polymeric substrates. Although this is a popular approach [55], it does separate substrate hydrolysis from bacterial growth, which is unlikely to reflect the situation in situ. Three polymeric organic substrates are considered by GRM, but it is assumed that the most significant of these in LLW disposal sites will be cellulose. The rate of polymer hydrolysis will depend on the ease of degradation, the ambient pH and temperature and the prevailing environment (i.e., aerobic/anoxic or anaerobic). The substrate removal rate within the saturated region can be expressed as:

$$\frac{dS}{dt} = -v_{i,j} F(T, \text{pH}) \theta_s S, \tag{130}$$

   where:

   - θ_s is the local saturated region moisture content;
   - S is the polymeric substrate concentration (mass per unit volume);

- $v_{i,j}$ is the hydrolysis rate. This depends on whether conditions are aerobic/anoxic ($i = 1$) or anaerobic ($i = 2$) and on whether the rate of degradation is classified as slow ($j = 3$), medium ($j = 2$) or fast ($j = 1$); and,
- pH cut-off factors are defined for both neutral and alkaline cellulose hydrolysis. These are the limiting pH values below which cellulose hydrolysis does not occur.

The function F is given by:

$$F(T, pH) = \frac{T \exp[-(\mathrm{pH} - \mathrm{pH_{opt}})^2 f]}{1 + \exp[\frac{T}{4} - 18]}, \tag{131}$$

where:

- T is the temperature, expressed here in centigrade units;
- $\mathrm{pH_{opt}}$ is the optimum pH for hydrolysis; and,
- f is a pH–dependence factor.

An option in GRM does however exist in which the temperature dependence of the hydrolysis rate may removed. If this option is chosen then the previous equation may be simplified to:

$$F(T, pH) = \exp[-(\mathrm{pH} - \mathrm{pH_{opt}})^2 f] \tag{132}$$

Hydrolysis rates within the unsaturated region are taken to be temperature and pH independent since neither quantity is defined within the unsaturated region. Similarly, no distinction is made between aerobic and anaerobic regimes. The substrate removal rate in this zone is therefore simplified to:

$$\frac{dS}{dt} = -v_i \theta_u S, \tag{133}$$

where:

- θ_u is the local unsaturated region moisture content; and,
- v_i is the hydrolysis rate, which can be classified as slow ($i = 3$), medium ($i = 2$) or fast ($i = 1$).

2. Bacterial Growth and Substrate Removal.
   These processes follow Michaelis-Menten (Monod) kinetics as described by McCarty and Mosey [13], with the addition of a pH control factor:

$$\frac{dS}{dt} = -\frac{VSX}{K_m + S} F_{\mathrm{pH}}, \tag{134}$$

   where:

   - V is the maximum substrate removal rate;
   - X is the biomass concentration, which evolves according to Eq. 135;
   - K_m is the half-saturation constant; and,
   - F_{pH} is a pH control factor, given by Eq. 136.

$$\frac{dX}{dt} = Y\frac{dS}{dt} - DX \tag{135}$$

$$F_{\mathrm{pH}} = \exp[-(\mathrm{pH} - \mathrm{pH_{opt}})^2 f] \tag{136}$$

   In the equations above we have introduced the parameters:

   - D, the biomass death rate;
   - Y, the yield coefficient; and,
   - $\mathrm{pH_{opt}}$, the optimum pH for metabolism.

The GRM user is able to control the nitrogen limitation of microbial growth with a switch in the `grm.dat` file, `INLIM`. If `INLIM` is set to unity, then the growth rate is limited by the availability of ammonia and/or nitrate.

If nitrogen limitation is switched off (by zeroing `INLIM`), the rate is calculated regardless of the amount of ammonia and nitrate present. Under these circumstances, the fixation of nitrogen is assumed.

8.6 Hydrolysis of Polymeric Organic Substrates

The hydrolysis of the three polymers considered within GRM is outlined below. The progress of the reactions discussed is modelled using the kinetic equations 130 and 133.

1. **Cellulose**
   Cellulose is considered to be a polymer of anhydroglucose which is hydrolysed to glucose through the action of bacteria. The general equation for this conversion is:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6. \quad (137)$$

   Alkaline hydrolysis is modelled by setting the optimum of the pH control function (Eq. 131) to an alkaline pH.

2. **Proteins**
   Since it is not possible to specify the elemental composition of any protein present in a disposal site, a representative 'average' protein is used [64]. Based on the empirical observations that such a protein would contain 50% carbon, 25% oxygen, 15% nitrogen and 7% hydrogen[23] this protein has the formula:

$$C_{46}H_{77}O_{17}N_{12}. \quad (138)$$

   Proteins are hydrolysed to soluble peptides of the same general formula.

3. **Fats**
   Fats are assumed to hydrolyse to long–chain carboxylic acids (free fatty acids: FFAs) and to glycerol [56]. The ratio of glycerol to acids in the hydrolysis products is specified by the user.

   Under anaerobic conditions FFAs are assumed to decompose to shorter–chain carboxylic acids: i.e., a mixture of acetic acid and volatile fatty acids (VFAs). This decomposition is represented by the following reaction:

$$(1+n+2f)H(CH_2)_mCOOH + 2(m-n-f+mf)H_2O \rightarrow$$
$$(1+m)H(CH_2)_nCOOH + f(1+m)CH_3COOH + (2m-2n-2f+2mf)H_2 \quad (139)$$

   where f is the user–defined molar ratio of acetic acid to VFAs in the decomposition products. This decomposition is assumed to be instantaneous and, therefore, the effects are modelled by simply increasing the relevant species concentrations by the required amounts and then setting the FFA concentration to zero.

[23] A small sulphur component is neglected in GRM.

8.7 Aerobic Metabolism

In regions where oxygen is present glucose, peptides, glycerol, acetic acid, VFAs and FFAs will all be consumed by the action of aerobic microbes. In reality these substrates would be degraded by a range of microbial groups at various rates. Due to the complexity of these processes and the probable absence of site–specific data, the aerobic degradation of these substrates is simplified by not ranking their degradability and instead adopting the concept of chemical oxygen demand (COD). A similar approach has also been followed in the modelling of activated–sludge wastewater treatment systems [57], where complex substrates are degraded aerobically. The COD value for a known quantity of a species is the amount of oxygen required to oxidise it completely. Thus, for the aerobic microbes, COD values are determined for the quantities of glucose, peptides, glycerol, acetic acid, VFAs and FFAs present. The activity of the microbes is then calculated based on the total COD rather than separately for each of the species.

As stated previously (Sec. 8.3), within GRM there are considered to be two types of aerobic bacteria: one which achieves maximum performance at neutral pH and an alkaliphilic type which performs best at a pH of around 9 (note, however, that the optimum pH values have been left as user–defined parameters in the code). Apart from different values for the kinetic constants (substrate utilisation rates, microbe yield coefficients etc.), the growth and activity of the two types of bacteria are identical.

The relevant oxidation reactions for the species concerned are given below.

Glucose:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \tag{140}$$

Peptides:

$$C_{46}H_{77}O_{17}N_{12} + \frac{191}{4}O_2 \rightarrow 46CO_2 + \frac{41}{2}H_2O + 12NH_3 \tag{141}$$

Glycerol:

$$C_3H_8O_3 + \frac{7}{2}O_2 \rightarrow 3CO_2 + 4H_2O \tag{142}$$

Acetic acid:

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O \tag{143}$$

Volatile fatty acids:

$$H(CH_2)_nCOOH + \frac{3n+1}{2}O_2 \rightarrow (n+1)CO_2 + (n+1)H_2O \tag{144}$$

Free fatty acids:

$$\mathrm{H(CH_2)_mCOOH} + \frac{3m+1}{2}\mathrm{O_2} \rightarrow (m+1)\mathrm{CO_2} + (m+1)\mathrm{H_2O} \tag{145}$$

COD values for the relevant species are calculated from:

$$\mathrm{COD_{sp}} = c_{\mathrm{sp}} \frac{\mathrm{MW_{O_2}}}{\mathrm{MW_{sp}}} \mathrm{SP}, \tag{146}$$

where:

- 'sp' labels the species (glucose, peptides, glycerol, acetic acid, VFA or FFA), which has a concentration (mass per unit volume) of 'SP';
- $\mathrm{MW_X}$ is the molecular weight of X; and,
- c_{sp} is the coefficient of O_2 in the relevant reaction equation (one of Eqs. 140 to 145).

Each of the substrates is also consumed to produce more bacteria. The primary source of nitrogen for these bacteria is NH_3 although, if there is an insufficient amount of this, NO_3^- may also be used. (Note that no external nitrogen source is required for the production of bacteria from peptides.) Again the COD concept is used by GRM to calculate the bacteria production (substrate consumption) rates. The bacteria–producing reactions considered are listed below.

Glucose:

$$5\mathrm{C_6H_{12}O_6} + 6\mathrm{NH_3} \rightarrow 6\mathrm{C_5H_7O_2N} + 18\mathrm{H_2O} \tag{147}$$

$$7\mathrm{C_6H_{12}O_6} + 6\mathrm{NO_3^-} + 6\mathrm{H^+} \rightarrow 6\mathrm{C_5H_7O_2N} + 12\mathrm{CO_2} + 24\mathrm{H_2O} \tag{148}$$

Glycerol:

$$10\mathrm{C_3H_8O_3} + 7\mathrm{NH_3} + 5\mathrm{CO_2} \rightarrow 7\mathrm{C_5H_7O_2N} + 26\mathrm{H_2O} \tag{149}$$

$$2\mathrm{C_3H_8O_3} + \mathrm{NO_3^-} + \mathrm{H^+} \rightarrow \mathrm{C_5H_7O_2N} + \mathrm{CO_2} + 5\mathrm{H_2O} \tag{150}$$

Acetic acid:

$$5\mathrm{CH_3COOH} + 2\mathrm{NH_3} \rightarrow 2\mathrm{C_5H_7O_2N} + 6\mathrm{H_2O} \tag{151}$$

$$7\mathrm{CH_3COOH} + 2\mathrm{NO_3^-} + 2\mathrm{H^+} \rightarrow 2\mathrm{C_5H_7O_2N} + 4\mathrm{CO_2} + 8\mathrm{H_2O} \tag{152}$$

VFAs:

$$10\mathrm{H(CH_2)_nCOOH} + (3n+1)\mathrm{NH_3} + 5(n-1)\mathrm{CO_2} \rightarrow$$

$$(3n+1)C_5H_7O_2N + 4(n+2)H_2O \tag{153}$$

$$14H(CH_2)_nCOOH + (3n+1)NO_3^- + (3n+1)H^+ \rightarrow$$
$$(3n+1)C_5H_7O_2N + (9-n)CO_2 + (5n+11)H_2O \tag{154}$$

FFAs:

$$10H(CH_2)_mCOOH + (3m+1)NH_3 + 5(m-1)CO_2 \rightarrow$$
$$(3m+1)C_5H_7O_2N + 4(m+2)H_2O \tag{155}$$

$$14H(CH_2)_mCOOH + (3m+1)NO_3^- + (3m+1)H^+ \rightarrow$$
$$(3m+1)C_5H_7O_2N + (9-m)CO_2 + (5m+11)H_2O \tag{156}$$

Peptides:

$$20C_{46}H_{77}O_{17}N_{12} + 35CO_2 \rightarrow 191C_5H_7O_2N + 49NH_3 + 28H_2O \tag{157}$$

Using a Michaelis–Menten formulation, the change in the total COD concentration is given by:

$$\frac{d(\mathrm{COD})}{dt} = -R_b X_b = -R_b^{\max}\frac{\mathrm{COD}}{K_b + \mathrm{COD}} F_{\mathrm{pH}} X_b, \tag{158}$$

where:

- $R_b^{\max}$ is the maximum rate of COD utilisation;
- K_b is a half-saturation constant;
- F_{pH} is an inhibition factor which is a function of pH and is given by an expression of the same form as Eq. 136; and,
- X_b is the local aerobe concentration.

The COD component species are assumed to be consumed on a pro rata basis so that the component concentrations at the end of a microbial timestep are:

$$\mathrm{SP} = \frac{\mathrm{COD}}{\mathrm{COD}^0} \cdot \frac{\mathrm{MW_{sp}}}{\mathrm{MW_{O_2}}} \cdot \frac{\mathrm{COD}^0_{\mathrm{sp}}}{c_{\mathrm{sp}}}, \tag{159}$$

the superscript 0 referring to quantities measured at the beginning of the microbial timestep.

The change in oxygen concentration is calculated from:

$$\frac{d(\mathrm{O_2})}{dt} = -(1 - Y_b) X_b R_b, \tag{160}$$

where Y_b is the fraction of COD used for microbe production. This quantity has components coming from the fractions of COD used to produce biomass from NH_3 and NO_3^- (Y_{NH_3} and Y_{NO_3} respectively -see section 8.7.1).

Unfortunately, for calculating the changes in other chemical concentrations the COD concept is not so helpful and we must consider the effect of each individual reaction separately. The remaining chemical concentration changes are calculated from:

$$\begin{aligned}\frac{d(\mathrm{CO_2})}{dt} = X_b \mathrm{MW}_{\mathrm{CO_2}} R_b \Big\{ & (C_{\mathrm{gluc}} + C_{\mathrm{ISA}}) \left(6 - 6Y_b + \frac{12}{7} Y_{\mathrm{NO_3}}\right) + C_{\mathrm{pep}} \left(46 - \frac{191}{4} Y_b\right) \\ & + C_{\mathrm{glyc}} \left(3 - 3Y_b + \frac{1}{2}(Y_{\mathrm{NO_3}} - Y_{\mathrm{NH_3}})\right) + C_{\mathrm{acet}} \left(2 - 2Y_b + \frac{4}{7} Y_{\mathrm{NO_3}}\right) \\ & + C_{\mathrm{VFA}} \left((n+1)(1 - Y_b) + \frac{1-n}{2} Y_{\mathrm{NH_3}} + \frac{9-n}{14} Y_{\mathrm{NO_3}}\right) \\ & + C_{\mathrm{FFA}} \left((m+1)(1 - Y_b) + \frac{1-m}{2} Y_{\mathrm{NH_3}} + \frac{9-m}{14} Y_{\mathrm{NO_3}}\right)\Big\}\end{aligned} \tag{161}$$

and:

$$\frac{d(\mathrm{NH_3})}{dt} = X_b \left(12 + \left(\frac{49}{20} - 12\right) Y_b\right) \mathrm{MW}_{\mathrm{NH_3}} R_b C_{\mathrm{pep}}, \tag{162}$$

where we have introduced the quantities C_{sp} defined by:

$$C_{\mathrm{sp}} = \frac{\mathrm{COD}^0_{\mathrm{sp}}}{\mathrm{COD}} \frac{1}{c_{\mathrm{sp}} \mathrm{MW}_{\mathrm{O_2}}}. \tag{163}$$

Note that Eq. 162 only accounts for NH_3 released in peptide reactions (Eqs. 141 and 157). In addition, NH_3 (and NO_3^-) may be consumed in microbe production. This is considered in the following subsection.

8.7.1 Microbe Production and Nitrogen Limitation

Apart from the concentration changes described above, NH_3 (and indeed NO_3^-) may be further consumed through microbe production. Since no external nitrogen is required for the production of microbes from peptides and since it is convenient to work in terms of

COD, we define a quantity Δcod given by the total COD consumption minus that coming from peptides:

$$\Delta\text{cod} \equiv \Delta\text{COD}\left(\frac{\text{COD}^0 - \text{COD}^0_{\text{pep}}}{\text{COD}^0}\right). \tag{164}$$

Let Y_b^i denote the ideal microbe yield (i.e., the fraction of COD which would be used in microbe production if there was sufficient nitrogen). Should sufficient nitrogen be present in the form of NH_3, then the corresponding increase in microbe concentration is:

$$\Delta\text{Bug} = Y_b^i \Delta\text{cod}\frac{\text{MW}_{\text{biomass}}}{5\text{MW}_{\text{O}_2}}. \tag{165}$$

The NH_3 requirement to produce this quantity of microbes is:

$$\frac{\text{MW}_{\text{NH}_3}}{\text{MW}_{\text{biomass}}}\Delta\text{Bug}. \tag{166}$$

If the NH_3 concentration is sufficient for this requirement then its concentration is reduced appropriately and the NO_3^- concentration is left unchanged. However, if there is insufficient NH_3 to produce the required quantity of microbes then the excess is produced from NO_3^-. In order to produce the ideal microbe yield in this way, the NO_3^- concentration must exceed the following:

$$\frac{5}{7}(Y_b^i - Y_{\text{NH}_3})\Delta\text{cod}\frac{\text{MW}_{\text{NO}_3}}{5\text{MW}_{\text{O}_2}}. \tag{167}$$

In the case where there is sufficient nitrogen in total to produce the ideal microbe yield, the available yields from NH_3 and NO_3^- are:

$$Y_{\text{NH}_3} = \frac{\text{NH}_3}{\Delta\text{cod}}\frac{5\text{MW}_{\text{O}_2}}{\text{MW}_{\text{NH}_3}} \tag{168}$$

$$Y_{\text{NO}_3} = \frac{7}{5}\frac{\text{NO}_3}{\Delta\text{cod}}\frac{5\text{MW}_{\text{O}_2}}{\text{MW}_{\text{NO}_3}}. \tag{169}$$

Once the actual microbe yields have been determined as described above, then the total change in microbe concentration can be evaluated from the following version of Eq. 135:

$$\frac{dX_b}{dt} = R_b X_b\left(Y_{\text{NH}_3} + \frac{5}{7}Y_{\text{NO}_3}\right)\left(\frac{\text{COD}^0 - \text{COD}^0_{\text{pep}}}{\text{COD}^0}\right) + \frac{191}{4}R_b X_b Y_b C_{\text{pep}}\text{MW}_{\text{O}_2} - k_b X_b, \tag{170}$$

where k_b is the aerobe death rate. The three terms on the right–hand side of the above equation represent production from non-peptide COD, production from peptides and death.

8.8 Denitrification

Denitrification is a general term for the reduction of nitrate or nitrite to dinitrogen or to gaseous oxides of nitrogen. Denitrifying bacteria utilise nitrate as a terminal electron acceptor in the absence of molecular oxygen. Within GRM the process is modelled in its most complete form of nitrate reduction to dinitrogen. This occurs via two routes, organotrophic and H_2-consumers, each being modelled with a distinct microbial population. The first group couples the oxidation of organic molecules to nitrate reduction; the second group couples to the oxidation of hydrogen. The hydrogen consumers are modelled assuming that these microbes derive carbon for biomass production from organic carbon sources. The relevant denitrifying reactions are as follows:

H_2-consuming:

$$5H_2 + 2NO_3^- + 2H^+ \rightarrow N_2 + 6H_2O \quad (171)$$

Organotrophic:

$$5C_6H_{12}O_6 + 24NO_3^- + 24H^+ \rightarrow 30CO_2 + 12N_2 + 42H_2O \quad (172)$$

$$10C_{46}H_{77}O_{17}N_{12} + 382NO_3^- + 382H^+ \rightarrow 460CO_2 + 191N_2 + 120NH_3 + 396H_2O \quad (173)$$

$$5C_3H_8O_3 + 14NO_3^- + 14H^+ \rightarrow 15CO_2 + 7N_2 + 27H_2O \quad (174)$$

$$5CH_3COOH + 8NO_3^- + 8H^+ \rightarrow 10CO_2 + 4N_2 + 14H_2O \quad (175)$$

$$5H(CH_2)_nCOOH + (6n+2)NO_3^- + (6n+2)H^+ \rightarrow (5n+5)CO_2 + (3n+1)N_2 + (8n+6)H_2O \quad (176)$$

$$5H(CH_2)_mCOOH + (6m+2)NO_3^- + (6m+2)H^+ \rightarrow (5m+5)CO_2 + (3m+1)N_2 + (8m+6)H_2O \quad (177)$$

As in the case of aerobic microbes (see Sec. 8.7), the organotrophs completely oxidise a range of substrates and it is therefore convenient to use the concept of COD, with values again given by Eq. 146. Each of the organic substrates is also consumed to produce more bacteria (both the H_2-consumers and the organotrophs). The primary source of nitrogen

for these bacteria is NH_3 although, if there is insufficient of this, NO_3^- may also be used. Microbe production proceeds via the reactions set out in Sec. 8.7 (Eqs. 147 to 157).

There is the option in the code of preventing the denitrifyers from consuming glucose. In effect, this assumes that they are unable to hydrolyse cellulose. The option is included because of suggestions that although cellulose hydrolysis by denitrifyers has been observed [58], it does not play a major role in determining microbial populations. Moreover, it has been claimed [59] that denitrifyers are much more likely to consume the end products of fermentative organisms.

A Michaelis–Menten formulation is used to describe the rates of utilisation of both hydrogen (R_n^a) and COD (R_n^o). Note that hydrogen is only consumed in the H_2-consuming energy reaction of Eq. 171, whereas COD is consumed by the other energy reactions (Eqs. 172 to 177) as well as in the production of both the organotrophic and the H_2-consuming microbes. The total change in COD concentration is then:

$$\frac{d(\mathrm{COD})}{dt} = -R_n^o X_o - R_n^a X_a Y_a \frac{5\mathrm{MW}_{\mathrm{O_2}}}{\mathrm{MW}_{\mathrm{biomass}}} \tag{178}$$

where X_o and X_a are the local organotroph and H_2-consumer concentrations respectively and Y_a is the H_2-consumer yield. Both this yield and the organotroph yield have component yields from NH_3 ($Y^o_{NH_3}$, $Y^a_{NH_3}$) and NO_3^- ($Y^o_{NO_3}$, $Y^a_{NO_3}$).

As in Sec. 8.7, COD component species are assumed to be consumed on a pro rata basis according to Eq. 159. The remaining chemical concentration changes are derived using the equations listed below:

$$\begin{aligned}
\frac{d(\mathrm{CO_2})}{dt} = {} & X_o \mathrm{MW}_{\mathrm{CO_2}} R_n^o \left\{ (C_{\mathrm{gluc}} + C_{\mathrm{ISA}}) \left(6 - 6Y_o + \frac{12}{7} Y^o_{\mathrm{NO_3}} \right) + C_{\mathrm{pep}} \left(46 - \frac{191}{4} Y_o \right) \right. \\
& + C_{\mathrm{glyc}} \left(3 - 3Y_o + \frac{1}{2}(Y^o_{\mathrm{NO_3}} - Y^o_{\mathrm{NH_3}}) \right) + C_{\mathrm{acet}} \left(2 - 2Y_o + \frac{4}{7} Y^o_{\mathrm{NO_3}} \right) \\
& + C_{\mathrm{VFA}} \left((n+1)(1-Y_o) + \frac{1-n}{2} Y^o_{\mathrm{NH_3}} + \frac{9-n}{14} Y^o_{\mathrm{NO_3}} \right) \\
& \left. + C_{\mathrm{FFA}} \left((m+1)(1-Y_o) + \frac{1-m}{2} Y^o_{\mathrm{NH_3}} + \frac{9-m}{14} Y^o_{\mathrm{NO_3}} \right) \right\} \\
& + X_a \mathrm{MW}_{\mathrm{CO_2}} \frac{5\mathrm{MW}_{\mathrm{O_2}}}{\mathrm{MW}_{\mathrm{biomass}}} R_n^a \left\{ (C_{\mathrm{gluc}} + C_{\mathrm{ISA}}) \frac{12}{7} Y^a_{\mathrm{NO_3}} - C_{\mathrm{pep}} \frac{7}{4} Y_a \right. \\
& \left. + C_{\mathrm{glyc}} \frac{1}{2} (Y^a_{\mathrm{NO_3}} - Y^a_{\mathrm{NH_3}}) + C_{\mathrm{acet}} \frac{4}{7} Y^a_{\mathrm{NO_3}} + C_{\mathrm{VFA}} \left(\frac{1-n}{2} Y^a_{\mathrm{NH_3}} + \frac{9-n}{14} Y^a_{\mathrm{NO_3}} \right) \right.
\end{aligned}$$

$$+C_{\mathrm{FFA}}\left(\frac{1-m}{2}Y^{o}_{\mathrm{NH_3}}+\frac{9-m}{14}Y^{o}_{\mathrm{NO_3}}\right)\Big\} \tag{179}$$

$$\frac{d(\mathrm{H_2})}{dt}=-R^{a}_{n}X_{a} \tag{180}$$

$$\frac{d(\mathrm{NO_3})}{dt}=-2R^{o}_{n}X_{o}(1-Y_{o})\mathrm{MW_{NO_3}}\Big\{\frac{12}{5}(C_{\mathrm{gluc}}+C_{\mathrm{ISA}})+\frac{4}{5}C_{\mathrm{acet}}+\frac{3n+1}{5}C_{\mathrm{VFA}}$$
$$+\frac{3m+1}{5}C_{\mathrm{FFA}}+\frac{7}{5}C_{\mathrm{glyc}}+\frac{191}{10}C_{\mathrm{pep}}\Big\}-R^{a}_{n}X_{a}\frac{2\mathrm{MW_{NO_3}}}{5\mathrm{MW_{H_2}}} \tag{181}$$

$$\frac{d(\mathrm{N_2})}{dt}=-\frac{\mathrm{MW_{N_2}}}{2\mathrm{MW_{NO_3}}}\frac{d(\mathrm{NO_3})}{dt} \tag{182}$$

$$\frac{d(\mathrm{NH_3})}{dt}=R^{o}_{n}X_{o}\mathrm{MW_{NH_3}}C_{\mathrm{pep}}\left(12-\frac{191}{20}Y_{o}\right)+R^{a}_{n}X_{a}Y_{a}\frac{5\mathrm{MW_{O_2}}}{\mathrm{MW_{biomass}}}\frac{49}{20}. \tag{183}$$

Note that, apart from the above concentration changes, NH_3 and NO_3^- may also be consumed in microbe production. This is considered later.

8.8.1 Substrate Limitation

The above method of calculation of chemical consumptions does not take into account how much of each species is present at the beginning of the timestep. It is therefore possible that some of the concentrations calculated using Eqs. 178 to 183 will be negative. Suppose for example that this possibility were to be realized for the COD. The decrease in COD concentration over a microbial timestep can be represented as:

$$\Delta\mathrm{COD}=\Delta_1+\Delta_2 Y_a\frac{5\mathrm{MW_{O_2}}}{\mathrm{MW_{biomass}}} \tag{184}$$

where Δ_1 is the consumption of COD due to all reactions involving the organotrophs and Δ_2 is the H_2 consumption by the energy reaction of Eq. 171. Now, if $\Delta\mathrm{COD} > \mathrm{COD}^0$ then new values are set for Δ_1 and Δ_2 such that $\Delta\mathrm{COD} = \mathrm{COD}^0$ and the ratio of Δ_1 to Δ_2 is maintained.

This process of reducing the chemical consumptions if necessary must be repeated for each of the species consumed to obtain a consistent set of new concentrations. However, the situation with NO_3^- is more complicated since this species is consumed by both the

energy reactions and the microbe synthesis reactions. Thus, the decrease in NO_3^- concentration over one timestep must take into account not only the changes described by Eq. 181, but also changes due to microbe synthesis. For calculational convenience, NO_3^- limitation is calculated under the assumption that all microbes are produced using NO_3^- as the nitrogen source. Thus:

$$\begin{aligned}\Delta NO_3 = \Delta_1(1-Y_o)2MW_{NO_3}\left\{\frac{12}{5}(C_{gluc}+C_{ISA})+\frac{4}{5}C_{acet}+\frac{3n+1}{5}C_{VFA}\right.\\ \left.+\frac{3m+1}{5}C_{FFA}+\frac{7}{5}C_{glyc}+\frac{191}{10}C_{pep}\right\}+\Delta_2\frac{2MW_{NO_3}}{5MW_{H_2}}\\ +\frac{5}{7}\Delta_1 f Y_o\frac{MW_{NO_3}}{5MW_{O_2}}+\frac{5}{7}\Delta_2 f Y_a\frac{MW_{NO_3}}{MW_{biomass}},\end{aligned} \tag{185}$$

where f is the fraction of COD not consisting of peptides. This assumption in determining NO_3^- limitation does not alter the fact that NH_3 is used in preference to NO_3^- for the production of microbes, but it may sometimes lead to an underprediction of the effects of denitrification. In practice this means that a few extra timesteps may be required to remove a given quantity of NO_3^- which, seen in the context of the GRM as a whole, is not expected to be significant.

8.8.2 Microbe Production and Nitrogen Limitation

These issues are discussed in the context of aerobic microbes in Sec. 8.7.1. A very similar process is followed in calculating denitrification processes. There are however, some slight modifications due to the presence of two microbe populations. Working with Δcod as in Eq. 164, the total increase in microbe concentration is:

$$\Delta Bug = Y_o^i \Delta cod\frac{MW_{biomass}}{5MW_{O_2}}+Y_a^i\Delta H_2, \tag{186}$$

where the superscript i denotes an ideal yield. The NH_3 requirement for this is the expression given in Eq. 166, with ΔBug as just given above. If there is insufficient nitrogen in the form of NH_3 then the ideal yields can still be produced if the NO_3^- concentration exceeds:

$$\frac{5}{7}(Y_o^i-Y_{NH_3}^o)\Delta cod\frac{MW_{NO_3}}{5MW_{O_2}}+\frac{5}{7}(Y_a^i-Y_{NH_3}^a)\Delta H_2\frac{MW_{NO_3}}{MW_{biomass}}. \tag{187}$$

All of the available NH_3 is known to be used for microbe production in preference to NO_3^-. However, this statement does not provide enough information to determine the

yields $Y^o_{\mathrm{NH_3}}$ and $Y^a_{\mathrm{NH_3}}$ that appear in the above equation. In order to do so, the ratio of these two is assumed to equal the ratio of the corresponding ideal yields. We then have that:

$$Y^a_{\mathrm{NH_3}} = \frac{\mathrm{NH_3}}{\mathrm{MW_{NH_3}}}\left[\frac{Y^i_o}{Y^i_a}\frac{\Delta\mathrm{cod}}{5\mathrm{MW_{O_2}}} + \frac{\Delta\mathrm{H_2}}{\mathrm{MW_{biomass}}}\right]^{-1} \tag{188}$$

$$Y^o_{\mathrm{NH_3}} = Y^a_{\mathrm{NH_3}}\frac{Y^i_o}{Y^i_a}. \tag{189}$$

In the case where there is insufficient nitrogen in total to produce the ideal microbe yield, Eqs. 188 and 189 still hold and Y^a_{NO3}, Y^o_{NO3} are found in a similar way to be:

$$Y^a_{\mathrm{NO_3}} = \frac{7}{5}\frac{\mathrm{NO_3}}{\mathrm{MW_{NO_3}}}\left[\frac{Y^i_o}{Y^i_a}\frac{\Delta\mathrm{cod}}{5\mathrm{MW_{O_2}}} + \frac{\Delta\mathrm{H_2}}{\mathrm{MW_{biomass}}}\right]^{-1} \tag{190}$$

$$Y^o_{\mathrm{NO_3}} = Y^a_{\mathrm{NO_3}}\frac{Y^i_o}{Y^i_a} \tag{191}$$

Once the actual microbe yields have been calculated, the organotroph and H_2-consumer concentrations, respectively, can be evaluated from:

$$\frac{dX_o}{dt} = R^o_n X_o\left(Y^o_{\mathrm{NH_3}} + \frac{5}{7}Y^o_{\mathrm{NO_3}}\right)\frac{\mathrm{MW_{biomass}}}{5\mathrm{MW_{O_2}}} + \frac{191}{20}R^o_n X_o Y_o \mathrm{MW_{biomass}} C_{\mathrm{pep}} - k_o X_o \frac{\mathrm{MW_{biomass}}}{5\mathrm{MW_{O_2}}} \tag{192}$$

$$\frac{dX_a}{dt} = R^a_n X_a\left(Y^a_{\mathrm{NH_3}} + \frac{5}{7}Y^a_{\mathrm{NO_3}}\right) + \frac{191}{20}R^a_n X_a Y_a 5\mathrm{MW_{O_2}} C_{\mathrm{pep}} - k_a X_a, \tag{193}$$

where k_o and k_a are the death rates.

8.9 Fermentation

There are three fermentative pathways considered within GRM and these are described below.

8.9.1 Fermentation of Glucose

Glucose fermentation generates acetic acid, carboxylic acids, hydrogen and carbon dioxide. The carboxylic acids produced are composite VFA, the carbon number of which can be

specified by the user. This allows glucose to be fermented to acetic and butyric acid or acetic and propionic acid or even an average VFA representing the mixture observed in an anaerobic environment. The overall chemical reaction is:

$$3C_6H_{12}O_6 + 4(4-n)H_2O \rightarrow$$
$$2H(CH_2)_nCOOH + CH_3COOH + 6(5-n)H_2 + 2(7-n)CO_2. \quad (194)$$

Synthesis of the glucose fermenting microbes proceeds via reaction 147, the only possible nitrogen source being NH_3.

A Michaelis–Menten formulation is again used in determining the rate of glucose utilisation, R_1. The resulting chemical concentration changes are given below:

$$\frac{d(\text{gluc})}{dt} = -R_1 X_A^1 \quad (195)$$

$$\frac{d(\text{acet})}{dt} = (1-Y_1)R_1 X_A^1 \frac{\text{MW}_{\text{acet}}}{\text{MW}_{\text{gluc}}} \frac{1}{3} \quad (196)$$

$$\frac{d(\text{VFA})}{dt} = (1-Y_1)R_1 X_A^1 \frac{\text{MW}_{\text{VFA}}}{\text{MW}_{\text{gluc}}} \frac{2}{3} \quad (197)$$

$$\frac{d(H_2)}{dt} = (1-Y_1)R_1 X_A^1 \frac{\text{MW}_{H_2}}{\text{MW}_{\text{gluc}}} 2(5-n) \quad (198)$$

$$\frac{d(CO_2)}{dt} = (1-Y_1)R_1 X_A^1 \frac{\text{MW}_{CO_2}}{\text{MW}_{\text{gluc}}} \frac{14-2n}{3} \quad (199)$$

$$\frac{d(NH_3)}{dt} = -Y_1 R_1 X_A^1 \frac{\text{MW}_{NH_3}}{\text{MW}_{\text{gluc}}} \frac{6}{5}, \quad (200)$$

where Y_1 is the fraction of glucose consumption used in biomass production. Note that the acidogenic microbes produced from glucose are not considered to be the same as those responsible for the fermentation of peptides or fats. The rate of change of the concentration of this microbe is:

$$\frac{dX_A^1}{dt} = (Y_A^1 R_1 - k_A^1)X_A^1, \quad (201)$$

where k_A^1 is the death rate and Y_A^1 is the microbe yield coefficient. The latter quantity is input by the user and is defined by:

$$\text{Increase in bug mass} = Y_A^1(\text{Total decrease in glucose mass}). \quad (202)$$

If there is sufficient nitrogen in the form of ammonia to produce the ideal microbe yield, the yield coefficient is related to Y_1 by:

$$Y_A^1 = Y_1 \frac{6\mathrm{MW_{biomass}}}{5\mathrm{MW_{gluc}}} \tag{203}$$

Note, however, that if there is insufficient ammonia to support the required microbe yield then Y_A^1 must be reduced.

8.9.2 Peptide Fermentation

The peptides produced by hydrolysis of proteins may ferment to produce a mixture of acetic acid, short–chain carboxylic acids, CO_2 and NH_3. The molar ratio of acetic acid to VFAs in the fermentation products (F_1) is defined by the GRM user. The appropriate chemical reaction is:

$$(6n{+}2{+}8F_1)\ C_{46}H_{77}O_{17}N_{12} + (68n + 150 + 218F_1)\ H_2O \rightarrow$$

$$191H(CH_2)_nCOOH{+}191F_1\ CH_3COOH + (85n{-}99{-}14F_1)\ CO_2 + (72n{+}24{+}96F_1)\ NH_3. \tag{204}$$

Competing with this fermentation reaction is the microbe synthesis reaction 157 which also consumes the peptides to produce acidogenic microbes.

A Michaelis–Menten formulation is again used in determining the rate of substrate utilisation, R_p. The resulting chemical concentration changes are given below:

$$\frac{d(\mathrm{pep})}{dt} = -R_p X_A^p \tag{205}$$

$$\frac{d(\mathrm{acet})}{dt} = (1 - Y_2) R_p X_A^p \frac{\mathrm{MW_{acet}}}{\mathrm{MW_{pep}}} \frac{191F_1}{6n + 2 + 8F_1} \tag{206}$$

$$\frac{d(\mathrm{VFA})}{dt} = (1 - Y_2) R_p X_A^p \frac{\mathrm{MW_{VFA}}}{\mathrm{MW_{pep}}} \frac{191}{6n + 2 + 8F_1} \tag{207}$$

$$\frac{d(CO_2)}{dt} = (1 - Y_2) R_p X_A^p \frac{\mathrm{MW_{CO_2}}}{\mathrm{MW_{pep}}} \frac{85n - 99 - 14F_1}{6n + 2 + 8F_1} - Y_2 R_p X_A^p \frac{\mathrm{MW_{CO_2}}}{\mathrm{MW_{pep}}} \frac{7}{4} \tag{208}$$

$$\frac{d(NH_3)}{dt} = (1 - Y_2) R_p X_A^p \frac{\mathrm{MW_{NH_3}}}{\mathrm{MW_{pep}}} \frac{36n + 12 + 48F_1}{3n + 1 + 4F_1} + Y_2 R_p X_A^p \frac{\mathrm{MW_{NH_3}}}{\mathrm{MW_{pep}}} \frac{49}{20}, \tag{209}$$

where Y_2 is the fraction of total peptide consumption used in acidogen production. The rate of change of the concentration of this microbe is:

$$\frac{dX_A^p}{dt} = (Y_A^p R_1 - k_A^p) X_A^p, \tag{210}$$

where k_A^p is the death rate and Y_A^p is the microbe yield coefficient. The latter quantity is input by the user and is defined analogously to Eq. 202. The fraction Y_2 is straightforward to calculate from Y_A^p.

8.9.3 Glycerol Fermentation

Glycerol is produced by the hydrolysis of fats and, like the peptides, may subsequently ferment to give a mixture of acetic acid, short–chain carboxylic acids and hydrogen. The molar ratio of these acids in the fermentation products (F_2) is again user–defined. The appropriate chemical reaction is:

$$(2F_2 + 1 + n)\mathrm{C_3H_8O_3} + 3(1-n)\mathrm{H_2O} \rightarrow$$
$$3\mathrm{H(CH_2)_nCOOH} + 3F_2\mathrm{CH_3COOH} + 2(F_2 + 2 - n)\mathrm{H_2}. \tag{211}$$

Glycerol fermenting microbes are produced via reaction 149.

A Michaelis–Menten formulation is again used in determining the rate of substrate utilisation, R_g. The resulting chemical concentration changes are given below:

$$\frac{d(\mathrm{glyc})}{dt} = -R_g X_A^g \tag{212}$$

$$\frac{d(\mathrm{acet})}{dt} = (1 - Y_g) R_g X_A^g \frac{\mathrm{MW_{acet}}}{\mathrm{MW_{glyc}}} \frac{3F_2}{2F_2 + 1 + n} \tag{213}$$

$$\frac{d(\mathrm{VFA})}{dt} = (1 - Y_g) R_g X_A^g \frac{\mathrm{MW_{VFA}}}{\mathrm{MW_{glyc}}} \frac{3}{2F_2 + 1 + n} \tag{214}$$

$$\frac{d(\mathrm{H_2})}{dt} = (1 - Y_g) R_g X_A^g \frac{\mathrm{MW_{H_2}}}{\mathrm{MW_{glyc}}} 2 \frac{F_2 + 2 - n}{2F_2 + 1 + n} \tag{215}$$

$$\frac{d(\mathrm{CO_2})}{dt} = -Y_g R_g X_A^g \frac{\mathrm{MW_{CO_2}}}{\mathrm{MW_{glyc}}} \frac{1}{2} \tag{216}$$

$$\frac{d(\mathrm{NH_3})}{dt} = -Y_g R_g X_A^g \frac{\mathrm{MW_{NH_3}}}{\mathrm{MW_{glyc}}} \frac{7}{10}, \tag{217}$$

where Y_g is the fraction of total glycerol consumption used to produce biomass from NH_3. Note that the acidogenic microbes produced from glycerol are not considered to be the same as those responsible for the fermentation of peptides or glucose. The rate of change of the concentration of this microbe is:

$$\frac{dX_A^g}{dt} = (Y_A^g R_g - k_A^g) X_A^g, \tag{218}$$

where k_A^g is the death rate and Y_A^g is the microbe yield coefficient. The latter quantity is input by the user and is defined analogously to Eq. 202. The fraction Y_g is straightforward to calculate from Y_A^g. Note, however, that if there is insufficient ammonia to support the required microbe yield then Y_A^g must be reduced.

8.10 Microbial Iron Reduction

Under anaerobic conditions, bacteria couple the reduction of available iron(III) to iron(II). This process is modelled via two routes, organotrophic and H_2-consumers, each having its own microbial population. The first group couple the oxidation of organic molecules to iron reduction, while the second group couple to the oxidation of hydrogen. Iron reduction at the expense of hydrogen has been observed both in the environment and the laboratory. Iron(III) is assumed to be present as amorphous ferric oxyhydroxides and is reduced until it is exhausted. The relevant iron–reducing reactions are as follows:

H_2-consuming:

$$\mathrm{H_2 + 2Fe^{3+} \rightarrow 2Fe^{2+} + 2H^+} \tag{219}$$

Organotrophic:

$$\mathrm{CH_3COOH + 8Fe^{3+} + 2H_2O \rightarrow 8Fe^{2+} + 2CO_2 + 8H^+} \tag{220}$$

$$\mathrm{H(CH_2)_nCOOH + (6}n\mathrm{ + 2)Fe^{3+} + 2}n\mathrm{H_2O \rightarrow}$$
$$\mathrm{(6}n\mathrm{ + 2)Fe^{2+} + (}n\mathrm{ + 1)CO_2 + (6}n\mathrm{ + 2)H^+}. \tag{221}$$

Acetic acid and VFAs are also consumed to produce biomass via reactions 151 and 153. The source of nitrogen for these bacteria is NH_3.

Due to the fact that the organotrophs act equally to oxidise two substrates, an equivalent total chemical oxygen demand (COD) is considered, as in Sec. 8.7, with values given

by Eq. 146. Indeed, the calculations of microbial iron reduction are essentially a generalization of the equations given in Secs. 8.7 and 8.8. A Michaelis–Menten formulation describes the rates of hydrogen (R_f^a) and COD (R_f^o) consumption and COD component species are then consumed by applying Eq. 159. The other chemical concentration changes are given by:

$$\frac{d(\mathrm{CO_2})}{dt} = R_f^o X_f^o \mathrm{MW_{CO_2}} \left\{ 2(1-Y_f^o) C_{\mathrm{acet}} + \left(n + 1 - \frac{1}{2} Y_f^o (3n-1) \right) C_{\mathrm{VFA}} \right\} - R_f^a X_f^a Y_f^a \mathrm{MW_{CO_2}} \frac{1}{2} (n-1) C_{\mathrm{VFA}} \frac{5\mathrm{MW_{O_2}}}{\mathrm{MW_{biomass}}} \quad (222)$$

$$\frac{d(\mathrm{Fe^{3+}})}{dt} = -\frac{d(\mathrm{Fe^{2+}})}{dt} = -R_f^o X_f^o (1-Y_f^o) \left[8C_{\mathrm{acet}} + 2(3n+1) C_{\mathrm{VFA}} \right] - 2R_f^a X_f^a, \quad (223)$$

where X_f^o and X_f^a are the local organotroph and H_2-consumer concentrations respectively and Y_f^o and Y_f^a are the corresponding yields.

Substrate and nitrogen limitation are both taken into account, using completely analogous procedures to those described in Secs. 8.8.1 and 8.8.2 respectively.

8.11 Sulphate Reduction

Under anaerobic conditions sulphate–reducing bacteria reduce available sulphate to sulphide (in the form of H_2S). Two sulphate reducing pathways are considered within GRM, each metabolised by a separate group of bacteria. The first of these, the H_2-consumers, couple sulphate reduction to hydrogen oxidation whereas the other group, organotrophs, utilise acetic acid and VFAs as electron donors. The relevant reactions are as follows:

H_2-consuming:

$$4\mathrm{H_2} + \mathrm{SO_4^{2-}} + 2\mathrm{H^+} \rightarrow \mathrm{H_2S} + 4\mathrm{H_2O} \quad (224)$$

Organotrophic:

$$\mathrm{CH_3COOH} + \mathrm{SO_4^{2-}} + 2\mathrm{H^+} \rightarrow 2\mathrm{CO_2} + \mathrm{H_2S} + 2\mathrm{H_2O} \quad (225)$$

$$4\mathrm{H(CH_2)_nCOOH} + (3n+1)\mathrm{SO_4^{2-}} + 2(3n+1)\mathrm{H^+} \rightarrow 4(n+1)\mathrm{CO_2} + (3n+1)\mathrm{H_2S} + 4(n+1)\mathrm{H_2O}. \quad (226)$$

Acetic acid and VFAs are also consumed to produce more bacteria in the same manner as described for the iron reducers: i.e., via reactions 151 and 153.

Due to the fact that the organotrophs act equally to oxidise two substrates, an equivalent total chemical oxygen demand (COD) is considered, as in Sec. 8.7, with values given by Eq. 146. Indeed, the calculations of microbial sulphate reduction are essentially a generalization of the equations given in Secs. 8.7 and 8.8. A Michaelis–Menten formulation describes the rates of hydrogen (R_s^a) and COD (R_s^o) consumption and COD component species are then consumed by applying Eq. 159. The other chemical concentration changes are given by:

$$\frac{d(\mathrm{CO_2})}{dt} = R_s^o X_s^o \mathrm{MW_{CO_2}} \left\{ 2(1-Y_s^o) C_{\mathrm{acet}} + \left(n+1-\frac{1}{2} Y_s^o (3n+1) \right) C_{\mathrm{VFA}} \right\} - R_s^a X_s^a Y_s^a \mathrm{MW_{CO_2}} \frac{1}{2}(n-1) C_{\mathrm{VFA}} \frac{5\mathrm{MW_{O_2}}}{\mathrm{MW_{biomass}}} \quad (227)$$

$$\frac{d(\mathrm{SO_4})}{dt} = -R_s^o X_s^o (1-Y_s^o) \mathrm{MW_{SO_4}} \left[C_{\mathrm{acet}} + \frac{3n+1}{4} C_{\mathrm{VFA}} \right] - R_s^a X_s^a (1-Y_s^a) \frac{\mathrm{MW_{SO_4}}}{4\mathrm{MW_{H_2}}} \quad (228)$$

$$\frac{d(\mathrm{H_2S})}{dt} = R_s^o X_s^o (1-Y_s^o) \mathrm{MW_{H_2S}} \left[C_{\mathrm{acet}} + \frac{3n+1}{4} C_{\mathrm{VFA}} \right] + R_s^a X_s^a (1-Y_s^a) \frac{\mathrm{MW_{H_2S}}}{4\mathrm{MW_{H_2}}}, \quad (229)$$

where X_s^o and X_s^a are the local organotroph and H_2-consumer concentrations respectively and Y_s^o and Y_s^a are the corresponding yields.

Substrate and nitrogen limitation are both take into account, using completely analogous procedures to those described in Secs. 8.8.1 and 8.8.2 respectively.

8.12 Acetogenesis

Under anaerobic conditions, acetogenic bacteria are responsible for breaking down long–chain VFAs into acetic acid, hydrogen and carbon dioxide. The reaction is:

$$\mathrm{H(CH_2)_nCOOH} + 2(n-1)\mathrm{H_2O} \rightarrow \mathrm{CH_3COOH} + 3(n-1)\mathrm{H_2} + (n-1)\mathrm{CO_2}. \quad (230)$$

As well as being consumed in the acetogenesis reaction, the VFAs are also used in bacteria growth through Eq. 153. The source of nitrogen for the bacteria is NH_3.

Acetogenesis by the above route is known to be inhibited by the free hydrogen concentration. This is included in the model in the manner described by Young [64]. A Michaelis–Menten formulation is used to determine the rate of VFA utilisation (R_v), but is corrected by using the inhibition factor $\chi\theta(\chi)$, where θ is a step function and:

$$\chi = \ln \frac{\mathrm{VFA}}{\mathrm{acet}.\mathrm{H_2^{4.63}}} \quad (231)$$

Thus, if $\chi \leq 0$ then acetogenesis is considered to be completely inhibited.

The chemical concentration changes resulting from the above acetogenesis reaction and the corresponding microbe synthesis reaction are calculated from the following equations:

$$\frac{d(\mathrm{VFA})}{dt} = -R_v X_v \tag{232}$$

$$\frac{d(\mathrm{acet})}{dt} = (1 - Y_v) R_v X_v \frac{\mathrm{MW_{acet}}}{\mathrm{MW_{VFA}}} \tag{233}$$

$$\frac{d(\mathrm{H_2})}{dt} = (1 - Y_v) R_v X_v 3(n-1) \frac{\mathrm{MW_{H_2}}}{\mathrm{MW_{VFA}}} \tag{234}$$

$$\frac{d(\mathrm{CO_2})}{dt} = (1 - Y_v) R_v X_v (n-1) \frac{\mathrm{MW_{CO_2}}}{\mathrm{MW_{VFA}}} - Y_v R_v X_v \frac{n-1}{2} \frac{\mathrm{MW_{CO_2}}}{\mathrm{MW_{VFA}}} \tag{235}$$

$$\frac{d(\mathrm{NH_3})}{dt} = -Y_v R_v X_v \frac{3n+1}{10} \frac{\mathrm{MW_{NH_3}}}{\mathrm{MW_{VFA}}}, \tag{236}$$

where Y_v is the fraction of VFA consumption used in biomass production. The rate of change of the concentration of this microbe is:

$$\frac{dX_v}{dt} = (Y_v^a R_v - k_v) X_v, \tag{237}$$

where k_v is the death rate and Y_v^a is the microbe yield coefficient. The latter quantity is input by the user and is defined analogously to Eq. 202. The fraction Y_v is straightforward to calculate from Y_v^a. Note, however, that if there is insufficient ammonia to support the required microbe yield then Y_v^a must be reduced.

8.13 Methane Production

Two basic methanogenic pathways are considered within GRM, the bacteria being divided into H_2-consumers, which consume hydrogen as a substrate, and organotrophs, which consume acetic acid. The relevant reactions are:

H_2-consuming:

$$\mathrm{CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O} \tag{238}$$

Organotrophic:

$$\mathrm{CH_3COOH \rightarrow CO_2 + CH_4}. \tag{239}$$

In the production of H_2-consuming biomass, the necessary carbon is supplied by carbon dioxide rather than organic sources. The H_2-consuming biomass synthesis reaction is thus:

$$5CO_2 + 10H_2 + NH_3 \rightarrow C_5H_7O_2N + 8H_2O, \tag{240}$$

while organotroph synthesis proceeds via reaction 151.

The methanogenic model is more complex than that applied to the other microbial groups because of the sensitive nature of the bacteria involved. Following Ref. [64], the methanogens have a temperature factor included in the specific rate equation (cf. Eq. 134):

$$\frac{dS}{dt} = -\frac{VSX}{K_m + S} F_{\mathrm{pH}}.F_{\mathrm{temp}}, \tag{241}$$

where:

$$F_{\mathrm{temp}} = \exp\left(\frac{-(T-35)^2}{100}\right). \tag{242}$$

In GRM an option exists where this temperature dependance may be switched off. In this case the function F_{temp} is simply set to unity.

The organotrophic methanogens also have temperature–dependent half-saturation constants. This follows the temperature evolution outlined by Lawrence and McCarty [60] and the implementation of Young [64]. Specifically:

$$K_m = \begin{cases} 869 \text{ mgl}^{-1} & \text{if } T \leq 25^o\text{C} \\ 333 + 536(6 - T/5)\text{mgl}^{-1} & \text{if } 25^o\text{C} < T \leq 30^o\text{C} \\ 172 + 161(7 - T/5) \text{ mgl}^{-1} & \text{if } 30^o\text{C} < T \leq 35^o\text{C} \\ 172 \text{ mgl}^{-1} & \text{if } T > 35^o\text{C}. \end{cases} \tag{243}$$

If the temperature dependence of methanogenesis is switched off, the organotrophic half-saturation constant is set to 869gm^{-3}

The chemical concentration changes resulting from all of the above reactions are calculated from the following equations:

$$\frac{d(H_2)}{dt} = -R_m^a X_m^a \tag{244}$$

$$\frac{d(\text{acet})}{dt} = -R_m^o X_m^o \tag{245}$$

$$\frac{d(CH_4)}{dt} = R_m^a X_m^a (1 - Y_m^a)\frac{\mathrm{MW}_{CH_4}}{4\mathrm{MW}_{H_2}} + R_m^o X_m^o (1 - Y_m^o)\frac{\mathrm{MW}_{CH_4}}{\mathrm{MW}_{\text{acet}}} \tag{246}$$

$$\frac{d(CO_2)}{dt} = -R_m^a X_m^a \left(\frac{1}{4} + \frac{1}{4}Y_m^a\right) \frac{MW_{CO_2}}{MW_{H_2}} + R_m^o X_m^o (1 - Y_m^o) \frac{MW_{CO_2}}{MW_{acet}} \quad (247)$$

$$\frac{d(NH_3)}{dt} = -R_m^a X_m^a Y_m^a \frac{MW_{NH_3}}{10MW_{H_2}} - R_m^o X_m^o Y_m^o \frac{2MW_{NH_3}}{5MW_{acet}}, \quad (248)$$

where Y_m^o and Y_m^a are respectively the organotroph and H_2-consumer microbe yields from NH_3. The rates of change of the methanogens are:

$$\frac{dX_m^a}{dt} = (Y_m^{a0} R_m^a - k_m^a) X_m^a \quad (249)$$

$$\frac{dX_m^o}{dt} = (Y_m^{o0} R_m^o - k_m^o) X_m^o, \quad (250)$$

where k_m^a and k_m^o are the respective death rates and Y_m^{a0} and Y_m^{o0} are microbe yield coefficients. These coefficients are input by the user and are defined analogously to Eq. 202. The fractions Y_m^a and Y_m^o are straightforward to calculate from Y_m^{a0} and Y_m^{o0} respectively. Note, however, that if there is insufficient ammonia to support the required microbe yields then the yield coefficients must be reduced accordingly.

The H_2-consumer synthesis is calculated in two steps, each with half of the normal microbial timestep. This splitting of the methanogenesis process allows for a degree of coupling with the acetogenesis processes.

8.14 Reoxidation

The growth and activity of bacteria responsible for the oxidation of inorganic substrates is modelled within GRM using two oxidising agents: oxygen and nitrate. Oxygen is used to oxidise Fe(II), sulphide, pyrite, and ammonia. Nitrate is used to oxidise Fe(II), sulphide and pyrite. These two processes are discussed below.

8.14.1 Nitrate Reoxidation

The quantity of oxidisable substrate is handled in the form of a total chemical nitrate demand (CND) which is similar to the chemical oxygen demand (COD) discussed previously. Substrate utilisation may either occur instantaneously or at a rate controlled by the local microbe concentration.

Before the usual growth and death calculations are performed microbe maintenance is considered. The maintenance requirement for a given microbe is the amount of nutrient

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(in the form of CND for example) which is required to keep it alive. A maintenance factor (MF) is specified by the user. The maintenance requirement (MR) for a given microbe is then given by:

$$\mathrm{MR} = \mathrm{MF}.\Delta t_{\mathrm{bug}}.X_r, \tag{251}$$

where X_r is the oxidising microbe concentration. If the amount of nutrient is less than the maintenance requirement then some proportion of the microbes will die, and the quantities of recycled and inert biomass are increased appropriately. Note that the inclusion of maintenance calculations in this section of the GRM code reflects the format in which kinetic data is often given for such microbes.

If microbial mediation has been specified, a Michaelis–Menten formulation is employed to find the rate of CND utilisation, R_N. Subject, of course, to availability, the changes in CND and the nitrate concentration are then given by:

$$\frac{d(\mathrm{CND})}{dt} = \frac{d(\mathrm{NO_3})}{dt} = -R_N X_r. \tag{252}$$

In addition to the oxidation of the inorganic substrates, microbe synthesis must also be taken into account. Since no organic carbon is involved, the carbon necessary for the production of new microbes is taken from CO_2, while the necessary nitrogen is supplied by ammonia. The microbe synthesis reaction is:

$$5\mathrm{CO_2} + \mathrm{NH_3} + 20\mathrm{H^+} + 20e^- \rightarrow \mathrm{C_5H_7O_2N} + 8\mathrm{H_2O}. \tag{253}$$

As usual, if there is insufficient nitrogen to produce the ideal microbe yield, the actual yield is reduced such that all the available nitrogen is used in microbe production. CO_2 limitation on the microbe growth is treated similarly.

8.14.2 Oxygen Reoxidation

The oxidation of inorganic substrates (iron II, sulphide, pyrite and ammonia) using oxygen as an agent is very similar to that discussed above when using nitrate, with the exception that COD rather than CND is used. Microbe synthesis can again occur through Eq. 253 and if there is insufficient CO_2 or nitrogen present to produce the required quantity of microbes, then the yield is reduced accordingly.

8.14.3 COD/CND Determinations

Before determining the COD and CND consumption for the oxygen and nitrate cases discussed above, it is necessary to determine the initial COD and CND values from

the appropriate reactions. Consider the oxygen case first. The oxidation of iron(II) species/minerals is described by the following reaction:

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightleftharpoons Fe^{3+} + \frac{1}{2}H_2O. \tag{254}$$

The corresponding COD for any iron(II) species/minerals is:

$$COD_{Fe(II)} = \frac{1}{4}[Fe(II)] \tag{255}$$

where [Fe(II)] is the total iron(II) concentration excluding pyrite. The mineral pyrite (FeS_2) must be considered separately since it is not in a completely reduced form (sulphur is in the -1 valence state rather than the -2 state). Oxidation of pyrite is usually represented in two stages, the first being:

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightleftharpoons Fe^{2+} + 2SO_4^{2-} + 2H^+, \tag{256}$$

and the second being as in reaction 254. Combining these reactions, the COD of any pyrite present is found to be:

$$COD_{pyr} = \frac{15}{4}[pyr]. \tag{257}$$

Sulphide oxidation is described by:

$$HS^- + 2O_2 + OH^- \rightleftharpoons SO_4^{2-} + H_2O, \tag{258}$$

so that the COD of any sulphide species/minerals is:

$$COD_S = 2[HS^-], \tag{259}$$

where $[HS^-]$ is the total HS^- concentration, again excluding any pyrite.

Ammonia oxidation is described by:

$$NH_4^+ + 2O_2 \rightleftharpoons NO_3^- + 2H^+ + H_2O, \tag{260}$$

so that the COD of any ammonia species is:

$$COD_{NH_3} = 2[NH_4^+], \tag{261}$$

where $[NH_4^+]$ is the total aqueous ammonia concentration, which includes all species containing the ammonia master species.

The total COD on which the reoxidising microbes act is simply the sum of Eqs. 255, 257, 261 and 259.

Now consider the case of reoxidation using nitrate. The half redox reaction for nitrate being reduced to nitrogen gas is:

$$NO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}N_2 + 3H_2O. \quad (262)$$

Thus one mole of nitrate reacts with 5 moles of available electrons, whereas 1 mole of oxygen gas reacts with 4 moles of available electrons since:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O. \quad (263)$$

The COD value for oxidation of iron(II), sulphide and pyrite using oxygen can then be converted into a nitrate demand equivalent (CND) through:

$$CND = \overline{COD}\frac{MW_{NO_3}}{MW_{O_2}}.\frac{4}{5}. \quad (264)$$

Where:

$$\overline{COD} = COD_{FeII} + COD_{sulphide} + COD_{pyrite}. \quad (265)$$

Given the above values for COD and CND the microbial consumptions can be evaluated using the methods of Secs. 8.14.1 and 8.14.2. The resulting chemical changes are then made.

8.15 Biomass Recycle

All bacterial groups within GRM are subject to death and decay. Dead biomass is split into degradable and non-degradable portions according to a ratio set by the user. The biomass is assumed to consist of approximately 50% protein with lesser amounts of fats, carbohydrates etc. For simplicity therefore, it is recycled only into proteins and FFAs via the following reaction:

$$(191 + 2F + 6mF)C_5H_7O_2N + 4(7 + 4F + 2mF)H_2O \rightarrow$$

$$20C_{46}H_{77}O_{17}N_{12} + 20FH(CH_2)_mCOOH + 5(7 - 2F + 2mF)CO_2 + (2F + 6mF - 49)NH_3, \quad (266)$$

where F is the molar ratio of FFAs to proteins in the recycled material. Since the biomass is already considered to be in the form of proteins etc., it should be stressed that

this reaction is purely a hypothetical concept to avoid violation of mass conservation. Thus there is no associated rate expression and the relevant concentrations are simply increased instantaneously. The inert non-degradable portion builds up within the model as a residual solid material.

8.16 Optional Treatment of HS^-

Sulphides from microbial processes may be produced in significant quantities in the presence of ferric iron. This could lead to a situation that is chemically unacceptable. In order to avoid it, the GRM user has the option (selected by setting the IHSRDX flag in grm.dat to unity) of allowing the sulphides and ferric iron to react. The reaction modelled is:

$$FeOOH + \frac{1}{8}HS^- + HCO_3^- + \frac{7}{8}H^+ \rightarrow FeCO_3 + \frac{1}{8}SO_4^{2-} + \frac{3}{2}H_2O. \qquad (267)$$

The extent to which the reaction occurs is such as to reduce either the sulphide or the ferric iron concentration to zero.

9 Corrosion Chemistry

GRM assumes the dominant metal in LLW disposal sites to be mild steel. The modelling of corrosion within GRM is not concerned with the integrity of metal containers containing waste or their times to failure or leakage. The focus is rather on the rate of formation of corrosion products, which could significantly affect the chemical evolution of the site.

The corrosion module in GRM treats saturated corrosion (iron in waterlogged conditions) differently to unsaturated corrosion (iron in damp/dry conditions), in terms of both the corrosion rates and the products formed. Acid corrosion is not taken into account since the pH is not expected to become very low in LLW sites[24].

9.1 Saturated Corrosion

The corrosion module simulates the aerobic and anaerobic degradation of mild steel. The iron is treated as a combination of three possible shapes (spheres, plates and rods), the rate of corrosion depending on the available surface area of the shapes present.

Corrosion in the saturated zone is modelled using the reactions shown below.

1. Aerobic corrosion:

$$4Fe + 10H_2O + 3O_2 \rightleftharpoons 4Fe(OH)_3{\cdot}H_2O. \tag{268}$$

2. Anaerobic corrosion products can be either Fe(III) or Fe(II) based depending on the initial conditions set by the GRM user. If Fe(III) products are chosen then anaerobic corrosion proceeds via the following reaction:

$$2Fe + 8H_2O \rightleftharpoons 2Fe(OH)_3{\cdot}H_2O + 3H_2. \tag{269}$$

Solid $Fe(OH)_3$ is formed if the pH is greater than some user–defined level, typically around 9. Otherwise, when the internal flag COLFLG is set to zero during execution, colloids and solid $Fe(OH)_3$ are formed and when it is set to unity, then dissolved ferric ions are produced. This flag is set to unity during GRM execution when the chemical speciation calculations predict that all of the $Fe(OH)_3$ dissolves into solution. If solid $Fe(OH)_3$ is formed, the fraction in static mineral and in mobile colloidal form can be

[24] Acid corrosion occurs at low pH ($\lesssim 4$) such as when organic acids are present: $Fe + 2CH_3COOH \rightleftharpoons Fe^{2+} + H_2 + 2CH_3COO^{2-}$. The rate of acid corrosion increases with falling pH, though the chemical reaction will push the solution towards higher pH. If there were a plentiful supply of organic acids and the solution is buffered at a low pH then acid corrosion would be an important process even in anaerobic conditions.

specified by the user in grm.cor. Sorption onto both of these products is taken into account. The sorption processes are treated as instantaneous and are discussed in Sec. 5.2.

In the case of Fe(II) products being chosen, anaerobic corrosion proceeds by:

$$\mathrm{Fe} + 2\mathrm{H_2O} \rightleftharpoons \mathrm{Fe(OH)_2} + \mathrm{H_2}, \tag{270}$$

when CO_2 is limiting and:

$$\mathrm{Fe} + \mathrm{CO_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{FeCO_3} + \mathrm{H_2}, \tag{271}$$

when CO_2 is available. Iron(II) colloids are not considered at present.

Under high pH conditions a passivity layer [25] forms which retards the rate of corrosion. The rate decreases as the layer forms until a minimum rate is reached. The corrosion rate is reduced under both aerobic and anaerobic conditions (different minimum rates can be specified for the two types of conditions), the decrease being dependent on the (user-defined) size of the passivity layer formed. In practice, the anaerobic corrosion rate will be substantially reduced by the passivity layer, but aerobic corrosion is little affected since it normally takes place at pH higher than 9.

In the course of each microbial timestep, the corroded volumes of spheres, plates and rods are updated using the following equations. Note that similar equations are applied for both aerobic and anaerobic corrosion.

- For spheres:

$$V_{\mathrm{sph}} = \frac{4}{3}\pi\left(r_{\mathrm{sph}}^3 - (r_{\mathrm{sph}} - \mathrm{cor_{sph}}.\Delta t_{\mathrm{bug}})^3\right)N_{\mathrm{sph}}, \tag{272}$$

where:

  - r_{sph} is the radius of the spheres;
  - N_{sph} is the number of spheres; and,
  - $\mathrm{cor_{sph}}$ is the linear corrosion rate for spheres.

- For plates:

$$V_{\mathrm{plt}} = \mathrm{SA_{plt}cor_{plt}}\Delta t_{\mathrm{bug}}, \tag{273}$$

where:

[25] A Passivity Layer forms under aerobic conditions always, but under anaerobic conditions it only forms if Fe(III) is specified as a product.

– SA_{plt} is the surface area of the plates; and,

– cor_{plt} is the linear corrosion rate for plates.

- For rods:

$$V_{rod} = \left(\pi.r_{rod}^2\ell_{rod} - \pi(\ell_{rod} - 2cor_{rod}.\Delta t_{bug})(r_{rod} - cor_{rod}.\Delta t_{bug})^2\right)N_{rod}, \quad (274)$$

where:

– r_{rod} is the radius of the rods;

– ℓ_{rod} is the length of the rods;

– N_{rod} is the number of rods; and,

– cor_{rat} is the linear corrosion rate for rods.

The volume of iron that can be corroded in aerobic conditions is limited by the available oxygen:

$$V_{max}^{aer} = [O_2]\frac{MW_{Fe}}{MW_{O_2}}\frac{4}{3}\frac{V_{sat}}{\rho_{iron}} \quad (275)$$

where:

- $[O_2]$ is the oxygen concentration (expressed as a mass per unit volume);
- ρ_{iron} is the density of iron;
- V_{sat} is the saturated volume; and,
- $\frac{4}{3}$ represents the number of moles of iron corroded for every mole of oxygen.

The sums of the corrosion volumes V_{sph}, V_{plt} and V_{rod} are compared for aerobic and anaerobic corrosion. Should there be insufficient oxygen for the desired amount of aerobic corrosion then V_{max}^{aer} is used as the aerobic volume in the comparison. The larger total corroded volume then defines the corrosion conditions for the present timestep. But if $[O_2] < 1E-10$ gm^{-3} conditions are automatically taken as anaerobic.

Should aerobic conditions prevail but be oxygen limited then the volume corroded must be reduced to V_{max}^{aer}. This is divided amongst spheres, plates and rods in proportion to their surface areas, with corresponding reductions to the linear corrosion rates.

In the case of anaerobic corrosion, the chemical changes will depend on whether Fe(II) or Fe(III) is the designated corrosion product. The hydrogen concentration following the anaerobic corrosion reactions can be expressed as:

$$\Delta[\mathrm{H_2}] = \left(\sum_{\text{shapes}} V_{\text{shape}}^{\text{ana}} - V_{\text{max}}^{\text{aer}} \right) \frac{\rho_{\text{iron}}}{V_{\text{sat}}} \frac{v_{\text{iron}}}{2} \frac{\mathrm{MW_{H_2}}}{\mathrm{MW_{Fe}}}, \tag{276}$$

where v is the valence of the iron product.

As well as the chemical changes due to iron corrosion during a timestep, the geometric iron parameters and the iron corrosion rates must be updated each time. The relevant equations are:

$$\mathrm{cor_{shape}}(t + \Delta t_{\text{bug}}) = \mathrm{cor_{shape}}(t) - \widetilde{\mathrm{cor}}_{\text{shape}}(t) \left(1 - \exp(\text{-pas}\Delta t_{\text{bug}})\right) \tag{277}$$

$$r_{\text{sph}}(t + \Delta t_{\text{bug}}) = r_{\text{sph}}(t) - \widetilde{\mathrm{cor}}_{\text{sph}}(t)\Delta t_{\text{bug}} \tag{278}$$

$$\mathrm{th_{plt}}(t + \Delta t_{\text{bug}}) = \mathrm{th_{plt}}(t) - 2\widetilde{\mathrm{cor}}_{\text{plt}}(t)\Delta t_{\text{bug}} \tag{279}$$

$$r_{\text{rod}}(t + \Delta t_{\text{bug}}) = r_{\text{rod}}(t) - \widetilde{\mathrm{cor}}_{\text{rod}}(t)\Delta t_{\text{bug}} \tag{280}$$

$$\ell_{\text{rod}}(t + \Delta t_{\text{bug}}) = \ell_{\text{rod}}(t) - 2\widetilde{\mathrm{cor}}_{\text{rod}}(t)\Delta t_{\text{bug}} \tag{281}$$

where:

- a tilded quantity refers to its value after possible reduction in aerobic conditions if the corrosion is oxygen limited;
- 'pas' is equal to zero unless a passivity layer is formed in which case it is equal to the user–defined rate of formation of the layer; and,
- $\mathrm{th_{plt}}$ is the thickness of the plates.

9.2 Unsaturated Corrosion

Corrosion in the unsaturated zone is based on a three-stage reaction as used in the GAMMON code [51]. GAMMON was devised to model the evolution of gases from deep depositories, arising from the corrosion of metals and the microbial degradation of cellulosic waste. The basic corrosion reactions assumed are:

1. Aerobic corrosion;

$$4\mathrm{Fe} + 3\mathrm{O_2} \rightleftharpoons 2\mathrm{Fe_2O_3} \tag{282}$$

2. Oxide depletion corrosion;

$$4Fe_2O_3 + Fe \rightleftharpoons 3Fe_3O_4 \tag{283}$$

3. Anaerobic corrosion;

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2. \tag{284}$$

The intermediate process (reaction 283) occurs once oxygen has become depleted, the ferric oxide being used to oxidise the iron metal in order to form magnetite, the reduced iron oxide. Only when all of the ferric oxide has been used does true anaerobic corrosion occur. The rate of corrosion for the intermediate process is assumed to be the same as that for anaerobic corrosion. The passivity layer is assumed only to form during aerobic corrosion since Fe_3O_4 has been found not to adhere to iron metal surfaces.

The same basic equations as those employed in calculating the saturated corrosion rates are used. However, the determination of the prevailing conditions is altered because there are three unsaturated reactions to consider. The maximum volume of iron that can be corroded without resort to true anaerobic corrosion is:

$$V_{\max}^{\text{oxid}} = < Fe_2O_3 > \frac{\text{MW}_{\text{Fe}}}{4\rho_{\text{iron}}} + \frac{V_{\max}^{\text{aer}}}{8}, \tag{285}$$

where:

- $< Fe_2O_3 >$ is the number of moles of Fe_2O_3 present;
- $\frac{1}{4}$ is the number of moles of iron corroded for every mole of Fe_2O_3; and,
- the term $V_{\max}^{\text{aer}}/8$ is due to Fe_2O_3 formed from all of the available oxygen, $V_{\max}^{\text{aer}}$ being given by replacing the saturated volume by the unsaturated volume in Eq. 275.

The sums of the corrosion volumes V_{sph}, V_{plt} and V_{rod} are compared for aerobic and anaerobic corrosion rates. Should there be insufficient oxygen for the desired amount of aerobic corrosion then $V_{\max}^{\text{aer}}$ is used as the aerobic volume in the comparison. The larger total corroded volume then defines the corrosion conditions for the present timestep.

Should aerobic conditions prevail, the methods used to determine the corrosion rate under limited oxygen conditions are the same as under saturated conditions. A passivity layer is only formed under aerobic conditions, a similar equation being used as for saturated corrosion. When oxide depletion occurs, it is assumed that any passivity layer is stripped off. Thus, if aerobic conditions occur again then the aerobic corrosion rate is at its maximum.

Should anaerobic conditions prevail then it is necessary to determine whether oxide depletion or true anaerobic corrosion reactions take place. Oxide depletion occurs unless the total anaerobic corroded volume exceeds the sum of $V_{\max}^{\text{aer}}$ and $V_{\max}^{\text{oxid}}$. In the oxide depletion case no hydrogen is evolved and the amounts of Fe_2O_3 lost and Fe_3O_4 formed are determined by:

$$\Delta < Fe_2O_3 >= \frac{V_{\max}^{\text{aer}} \rho_{\text{iron}}}{2\text{MW}_{\text{Fe}}} - \left(\sum_{\text{shapes}} V_{\text{shape}}^{\text{ana}} - V_{\max}^{\text{aer}} \right) \frac{\rho_{\text{iron}}}{4\text{MW}_{\text{Fe}}} \tag{286}$$

$$\Delta < Fe_3O_4 >= \left(\sum_{\text{shapes}} V_{\text{shape}}^{\text{ana}} - V_{\max}^{\text{aer}} \right) \frac{\rho_{\text{iron}}}{3\text{MW}_{\text{Fe}}}. \tag{287}$$

In the true anaerobic case, any remaining Fe_2O_3 is converted into Fe_3O_4. The amount of hydrogen evolved is:

$$\Delta[H_2] = \left(\sum_{\text{shapes}} V_{\text{shape}}^{\text{ana}} - V_{\max}^{\text{aer}} \right) \frac{\rho_{\text{iron}}}{V_{\text{sat}}} \frac{4}{3} \frac{\text{MW}_{H_2}}{\text{MW}_{\text{Fe}}}. \tag{288}$$

10 Radioactive Decay Processes

Problems of solute transport involving sequential first–order decay reactions frequently occur in modelling soil systems. As well as radioactive chain members, the decay of other materials (such as interacting nitrogen species, organic phosphates and pesticides) has been considered in some models. Additional complexities arise within GRM since multi-phase media are considered: i.e., solute, sorbate and precipitate. Decay within the solute is treated as within the transport/decay literature. That is, the energy of the decay reaction severs the bond between the complexed parent and its ligands with the daughter product going into solution. For the sorbed and precipitated phases a simplifying assumption is made that the recoil energy of the radionuclide is sufficient to eject it into the solute.

In all cases, therefore, the daughter product is taken to be released into solution. Of course, subsequent determinations of the microelement speciation will then be able to move the daughter into the appropriate phase should this be required for chemical equilibrium. Errors introduced by the assumption will therefore only persist between the time of decay and the time of the next speciation call. Hence, they should be small and closely controlled.

The decay equation for the i th member of a chain is:

$$\frac{dN_i}{dt} = -\lambda_i N_i + \lambda_{i-1} N_{i-1} \tag{289}$$

with $\lambda_0 \equiv 0$. The general solution to a sequence of such equations is well known to be a sum of exponential terms, given originally by Bateman [61]. Numerically, however, direct use of the Bateman formalism can lead to difficulties for long decay chains (with more than about seven members) due to rounding errors in the calculation of small differences between large terms. Such problems are more likely to occur if the timesteps are small and the nuclide half lives are close together. The accent for GRM numerical calculations is to prefer the robust to the spuriously accurate method[26]. The GRM code therefore solves the decay equations to $\mathcal{O}(\delta t)$ for each transport timestep. Provided that the transport step is considerably smaller than all of the nuclide half lives, the errors induced by this approximation should be insignificant.

[26] Firstly, because a search for very high accuracy would not be justified by the model and could increase run time. Secondly, because the code must be able to run to completion given a wide variety of numerical situations (varying numerics may arise even in the course of a single run).

10.1 Decay Chains

Within the GRM, it is possible to trace the components of a particular nuclide concentration back to the relevant parent in the original disposed inventory. The option to follow decay chains can be selected by the user by setting the ICHAIN flag to unity in the main input file grm.dat.

Consider for example the decay chain $N_1 \rightarrow N_2 \rightarrow N_3$. From this, the code identifies three decay subchains:

1. $N_1 \rightarrow N_2 \rightarrow N_3 \rightarrow X$;
2. $N_2 \rightarrow N_3 \rightarrow X$; and,
3. $N_3 \rightarrow X$

where X is not followed. Any initial inventory of N_1 is used to seed the first subchain; any initial inventory of N_2 is used to seed the second subchain and any initial inventory of N_3 is used to seed the third subchain. Decay within each of the subchains is treated separately, and therefore the user can be provided with that part of the subsequent inventory of the nuclide N_i which exists because of the presence of nuclide N_j $(j \leq i)$ in the starting inventory. Output for each subchain is given in the output files chain.out and chtot.out.

Suppose that as well as the chain $N_1 \rightarrow N_2 \rightarrow N_3$, there is also a second chain of the form $M_1 \rightarrow N_2 \rightarrow N_3$ (i.e., the nuclides N_1 and M_1 have the same daughter). Repeated subchains would then arise. The GRM code will ignore all repeated subchains except for the last occasion they appear[27]. In chain.out and chtot.out therefore, the user will find that the output data for subchains that recur later in the sequence will be always zero.

Each member of each decay subchain is treated as a separate 'nuclide component' and the corresponding concentrations are summed to give the total radioelement concentrations before speciation. This is necessary because of the potential for a situation in which the total concentration of a particular radioelement is above its solubility limit, but the individual component concentrations are lower than this limit. Without the summation, precipitation would not occur.

While chain.out allows calculation of nuclide fluxes within groundwater, chtot.out refers to the total concentrations within each cell (both saturated and unsaturated regions)rather than simply the liquid phase. There are however two other differences between chain.out and chtot.out:

[27] The order is defined by the listing of master decay chains in the grm.dcy input file.

1. Whereas external water flows are written to file `chain.out` for each print time, these are not relevant in the case of human intrusion calculations so no flow data are written to `chtot.out`.

2. Nuclide concentrations are written to file `chain.out` as moles per litre of porewater, whereas the units used for `chtot.out` are moles per litre of total cell volume.

10.2 Following of Active Carbon

As well as the radioactive decay processes for microspecies, there is an option in `GRM` which allows the user to follow active carbon 14. The inventory of ^{14}C is given by specifying it as a fraction of each carbon bearing species on a cell by cell basis, and it is these fractions which are updated as necessary through the transport, speciation, microbial and corrosion modules of the code. If the option is chosen (by setting `C14SWT` to unity in `grm.dat`), the active fraction data file, `grm.act` (Sec. 12.1) is opened and read in.

Within the transport module of the code, calculations are made of the amount of ^{14}C lost to the external environment. Moreover, the individual ^{14}C species concentration, in each cell, is allowed to decay with a hardwired half life of 5730 years. It is assumed that there is no active ^{14}C entering the model domain in the incoming groundwater, although it is allowed to leave via seepage etc. As far as sorption processes are concerned, ^{14}C is treated similarly to other species in that it can be sorbed onto the waste/geomatrix.

The active fraction of ^{14}C in any species containing carbon is updated due to transport and speciation. For transport, the following relation is used:

$$f_{i,j}^{\text{new}} = \frac{C_{i,j}^{\text{old}} f_{i,j} + \Delta C_{i,j+1} f_{i,j+1}}{C_{i,j}^{\text{old}} + \Delta C_{i,j+1}}, \tag{290}$$

where:

- $f_{i,j}$ is the active fraction in cell (i,j); i.e. the fraction of total C which is ^{14}C.
- $C_{i,j}$ is species concentration in cell (i,j); and,
- $\Delta C_{i,j+1}$ is the change in the cell (i,j) species concentration due to transport from cell $(i,j+1)$.

Similar expressions are used to update the fraction for all cells surrounding the cell of interest, and for any boundary flows. Other updates use analogous relations.

10.2.1 Other Minor Active Isotopes

In addition to ^{14}C, radon (^{222}Rn) and tritium (^{3}H) can also be followed. These options are switched on using the flags `IFLGH3` and `IFLGRN` respectively in the file `grm.dat`.

^{222}Rn is a highly soluble gas and is assumed to be non-sorbing. It is produced by the decay of ^{226}Ra and decays with a half life of just 3.8 days. The decay products of ^{222}Rn are short–lived and non-gaseous and are therefore not followed within `GRM`. Transportation of dissolved ^{222}Rn is treated in exactly the same manner as for other dissolved species.

Tritium is assumed to exist in the form of tritiated water. It is allowed to leave the modelled domain either as aqueous groundwater or as water vapour vented through the repository cap.

Partioning of both ^{222}Rn and tritium is discussed in Secs. 6.5 and 6.6.

11 Running GRM

11.1 Residence of the Current Master Version of GRM

The FORTRAN source files required to compile version 4.1 of the code are listed in the file:

`/home/grm/bld/4.1/log4.1`

These files are held in the RCS directory:

`/home/grm/src/RCS`

An executable for GRM version 4.1 is available at:

`/home/grm/bin/grm4.1_irix6.5`

11.2 Procedure for Running GRM

GRM version 4.1 may be run by following the simple steps below.

1. Create a directory in your workspace from which you intend to run the code and move to that directory (the run directory).
2. Create the appropriate input files `grm.*`. The format and contents of each of these files is described in Sec. 12.
3. Create a dummy file called `RUNNER`. The contents of this file are never read and are therefore irrelevant. The GRM code attempts to open this file before each transport timestep. If the file cannot be found in the run directory then a full set of output will be produced and execution is terminated. Halting execution by deleting (or renaming) the `RUNNER` file may be preferable to simply killing the relevant process since the former method will provide the user with potentially useful output at the time of termination, including restart files which may be used to continue the run at a later time.
4. Ensure that a file `grm.out` does not exist in the run directory. If such a file is present, the GRM execution will terminate immediately with the issue of an appropriate error message. The purpose of this is to ensure that the main output file from a previous GRM run is not inadvertantly overwritten. A `grm.out` file in the run directory should

be either deleted or renamed. Note, however, that existing output files other than the main one are not protected in this way.

5. Once all files have been set up correctly, GRM is run by typing the name of the executable (with the appropriate path). The location of the current GRM executable is given in Sec. 11.1 above.

6. If execution is terminated before the specified endtime, information on why this has occurred may be provided in the form of an error message to the main output file `grm.out` (and also to the screen if the run was performed in the foreground). A description of possible error messages is given in Sec. 11.5.

11.3 Restart Facility

The GRM user is able to stop and subsequently restart a simulation. This option may be useful if some of the input parameters (such as the flags for different process modules) are to be changed in the course of a simulation. Use of the restart facility is controlled by two parameters (RSTTIME and RSTINT) in the main input file, `grm.dat`. These represent a termination time and a restart interval and must always be set. If these times are greater than the endtime of the simulation, the restart files will not be written. If the current simulation time reaches an integer multiple of RSTINT then restart files are written and code execution continues. If the simulation time reaches RSTTIME then restart files are written and code execution terminates.

When written, the restart files (RESTART and RESTART1) contain all the information about the current state of the simulation. On beginning a new GRM run the code will read in these files if they exist in the run directory and attempt to continue the old simulation from where it left off.

If no changes are made to the data files then the results produced by the restarted run will be identical to those which would have been produced by continuing the original run. An exception to this statement applies to the contents of the files `chain.out` and `chtot.out`. Thus, the option for decay chain following is not compatible with the restart facility[28].

In practice, the restart files simply list the contents of a large number of calculated variables and arrays. RESTART1 in particular is often a very large file. Should one wish to make a copy of it for some reason then a symbolic link is to be preferred to a direct copy.

[28] It is anticipated that code development will resolve this issue in a future version of GRM.

The restart facility is mainly designed to allow the user to alter information supplied through the input data files. Any alteration to the contents of the restart files should be done with care since it could easily have unforeseen consequences. It is not recommended without having first made a careful study of the Programmer's Guide [1].

11.4 Variable Timesteps

Within GRM there are five different timesteps that are specified by the user. The main input file `grm.dat` contains the transport and speciation timesteps, the output print frequency and pH/pe print frequency. The `grm.bug` file contains the microbial timestep.

Depending on the chemical and transport properties, the speciation module of GRM may need small timesteps in order to perform satisfactory equilibration at the start of a simulation, but then be able to function with a larger timestep at later times (i.e., once the system has reached a steady or slowly–evolving state). For such reasons, the GRM user is allowed to vary the microbial, transport and speciation timesteps over the course of the run. In each case, a maximum of 9 changes to the initial step size are permitted. The form of the input is described in Secs. 12.3 and 12.6.

In addition, one may require more detailed output at certain times within the run. Therefore, the frequencies at which information is written to the output files can be varied in a very similar fashion.

11.5 Error Messages

As far as practicable, the GRM code has been written with a view to providing good error trapping. If an error or inconsistency is detected, then an error code and short message are written both to standard output and to the main output file `grm.out`. Execution is then terminated. Several errors of execution, such as overflow/underflow, divide by zero, address out of range and I/O format should be handled by the local compiler/operating system, which will display sufficient information to locate the fault. Such errors should not occur if the data set has been correctly configured.

Errors detected by the GRM code itself are discussed below. Some of these are assigned code numbers, which are listed along with the description of the errors.

1. GRM has not been able to open the named file. Check that all necessary input files (as listed in Table 3) exist in the run directory.

3. While reading one of the input files, GRM was expecting to find the named keyword[29]. The string actually read is written as part of the error message. From this information it should be relatively easy to find the error in the relevant input file. Spelling mistakes, extra lines of numerical data before the keyword and simply missing out the keyword are all examples of errors which may have occurred.

4. In the RUN TIME OPTIONS section of the main input file grm.dat each of the flags should either be set to 0 or 1. If this is not the case, the offending variable is indicated.

5. Two of the RUN TIME OPTIONS flags are in conflict. For example, this would be signalled if IREOX was set to 1 (indicating that microbial reoxidation of reduced minerals is to be performed) while YESBUG is set to 0 (indicating that microbial activity is not included in the current simulation).

6. The named integer parameter is above the maximum allowable value, which is also indicated.

7. One of the species identification numbers listed in either grm.bcs or grm.kds is not recognised as a transported species (it does not appear in the MACROSPECIES PHREEQE ID NUMBERS or MICROSPECIES ID NUMBERS sections of the main input file grm.dat).

8. The number of colloids specified in the INTEGER PARAMETERS section of the main input file grm.dat is outside the allowable range (0 to 3 inclusive).

10. For each microelement included in the bulk chemistry, the corresponding master species (species number 3**01) must appear in the list of transported species (as specified in the MICROSPECIES ID NUMBERS section of the main input file grm.dat). An error is signalled should this not be the case.

11. The element, species and mineral names appearing in the PRINT DATA, MICROMINERALS IN INITIAL INVENTORY and MACROMINERALS IN INITIAL INVENTORY sections of the main input file grm.dat must be exactly as they appear in the PHREEQE database. An error is signalled should this not be the case.

12. Due to the way in which the microelement inventory is apportioned between different phases and regions within the current version of GRM, no finite–difference cell may

[29] Note that all keywords are preceeded by an asterisk.

be fully saturated if the simulation includes at least one microelement. A possible solution is to assign each cell a nominal headspace.

14. One of the microelements listed in file `grm.kds` is not recognised as a transported element (as specified in the `MICROSPECIES ID NUMBERS` section of the main input file `grm.dat`).

20. The implicit finite–differencing transport solver has been chosen (flag `ISLVBK` set to 1 in the `RUN TIME OPTIONS` section of the main input file `grm.dat`). This option is disabled in the current version of the code and one must select the explicit–differencing solver instead, by setting `ISLVBK` to 0.

50. The value of the named parameter is outside the permitted range, which is stated.

The following errors are also detected by `GRM`. They have not been assigned code numbers but are fully described by an output message.

- The gas flow calculations include a self-consistency check.
- The names of any ion-exchange species are checked. They must be exactly as they appear in the `PHREEQE` database.
- The name of any ion-exchange species for which data is to be output must agree with the name of a species that is followed in the run.
- An error in opening `grm.bcs`, `grm.grd`, `grm.flw`, `modf.grd`, `modf.hds` or `modf.cbb` is captured.
- A check is made that `modf.grd` has the header line `MCAD386`, which it must if it is a valid `MODFLOW` file.
- Any cell numbers listed in the `grm.bcs` file for local boundary conditions are checked. They must not fall outside the range of the finite difference grid specified in `grm.grd`.
- Local boundary conditions set in `grm.bcs` have a data entry for the boundary condition type. This must be either 0, 1 or 2 (see Sec. 12.2).
- A check is made that the grid sizes in `modf.grd` do not exceed the maximum permitted values.
- Checks are made that the grid sizes in `modf.cbb`, `modf.crc`, `modf.hds` and in `modf.cbw` agree with those in `modf.grd`.

- Before calling PHREEQE a check is made that all of the elements to be speciated are in its database.
- Kinetic minerals listed in `grm.kin` are checked to ensure that they appear in the database.
- The sorption data read from `grm.kds` is checked to ensure that only positive values occur.

12 Input Deck

The input data required for a GRM run is supplied through a number of files, which are generally named grm.***. The only exceptions to this are the MODELCAD/MODFLOW data files which are named as modf.*** and the PHREEQC database file phreeqc.dat. A list of all possible data files is given in Table 3 below, together with a brief description of each. The third column of the table indicates whether each file is optional and, if so, specifies which flag or parameter controls the need for its presence. All of these flags are set in the main data file grm.dat. The file grm.flw, for example, is required if and only if the flag IMDFLW is set to zero.

Each of the input files is described separately in the following sections. Note that reference is often made to 'keywords'. These must appear in the input file exactly as stated and be preceded by a single asterisk. Examples of the input files are available in the appendices. These have been included for illustrative purposes only and were not designed to be consistent with each other. The data included in the files should not be regarded as realistic.

Name	Description	Optional?
grm.act	Active fraction data	Yes (C14SWT=1)
grm.bcs	Solute boundary conditions	No
grm.bug	Microbial data	Yes (YESBUG=1 or YESCOR=1)
grm.cem	Cement dissolution data	Yes (ICEM=1)
grm.cor	Corrosion data	Yes (YESCOR=1)
grm.dat	Main input file	No
grm.dcy	Radioactive decay database	Yes (NME>0)
grm.flw	Groundwater flow data	Yes (IMDFLW=0)
grm.grd	Geometry data	Yes (IMDFLW=0)
grm.iex	Ion-exchange data	Yes (YESX=1)
grm.inv	Initial inventory data	No
grm.kin	Kinetic mineral dissolution data	Yes (NKIN>0)
grm.kds	Sorption/release database	No
grm.phr	PHREEQE database	Yes (YESPC=0. YESCHM=1)
phreeqc.dat	PHREEQC database	Yes (YESPC=1. YESCHM=1)
grm.phc	PHREEQC header file	Yes (YESPC=1. YESCHM=1)
grm.rel	Microelement release data	Yes (NME>0)
modf.cbb	MODFLOW internal flow data	Yes (IMDFLW=1)
modf.cbw	MODFLOW well flow data	Yes (IMDFLW=1)
modf.crc	MODFLOW recharge flow data	Yes (IMDFLW=1)
modf.grd	MODFLOW grid data	Yes (IMDFLW=1)
RESTART	Time data used in the restart facility	Yes (see Sec. 11.3)
RESTART1	Other data used in the restart facility	Yes (see Sec. 11.3)

Table 3: GRM input files.

12.1 grm.act

This data file contains the active fraction information for ^{14}C in each cell. An example file can be seen in Appendix A. The format of the file is as follows:

- Line 1 - Keyword `CELLULOSE TYPE 1`.
- The next `NY` lines contain the active fractions of ^{14}C in cellulose type 1 for each of the `NX` cells.
- Line 2 + `NY`- Keyword `CELLULOSE TYPE 2`.
- The next `NY` lines contain the active fractions of ^{14}C in cellulose type 2 for each of the `NX` cells.
- Line 3 + `2NY` - Keyword `CELLULOSE TYPE 3`.
- The next `NY` lines contain the active fractions of ^{14}C in cellulose type 3 for each of the `NX` cells.
- Line 4 + `3NY` - Keyword `PROTEIN TYPE 1`.
- The next `NY` lines contain the active fractions of ^{14}C in protein type 1 for each of the `NX` cells.
- Line 5 + `4NY` - Keyword `PROTEIN TYPE 2`.
- The next `NY` lines contain the active fractions of ^{14}C in protein type 2 for each of the `NX` cells.
- Line 6 + `5NY` - Keyword `PROTEIN TYPE 3`.
- The next `NY` lines contain the active fractions of ^{14}C in protein type 3 for each of the `NX` cells.
- Line 7 + `6NY` - Keyword `FAT TYPE 1`.
- The next `NY` lines contain the active fractions of ^{14}C in fat type 1 for each of the `NX` cells.
- Line 8 + `7NY` - Keyword `FAT TYPE 2`.

- The next NY lines contain the active fractions of ^{14}C in fat type 2 for each of the NX cells.
- Line 9 + 8NY - Keyword FAT TYPE 3.
- The next NY lines contain the active fractions of ^{14}C in fat type 3 for each of the NX cells.
- Next Line - Keyword NUMBER OF MACROELEMENTS TO BE READ.
- Next Line - Number (ELCNT) of carbon macroelements which have an active fraction that are involved in the GRM run.
- Next Line - Keyword PHREEQE NUMBER AND ACTIVE FRACTION.
- For each macroelement with a carbon active fraction (ELCNT in total):
  - Next Line: Element PHREEQE number.
  - Next NY Lines: The active fractions of ^{14}C for this element in each of the NX cells.
- Next Line - Blank.
- Next Line - Keyword NUMBER OF MICROSPECIES TO BE READ.
- Next Line - Number (MICNM) of microspecies which have an active fraction of ^{14}C that are involved in the GRM run.
- Next Line- Keyword MICROSPECIES NUMBER AND ACTIVE FRACTION.
- For each microspecies with a carbon active fraction (MICNM in total):
  - Next Line: Microspecies PHREEQE number.
  - Next NY Lines: The active fractions of ^{14}C for this microspecies in each of the NX cells.
- Next Line - Blank.
- Next Line - Keyword NUMBER OF MACROMINERALS TO BE READ.
- Next Line - Number (NOMORE1) of macrominerals which have an active fractionf ^{14}C.
- Next Line- Keyword MINERAL NAME AND ACTIVE FRACTION.

- For each macromineral with a carbon active fraction (NOMORE1 in total):
  - Next Line: Macromineral PHREEQE name.
  - Next NY Lines: The active fractions of ^{14}C for this mineral in each of the NX cells.

12.2 grm.bcs

This data file contains information concerning the chemistry of influent streams. It may take either of two forms (Sec. 3.5), depending on whether constant or time–dependent boundary conditions have been specified (using flag ITDBCS in the main data file grm.dat). Only macrospecies and colloid concentrations may be set in the time–independent case, while microspecies concentrations may also be set if the time–dependent form is used. (In both forms the pH and pe of each external stream are also set. Although these values are read by GRM their values are not used in the code calculations and they may therefore be given arbitrary values.)

The boundary conditions are specified using a combination of global and local conditions, with any local values given overwriting the global values in the relevant cells.

12.2.1 Time–independent form

Used if ITDBCS = 0. In the time–independent form, global concentrations must be set for every macrospecies and colloid. An example file can be seen in Appendix B.1. The format of the file is as follows:

- Line 1 - Keyword GLOBAL BOUNDARY CONCENTRATIONS.
- Line 2 - Caption (text unimportant).
- Next NC lines (NC = number of macrospecies):
  1. Global species concentration in constant head flows (moll^{-1} of porewater);
  2. Global species concentration in well flows (moll^{-1} of porewater);
  3. Global species concentration in recharge flows (moll^{-1} of porewater).

  This data should be written in the same order in which the macrospecies PHREEQE numbers are specified in the main input file grm.dat.
- Next NCOL lines (NCOL = number of colloids):

1. Global colloid concentration in constant head flows (gl^{-1} of porewater);
2. Global colloid concentration in well flows (gl^{-1} of porewater);
3. Global colloid concentration at boundary of recharge cells (gl^{-1} of porewater).

- Blank line.
- Next line - Keyword `GLOBAL BOUNDARY PH`.
- Next line:
  1. Global pH in constant head flows;
  2. Global pH in well flows;
  3. Global pH in recharge flows.
- Blank line.
- Next line - Keyword `GLOBAL BOUNDARY PE`.
- Next line:
  1. Global pe in constant head flows;
  2. Global pe in well flows;
  3. Global pe in recharge flows.
- Blank line.
- Next line - Keyword `LOCAL BOUNDARY CONCENTRATIONS`.
- Next line - Number (`N`) of local boundary concentrations to be set for the first macrospecies.
- For each local boundary concentration to be set for this macrospecies (`N` in total):
  - Next `N` lines:
    1. Y-position of cell (row number);
    2. X-position of cell (column number);
    3. Type of boundary flow (0 = constant head, 1 = well, 2 = recharge);
    4. Macrospecies concentration in boundary stream ($moll^{-1}$ of porewater).

– Blank line.

The previous 2N +1 lines are repeated for each macrospecies (i.e. NC times).

- Next line - Number (N1) of local boundary concentrations to be set for this colloid.
- For each local boundary concentration to be set for this colloid ((N1 in total):
  - Next N lines:
    1. Y-position of cell (row number);
    2. X-position of cell (column number);
    3. Type of boundary flow (0 = constant head, 1 = well, 2 = recharge);
    4. Colloid concentration in boundary stream (gl^{-1} of porewater).
  - Blank line.

The previous 2N1 +1 lines are repeated for each colloid (i.e. NCOL times).

- Next line - Keyword LOCAL BOUNDARY PH, PE.
- Next line - Number of local boundary pH/pe values to be set (M).
- Next M lines:
  1. Y-position of cell (row number);
  2. X-position of cell (column number);
  3. Type of boundary flow (0 = constant head, 1 = well, 2 = recharge);
  4. pH of boundary stream;
  5. pe of boundary stream.

12.2.2 Time–dependent form

Used if ITDBCS = 1. Time–dependent boundary conditions may be expressed in either of two ways. In the first way, each time–dependent quantity is represented by a series of straight lines. This enables the user to make a fit to the time profile of the relevant

quantity, which may have been determined elsewhere. Thus, for example, a time varying species concentration is represented as:

$$c(t) = \begin{cases} c_0 + m_0(t - t_0) & t_0 \leq t < t_1 \\ c_1 + m_1(t - t_1) & t_1 \leq t < t_2 \\ \text{etc.} \end{cases} \quad (291)$$

where t_0, t_1 etc. are the start times of successive periods. In each period, the concentration profile is approximated by a straight line starting from the values c_0, c_1 etc. and having gradients m_0, m_1 etc.

The second method of expressing the time–dependent boundary conditions is analogous to the first except that now the straight lines describe the logarithm of the relevant quantity. Thus, a species concentration would be represented by:

$$c(t) = \begin{cases} c_0 10^{m_0(t-t_0)} & t_0 \leq t < t_1 \\ c_1 10^{m_1(t-t_1)} & t_1 \leq t < t_2 \\ \text{etc.} \end{cases} \quad (292)$$

In the time–dependent form of `grm.bcs`, it is not necessary to specify boundary concentrations for every species and colloid, the default values being zero. An example file can be seen in Appendix B.2. The format of the file is as follows:

- Line 1 - Keyword `IBCLOG`.
- Line 2 - Flag indicating whether linear or logarithmic time–dependence is used (0=linear, 1=logarithmic).
- Line 3 - Keyword `WELL CELLS`.
- Line 4 - Keyword `GLOBAL WELL CONCENTRATIONS`.
- The following format is used in turn for each species for which non-zero concentrations are to be specified:
  - Next line - The number of the species as it appears in the `PHREEQE` database. Note that if a '-' sign appears here it signifies that there are no more global well concentrations to be read. Colloids may be specified as "col1","col2", or "col3".
  - If the current species is a microspecies then for each isotope:
    * Next line - Isotope fraction of this isotope.

- Next line - Number of time periods used to define the time–dependence (NT).
- Next NT lines:
  1. Period start time (yr);
  2. Period end time (yr);
  3. Species concentration at period start time ($moll^{-1}$ for liquid species, gl^{-1} for colloids);
  4. Slope of either the concentration profile or the logarithm of it during the period ($moll^{-1}yr^{-1}$ and $gl^{-1}yr^{-1}$ for liquid species and colloids respectively if a linear time–dependence is used; yr^{-1} for both liquid species and colloids if logarithmic dependence is used);
  5. Species concentration at period end time ($moll^{-1}$ for liquid species, gl^{-1} for colloids).

- Next line - Keyword GLOBAL WELL PH.
- Next line - Number of time periods used to define time–dependence of pH (NPH).
- Next NPH lines:
  1. Period start time (yr);
  2. Period end time (yr);
  3. pH at period start time;
  4. Slope of either pH or log pH profile during the period;
  5. pH at period end time.
- Next line - Keyword GLOBAL WELL PE.
- Next line - Number of time periods used to define time–dependence of pe (NPE).
- Next NPE lines:
  1. Period start time (yr);
  2. Period end time (yr);
  3. pe at period start time;
  4. Slope of either pH or log pH profile during the period;
  5. pe at period end time.

- Next line - Keyword `LOCAL WELL CONCENTRATIONS`.
- The following format is used in turn for each species for which local concentrations are to be specified:
  - Next line - The number of the species as it appears in the `PHREEQE` database. Note that if a '-' sign appears here it signifies that there are no more local well concentrations to be read. Colloids may be specified as "col1","col2", or "col3".
  - Next line - The number of cells for which local well concentrations are required for this species (`NC`).
  - Next set of lines repeated `NC` times:
    * Next line:
      1. Column number (X-position) of this cell;
      2. Row number (Y-position) of this cell;
      3. Number of time periods used to define time–dependence (`NT`).
    * If the current species is a microspecies then for each isotope:
      · Next line - Isotope fraction of this isotope.
    * Next `NT` lines:
      1. Period start time (yr);
      2. Period end time (yr);
      3. Species concentration at period start time ($moll^{-1}$ for liquid species, gl^{-1} for colloids);
      4. Slope of either the concentration profile or the logarithm of it during the period ($moll^{-1}yr^{-1}$ and $gl^{-1}yr^{-1}$ for liquid species and colloids respectively if a linear time–dependence is used; yr^{-1} for both liquid species and colloids if logarithmic dependence is used);
      5. Species concentration at period end time ($moll^{-1}$ for liquid species, gl^{-1} for colloids).
- Next line - Keyword `LOCAL WELL PH`.
- Next line - Number of cells for which a local well pH value is required (`NCPH`).
- Next set of lines repeated `NCPH` times:
  - Next line:

1. Column number (X-position) of this cell;
2. Row number (Y-position) of this cell;
3. Number of time periods used to define time–dependence of pH in this cell (NPH).

– Next NPH lines:

1. Period start time (yr);
2. Period end time (yr);
3. pH at period start time;
4. Slope of either pH or log pH profile during the period;
5. pH at period end time.

- Next line - Keyword LOCAL WELL PE.
- Next line - Number of cells for which a local well pe value is required (NCPE).
- Next set of lines repeated NCPE times:

– Next line:

1. Column number (X-position) of this cell;
2. Row number (Y-position) of this cell;
3. Number of time periods used to define time–dependence of pe in this cell (NPE).

– Next NPE lines:

1. Period start time (yr);
2. Period end time (yr);
3. pe at period start time;
4. Slope of either pe or log pe profile during the period;
5. pe at period end time.

- Blank line.

All of the above (apart from lines 1 and 2) is repeated for the recharge and the constant head boundary conditions in turn.

12.3 grm.bug

This file contains all the microbial data necessary for a GRM run. It is only required as input if microbial or corrosion calculations are to be performed: i.e., if the flag YESBUG or the flag YESCOR is set to 1 in the RUN TIME OPTIONS section of the main data file grm.dat. An example file can be seen in Appendix C. The format of the file is as follows:

- Line 1 - Keyword CARBOXYLIC ACID CARBON NUMBERS.
- On subsequent lines:
  - Number of carbon atoms minus one (since formula is $H(CH_2)_nCOOH$) in one molecule of the 'average' volatile fatty acid (VFA).
  - Number of carbon atoms minus one in one molecule of the 'average' free fatty acid (FFA).
- Line 4 - Keyword CELLULOSE HYDROLYSIS DATA.
- On subsequent lines:
  - Aerobic hydrolysis rate constant for type 1 cellulose (s^{-1}).
  - Anaerobic hydrolysis rate constant for type 1 cellulose (s^{-1}).
  - Aerobic hydrolysis rate constant for type 2 cellulose (s^{-1}).
  - Anaerobic hydrolysis rate constant for type 2 cellulose (s^{-1}).
  - Aerobic hydrolysis rate constant for type 3 cellulose (s^{-1}).
  - Anaerobic hydrolysis rate constant for type 3 cellulose (s^{-1}).
  - Optimum pH for cellulose hydrolysis.
  - pH factor for cellulose hydrolysis.
  - pH cut-off for cellulose hydrolysis. Below this value hydrolysis will not occur.
  - Alkaline aerobic hydrolysis rate constant for type 1 cellulose (s^{-1}).
  - Alkaline anaerobic hydrolysis rate constant for type 1 cellulose (s^{-1}).
  - Alkaline aerobic hydrolysis rate constant for type 2 cellulose (s^{-1}).
  - Alkaline anaerobic hydrolysis rate constant for type 2 cellulose (s^{-1}).
  - Alkaline aerobic hydrolysis rate constant for type 3 cellulose (s^{-1}).
  - Alkaline anaerobic hydrolysis rate constant for type 3 cellulose (s^{-1}).

- Optimum pH for alkaline hydrolysis.
- pH factor for alkaline hydrolysis.
- pH cut-off for alkaline hydrolysis. Below this value hydrolysis will not occur.
- Glucose recycle switch. If this switch has a value greater than or equal to 1.0, excess glucose is converted back into cellulose.
- Unsaturated hydrolysis rate for type 1 cellulose (s^{-1}).
- Unsaturated hydrolysis rate for type 2 cellulose (s^{-1}).
- Unsaturated hydrolysis rate for type 3 cellulose (s^{-1}).

- Line 27 - Keyword `PROTEIN HYDROLYSIS DATA`.
- On subsequent lines:
  - Aerobic hydrolysis rate constant for type 1 protein (s^{-1}).
  - Anaerobic hydrolysis rate constant for type 1 protein (s^{-1}).
  - Aerobic hydrolysis rate constant for type 2 protein (s^{-1}).
  - Anaerobic hydrolysis rate constant for type 2 protein (s^{-1}).
  - Aerobic hydrolysis rate constant for type 3 protein (s^{-1}).
  - Anaerobic hydrolysis rate constant for type 3 protein (s^{-1}).
  - Optimum pH for protein hydrolysis.
  - Constant in pH control factor for protein hydrolysis. The larger the value, the narrower the pH range over which hydrolysis will occur.
  - pH cut-off for protein hydrolysis. Below this value hydrolysis will not occur.
  - Unsaturated hydrolysis rate for type 1 protein (s^{-1}).
  - Unsaturated hydrolysis rate for type 2 protein (s^{-1}).
  - Unsaturated hydrolysis rate for type 3 protein (s^{-1}).
- Line 40 - Keyword `FAT HYDROLYSIS DATA`.
- On subsequent lines:
  - Aerobic hydrolysis rate constant for type 1 fats (s^{-1}).
  - Anaerobic hydrolysis rate constant for type 1 fats (s^{-1}).

- Aerobic hydrolysis rate constant for type 2 fats (s^{-1}).
- Anaerobic hydrolysis rate constant for type 2 fats (s^{-1}).
- Aerobic hydrolysis rate constant for type 3 fats (s^{-1}).
- Anaerobic hydrolysis rate constant for type 3 fats (s^{-1}).
- Optimum pH for fat hydrolysis.
- Constant in pH control factor for fat hydrolysis. The larger the value, the narrower the pH range over which hydrolysis will occur.
- pH cut-off for fat hydrolysis. Below this value hydrolysis will not occur.
- Mass ratio of glycerol to FFAs in fat hydrolysis products.
- Unsaturated hydrolysis rate for type 1 fats (s^{-1}).
- Unsaturated hydrolysis rate for type 2 fats (s^{-1}).
- Unsaturated hydrolysis rate for type 3 fats (s^{-1}).

• Line 54 - Keyword `AEROBIC BACTERIA DATA`.

• On subsequent lines:

- Initial concentration of neutraphilic aerobes (gm^{-3}).
- Maximum substrate (COD) utilisation rate by aerobes (s^{-1}).
- Half-saturation constant for substrate utilisation by aerobes (gm^{-3}).
- Aerobic biomass yield coefficient (g biomass per g substrate).
- Aerobic biomass death rate (s^{-1}).
- Optimum pH for neutraphilic aerobic activity.
- Constant in pH control factor for aerobic activity. The larger the value, the narrower the pH range over which aerobic activity will occur.
- Initial concentration of alkaliphilic aerobes (gm^{-3}).
- Maximum substrate (COD) utilisation rate by alkaliphilic aerobes (s^{-1}).
- Half-saturation constant for substrate utilisation by alkaliphilic aerobes (gm^{-3}).
- Alkaliphilic aerobic biomass yield coefficient (g biomass per g substrate).
- Alkaliphilic aerobic biomass death rate (s^{-1}).
- Optimum pH for alkaliphilic aerobic activity.

  - Constant in pH control factor for alkaliphilic aerobic activity. The larger the value, the narrower the pH range over which aerobic activity will occur.
  - Aerobic degradation switch. If this switch has a value less than or equal to 0.0, instantaneous aerobic degradation occurs; otherwise Monod kinetics are used.

- Line 70 - Keyword `DENITRIFYING BACTERIA DATA`.
- On subsequent lines:
  - Initial concentration of neutraphilic, organotrophic denitrifiers (gm^{-3}).
  - Maximum substrate (COD) utilisation rate by organotrophic denitrifiers (s^{-1}).
  - Half-saturation constant for substrate utilisation by organotrophic denitrifiers (gm^{-3}).
  - Organotrophic denitrifier biomass yield coefficient (g biomass per g substrate).
  - Organotrophic denitrifier biomass death rate (s^{-1}).
  - Initial concentration of alkaliphilic, organotrophic denitrifiers (gm^{-3}).
  - Maximum substrate (COD) utilisation rate by alkaliphilic organotrophic denitrifiers (s^{-1}).
  - Half-saturation constant for substrate utilisation by alkaliphilic organotrophic denitrifiers (gm^{-3}).
  - Alkaliphilic organotrophic denitrifier biomass yield coefficient (g biomass g substrate^{-1}).
  - Alkaliphilic organotrophic denitrifier biomass death rate (s^{-1}).
  - Glucose degradation switch. If this switch has a value less than or equal to 0.0, glucose can be consumed along with other substrates; otherwise only fermentation end products are consumed.
  - Initial concentration of neutraphilic, H_2-consuming denitrifiers (gm^{-3}).
  - Maximum substrate (H_2) utilisation rate by H_2-consuming denitrifiers (s^{-1}).
  - Half-saturation constant for substrate utilisation by H_2-consuming denitrifiers (gm^{-3}).
  - H_2-consuming denitrifier biomass yield coefficient(g biomass g substrate^{-1}).
  - H_2-consuming denitrifier biomass death rate (s^{-1}).

- Initial concentration of alkaliphilic, H_2-consuming denitrifiers (gm^{-3}).
- Maximum substrate (H_2) utilisation rate by alkaliphilic H_2-consuming denitrifiers (s^{-1}).
- Half-saturation constant for substrate utilisation by alkaliphilic H_2-consuming denitrifiers (gm^{-3}).
- Alkaliphilic H_2-consuming denitrifier biomass yield coefficient (g biomass g substrate^{-1}).
- Alkaliphilic H_2-consuming denitrifier biomass death rate (s^{-1}).
- Optimum pH for neutraphilic denitrifying activity.
- Constant in pH control factor for neutraphilic denitrifying activity. The larger the value, the narrower the pH range over which activity will occur.
- Optimum pH for alkaliphilic denitrifying activity.
- Constant in pH control factor for alkaliphilic denitrifying activity. The larger the value, the narrower the pH range over which activity will occur.

- Line 96 - Keyword `GLUCOSE ACIDOGEN DATA`.
- On subsequent lines:
  - Initial concentration of neutraphilic glucose fermenting biomass (gm^{-3}).
  - Maximum substrate (glucose) utilisation rate by glucose fermenting biomass (s^{-1}).
  - Half-saturation constant for substrate utilisation by glucose fermenting biomass (gm^{-3}).
  - Glucose fermenting biomass yield coefficient (g biomass per g substrate).
  - Glucose fermenting biomass death rate (s^{-1}).
  - Optimum pH for neutraphilic glucose fermenting activity.
  - Constant in pH control factor for glucose fermenting activity. The larger the value, the narrower the pH range over which activity will occur.
  - Initial concentration of alkaliphilic glucose fermenting biomass (gm^{-3}).
  - Initial concentration of alkaliphilic ISA[30] fermenting biomass (gm^{-3}).

[30] See the note on ISA in Sec. 8.3.

- Maximum substrate (glucose) utilisation rate by alkaliphilic glucose fermenting biomass (s^{-1}).
- Half-saturation constant for substrate utilisation by alkaliphilic glucose fermenting biomass (gm^{-3}).
- Alkaliphilic glucose fermenting biomass yield coefficient (g biomass per g substrate).
- Alkaliphilic glucose fermenting biomass death rate (s^{-1}).
- Optimum pH for alkaliphilic glucose fermenting activity.
- Constant in pH control factor for alkaliphilic glucose fermenting activity. The larger the value, the narrower the pH range over which activity will occur.

- Line 112 - Keyword `PEPTIDE ACIDOGEN DATA`.
- On subsequent lines:
  - Initial concentration of neutraphilic peptide fermenting biomass (gm^{-3}).
  - Maximum substrate (peptide) utilisation rate by peptide fermenting biomass (s^{-1}).
  - Half-saturation constant for substrate utilisation by peptide fermenting biomass (gm^{-3}).
  - Peptide fermenting biomass yield coefficient (g biomass per g substrate).
  - Peptide fermenting biomass death rate (s^{-1}).
  - Optimum pH for neutraphilic peptide fermenting activity.
  - pH factor for neutraphilic peptide fermenting activity.
  - Initial concentration of alkaliphilic peptide fermenting biomass (gm^{-3}).
  - Maximum substrate (peptide) utilisation rate by alkaliphilic peptide fermenting biomass (s^{-1}).
  - Half-saturation constant for substrate utilisation by alkaliphilic peptide fermenting biomass (gm^{-3}).
  - Alkaliphilic peptide fermenting biomass yield coefficient (g biomass per g substrate).
  - Alkaliphilic peptide fermenting biomass death rate (s^{-1}).

- Optimum pH for alkaliphilic peptide fermenting activity.
- pH factor for alkaliphilic peptide fermenting activity.
- Molar ratio of acetic acid to VFAs in peptide fermentation products.

- Line 128 - Keyword `GLYCEROL ACIDOGEN DATA`.
- On subsequent lines.
  - Initial concentration of neutraphilic glycerol fermenting biomass (gm^{-3}).
  - Maximum substrate (glycerol) utilisation rate by glycerol fermenting biomass (s^{-1}).
  - Half-saturation constant for substrate utilisation by glycerol fermenting biomass (gm^{-3}).
  - Glycerol fermenting biomass yield coefficient (g biomass per g substrate).
  - Glycerol fermenting biomass death rate (s^{-1}).
  - Optimum pH for neutraphilic glycerol fermenting activity.
  - Constant in pH control factor for glycerol fermenting activity. The larger the value, the narrower the pH range over which activity will occur.
  - Initial concentration of alkaliphilic glycerol fermenting biomass (gm^{-3}).
  - Maximum substrate (glycerol) utilisation rate by alkaliphilic glycerol fermenting biomass (s^{-1}).
  - Half-saturation constant for substrate utilisation by alkaliphilic glycerol fermenting biomass (gm^{-3}).
  - Alkaliphilic glycerol fermenting biomass yield coefficient (g biomass per g substrate).
  - Alkaliphilic glycerol fermenting biomass death rate (s^{-1}).
  - Optimum pH for alkaliphilic glycerol fermenting activity.
  - Constant in pH control factor for alkaliphilic glycerol fermenting activity. The larger the value, the narrower the pH range over which activity will occur.
  - Molar ratio of acetic acid to VFAs in glycerol fermentation products.
- Line 144 - Keyword `IRON REDUCING BACTERIA DATA`.
- On subsequent lines.

- Initial concentration of neutraphilic, organotrophic iron reducers (gm^{-3}).
- Maximum substrate (COD) utilisation rate by organotrophic iron reducers (s^{-1}).
- Half-saturation constant for substrate utilisation by organotrophic iron reducers (gm^{-3}).
- Organotrophic iron–reducing biomass yield coefficient (g biomass per g substrate).
- Organotrophic iron–reducing biomass death rate (s^{-1}).
- Initial concentration of alkaliphilic, organotrophic iron reducers (gm^{-3}).
- Maximum substrate (COD) utilisation rate by alkaliphilic organotrophic iron reducers (s^{-1}).
- Half-saturation constant for substrate utilisation by alkaliphilic organotrophic iron reducers (gm^{-3}).
- Alkaliphilic iron–reducing biomass yield coefficient (g biomass per g substrate).
- Alkaliphilic iron–reducing biomass death rate (s^{-1}).
- Initial concentration of neutraphilic, H_2-consuming iron reducers (gm^{-3}).
- Maximum substrate (H_2) utilisation rate by H_2-consuming iron reducers (s^{-1}).
- Half-saturation constant for substrate utilisation by H_2-consuming iron reducers (gm^{-3}).
- H_2-consuming iron–reducing biomass yield coefficient (g biomass per g substrate).
- H_2-consuming iron–reducing biomass death rate (s^{-1}).
- Initial concentration of alkaliphilic, H_2-consuming iron reducers (gm^{-3}).
- Maximum substrate (H_2) utilisation rate by alkaliphilic H_2-consuming iron reducers (s^{-1}).
- Half-saturation constant for substrate utilisation by alkaliphilic H_2-consuming iron reducers (gm^{-3}).
- Alkaliphilic H_2-consuming iron–reducing biomass yield coefficient (g biomass g substrate^{-1}).
- Alkaliphilic H_2-consuming iron–reducing biomass specific death rate (s^{-1}).
- Optimum pH for neutraphilic iron–reducing activity.

  - Constant in pH control factor for neutraphillic iron–reducing activity. The larger the value, the narrower the pH range over which activity will occur.
  - Optimum pH for alkaliphilic iron–reducing activity.
  - Constant in pH control factor for alkaliphilic iron–reducing activity. The larger the value, the narrower the pH range over which activity will occur.

- Line 169 - Keyword `SULPHATE REDUCING BACTERIA DATA`.
- On subsequent lines.
  - Initial concentration of neutraphilic, organotrophic sulphate reducers (gm^{-3}).
  - Maximum substrate (COD) utilisation rate by organotrophic sulphate reducers (s^{-1}).
  - Half-saturation constant for substrate utilisation by organotrophic sulphate reducers (gm^{-3}).
  - Organotrophic sulphate–reducing biomass yield coefficient (g biomass per g substrate).
  - Organotrophic sulphate–reducing biomass death rate (s^{-1}).
  - Initial concentration of alkaliphilic, organotrophic sulphate reducers (gm^{-3}).
  - Maximum substrate (COD) utilisation rate by alkaliphilic organotrophic sulphate reducers (s^{-1}).
  - Half-saturation constant for substrate utilisation by alkaliphilic organotrophic sulphate reducers (gm^{-3}).
  - Alkaliphilic organotrophic sulphate–reducing biomass yield coefficient (g biomass g substrate^{-1}).
  - Alkaliphilic organotrophic sulphate–reducing biomass death rate (s^{-1}).
  - Initial concentration of neutraphilic, H_2-consuming sulphate reducers (gm^{-3}).
  - Maximum substrate (H_2) utilisation rate by H_2-consuming sulphate reducers (s^{-1}).
  - Half-saturation constant for substrate utilisation by H_2-consuming sulphate reducers (gm^{-3}).
  - H_2-consuming sulphate–reducing biomass yield coefficient (g biomass g substrate^{-1}).

- H_2-consuming sulphate–reducing biomass death rate (s^{-1}).
- Initial concentration of alkaliphilic, H_2-consuming sulphate reducers (gm^{-3}).
- Maximum substrate (H_2) utilisation rate by alkaliphilic H_2-consuming sulphate reducers (s^{-1}).
- Half-saturation constant for substrate utilisation by alkaliphilic H_2-consuming sulphate reducers (gm^{-3}).
- Alkaliphilic H_2-consuming sulphate–reducing biomass yield coefficient (g biomass g substrate^{-1}).
- Alkaliphilic H_2-consuming sulphate–reducing biomass death rate (s^{-1}).
- Optimum pH for neutraphilic sulphate–reducing activity.
- Constant in pH control factor for neutraphillic sulphate–reducing activity. The larger the value, the narrower the pH range over which activity will occur.
- Optimum pH for alkaliphilic sulphate–reducing activity.
- Constant in pH control factor for alkaliphilic sulphate–reducing activity. The larger the value, the narrower the pH range over which activity will occur.

• Line 194 - Keyword `ACETOGENIC BACTERIA DATA`.

• On subsequent lines.

- Initial concentration of neutraphilic acetogens (gm^{-3}).
- Maximum substrate (VFA) utilisation rate by acetogens (s^{-1}).
- Half-saturation constant for substrate utilisation by acetogens (gm^{-3}).
- Acetogenic biomass yield coefficient (g biomass g substrate^{-1}).
- Acetogenic biomass death rate (s^{-1}).
- Optimum pH for neutraphilic acetogenic activity.
- Constant in pH control factor for neutraphillic acetogenic activity. The larger the value, the narrower the pH range over which acetogenic activity will occur.
- Initial concentration of alkaliphilic acetogens (gm^{-3}).
- Maximum substrate (VFA) utilisation rate by alkaliphilic acetogens (s^{-1}).
- Half-saturation constant for substrate utilisation by alkaliphilic acetogens (gm^{-3}).

- Alkaliphilic acetogenic biomass yield coefficient (g biomass per g substrate).
- Alkaliphilic acetogenic biomass death rate (s^{-1}).
- Optimum pH for alkaliphilic acetogenic activity.
- Constant in pH control factor for alkaliphilic acetogenic activity. The larger the value, the narrower the pH range over which acetogenic activity will occur.

- Line 209 - Keyword `METHANOGENIC BACTERIA DATA`.
- On subsequent lines.
  - Initial concentration of neutraphilic organotrophic methanogens (gm^{-3}).
  - Maximum substrate (acetic acid) utilisation rate by organotrophic methanogens (s^{-1}).
  - Organotrophic methanogenic biomass yield coefficient (g biomass per g substrate).
  - Organotrophic methanogenic biomass death rate (s^{-1}).
  - Optimum pH for neutraphilic organotrophic methanogen activity.
  - Constant in pH control factor for neutraphilic organotrophic methanogen activity. The larger the value, the narrower the pH range over which activity will occur.
  - Initial concentration of alkaliphilic organotrophic methanogens (gm^{-3}).
  - Maximum substrate (acetic acid) utilisation rate by alkaliphilic organotrophic methanogens (s^{-1}).
  - Alkaliphilic organotrophic methanogenic biomass yield coefficient (g biomass g substrate^{-1}).
  - Alkaliphilic organotrophic methanogenic biomass death rate (s^{-1}).
  - Optimum pH for alkaliphilic organotrophic methanogen activity.
  - Constant in pH control factor for alkaliphilic organotrophic methanogen activity. The larger the value, the narrower the pH range over which activity will occur.
  - Initial concentration of neutraphilic H_2-consuming methanogens (gm^{-3}).
  - Maximum substrate (hydrogen) utilisation rate by H_2-consuming methanogens (s^{-1}).

- H_2-consuming methanogenic biomass yield coefficient (g biomass per g substrate).
- H_2-consuming methanogenic biomass death rate (s^{-1}).
- Optimum pH for neutraphilic H_2-consuming methanogen activity.
- Constant in pH control factor for neutraphillic H_2-consuming methanogen activity. The larger the value, the narrower the pH range over which activity will occur.
- Initial concentration of alkaliphilic H_2-consuming methanogens (gm^{-3}).
- Maximum substrate (hydrogen) utilisation rate by alkaliphilic H_2-consuming methanogens (s^{-1}).
- Alkaliphilic H_2-consuming methanogenic biomass yield coefficient (g biomass g substrate^{-1}).
- Alkaliphilic H_2-consuming methanogenic biomass death rate (s^{-1}).
- Optimum pH for alkaliphilic H_2-consuming methanogen activity.
- Constant in pH control factor for alkaliphilic H_2-consuming methanogen activity. The larger the value, the narrower the pH range over which activity will occur.

- Line 234 - Keyword `OXYGEN REOXIDISER DATA`.
- On subsequent lines.
  - Initial concentration of neutraphilic reoxidising biomass (gm^{-3}).
  - Maximum substrate (COD) utilisation rate by reoxidising biomass (s^{-1}).
  - Half-saturation constant for substrate utilisation by reoxidising biomass (gm^{-3}).
  - Reoxidising biomass yield coefficient (g biomass g substrate^{-1}).
  - Reoxidising biomass death rate (s^{-1}).
  - Optimum pH for neutraphilic reoxidising activity.
  - Constant in pH control factor for neutraphillic reoxidising activity. The larger the value, the narrower the pH range over which activity will occur.
  - Maintenance factor for neutraphilic microbes (s^{-1}).
  - Initial concentration of alkaliphilic reoxidising biomass (gm^{-3}).
  - Maximum substrate (COD) utilisation rate by alkaliphilic reoxidising biomass (s^{-1}).

- Half-saturation constant for substrate utilisation by alkaliphilic reoxidising biomass (gm^{-3}).
- Alkaliphilic reoxidising biomass yield coefficient (g biomass per g substrate).
- Alkaliphilic reoxidising biomass death rate (s^{-1}).
- Optimum pH for alkaliphilic reoxidising activity.
- Constant in pH control factor for alkaliphilic reoxidising activity. The larger the value, the narrower the pH range over which activity will occur.
- Maintenance factor for alkaliphilic microbes (s^{-1}).
- Reoxidation switch. If this switch has a value less than or equal to 0.0, instantaneous reoxidation occurs; otherwise Monod kinetics are used.

- Line 252 - Keyword `NITRATE REOXIDISER DATA`.
- On subsequent lines:
  - Initial concentration of neutraphilic nitrate reoxidising biomass (gm^{-3}).
  - Maximum substrate (COD) utilisation rate by nitrate reoxidising biomass (s^{-1}).
  - Half-saturation constant for substrate utilisation by nitrate reoxidising biomass (gm^{-3}).
  - Nitrate reoxidising biomass yield coefficient (g biomass per g substrate).
  - Nitrate reoxidising biomass death rate (s^{-1}).
  - Optimum pH for neutraphilic nitrate reoxidising activity.
  - Constant in pH control factor for neutraphillic nitrate reoxidising activity. The larger the value, the narrower the pH range over which activity will occur.
  - Maintenance factor for neutraphilic microbes (s^{-1}).
  - Initial concentration of alkaliphilic nitrate reoxidising biomass (gm^{-3}).
  - Maximum substrate (COD) utilisation rate by alkaliphilic nitrate reoxidising biomass (s^{-1}).
  - Half-saturation constant for substrate utilisation by alkaliphilic nitrate reoxidising biomass (gm^{-3}).
  - Alkaliphilic nitrate reoxidising biomass yield coefficient (g biomass per g substrate).

- Alkaliphilic nitrate reoxidising biomass death rate (s^{-1}).
- Optimum pH for alkaliphilic nitrate reoxidising activity.
- Constant in pH control factor for alkaliphilic nitrate reoxidising activity. The larger the value, the narrower the pH range over which activity will occur.
- Maintenance factor for alkaliphilic microbes (s^{-1}).
- Nitrate reoxidation switch. If this switch has a value less than or equal to 0.0, instantaneous reoxidation occurs; otherwise Monod kinetics are used.

- Line 270 - Keyword `AMMONIA REOXIDISER DATA`.
- On subsequent lines:
  - Initial concentration of neutraphilic ammonia reoxidising biomass (gm^{-3}).
  - Maximum substrate (COD) utilisation rate by ammonia reoxidising biomass (s^{-1}).
  - Half-saturation constant for substrate utilisation by ammonia reoxidising biomass (gm^{-3}).
  - Ammonia reoxidising biomass yield coefficient (g biomass per g substrate).
  - Ammonia reoxidising biomass death rate (s^{-1}).
  - Optimum pH for neutraphilic ammonia reoxidising activity.
  - Constant in pH control factor for neutraphillic ammonia reoxidising activity. The larger the value, the narrower the pH range over which activity will occur.
  - Maintenance factor for neutraphilic microbes (s^{-1}).
  - Initial concentration of alkaliphilic ammonia reoxidising biomass (gm^{-3}).
  - Maximum substrate (COD) utilisation rate by alkaliphilic ammonia reoxidising biomass (s^{-1}).
  - Half-saturation constant for substrate utilisation by alkaliphilic ammonia reoxidising biomass (gm^{-3}).
  - Alkaliphilic ammonia reoxidising biomass yield coefficient (g biomass per g substrate).
  - Alkaliphilic ammonia reoxidising biomass death rate (s^{-1}).
  - Optimum pH for alkaliphilic ammonia reoxidising activity.

- Constant in pH control factor for alkaliphilic nitrate reoxidising activity. The larger the value, the narrower the pH range over which activity will occur.
- Maintenance factor for alkaliphilic microbes (s^{-1}).
- Ammonia reoxidation switch. If this switch has a value less than or equal to 0.0, instantaneous reoxidation occurs; otherwise Monod kinetics are used.

- Line 288 - Keyword `TIME DATA`.
- Time `TENDBUG`, beyond which microbial calculations are no longer required (yr). On subsequent lines:
  - Number (`NBGDT`) of variable microbial timesteps (maximum 10).
  - The next line is repeated `NBGDT` times.
    - Endtime (yr) and microbial timestep (s) for this period.
- Line 290 + `NBGDT` - Keyword `OTHER DATA`.
- On subsequent lines:
  - Minimum value for biomass concentrations (gm^{-3}).
  - Ionic strength of the solution.
  - Degradable fraction of dead biomass.
  - Molar ratio of FFAs to protein in recycled biomass.
  - Molar ratio of acetic acid to VFAs in FFA decomposition products.
  - Initial concentration of inert biomass (gm^{-3}).
  - Log dissociation constant for oxygen dissolution.
  - DH factor for oxygen used in Van't Hoff calculation.
  - Log dissociation constant for nitrogen dissolution.
  - DH factor for nitrogen used in Van't Hoff calculation.
  - Log dissociation constant for CH_4 dissolution.
  - DH factor for CH_4 used in Van't Hoff calculation.
  - Combined partial pressure of N_2 and Ar gases in air (atm).
  - Partial pressure of O_2 in air (atm).

- Partial pressure of CO_2 in air (atm).
- O_2 dissolution switch. O_2 is considered to be soluble if this switch is equal to 1; otherwise it is insoluble.
- N_2 dissolution switch. N_2 is considered to be soluble if this switch is equal to 1; otherwise it is insoluble.
- CH_4 dissolution switch. CH_4 is considered to be soluble if this switch is equal to 1; otherwise it is insoluble.
- Switch for temperature-dependence of hydrolysis. Hydrolysis is considered to be temperature-dependent if this switch is equal to 1; otherwise it is temperature-independent.
- Switch for temperature-dependence of methanogenesis. Methanogenesis is considered to be temperature-dependent if this switch is equal to 1; otherwise it is temperature-independent.
- Switch for controlling use of O_2 in pe calculations. The oxygen couple is included in the redox cascade if this switch is equal to 1; otherwise O_2 is not included in the calculations.
- Switch for controlling use of NO_3^- in pe calculations. The nitrate couple is included in the redox cascade if this switch is equal to 1; otherwise NO_3^- is not included in the calculations.
- Permeability of headspace cap ($m^3s^{-1}atm^{-1}$).

- Line 310 + NBGDT - Keyword TEMPERATURE ARRAY.
  - The next NY lines contain the local temperatures (°C) for use in microbial calculations. Each line contains NX terms. (NX and NY are the number of columns and rows in the finite difference grid respectively).
- Line 311 + NY + NBGDT - Keyword MOISTURE CONTENT IN SATURATED ZONE.
- On subsequent lines:
  - The next NY lines contain the moisture content in the saturated zone for each of NX cells.
- Line 312 + NBGDT + 2NY - Keyword MOISTURE CONTENT IN UNSATURATED ZONE.
- On subsequent lines:

  - The next NY lines contain the moisture content in the unsaturated zone for each of NX cells.

- Line 313 + NBGDT + 3NY - Keyword SLUMPING FLAGS.
- On subsequent lines:
  - The next NY lines contain flags for the waste settling calculations for each of NX cells (=1 if waste settling is to occur in the cell). Note that the term slumping is used as a synonym for waste settling within the code itself.
- Line 314 + NBGDT + 4NY - Keyword SLUMPING DENSITIES.
- On subsequent lines:
  - Densities for the three types of cellulose (kgm^{-3}).
  - Densities for the three types of proteins (kgm^{-3}).
  - Densities for the three types of fats (kgm^{-3}).
  - The density of minerals (kgm^{-3}).
  - The density of iron (kgm^{-3}).
  - The density of the corrosion product Fe_2O_3 (kgm^{-3}).
  - The density of the corrosion product Fe_3O_4 (kgm^{-3}).

12.4 grm.cem

This data file contains information required to model the dissolution of cements, specifically the incongruent dissolution of the calcium silicate hydrogel (CSH). It is only required if the flag `ICEM` is set to 1 in the main data file `grm.dat`. An example file can be seen in Appendix D. The format of the file is as follows:

- Line 1 - Caption (text unimportant).
- Line 2 - Number of mineral phases (`NCEM`) that constitute the CSH phase.
- Line 3 - Caption (text unimportant).
- Lines 4 to 3 + `NCEM` - Names of the CSH minerals.
- Line 4 + `NCEM` - Caption (text unimportant).
- Next `NY` lines (`NY` = number of rows, `NX` = number of columns):
  1. Ca:Si ratio in each of the `NX` cells on the row.
- Next line - Caption (text unimportant).
- Next `NY` lines:
  1. Concentration of CSH in each of the `NX` cells on the row (moll^{-1} of porewater).

12.5 grm.cor

This file contains information for the corrosion module of the code. It is only required if the flag YESCOR is set to 1 in the main data file `grm.dat`. An example file can be seen in Appendix E. The format of the file is as follows:

- Line 1 - Caption (text unimportant).
- Line 2 - Density of mild steel (kgm^{-3}).
- Line 3 - Caption (text unimportant).
- Line 4 - Initial saturated aerobic corrosion rate (ms^{-1}).
- Line 5 - Caption (text unimportant).
- Line 6 - Initial saturated anaerobic corrosion rate (ms^{-1}).
- Line 7 - Caption (text unimportant).
- Line 8 - Initial unsaturated aerobic corrosion rate (ms^{-1}).
- Line 9 - Caption (text unimportant).
- Line 10 - Initial unsaturated anaerobic corrosion rate (ms^{-1}).
- Line 11 - Caption (text unimportant).
- Line 12 - Minimum aerobic corrosion rate (ms^{-1}).
- Line 13 - Caption (text unimportant).
- Line 14 - Minimum anaerobic corrosion rate (ms^{-1}).
- Line 15 - Caption (text unimportant).
- Line 16 - Passivity rate (yr^{-1}).
- Line 17 - Caption (text unimportant).
- Line 18 - Molecular weight of iron ($gmol^{-1}$).
- Line 19 - Caption (text unimportant).
- Line 20 - Average initial sphere radius (m).

- Line 21 - Caption (text unimportant).
- Line 22 - Average initial plate thickness (m).
- Line 23 - Caption (text unimportant).
- Line 24 - Average initial rod radius (m).
- Line 25 - Caption (text unimportant).
- Line 26 - Average initial rod length (m).
- Line 27 - Caption (text unimportant).
- Next NY lines (NY = number of rows, NX = number of columns):
  1. Initial mass of spheres (kg) in each of the NX cells on the row.
- Next line - Caption (text unimportant).
- Next NY lines:
  1. Initial mass of plates (kg) in each of the NX cells on the row.
- Next line - Caption (text unimportant).
- Next NY lines:
  1. Initial mass of rods (kg) in each of the NX cells on the row.
- Next line - Caption (text unimportant).
- Next NY lines:
  1. Initial inventory of Fe_2O_3 (mol) in each of the NX cells on the row.
- Next line - Caption (text unimportant).
- Next NY lines:
  1. Initial inventory of Fe_3O_4 (mol) in each of the NX cells on the row.
- Next line - Caption (text unimportant).
- Next line - Fraction of $Fe(OH)_3$ which forms colloids.
- Next line - Caption (text unimportant).
- Next line - pH threshold for formation of passivity layer.

12.6 grm.dat

This is the main data file for a GRM run. The following format refers to the use of PHREEQE as the chemical solver (YESPC = 0). Section 12.7 gives details of format when using PHREEQC. An example of a PHREEQE configured input file can be seen in Appendix F.1. The format of the file is as follows:

- Line 1 - Keyword TITLE.
- Line 2 - Text describing current run (up to 70 characters).
- Line 3 - Keyword RUN TIME OPTIONS.
- Line 4:
  1. YESCHM speciation flag. This should be set to 1 if speciation calculations are required. Otherwise it must be zeroed.
  2. YESBUG microbiology flag. This should be set to 1 if microbial calculations are required. Otherwise it must be zeroed.
  3. YESCOR corrosion flag. This should be set to 1 if corrosion calculations are required. Otherwise it must be zeroed.
  4. YESX ion-exchange flag. This should be set to 1 if ion-exchange calculations are required. Otherwise it must be zeroed.
- Line 5:
  1. IMDFLW: This should be set to 1 if MODFLOW/MODELCAD are used to specify the finite–difference grid and flowfield (via files modf.xxx). Otherwise it must be zeroed and the grid and the flowfield specified through the files grm.grd and grm.flw respectively.
  2. ITDBCS: This should be set to 1 if the boundary conditions file is given in the time–dependent form (see Sec. 12.2). Otherwise it must be zeroed and the time–independent form used.
  3. IFKD: This should be set to 1 if pH-dependent sorption K_d's are given in grm.kds (see Sec. 12.14). Otherwise it must be zeroed and the species–dependent format used.

4. ISLVBK: This should be set to 1 if the implicit transport solver is used. Otherwise it must be zeroed and the explicit solver is used. Note that the implicit solver is disabled in the current version of the code and so this flag must be zeroed.

- Line 6:

1. YESPE: This should be set to 1 if pe calculations are required, otherwise it must be zeroed.
2. PEO2: If this is set to 1 then the oxygen redox couple is used to determine the pe until such time as the oxygen runs out, when the pe is fixed at the value PEHELD. Note that the flag is usually zeroed to enable a full pe calculation to be performed (assuming YESPE = 1).
3. PEHELD: See previous item.
4. IHSRDX: If this is set to 1 then HS^- formed within the microbial module is allowed to react via redox reaction with Fe^{3+} to give SO_4^{2-} and Fe^{2+} (see Sec. 8.16). Otherwise the flag must be zeroed.

- Line 7:

1. ISORCP sorption flag. If this is set to 1 then sorption is coupled to microelement speciation (and there is no macroelement sorption; see Sec. 5.1). Otherwise the flag must be zeroed and sorption and speciation are completely uncoupled (see Sec. 5.2).
2. IH2NRM: If this is set to 1 then hydrogen is treated like the other gases in the model. Otherwise, the flag must be zeroed and hydrogen is vented instantaneously to atmosphere at end of each microbial timestep (see Sec. 6.3).
3. ISPWRN: If this is set to 1 then a warning will be written to standard output if a species present in significant quantities is not included in the transport calculations. Otherwise the flag must be zeroed and the warning message is suppressed.
4. IFE2CR: If this is set to 1 then Fe^{2+} is formed in saturated anaerobic corrosion (see Sec. 9.1). Otherwise the flag must be zeroed and Fe^{3+} is formed.

- Line 8:

1. IREOX microbial reoxidation flag. This should be set to 1 if reoxidation of reduced species/minerals is to be performed (see Sec. 8.14). Otherwise it must be zeroed.

2. INLIM nitrogen limitation flag. If this is set to 1 then microbe growth is limited by nitrogen availability. Otherwise the flag must be zeroed.
3. ICEM: This should be set to 1 if the dissolution of cement is to be modelled (see Sec. 4.7). Otherwise it must be zeroed.
4. IMSBAL: This should be set to 1 if nuclide mass balance calculations are required (see Sec. 3.4). Otherwise it must be zeroed.

- Line 9:

1. ICHAIN: This should be set to 1 if decay chains are to be followed (see Sec. 10.1). Otherwise it must be zeroed.
2. C14SWT: This should be set to 1 if ^{14}C is to be followed (see Sec. 10.2). Otherwise it must be zeroed.
3. IFLGH3: This should be set to 1 if tritium is to be followed (see Sec. 10.2.1). Otherwise it must be zeroed.
4. IFLGRN: This should be set to 1 if ^{222}Rn is to be followed (see Sec. 10.2.1). Otherwise it must be zeroed.

- Line 10:

1. IDROP: This should be set to 1 if waste settling is to be modelled (see Sec. 3.6). Otherwise it must be zeroed.
2. YESPC: - PHREEQC used. [31]
3. YESSCM: - SCM modelled.
4. YESPPC: - Extra PHREEQC output produced.

- Line 11 - Keyword INTEGER PARAMETERS.
- Line 12:

1. NE: The number of bulk (macro) elements
2. NC: The number of bulk (macro) species.

- Line 13:

1. NME: The number of microelements.

[31] See Appendix O for format changes when using PHREEQC.

2. (NMSP(i) i=1,NME): The number of species containing each microelement.

- Line 14:
  1. NEMIC: The number of microelements to be included in the bulk chemistry calculations.
  2. (NBLKMIC(i) i=1,NEMIC): The PHREEQE element identification numbers corresponding to each microelement to be included in the bulk chemistry calculations.
- Line 15:
  1. MACROM: The number of macrominerals included in the initial inventory.
  2. MICROM: The number of microminerals included in the initial inventory.
  3. NKIN: The number of minerals for which kinetic dissolution data is supplied.
  4. NCOL: The number of colloidal types.
- Line 16 - Keyword MICROSPECIES ID NUMBERS.
- Next NMSP lines (NMSP = total number of microspecies):
  1. Microspecies identification number.
  2. The first flag is set to 1 if isotope number 1 is to be included in the calculations.
  3. The second flag is set to 1 if isotope number 2 is to be included in the calculations.
  4. The third flag is set to 1 if isotope number 3 is to be included in the calculations.
  5. The fourth flag is set to 1 if isotope number 4 is to be included in the calculations.
  6. The fifth flag is set to 1 if isotope number 5 is to be included in the calculations.
  7. The sixth flag is set to 1 if isotope number 6 is to be included in the calculations.
- Next line - Keyword MACROELEMENT PHREEQE ID NUMBERS.
- Next line - PHREEQE identification numbers for each of the NE macroelements.
- Next line - Keyword MACROSPECIES PHREEQE ID NUMBERS.
- Next line - PHREEQE identification numbers for each of the NC macrospecies.

- Next line - Keyword SPECIES SPECIFIC PHREEQE NUMBERS.

  NOTE that the numbers in the following 7 lines should only be set if the relevant species is transported. Otherwise they should be zeroed.

- Next line:
  1. PHREEQE identification number for species CO_3^{2-}.
  2. PHREEQE identification number for species HCO_3^-.
  3. PHREEQE identification number for species H_2CO_3.
  4. PHREEQE identification number for species CO_2 gas.
- Next line:
  1. PHREEQE identification number for species CH_3COO^- ($ACET^-$).
  2. PHREEQE identification number for species CH_3COOH (ACET).
- Next line:
  1. PHREEQE identification number for species HS^-.
  2. PHREEQE identification number for species H_2S(aq).
  3. PHREEQE identification number for species S^{2-}.
  4. PHREEQE identification number for species H_2S gas.
  5. PHREEQE identification number for species SO_4^{2-}.
- Next line:
  1. PHREEQE identification number for species O_2(aq).
  2. PHREEQE identification number for species NO_3^-.
  3. PHREEQE identification number for species Cl^-.
- Next line:
  1. PHREEQE identification number for species $RCOO^-$ ($PROP^-$).
  2. PHREEQE identification number for species RCOOH (PROP).
- Next line:

1. PHREEQE identification number for species Fe^{3+}.
2. PHREEQE identification number for species Fe^{2+}.

- Next line:

1. PHREEQE identification number for species NH_4^+.
2. PHREEQE identification number for species $NH_3(aq)$.
3. PHREEQE identification number for species NH_4Cl.
4. PHREEQE identification number for species NH_4NO_3.
5. PHREEQE identification number for species $NH_4SO_4^-$.
6. PHREEQE identification number for species NH_3 gas.

- Next line - Keyword `MICROMINERALS IN INITIAL INVENTORY`.
- Next `MICROM` lines:

1. Name of micromineral. Note that these names must be identical to microminerals that appear in the PHREEQE database.

- Next line - Keyword `MACROMINERALS IN INITIAL INVENTORY`.
- Next `MACROM` lines:

1. Name of macromineral. Note that these names must be identical to macrominerals that appear in the PHREEQE database.

- Next line - Keyword `TIME DATA`.
- Next line - `ENDTIME`: Duration of the simulation (yr).
- Next line - Number of different transport timesteps (`NDT`)- Max 10.
- Next `NDT` lines:

1. Endtime for the transport timestep (yr).
2. Transport timestep to be used until the corresponding endtime (yr).

- Next line - `TENDCHEM`: Time beyond which the bulk chemistry is frozen and macrochemical calculations are no longer performed (yr).

- Next line - Number of different speciation timesteps (NDS)- Max 10.
- Next NDS lines:
  1. Endtime for the speciation timestep (yr).
  2. Speciation timestep to be used until the corresponding endtime (yr).
- Next line - Number of different output frequencies (NTV)- Max 10.
- Next NTV lines:
  1. Endtime for the use of the output frequency (yr).
  2. Number of times at which output data is to be written. (Note that the total number of output times for any run must not be greater than 300).
- Next line - Number of different pH output frequencies (NPHP)- Max 10.
- Next NPHP lines:
  1. Endtime for the use of the pH output frequency (yr).
  2. Frequency for the pH output to be used until the corresponding endtime (yr).
- Next line - Keyword RESTART DATA.
- Next line:
  1. RSTTIME: Restart time. If the model time reaches RSTTIME then the restart files are written out, and execution is terminated (yr).
  2. RSTINT: If the model time reaches a whole number multiple of RSTINT then the restart files are written out and execution continues (yr).
- Next line - Keyword PHREEQE CONVERGENCE TOLERANCE.
- Next line - Tolerance level ECLOSE for determining PHREEQE convergence (see Sec. 4.3).
- Next line - Keyword BACKWARD-DIFFERENCE TRANSPORT SOLVER DATA.
- Next line:- This data is currently irrelevant since the implicit transport solver is disabled

1. NITSOR: The maximum number of iterations performed in determining the solution of the transport equations. This parameter is only relevant if ISLVBK is set to 1.
2. TOLSOR: Convergence parameter in establishing a solution to the transport equations. This parameter is only relevant if ISLVBK is set to 1.
3. OMEGA: Over–relaxation parameter used in solving the transport equations. This parameter is only relevant if ISLVBK is set to 1.

- Next line - Keyword PRINT DATA.
- Next line:

1. NOUT: Number of species for which detailed output is required in the main output file.
2. MASSOUT: Flag specifying the units used in the output. If MASSOUT is set to 1 then mass units are output; otherwise concentration units are used. If MASSOUT is set to 2 then total liquid concentrations for each macroelement are also output.

- Next line:

1. (NSOUT(i) i=1,NOUT): GRM species numbers for those species for which detailed output is required in the main output file.

- Next line - Number of species for which output is required external to the main output file (NPRNS).
- Next NPRNS lines:

1. Names of the species for which output is required external to the main output file. Note that these names must be identical to species that appear in the PHREEQE database.

- Next line - Number of elements for which output is required external to the main output file (NPRNE).
- Next NPRNE lines:

1. Names of the elements for which output is required external to the main output file. Note that these names must be identical to elements that appear in the PHREEQE database.

- Next line - Number of cells at which output is required external to the main output file (`NPRNC`).
- Next `NPRNC` lines:
  1. Column number of a cell at which output is required external to the main output file.
  2. Row number of the cell.
- Next line - Number of times at which output is required external to the main output file (`NPRNT`). (The simulation time is divided into `NPRNT` equal intervals, at the end of each of which the output is written.)
- Next line - `IPREXT`. This flag is set to 1 if cumulative quantities of the specified species crossing external boundaries are to be output.

12.7 Changes to grm.dat for PHREEQC option

Use of the PHREEQC chemical speciation module in GRM (YESPC = 1) requires modification of the grm.dat file to include species names rather than index numbers. An example file can be seen in Appendix F.2. The keywords used are listed below with detail of those required for new PHREEQC format (YESPC = 1).

- Line 1 - Keyword TITLE. (same as YESPC =0)
- Line 3 - Keyword RUN TIME OPTIONS. (same as YESPC =0)
- Line 11 - Keyword INTEGER PARAMETERS.(same as YESPC =0)
- Line 16 - Keyword MICROSPECIES NAMES. [32]
- Next line - Keyword MACROSPECIES NAMES.
- Next line - PHREEQC names for each of the NC macrospecies. FORMAT (6A12)
- Next line - Keyword MACROMINERAL NAMES .
- Next line - PHREEQC names for each of the NUMIN macrominerals to be considered in the model. FORMAT (6A12)
- If Surface Complexation is included (SCM =1)
  1. Next line - Keyword SURFACE SITES.
  2. Next NSURF lines - For each surface the names of each surface site (NSCM(NSURF)) FORMAT (6A12). The names of each surface site should use the PHREEQC format [6] where the surface is identified by characters preceding an underscore character and sites are identified by characters following the underscore e.g. Hfo_sOH
- If Ion Exchange is included (YESX =1)
  1. Next line - Keyword EXCHANGE SITES.
  2. Next NIEX lines - The names of each exchange site.
- Next line - Keyword MICROMINERALS IN INITIAL INVENTORY. [33]
- Next line - Keyword MACROMINERALS IN INITIAL INVENTORY.

[32] Radioactive decay currently unsupported in version 4.1 for YESPC = 1, keyword retained for future development
[33] Radioactive decay currently unsupported in version 4.1 for YESPC = 1, keyword retained for future development

- Next MACROM lines:
- Name of each macromineral, these names must be identical to macrominerals that appear in the PHREEQC database.
- Next line - Keyword TIME DATA. (same as YESPC =0)
- Next line - TENDCHEM. (same as YESPC =0)
- Next line - Keyword PHREEQE CONVERGENCE TOLERANCE. (same as YESPC =0)
- Next line - Keyword IMPLICIT TRANSPORT SOLVER DATA. (same as YESPC =0)
- Next line - Keyword PRINT DATA. (same as YESPC =0)

12.8 grm.dcy

This is the decay database for a GRM run. The nuclides are listed under master decay chains, which form the basis for the nuclide subchains used in the code (see Sec. 10.1). At the head of each master chain is a nuclide which cannot be ingrown. Each nuclide in the chain decays to the succeeding one, although decay products of the final nuclide are not followed. An example file can be seen in Appendix G. The format of the file is as follows:

- Line 1 - Number of master decay chains (NCHN).
- Line 2 - Number of nuclides in the first master decay chain (NCOM).
- Line 3 - Name of the first nuclide in master decay chain 1. Note that the nuclide names in grm.dcy are for annotation purposes only, except for the case of radium-226. This nuclide is the parent of radon-222 which can be treated as a soluble gas within GRM (see Sec. 10.2.1). In order that radium-226 can be recognized as a source for this gas through decay its name must be given as one of the following: Ra-226, RA-226, Ra226 or RA226.
- Line 4:
  1. PHREEQE element identification number for first nuclide in master decay chain 1.
  2. Isotope number of first nuclide in master decay chain 1.
  3. Half life of first nuclide in master decay chain 1 (yr).
- Lines 3 and 4 are repeated for each nuclide in the master decay chain: i.e., their format is followed NCOM times.
- Lines 2 to 2 NCOM + 2 are repeated for each master decay chain: i.e., their format is followed NCHN times.

12.9 grm.flw

This data file defines the groundwater flowfield used in a GRM run. It is only required if the flag IMDFLW is set to 0 in the main data file grm.dat; otherwise the flowfield (and grid) are specified using the MODELCAD/MODFLOW packages (via files modf.xxx).

Note that in the following file description, the 'right face' of cell (i, j) is the boundary between cell (i, j) and cell $(i + 1, j)$, while the 'front face' is the boundary between cell (i, j) and cell $(i, j + 1)$. An example flowfield file can be seen in Appendix H. The format of the file is as follows:

- Line 1 - Keyword NUMBER OF FLOWFIELD PERIODS.
- Line 2 - Number of flowfield periods.
- Line 3 - Blank.
- Line 4 - Keyword ENDTIME FOR FLOWFIELD PERIOD.
- Line 5 - The endtime for the current flowfield period (yr). Note that if this is the last flowfield period then the endtime must be greater than or equal to the simulation endtime, as specified in grm.dat.
- Line 6 - Keyword FLOWS THROUGH RIGHT FACES.
- Lines 7 to 6 + NY (NY = number of rows, NX = number of columns):
  1. Flows through the right–hand faces of each of the NX cells on the row ($m^3 day^{-1}$). If the right–hand face of a cell is an external boundary of the modelled domain, then the right face flow should zeroed, with any flow represented using one of the boundary flow types.
- Line 7 + NY - Keyword FLOWS THROUGH FRONT FACES.
- Lines 8 + NY to 7 + 2NY:
  1. Flows through the front faces of each of the NX cells on the row ($m^3 day^{-1}$). If the front face of a cell is an external boundary of the modelled domain, then the front face flow should zeroed, with any flow represented using one of the boundary flow types.
- Line 8 + 2NY - Keyword FLOWS INTO WELL CELLS.

- Lines 9 + 2NY to 8 + 3NY:

  1. External well flows into each of the NX cells on the row (m^3day^{-1}). (Positive values represent flow into the cell; negative values flow out of the cell.) The name 'well cell' in this context has no physical significance. A flow entered here could represent, for example, groundwater flow through an external boundary, or seepage through the base of the modelled region.

- Line 9 + 3NY - Keyword FLOWS INTO RECHARGE CELLS.

- Lines 10 + 3NY to 9 + 4NY:

  1. External recharge flows into each of the NX cells on the row (m^3day^{-1}). (Positive values represent flow into the cell; negative values flow out of the cell.) Recharge flows into the modelled domain are used to represent infiltration from above. Thus, if a cell contains an unsaturated headspace (i.e., if the hydraulic head is less than the elevation of the cell top), then any specified recharge flow may be used to leach microelements from the unsaturated region (see Sec. 3.6).

- Line 10 + 4NY - Keyword FLOWS INTO CONSTANT HEAD CELLS.

- Lines 11 + 4NY to 10 + 5NY:

  1. External constant head flows into each of the NX cells on the row (m^3day^{-1}). (Positive values represent flow into the cell; negative values flow out of the cell.) The name 'constant head cell' in this context has no physical significance. A flow entered here could represent, for example, groundwater flow through an external boundary, or seepage through the base of the modelled region.

- Line 11 + 5NY - Keyword POROSITIES.

- Lines 12 + 5NY to 11 + 6NY:

  1. Porosities of each of the NX cells on the row.

- Line 12 + 6NY - Keyword LONGITUDINAL DISPERSIVITIES.

- Lines 13 + 6NY to 12 + 7NY:

  1. Longitudinal dispersivity values (m) for each of the NX cells on the row.

- Line 13 + 7NY - Keyword TRANSVERSE DISPERSIVITIES.

- Lines 14 + 7NY to 13 + 8NY:
  1. Transverse dispersivity values (m) for each of the NX cells on the row.
- Line 14 + 8NY - Blank.
- If there is more than one flowfield period, then the format of lines 4 to 14 + 8NY (from the ENDTIME FOR FLOWFIELD PERIOD header onwards) is repeated for each flowfield period in turn.

12.10 grm.grd

This data file defines the finite–difference grid used in a GRM run. It is only required if the flag IMDFLW is set to 0 in the main data file grm.dat; otherwise the flowfield (and grid) are specified using the MODELCAD/MODFLOW packages (via files modf.xxx).

Note that in the following file description, the 'right face' of cell (i, j) is the boundary between cell (i, j) and cell $(i + 1, j)$, while the 'front face' is the boundary between cell (i, j) and cell $(i, j + 1)$. An example grid file can be seen in Appendix I. The format of the file is as follows:

- Line 1 - Keyword NUMBER OF COLUMNS.
- Line 2 - Number of columns in the grid (NX).
- Line 3 - Keyword COLUMN GRID LINE CO-ORDINATES.
- Line 4:
  1. The distances of each of the NX right–hand faces from the left–hand face of the first column (m).
- Line 5 - Keyword NUMBER OF ROWS.
- Line 6 - Number of rows in the grid (NY).
- Line 7 - Keyword ROW GRID LINE CO-ORDINATES.
- Line 8:
  1. The distances of each of the NY front faces from the back face of the first row (m).
- Line 9 - Keyword ELEVATION OF CELL TOPS.
- Lines 10 to 9 + NY:
  1. For each of the NX cells on a row, the elevations of the cell tops above some fixed level are given (m).
- Line 10 + NY - Keyword ELEVATION OF CELL BOTTOMS.
- Lines 11 + NY to 10 + 2NY:

1. For each of the NX cells on a row, the elevations of the cell bottoms are given, above the same fixed level as was used to define the elevation of the cell tops (m).

- Line 11 + 2NY - Keyword HYDRAULIC HEADS.
- Lines 12 + 2NY to 11 + 3NY:

1. For each of the NX cells on a row, elevations of the water table are given, above the same fixed level as was used to define the elevation of the cell tops (m). Note that a value of 999.99 can be entered to indicate that the relevant cell is inactive (i.e., is impermeable to flow and does not take part in any calculations).

   A value greater than the elevation of the cell top simply means that the cell is fully saturated. However, if microelements are included in the run then the method of inventory specification used in the code requires that no cells be fully saturated. It would therefore be necessary to define a negligibly small headspace in such fully saturated cells.

12.11 grm.iex

This file contains ion-exchange data in cases where PHREEQE is used for chemical speciation. It is only required if ion-exchange calculations are to be performed in the GRM run (i.e., if the flag YESX is set to 1 in the RUN TIME OPTIONS section of the main data file grm.dat). Section 12.12 gives details of the format when using PHREEQC. An example file can be seen in Appendix J.1. The format of the file is as follows:

- Line 1 - Caption (text unimportant).
- Line 2 - Number of types of ion-exchange sites (NIEX).
- Next NIEX lines:
  1. Name of each ion-exchange type. Note that these names must be identical to names that appear in the PHREEQE database.
- Next line - Caption (text unimportant).
- Next line - Number of bulk (macro) ion-exchange species (NIEXSP).
- Next NIEXSP lines:
  1. Name of each bulk ion-exchange species. Note that these names must be identical to species that appear in the PHREEQE database.
- Next line - Caption (text unimportant).
- Next line - Number of ion-exchange microspecies (NIEXM).
- Next NIEXM lines:
  1. Name of each ion-exchange microspecies. Note that these names must be identical to species that appear in the PHREEQE database.
- For each of the NIEX types of ion-exchange site:
  - Next line - Caption (text unimportant).
  - Next NY lines (NY = number of rows, NX = number of columns):
    1. Cation exchange capacity (CEC) for this type of ion-exchange site in each of the NX cells on the row (mol(eq)l^{-1}).

- Next line - Caption (text unimportant).
- Next line - Number of bulk (macro) ion-exchange species for which output is required (`OUTEXS`).
- Next `OUTEXS` lines:
  1. Name of each bulk ion-exchange species for which output is required. Note that these names must be identical to species that appear in the `PHREEQE` database.
- Next line - Caption (text unimportant).
- Next line - Number of ion-exchange microspecies for which output is required (`OUTEXM`).
- Next `OUTEXM` lines:
  1. Name of each ion-exchange microspecies for which output is required. Note that these names must be identical to species that appear in the `PHREEQE` database.

12.12 grm.iex PHREEQC option

This file contains ion-exchange data when the PHREEQC chemical speciation module is used (YESPC =1). The file is only required if ion-exchange calculations are to be performed in the GRM run (i.e., if the flag YESX is set to 1 in the RUN TIME OPTIONS section of the main data file grm.dat). An example file can be seen in Appendix J.2. The format of the file is as follows:

For each NIEX Ion exchanger listed in grm.dat the following data are required

- Caption (text unimportant).
- Cation exchange capacity (CEC) for this type of ion-exchange site in each of the NX cells on the row (mol(eq)l^{-1}).

12.13 grm.inv

This data file contains information on the initial site inventory for a GRM run. An example file can be seen in Appendix K. The format of the file is as follows:

- Line 1 - Keyword SITE TEMPERATURE.
- Line 2 - Site temperature (°C). Except for the temperature values used in the microbial calculations (see Sec. 12.3), this temperature is a single value used throughout the model.
- For each microelement:
  - For each isotope of the microelement:
    - Next line - Keyword SOLID.
    - Next NY lines (NY = number of rows, NX = number of columns):
      1. Concentrations of this isotope of this microelement in the solid phase in each of the NX cells on the row (moll^{-1} of porewater).
  - Next line - Keyword LIQUID.
  - Next NY lines:
    1. Concentrations of this microelement in the liquid phase in each of the NX cells on the row (moll^{-1} of porewater).
  - For each colloidal type:
    - Next line - Keyword COLLOID.
    - Next NY lines:
      1. Quantities of this microelement sorbed onto this type of colloid in each of the NX cells on the row (kmol).
  - Next line - Keyword ADSORB.
  - Next NY lines:
    1. Quantities of this microelement sorbed onto the geomatrix/waste in each of the NX cells on the row (kmol).
- For each bulk (macro) element (excluding oxygen):
  - Next line - Keyword LIQUID MACROSPECIES.
  - Next NY lines:

1. Concentrations of this macroelement in the liquid phase in each of the NX cells on the row (moll^{-1} of porewater).

- Next line - Keyword LIQUID MACROSPECIES.
- Next NY lines:
  1. Oxygen concentrations in the liquid phase for each of the NX cells on the row (moll^{-1} of porewater).
- If tritium is to be followed in the simulation (i.e., if the flag IFLGH3 is set to 1 in the RUN TIME OPTIONS section of grm.dat) then:
  - Next line - Keyword TRITIUM LIQUID CONCENTRATION.
  - Next NY lines:
    1. Initial concentration of tritium in each of the NX cells on the row (moll^{-1} of porewater)
- For each type of colloid:
  - Next line - Keyword COLLOID.
  - Next NY lines:
    1. Quantities of this type of colloid present in each of the NX cells on the row (kgm^{-3}).
- For each type of colloid:
  - Next line - Keyword RELEASE COEFFICIENT.
  - Next NY lines:
    1. Release coefficients for this type of colloid in each of the NX cells on the row.
- For the headspace gases (Note that inventories must be specified for seven gases and that their order is hardwired as CO_2, CH_4, H_2, N_2, O_2, H_2S and NH_3):
  - Next line - Keyword PARTIAL PRESSURE.
  - Next NY lines
    1. Partial pressures of this gas in each of the NX cells on the row (atm).

- For each type of cellulose (Note that the number of cellulose types is hardwired as 3):
  - Next line - Keyword `CELLULOSE`.
  - Next `NY` lines:
    1. Masses of this type of cellulose in each of the `NX`cells on the row (kg).
- For each type of protein (Note that the number of protein types is hardwired as 3):
  - Next line - Keyword `PROTEINS`.
  - Next `NY` lines:
    1. Masses of this type of protein in each of the `NX` cells on the row (kg).
- For each type of fat (Note that the number of fat types is hardwired as 3):
  - Next line - Keyword `FATS`.
  - Next `NY` lines:
    1. Masses of this type of fat in each of the `NX` cells on the row (kg).
- Next line - Keyword `PH ARRAY`.
- Next `NY` lines:
  1. Initial pH values for each of the `NX` cells on the row.
- Next line - Keyword `PE ARRAY`.
- Next `NY` lines:
  1. Initial pe values for each of the `NX` cells on the row.
- For each micromineral present initially (as specified in the main data file `grm.dat`):
  - Next line - Name of the micromineral as it appears in the `PHREEQE` database (and also in the main data file `grm.dat`). This name should be written as a keyword (i.e., preceeded by an asterisk).
  - Next `NY` lines:
    1. Concentrations of this micromineral in each of the `NX` cells on the row (moll^{-1} of porewater).

- For each macromineral present initially (as specified in the main data file `grm.dat`):
  - Next line - Name of the macromineral as it appears in the `PHREEQE` database (and also in the main data file `grm.dat`). This name should be written as a keyword (i.e., preceeded by an asterisk).
  - Next `NY` lines:
    1. Concentrations of this macromineral in each of the `NX` cells on the row ($moll^{-1}$ of porewater).
- In the case of Surface Complexation (`YESSCM =1`) (Example Appendix K.1) for each surface type present (as specified in the main data file `grm.dat NSURF`):
  1. Next line Caption (Text unimportant)
  2. Next line Specific surface area of the surface type in each of the `NX` cells on the row (m^2g^{-1}).
  3. Next line Caption (Text unimportant)
  4. Next line Mass of the surface type in each of the `NX` cells on the row (g).
  5. For each surface site on the surface type `NSCM`)
     (a) Next line Caption (Text unimportant)
     (b) Next line Site density of surface site in each of the `NX` cells on the row (sites per nm^2).
- Next line - Keyword `DENSITY OF WASTE`.
- Next `NY` lines:
  1. Bulk density of the waste/soil matrix in each of the `NX` cells on the row (kgm^{-3}).

12.14 grm.kds

This data file contains sorption information. It may take either of two forms (see Sec. 5), depending on whether species–dependent or pH-dependent sorption has been specified for the microelements (the choice is made using the flag `IFKD` in the main data file `grm.dat`). The means of specification of microspecies sorption data is identical in both cases. For each species or element, six sets of sorption data are provided. Each cell is then assigned a sorption type index to identify which of these data sets should be used within the cell.

As described in Sec. 3.6, there are two models available in the `GRM` code for the release of microspecies from the unsaturated region. Although release coefficients appear in the present input file, they do so for historical reasons only. The actual values used are taken from the `grm.rel` input file. Thus, the entries in `grm.kds` are needed for formatting reasons only, their values being irrelevant.

12.14.1 Species–dependent form

This form of `grm.kds` is used if the flag `IFKD` is set to 0 in the main data file `grm.dat`. For macrospecies, a default set of sorption data is read. This may be followed by data for individual macrospecies which overrides the default set.

The situation for microspecies is similar, except that default data may also be set at the elemental level. Thus, all microspecies are initially assigned the default microspecies data. Should default microelement data be specified then the microspecies defaults are overridden for all species of the microelement. Finally, should individual microspecies data be specified then both the microspecies and microelement defaults are overridden. The scheme allows for an economic definition of sorption data when individual microspecies sorption characteristics may be unknown.

An example file can be seen in Appendix L.1. The format of the file is as follows:

- Line 1 - Keyword `SORPTION TYPE IN EACH CELL.`
- Next `NY` lines (`NY` = number of rows, `NX` = number of columns):
  1. Sorption type indices for each of the `NX` cells on the row.
- Next line - Blank.
- Next line - Keyword `DEFAULT MACROSPECIES SORPTION DATA.`
- Next 6 lines (The i th of these lines corresponds to sorption type i.):

1. Dummy number to aid user (this is not used within the code).
2. Distribution coefficient (K_d) for sorption onto the geomatrix/waste (m^3kg^{-1}).
3. Rate constant for sorption onto the geomatrix/waste (s^{-1}).
4. Release coefficient from the unsaturated region (not used – see above).
5. Distribution coefficient (K_d) for sorption onto colloidal type 1 (m^3kg^{-1}).
6. Rate constant for sorption onto colloidal type 1 (s^{-1}).
7. Distribution coefficient (K_d) for sorption onto colloidal type 2 (m^3kg^{-1}).
8. Rate constant for sorption onto colloidal type 2 (s^{-1}).
9. Distribution coefficient (K_d) for sorption onto colloidal type 3 (m^3kg^{-1}).
10. Rate constant for sorption onto colloidal type 3 (s^{-1}).

- Next line - Blank.
- Next line - Keyword `INDIVIDUAL MACROSPECIES SORPTION DATA`.
- For each macrospecies for which individual sorption data is to be specified:
  - Next line - Number of the species as it appears in the `PHREEQE` database. The number 0 is used to indicate that there is no more individual macrospecies data to be read.
  - The next 6 lines give sorption data in the same format as the default data above.
- Next line - Blank.
- Next line - Keyword `DEFAULT MICROSPECIES SORPTION DATA`.
- The next 6 lines give default microspecies data as above for default macrospecies.
- Next line - Blank.
- Next line - Keyword `DEFAULT MICROELEMENT SORPTION DATA`.
- For each microelement for which individual sorption data is to be specified:
  - Next line - Number of the microelement as it appears in the `PHREEQE` database. The number 0 is used to indicate that there is no more individual microelement data to be read.

– The next 6 lines give sorption data in the same format as the default data above.

- Next line - Blank.
- Next line - Keyword `INDIVIDUAL MICROSPECIES SORPTION DATA`.
- For each microspecies for which individual sorption data is to be specified:
  - Next line - Number of the microspecies (e.g., 30101). The number 0 is used to indicate that there is no more individual microspecies data to be read.
  - The next 6 lines give sorption data in the same format as the default data above.

12.14.2 pH-dependent form

This form of `grm.kds` is used if the flag `IFKD` is set to 1 in the main data file `grm.dat`. For macrospecies, a default set of sorption data is read. This may be followed by data for individual macrospecies which overrides the default set.

Microelement data is specified in a similar way, except that the K_d's for sorption onto the geomatrix/waste are allowed to vary with pH according to the empirical rise function of Eqs. 60 and 61.

An example file can be seen in Appendix L.2. The format of the file is as follows:

- Line 1 - Keyword `SORPTION TYPE IN EACH CELL`.
- Next `NY` lines (`NY` = number of rows, `NX` = number of columns):
  1. Sorption type indices for each of the `NX` cells on the row.
- Next line - Blank.
- Next line - Keyword `DEFAULT MACROSPECIES SORPTION DATA`.
- Next 6 lines (The i th of these lines corresponds to sorption type i.):
  1. Dummy number to aid user (this is not used within the code).
  2. Distribution coefficient (K_d) for sorption onto the geomatrix/waste (m^3kg^{-1}).
  3. Rate constant for sorption onto the geomatrix/waste (s^{-1}).
  4. Release coefficient from the unsaturated region (not used – see above).
  5. Distribution coefficient (K_d) for sorption onto colloidal type 1 (m^3kg^{-1}).

6. Rate constant for sorption onto colloidal type 1 (s^{-1}).
7. Distribution coefficient (K_d) for sorption onto colloidal type 2 (m^3kg^{-1}).
8. Rate constant for sorption onto colloidal type 2 (s^{-1}).
9. Distribution coefficient (K_d) for sorption onto colloidal type 3 (m^3kg^{-1}).
10. Rate constant for sorption onto colloidal type 3 (s^{-1}).

- Next line - Blank.
- Next line - Keyword `INDIVIDUAL MACROSPECIES SORPTION DATA`.
- For each macrospecies for which individual sorption data is to be specified:
  - Next line - Number of the species as it appears in the PHREEQE database. The number 0 is used to indicate that there is no more individual macrospecies data to be read.
  - The next 6 lines give sorption data in the same format as the default data above.
- Next line - Blank.
- Next line - Keyword `DEFAULT MICROELEMENT SORPTION DATA`.
- Next 6 lines (The i th of these lines corresponds to sorption type i.):
  1. Dummy number to aid user (this is not used within the code).
  2. Parameter a in Eq. 61 for the distribution coefficient describing sorption onto the geomatrix/waste.
  3. Parameter b in Eq. 61 for the distribution coefficient describing sorption onto the geomatrix/waste.
  4. Parameter c in Eq. 61 for the distribution coefficient describing sorption onto the geomatrix/waste.
  5. Parameter d in Eq. 61 for the distribution coefficient describing sorption onto the geomatrix/waste.
  6. Rate constant for sorption onto the geomatrix/waste (s^{-1}).
  7. Release coefficient from the unsaturated region (not used – see above).
  8. Distribution coefficient (K_d) for sorption onto colloidal type 1 (m^3kg^{-1}).
  9. Rate constant for sorption onto colloidal type 1 (s^{-1}).

10. Distribution coefficient (K_d) for sorption onto colloidal type 2 (m^3kg^{-1}).
11. Rate constant for sorption onto colloidal type 2 (s^{-1}).
12. Distribution coefficient (K_d) for sorption onto colloidal type 3 (m^3kg^{-1}).
13. Rate constant for sorption onto colloidal type 3 (s^{-1}).

- Next line - Blank.
- Next line - Keyword `INDIVIDUAL MICROELEMENT SORPTION DATA`.
- For each microelement for which individual sorption data is to be specified:
  - Next line - number of the microelement as it appears in the `PHREEQE` database. The number 0 is used to indicate that there is no more individual microelement data to be read.
  - The next 6 lines give sorption data in the same format as the default microelement data above.

12.15 grm.kin

This file contains the data required for the kinetic mineral dissolution calculations of Sec. 4.8. It is only required if there are kinetic minerals included in the run: i.e., if `NKIN` has a value greater than zero in the `INTEGER PARAMETERS` section of the main data file `grm.dat`. An example file can be seen in Appendix M. The format of the file is as follows:

- For each of the `NKIN` kinetic minerals:
  1. Name of the kinetic mineral. Note that these names must be identical to minerals that appear in the `PHREEQE` database.
  2. The constant k_1 from Eq. 57.
  3. The constant k_2 from Eq. 57.
  4. The constant k_3 from Eq. 57.

Note that the above items are format sensitive. Item 1 is a string of 12 characters and items 2 to 4 are read in with the FORTRAN format `D12.4`.

12.16 grm.phr

This file contains thermodynamic data, which are required in many GRM calculations, notably those of chemical speciation. The file should be written in the standard PHREEQE database format [5], with the addition of microspecies. It should not be necessary, however, for the GRM user to generate the file by hand. A utility program is available which enables PHREEQE database files to be generated automatically.

The program is called PICKER and is described in Ref. [62]. It selects from a quality–assured thermodynamic database the data relevant to the reactions involving the specified elements or master species. At present the NIREX database is used [63]. The NEA12 database [10] has now also become available and an additional option for its use will be introduced into PICKER in the near future. The program is executed using the following command:

```
/home/trivedi/bin/picker
```

This command file could be copied into the user's /home/bin/ directory for ease of use. If the command is typed without any arguments then the following on-screen message will be displayed:

```
picker:  [-s|m] [-I<file>] [-O<file>]

options
s Use standard database (default)
m use modified database
I <file> Input file
O <file> Output file
```

The various flags are described below.

-s Selects the standard NIREX database as received by BNFL from AEA Technology at Harwell. This database was described in detail by Cross et al [63].

-m Selects a modified version of the NIREX database in which the redox states of some of the bulk chemicals have been separated.

-I Followed by the name of a file, this flag specifies an input file name. The default name is `pick.inp`.

-O Followed by the name of a file, this flag specifies an output file name. The default name is `pick.out`.

The input file lists the species for which data is required. The format of this file is straightforward. The first n lines contain the names of the n macroelements to be considered. These should be followed by two blank lines and then m further lines which list the names of the m microelements to be considered. One more blank line is required, followed by a line which simply contains the word `END`.

If the input file were saved as `test.inp`, for instance, and one wished to run `PICKER` using the modified database, then the command would be:

```
picker -m -I test.inp -O test.out
```

This would produce the file `test.out` in the current directory, provided that such a file did not previously exist. The output file is suitable for direct input into the `GRM` code (after being renamed grm.phr).

Following generation of `grm.phr` the user should consider which mineral phases would realistically be formed under the conditions modelled. The `GRM` code precipitates the most stable mineral phases included in `grm.phr`. However, such phases may not actually form in practice owing to kinetic constraints.

12.17 grm.rel

This input file is the database for nuclide release from the unsaturated region within a GRM run. The file is required whenever microelements are included in a run. Release is performed on an elemental level: i.e., the rate of release of a particular microelement is the same for all isotopes and species of that element. There are two release models available within the GRM (see Sec. 3.6), a simple linear model, and a more mechanistic treatment. The model to be used for each radioelement in each finite–difference cell is selected by flags in the current file.

An example grm.rel file can be seen in Appendix N. The format of the file is as follows:

- Line 1 - Number of microelements in the release database (NMREL). Note that this should be equal to the number of microelements in the simulation, as specified in the main data file grm.dat.
- The following format is repeated NMREL times:
  - Next line:
    1. The PHREEQE identification number for this microelement.
    2. Effective solubility limit for use with the mechanistic model (moll^{-1}) (this is the parameter c_s of Sec. 3.6).
    3. Distribution coefficient for use with the mechanistic model (m^3kg^{-1}) (this is the parameter K_d of Sec. 3.6).
    4. Release coefficient for use with the simple linear model (this is the dimensionless parameter r of Sec. 3.6).
  - Next NY lines (NY = number of rows, NX = number of columns):
    1. Release model flags for each of the NX cells on the row. Values of 0 indicate that the simple linear model is to be used in the cell; values of 1 are used to select the more mechanistic model.

12.18 modf.cbb, modf.cbw, modf.crc and modf.grd

These files contain the data that describes the finite–difference grid and the flowfield in cases where such data is generated using the MODFLOW [18] and MODELCAD [19] packages. The use of these codes is signalled to GRM by setting the flag IMDFLW to 1 in the RUN TIME OPTIONS section of the main data file grm.dat.

MODELCAD is used to generate the finite–difference grid and various boundary condition and cell property data. After a grid has been generated by MODELCAD, a file with extension .grd is produced. This is an ASCII formatted DOS file and contains the following data:

- The number of rows, columns (and layers) in the grid;
- The x- and y-coordinates of the grid lines (the position of the first grid line in each case is not given since these are assumed to lie along the axes);
- An array is given which contains information about each of the cells. This can be used to identify any inactive cells in the grid; and,
- Various zones can be defined for each of the following properties:
  1. Conductivity;
  2. Storage;
  3. Specific yield;
  4. *Porosity*;
  5. Leakance;
  6. *Top elevation*;
  7. *Bottom elevation*;
  8. Evapotranspiration; and,
  9. *Dispersivity*,

with those in italics being relevant in a GRM model. The zoning system of MODELCAD allows for variation in the aquifer properties across the grid. For instance, it is possible to slope the aquifer by defining zones of differing top and bottom elevations.

Once the grid and associated data have been determined then the groundwater flow field can be calculated (again externally to the GRM) by using the MODFLOW [18] package. This results in the output of volumetric flows in each cell to an unformatted file with

suffix `.cbb`. This file should be renamed `modf.cbb` and is read by the GRM during the data initialisation stage.

The boundary conditions within GRM fall into two categories:

1. groundwater flowfield boundary conditions; and,
2. chemical speciation boundary conditions.

Conditions in the second of these categories are specified within file `grm.bcs` (see Sec. 12.2). Conditions falling into the first of the above categories can be set within MODFLOW and the corresponding output files are simply picked up by GRM during its input stage. MODFLOW (and GRM) allow for three possible types of flowfield boundary condition (constant head, wells and recharge). If one or more constant head cells have been specified, then an extra block of data appears in the `.cbb` file, which contains the boundary flows within such cells. If one or more well cells are specified, then an unformatted `.cbw` file is created. Although the file describes flows at every cell in the model, only those designated as well cells will have non-zero flow values. Recharge cells are handled similarly to well cells, the appropriate MODFLOW file having the suffix `.crc`.

Note that time–dependent flows are not catered for when using MODFLOW input files. Thus, the specified flowfield and any specified flow boundary conditions are operative for the entire simulation period.

13 Output Files

A list of all the possible GRM output files is given in Table 4 below. All but two of the output files are optional, and their creation depends on various flags and print parameters which are set in the main input file grm.dat. The second column of the table indicates the relevant flags and print parameters for each file.

Name	Optional?
grm.out	No
gen.out	No
grm.bal	Yes (IMSBAL=1)
chain.out	Yes (ICHAIN=1 and NME>0)
chtot.out	Yes (ICHAIN=1 and NME>0)
extsp.*	Yes (IPREXT=1 and NPRNS>0)
extspw.*	Yes (IPREXT=1 and NPRNS>0)
extspr.*	Yes (IPREXT=1 and NPRNS>0)
extsph.*	Yes (IPREXT=1 and NPRNS>0)
extel.*	Yes (IPREXT=1 and NPRNE>0)
extelw.*	Yes (IPREXT=1 and NPRNE>0)
extelr.*	Yes (IPREXT=1 and NPRNE>0)
extelh.*	Yes (IPREXT=1 and NPRNE>0)
macel.c*	Yes (NPRNE>0 and NPRNC>0)
spec.c*	Yes (NPRNS>0 and NPRNC>0)
out.c	Yes (NPRNE>0 and NPRNC>0)
macel.t*	Yes (NPRNE>0 and NPRNT>0)
micel.t*	Yes (NPRNE>0 and NPRNT>0)
spec.t*	Yes (NPRNS>0 and NPRNT>0)
phreeqc.out	Yes (YESPC= 1 and YESPPC= 1)
RESTART	Yes (see Sec. 11.3)
RESTART1	Yes (see Sec. 11.3)

Table 4: GRM output files.

The contents of each output file are intended to be self-explanatory. However, for completeness, the various files are summarised in the following sections.

13.1 grm.out

This is the main GRM output file. If an error occurs during execution then a brief description of the problem is written at the foot of this file (see Sec. 11.5). All being well, however, the file will first echo some of the input data and then give a description of the state of the system at the print out times defined in the main data file `grm.dat`. The description includes the current inventories of microbial[34], chemical and nuclear components.

The user should note that `grm.out` can be a large file and so it is often convenient to interrogate it with tools such as UNIX awk scripts.

The contents of the file are briefly described below, in the order in which they appear. Some of the items may or may not appear in the output file, according to whether the appropriate flag has been set (for example, the tritium inventory would not be written if `IFLGH3` were set to 0, so that tritium was not followed in the run). Units for the various quantities are given as part of headers within the file, and may depend on the print parameters selected in the input files:

- A header, which includes the current version number of the code and the date on which it was run;
- The title of the run;
- A summary of the options selected within the `RUN TIME OPTIONS` section of the main input file `grm.dat`;
- The numbers of macroelements, microelements and species included in the run;
- The number of microelements that are involved in bulk chemistry calculations;
- The numbers of macrominerals and microminerals that are included in the initial inventory;
- The number of types of colloid;
- A list of any microelements that are involved in bulk chemistry calculations;
- A summary of the finite–difference grid data, consisting of the following items,
  - The number of rows and columns;
  - The number of inactive cells;

[34] See the note on references to ISA in Sec. 8.3.

  - The grid co-ordinates; and,
  - The positions of the cell tops and bottoms, relative to some fixed level.
- A summary of the flowfield data, consisting of the following items for each flowfield period,
  - The flows through the right–hand faces and the front faces of each cell;
  - The external flows (recharge, well and constant head) for each cell;
  - The cell porosities; and,
  - The longitudinal and transverse dispersivities.
- Lists of the transported macrospecies and microspecies;
- Lists of the macrominerals and microminerals that are included in the initial inventory;
- Lists of the SCM and ion-exchange names for `PHREEQC`;
- A list of all nuclide subchains used in the code;
- At each print time the following data is written,
  - The bulk element concentrations in each cell;
  - The tritium liquid concentrations in each cell;
  - The Rn-222 liquid concentrations in each cell;
  - The nitrogen liquid concentrations in each cell;
  - The methane liquid concentrations in each cell;
  - The liquid, colloidal and adsorbed amounts of species for which detailed output has been requested (by means of the `grm.dat` file);
  - The amounts of bulk and micro ion-exchange species in each cell;
  - The total amount of waste material;
  - The total mass of all colloidal material;
  - The amounts of each colloidal type;
  - If microbial calculations are performed then the following data is given,

* The amounts of each type of cellulose in the unsaturated and in the saturated zones;
* The amounts of each type of protein in the unsaturated and in the saturated zones;
* The amounts of peptides;
* The amounts of glycerol;
* The amounts of ISA;
* The amounts of FFA;
* The amounts of each type of fat in the unsaturated and in the saturated zones;
* The amounts of glucose;
* The amounts of inert biomass;
* The populations of non-alkaliphilic aerobic bacteria;
* The populations of non-alkaliphilic H_2-consuming denitrifying bacteria;
* The populations of non-alkaliphilic organotrophic denitrifying bacteria;
* The populations of non-alkaliphilic H_2-consuming sulphate–reducing bacteria;
* The populations of non-alkaliphilic organotrophic sulphate–reducing bacteria;
* The populations of non-alkaliphilic organotrophic glucose acidogen bacteria;
* The populations of non-alkaliphilic organotrophic peptide acidogen bacteria;
* The populations of non-alkaliphilic organotrophic glycerol acidogen bacteria;
* The populations of non-alkaliphilic acetogenic bacteria;
* The populations of non-alkaliphilic H_2-consuming methanogenic bacteria;
* The populations of non-alkaliphilic organotrophic methanogenic bacteria;
* The populations of non-alkaliphilic H_2-consuming iron–reducing bacteria;
* The populations of non-alkaliphilic organotrophic iron–reducing bacteria;
* The populations of non-alkaliphilic oxygen reoxidising bacteria;
* The populations of non-alkaliphilic nitrate reoxidising bacteria;
* The populations of alkaliphilic aerobic bacteria;
* The populations of alkaliphilic H_2-consuming denitrifying bacteria;
* The populations of alkaliphilic organotrophic denitrifying bacteria;

  * The populations of alkaliphilic H_2-consuming sulphate–reducing bacteria;
  * The populations of alkaliphilic organotrophic sulphate–reducing bacteria;
  * The populations of alkaliphilic organotrophic glucose acidogen bacteria;
  * The populations of alkaliphilic organotrophic ISA acidogen bacteria;
  * The populations of alkaliphilic organotrophic peptide acidogen bacteria;
  * The populations of alkaliphilic organotrophic glycerol acidogen bacteria;
  * The populations of alkaliphilic acetogenic bacteria;
  * The populations of alkaliphilic H_2-consuming methanogenic bacteria;
  * The populations of alkaliphilic organotrophic methanogenic bacteria;
  * The populations of alkaliphilic H_2-consuming iron–reducing bacteria;
  * The populations of alkaliphilic organotrophic iron–reducing bacteria;
  * The populations of alkaliphilic oxygen reoxidising bacteria;
  * The populations of alkaliphilic nitrate reoxidising bacteria; and,
  * The total amount of biomass in each cell.
- The amounts of macrominerals and microminerals in each cell;
- The amounts in each cell of each microelement in solution, as colloids, as adsorbed material and as minerals;
- The amounts in each cell of each microelement in the unsaturated and in the saturated zones;
- The total amounts of each microelement in each cell;
- The isotope fractions in each cell for each microelement in the unsaturated and in the saturated zone;
- The amounts of Fe_2O_3 and Fe_3O_4 in the unsaturated zone;
- The amounts in each cell of uncorroded iron in the unsaturated and in the saturated zone;
- The partial pressures in each cell of each type of headspace gas, including water vapour, tritiated water vapour and radon;
- The total gas pressures in each cell in the headspace;
- The total amounts of each type of gas evolved in each cell by that time, including data for tritiated water vapour and radon;

- The current rate of evolution in each cell of each type of gas, including data for tritiated water vapour and radon;
- The active fractions in each cell of carbon–containing macrospecies and macrominerals;
- The active fractions in each cell of vented carbon dioxide and methane;
- The active fractions in each cell of inert biomass;
- The total amounts of each bulk element;
- The total amounts of each type of gas evolved;
- The total amount of carbon dioxide drawn in from the atmosphere;
- The total amounts of each type of protein and of each type of cellulose;
- The total amounts of peptides, glycerol, ISA and FFA;
- The total amount of biomass;
- The total amounts of recycled and of inert biomass;
- The total amount of each macromineral;
- The total amount of carbon 14 in each macromineral;
- The total amount of carbon 14 in each carbon–containing macrospecies;
- The total amounts of carbon 14 in CO_3^{2-}, CH_3COO^- and $RCOO^-$;
- The total amount of carbon 14 in each type of protein, fat and cellulose;
- The total amounts of carbon 14 in glycerol, ISA, FFA, glucose, peptides, inert biomass and headspace and vented carbon dioxide and methane;
- The total amounts of carbon 14 lost to the external environment through well, recharge and constant head flows;
- The total amount of sorbed carbon 14; and,
- The total amount of carbon 14 in the saturated zone.

• The following information is also written at every pH print time, as defined through the main data file `grm.dat`,

- The pH and the pe in each cell; and,
- The dominant redox couples currently being used to calculate the pe of each cell.

13.2 grm.bal

This file gives detailed information about the evolution of microelement inventories with time. Its main purpose is to provide a mass balance check on the GRM calculations. The file provides data at each of the print out times defined in the main data file grm.dat.

The contents of the file are briefly described below, in the order in which they appear:

- The title of the run; and,
- At each print time, the current time is written (yr), along with the following data for each microelement:
  - The total initial inventory (kmol);
  - The total amount that has entered the model domain from the external environment (kmol);
  - The total amount that has left the model domain and entered the external environment (kmol);
  - The current total inventory (kmol);
  - The change in the microelement inventory due to radioactive decay and ingrowth (kmol); and,
  - Any imbalance between the above data is written as an absolute value (kmol) and as a percentage of the initial inventory plus the total entered from the external environment.

13.3 chain.out

This file gives information for the decay subchains described in Sec. 10.1. It provides data on the boundary flows and on the concentrations of all components of all subchains at each of the print out times defined in the main data file `grm.dat`. The data in this file may be used to calculate nuclide fluxes leaving the modelled domain.

The contents of the file are briefly described below, in the order in which they appear:

- The numbers of rows and columns in the finite–difference grid;
- A list of all nuclide subchains used in the code; and,
- At each print time, both the current time and the mid-time between current and previous times are written (yr), along with the following data:
  - The well, recharge and constant head flows (lyr^{-1}) for each active cell (Only if the flow is out of the model. Inward flows are given as zero); and,
  - The average concentrations ($moll^{-1}$ of porewater) in each active cell since the previous output time. These are given for each component of each subchain. Average concentrations are used to avoid missing peaks occuring between print times

13.4 chtot.out

This file gives information for the decay subchains described in Sec. 10.1. It is exactly analogous to `chain.out`, except that the concentrations refer to total concentrations within a cell (both saturated and unsaturated regions) rather than simply the liquid phase. All data is described relative to the print out times defined in the main data file `grm.dat`. This data may be useful in human intrusion calculations.

The contents of the file are briefly described below, in the order in which they appear:

- The numbers of rows and columns in the finite–difference grid;
- A list of all nuclide subchains used in the code; and,
- At each print time, the current time is written (yr) (again the mid-time between current and previous printouts is also given) , along with the average concentrations ($moll^{-1}$ of total cell volume) since the previous output time. These are given for each component of each subchain.

13.5 Other Output Files

gen.out

This file is produced for debugging purposes only, and is generally empty.

RESTART

This file contains time data for use with the restart facility (see Sec. 11.3).

RESTART1

This file contains all other data that is required for use with the restart facility (see Sec. 11.3). It gives the contents of many internal code variables at the time when the restart was made.

extsp.*

Gives a time profile of the cumulative losses for specified species (kmol) from specified cells, summed over each of the 3 boundary flow types. A seperate file is produced for each cell, the file extension denoting the cell as follows: If the model contains NX columns and NY rows, the file extension for cell (i,j) is i + (j-1) * NX.

extspw.*

Gives a time profile of the cumulative losses for specified species (kmol) from specified cells, due to associated well flows. A seperate file is produced for each cell, the file extension denoting the cell as follows: If the model contains NX columns and NY rows, the file extension for cell (i,j) is i + (j-1) * NX.

extspr.*

Gives a time profile of the cumulative losses for specified species (kmol) from specified cells, due to associated recharge flows. A seperate file is produced for each cell, the file extension denoting the cell as follows: If the model contains NX columns and NY rows, the file extension for cell (i,j) is i + (j-1) * NX.

extsph.*

Gives a time profile of the cumulative losses for specified species (kmol) from specified cells, due to associated constant head flows. A seperate file is produced for each cell, the file extension denoting the cell as follows: If the model contains NX columns and NY rows, the file extension for cell (i,j) is i + (j-1) * NX.

extel.*

Gives a time profile of the cumulative losses for specified elements (kmol) from specified cells, summed over each of the 3 boundary flow types. A seperate file is produced for each cell, the file extension denoting the cell as follows: If the model contains NX columns and NY rows, the file extension for cell (i,j) is i + (j-1) * NX.

extelw.*

Gives a time profile of the cumulative losses for specified elements (kmol) from specified cells, due to associated well flows. A seperate file is produced for each cell, the file extension denoting the cell as follows: If the model contains NX columns and NY rows, the file extension for cell (i,j) is i + (j-1) * NX.

extelr.*

Gives a time profile of the cumulative losses for specified elements (kmol) from specified cells, due to associated recharge flows. A seperate file is produced for each cell, the file extension denoting the cell as follows: If the model contains NX columns and NY rows, the file extension for cell (i,j) is i + (j-1) * NX.

extelh.*

Gives a time profile of the cumulative losses for specified elements (kmol) from specified cells, due to associated constant head flows. A seperate file is produced for each cell, the file extension denoting the cell as follows: If the model contains NX columns and NY rows, the file extension for cell (i,j) is i + (j-1) * NX.

macel.c*

Gives time profiles of macroelement liquid concentrations (moll^{-1} of porewater) in a particular cell. The file extension denotes the cell.

spec.c*

Gives time profiles of species concentrations (moll^{-1} of porewater) in a particular cell. For each specified species, concentrations are given in the order:

- liquid;
- sorbed to colloids; and,
- sorbed to geomatrix.

The file extension denotes the cell.

***out.c* (e.g. Uout.c* for uranium, PUout.c* for plutonium etc...):**

Gives time profiles of microelement concentrations (moll^{-1} of porewater) in a particular cell, for a particular microelement. Concentrations are given in the order:

- liquid;
- sorbed to colloids;
- sorbed to geomatrix;
- mineral;
- unsaturated zone;
- saturated zone;
- total;
- isotope fractions in the saturated zone; and,
- isotope fractions in the unsaturated zone.

The file extension denotes the cell.

macel.t*

Gives spatial profiles of macroelement liquid concentrations ($moll^{-1}$ of porewater) at a specified time. The file extension denotes the time.

spec.t*

Gives spatial profiles of species liquid concentrations ($moll^{-1}$ of porewater) at a specified time. The file extension denotes the time.

micel.t*

Gives spatial profiles of microelement concentrations ($moll^{-1}$ of porewater) at a specified time. For each specified microelement, concentrations are given in the order:

- liquid;
- sorbed to geomatrix; and,
- mineral.

The file extension denotes the time.

phreeqc.out

When YESPPC=1, the PHREEQC module outputs the standard output for PHREEQC speciation calculations for each cell, at each speciation timestep. This file is used for setting up runs to investigate the behaviour of the PHREEQC module. The file is not normally produced in runs with more than a few timesteps.

References

[1] S. Kwong., *Program Programmer's Guide for the code GRM, Version 4.1*, BNFL Report 00/EN0127/7/3 (2001).

[2] J. Graham, G. Towler, P. Abraitis, and J. Small. *Program Verification Report for GRM, Version 4.1, Issue 2*, BNFL Report 00/EN0127/7/2 (2003).

[3] M. W. Kozac and N. E. Olague, *Updated Recommendations for Low-Level Waste Performance Assessment*, Proc. Symp. Waste Manage., Waste Management 93, pp371-376 (1993).

[4] A. C. Campbell, F. W. Ross, and T. J. Nicholson, *Low-Level Radioactive Waste Performance Assessment Technical Issues and Branch Technical Position*, Proc. Symp. Waste Manage., Waste Management 93, pp367-370 (1993).

[5] D. L. Parkhurst, D. C. Thorstenson and L. N. Plummer `PHREEQE` — *A Computer Program for Geochemical Calculations*, U.S. Geological Survey (1980).

[6] D. L. Parkhurst *User's Guide to PHREEQC - a Computer Program for Speciation, Reaction - Path, Advective - Transport. And Inverse Geochemical Calculations.* Water - Resources Investigations Report 95 - 4227, U.S. Geological Survey, Lakewood, Coloradao, USA (1995).

[7] J. I. Drever, *The geochemistry of natural waters: surface and groundwater environments.* 3rd ed. Prentice Hall (p.25) pp.436. (1997).

[8] J. W. Zhang and G. H. Nancollas. *Mechanisms of growth and dissolution of sparingly soluble salts.* In M.F. Hochella, Jr., and A.F. White (Eds.),Mineral Water Interface Geochemistry (pp. 365 -395). Reviews in Mineralogy Vol. 23. Washington, D.C. Mineralogical Society of America.

[9] W. Stumm and J. J. Morgan, *Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters*, Third Edition, John Wiley (1996).

[10] *HATCHES (Harwell/Nirex Thermodynamic Database for Chemical Equilibrium Studies) Database*, published by AEA Technology Environment. Derived from Nuclear Energy Agency, OECD (Paris)as NEA Version NEA12_R2 (9 November 1999).

[11] M. El-Fadel, A. N. Findikakis and J. O. Leckie, *A Numerical Model for Methane Production in Managed Sanitary Landfills*, Waste Man. Res. **7**, pp31-42 (1989).

[12] J. S. Kindred and M. Celia, *Contaminant Transport and Biodegradation 2. Conceptual Model and Test Simulations*, Water Resour. Res. **25**, pp1149-1159 (1989)

[13] P. L. McCarty and F. E. Mosey, *Modelling of Anaerobic Digestion Processes (A Discussion of Concepts)*, Water Sci. Technol. **24** No.8, pp17-33 (1991).

[14] J. Bear and A. Verruijt, *Modelling Groundwater Flow and Pollution*, D. Reidel Publishing Company (1987).

[15] W. Kinzelbach and W. Schafer, *Numerical Modelling of Natural and Enhanced Denitrification Processes in Aquifers*, Water Resour. Res. **27** No.6, pp1123-1135 (1991).

[16] G. T. Yeh and V. S. Tripathi, *A Critical Evaluation of Recent Developments in Hydrogeochemical Transport Models of Reactive Multichemical Components*, Water Resour. Res. **25** No.1, pp93-108 (1989).

[17] D. H. Smalley, R. Plant and N. S. Cooper, *Program User's Guide for the MONDRIAN Groundwater Flow Code GRWOLF, Version 4.2.2, Issue 2*, BNFL Report EN0055/06/22 (2002).

[18] M. G. McDonald and A. W. Harbaugh, *A Modular Three-Dimensional Finite-Difference Groundwater Flow Model*, U.S. Geological Survey Report 83-875 (1988).

[19] J. O. Rumbaugh III, *ModelCad*^{386} *Volume 1, Documentation*, Geraghty and Miller Inc. (1988).

[20] A. A. Anderson, J. C. Tannehill and R. H. Pletcher, *Computational Fluid Mechanics and Heat Transfer*, Hemisphere Publishing Corporation, New York (1984).

[21] C. I. Voss, *A Finite-Element Simulation Model for Saturated-Unsaturated, Fluid-Density-Dependent Groundwater Flow with Energy Transport or Chemically-Reactive Single-Species Solute Transport*, U.S. Geological Survey (1984).

[22] D. H. Smalley, P. N. Humphreys, T. Johnstone and M. Randall, *A Two Parameter Release Model in Low Level Waste Disposal Sites*, Computational Methods in Water Resources XII, Vol. 1, Computational Mechanics Publications (1998).

[23] A. B. Kersting, D. W. Efurd, D. L. Finnegan, D. J. Rokop, D. K. Smith and J. L. Thompson, *Migration of Plutonium in Groundwater at the Nevada Test Site*, Nature **397** No.7 p56-59 (1999).

[24] *Suspended Particles, Colloids and Radionuclide Transport*, NAGRA Bulletin 1/93 (1993).

[25] G. G. Eichholz, B. Wahlig, G. F. Powell and T. F. Craft, *Subsurface Migration of Radioactive Waste Materials by Particulate Transport*, Nucl. Tech. **58** pp511 (1982).

[26] R. W. Buddemeier and J. R. Hunt, *Transport of Colloidal Contaminants in Groundwater Radionuclide Migration at the Nevada Test Site*, Appl. Geochemistry **3** pp535-548 (1988).

[27] Kristallin-1 Safety Assessment Report, NAGRA Technical Report 93-22 (1994).

[28] C. W. Liu and T. N. Narasimhan, *Redox–Controlled Multiple Species Reactive Chemical Transport: 1. Model Development*, Water Resour. Res. **25** No.5, pp869-882 (1989).

[29] B. Noble, *Numerical Methods I: Iteration, Programming and Algebraic Equations*, Oliver and Boyd (1964).

[30] *Ionic Strength Report: CEC Report*, Nuclear Science and Technology EUR 12975 EN.

[31] U. R. Berner, *Evolution of Porewater Chemistry during Degradation of Cement in a Radioactive Waste Repository Environment*, Waste Management **12** pp201 (1992).

[32] D. G. Bennet, D. Read, M. Atkins and F. P. Glasser, *A Thermodynamic Model for Blended Cements: II Cement Hydrate Phases; Thermodynamic Values and Modelling Studies*, J. Nucl. Materials **190** pp315 (1992).

[33] C. A. J. Appelo and D. Postma, *Geochemistry, Groundwater and Pollution*, A. A. Bulkema, Rotterdam, Netherlands (1993).

[34] A. E. Neilsen, *Electrolyte Crystal Growth Mechanisms*, Journal of Crystal Growth **67** pp289-310 (1984).

[35] H. C. Helgeson, W. M. Murphy and P. Aagaard, *Thermodynamics and Kinetic Constraints on Reaction Rates Among Minerals and Aqueous solutions II: Rate Constants, Effective Surface Area and the Hydrolysis of Feldspars*, Geochimica et Cosmochimica Acta **48** pp2405-2432 (1984).

[36] B. Grambow, *A General Rate Equation for Nuclear Glass Corrosion*, Material Research Society Symposia Proc. **44** pp15-24 (1995).

[37] C. I. Steefal and P. Van-Cappellen, *A New Kinetic Approach to Modelling Water–Rock Interactions*, Geochimica et Cosmochimica Acta **54** pp2657-2677 (1990).

[38] D. J. Noy, PRECIP*: A Program for Coupled Groundwater Flow and Precipitation/Dissolution Reaction*, NSS/R275 or BDS report WE/90/38C.

[39] P. Zuidema et al., *Gas Formation and Release in Repositories for Low and Intermediate Level Wastes: An Issue of Potentially Decisive Importance*, Proc. 1989 Paris Symp. on Safety Assessments of Radioactive Waste Repositories, pp581-594, OECD, Paris (1990).

[40] D. E. Metcalfe and G. J. Farquar, *Modelling Gas Migration Through Unsaturated Soils from Waste Disposal Sites*, Water, Air and Soil Pollution **32** pp247-259 (1987).

[41] *Handbook of Chemistry and Physics*, CRC Press (1982).

[42] J. Simunek and D. L. Suarez, *Two Dimensional Transport Model for Variably Saturated Porous Media with Major Ion Transport*, Water Resour. Res. **30** No.4, pp 1115-1133 (1994).

[43] M-S Yim et al., *Modelling of Gas–Phase Radionuclide Release from Low–Level Waste Disposal Facilities*, Migration 93 (1993).

[44] A. H. Lu and Matusek, *Transport Through a Trench Cover of Gaseous Tritiated Compounds from Buried Nuclear Wastes*, IAEA-SM-232/60 (1978).

[45] R. V. Nicholson, J. A. Cherry and E. J. Reardon, *Migration of Contaminants in Groundwater at a Landfill: A Case Study*, J. Hydrology **63** pp131-176 (1983).

[46] A. J. B. Zehnder and W. Stumm, *Geochemistry and Biogeochemistry of Anaerobic Habitats*, in *Biology of Anaerobic Microorganisms*, edited by A. J. B. Zehnder, John Wiley and Sons, New York, pp1-38 (1988).

[47] J. R. Postgate, *The Sulphate Reducing Bacteria*, 2 nd Edition, Cambridge University Press (1984).

[48] J. S. Small, *Drigg Far Field Geochemical Interpretation*, BNFL Technical Note TN0039 (1999).

[49] W. D. Guenzi and W. E. Beard, *Volatile Fatty Acids in a Redox–Controlled Cattle Manure Slurry*, J. Environ. Qual. **10** No.4 pp427-482 (1981).

[50] R. G. Bell, *Studies on the Decomposition of Organic Matter in Flooded Soil*, Soil Biology **1** pp105-116 (1969).

[51] P. J. Agg, A. D. Moreton, J. H. Rees, W. R. Rodwell and P. J. Sumner, *Gas Generation and Migration*, NSARP Reference Document, Nirex Report No. 313 (1992).

[52] P. J. Agg and P. J. Sumner, *Modelling of Gas Generation in Radioactive Waste Repositories*, p189-199 of *Gas Generation and Release from Radioactive Waste Repositories*, OECD (1992).

[53] B. E. Jones, W. D. Grant, N. C. Collins and W. E. Mwatha, *Alkaliphiles: Diversity and Identification*, in *Bacterial Diversity and Systematics*, edited by F. G. Priest et al., Plenum Press, New York, pp195-230 (1994).

[54] P. L. McCarty, *Stoichiometry of Biological Reactions*, Progress in Water Technology **7** pp157-172 (1975).

[55] S. G. Pavlostathis and E. Giraldo–Gomez, *Kinetics of Anaerobic Treatment*, Water Sci. Tech. **24** No.8 pp35-59 (1991).

[56] M. J. McInery, *Anaerobic Hydrolysis and Fermentation of Fats and Proteins*, Chp. 8 of *Biology of Anaerobic Microorganisms*, edited by A. J. B. Zehnder, John Wiley and Sons (1998).

[57] M. Henze, C. P. L. Grady, W. Gujer, G. V. R. Marias and T. Matsuo, *Activated Sludge Model No. 1*, Task Group on Mathematical Modelling for Design and Operation of Biological Wastewater Treatment, IAWQ (1986).

[58] K. Sommer and J. C. G. Ottow, *Denitrifikation mit Cellulose als einzigem Wasserstoffdonator*, J. Basic. Microbiolo. **25** No.1 pp77-80 (1985).

[59] E. G. Beauchamp, J. T. Trevors and J. W. Paul, *Carbon Sources for Bacterial Denitrification*, Advance in Soil Science **10** pp113-142 (1989).

[60] A. W. Lawrence and P. L. McCarty, *Kinetics of Methane Fermentation in Anaerobic Treatment*, J. Wat. Pol. Con. Fed. **41** No.2 (1969).

[61] H. Bateman, *The Solution of a System of Differential Equations Occurring in the Theory of Radioactive Transformations*, Proc. Cambridge Phil. Soc. **15** pp423 (1910).

[62] G. Towler and A. E. Bond, *Supporting software and data used in the Drigg Technical Programme*, BNFL Technical Note DTP 01/02 TN100 (2003).

[63] J. E. Cross, F. T. Ewart and C. J. Tweed, *Thermochemical Modelling with Application to Nuclear Waste Processing and Disposal*, UKAEA Report AERE-R 12324, Harwell Laboratory (June 1987).

[64] A. Young, *Simulating Methanogenesis in Landfills*, pp62-86 of *Landfill Microbiology: R&D Workshop*, edited by P. Lawson and Y. R. Alston, ETSU Harwell (1989).

A Input File grm.act

```
*CELLULOSE TYPE 1
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
*CELLULOSE TYPE 2
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
*CELLULOSE TYPE 3
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9 1.5E-9
*PROTEIN TYPE 1
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
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0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
*PROTEIN TYPE 2
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*PROTEIN TYPE 3
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0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
*FAT TYPE 1
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
```

```
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
*FAT TYPE 2
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
*FAT TYPE 3
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
*NUMBER OF MACROELEMENTS TO BE READ
1
*PHREEQE NUMBER AND ACTIVE FRACTION
11
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000

*NUMBER OF MICROSPECIES TO BE READ
0
*MICROSPECIES NUMBER AND ACTIVE FRACTION

*NUMBER OF MACROMINERALS TO BE READ
1
*MINERAL NAME AND ACTIVE FRACTION
CALCITE
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
```

B Input File grm.bcs

B.1 Time–independent form

```
*GLOBAL BOUNDARY CONCENTRATIONS     ( mol/l for species, g/l for colloids )
*Cnst.hd.  Well           Recharge
0.0      5.290E-03       0.0             4 (PHREEQE ID No.)     Ca(Species name)
0.0      7.986E-03       0.0             5                      Na+
0.0      9.964E-03       0.0             6                      Cl-
0.0      9.158E-06       0.0             7                      CO3-2
0.0      6.164E-06       0.0             8                      K+
0.0      4.720E-03       0.0             9                      ClO4
0.0      4.056E-03       0.0             34                     HCO3-
0.0      2.459E-04       0.0             36                     H2CO3
0.0      2.185E-08       0.0             37                     Ca(OH)+
0.0 0.0 0.0 colloid 1
0.0 0.0 0.0 colloid 2
0.0 0.0 0.0 colloid 3

*GLOBAL BOUNDARY PH
12.5 7.5 12.5

*GLOBAL BOUNDARY PE
2.4 2.40 2.40

*LOCAL BOUNDARY CONCENTRATIONS
0 Ca

0 Na

4 CL-
5 1 0 1.34e-3

5 2 2 1.34e-3

5 3 1 1.34e-3

5 4 2 1.34e-3

0 CO3-2
```

```
0 K+

0 ClO4

0 HCO3-

0 H2CO3

0 Ca(OH)+

0 colloid 1

2 colloid 2
3 1 1 1.97e-3

4 2 1 2.34e-3

0 colloid 3

*LOCAL BOUNDARY PH, PE
0
```

B.2 Time–dependent form

```
*IBCLOG  (Data read in logarithmic form if = 1)
0
*WELL CELLS
*GLOBAL WELL CONCENTRATIONS:  (mol/l for species, g/l for colloids)
4 Ca
1
0. 150. 4.43e-4 0. 4.43e-4
5 Mg
1
0. 150. 1.87e-4 0. 1.87e-4
30002 U
0.15 U-234
0.85 U-235
0. 150. 1.2e-10 0. 1.2e-10
-
*GLOBAL WELL PH
1
0. 150. 7.48 0. 7.48
*GLOBAL WELL PE
1
0. 150. 2.40 0. 2.40
*LOCAL WELL CONCENTRATIONS
4  CA
2 (NC)
1 5 4 (I,J,NT)
0.000000 10.000000 3.858378e-02 0.000000e+00 3.858378e-02
10.000000 50.000000 3.858378e-02 3.192867e-03 1.662985e-01
50.000000 100.000000 1.662985e-01 -6.851670e-04 1.320401e-01
100.000000 150.000000 1.320401e-01 -1.481810e-03 5.794961e-02
1 7 4 (I,J,NT)
0.000000 10.000000 3.880743e-04 0.000000e+00 3.880743e-04
10.000000 50.000000 3.880743e-04 7.575514e-06 6.910949e-04
50.000000 100.000000 6.910949e-04 -9.059822e-06 2.381038e-04
100.000000 150.000000 2.381038e-04 -1.423028e-06 1.669524e-04
-
*LOCAL WELL PH
0
*LOCAL WELL PE
0
```

```
*RECHARGE CELLS
*GLOBAL RECHARGE CONCENTRATIONS:  (mol/l for species, g/l for colloids)
-
*GLOBAL RECHARGE PH
0
*GLOBAL RECHARGE PE
0
*LOCAL RECHARGE CONCENTRATIONS
-
*LOCAL RECHARGE PH
0
*LOCAL RECHARGE PE
0

*CONSTANT HEAD CELLS
*GLOBAL CONSTANT HEAD CONCENTRATIONS:  (mol/l for species, g/l for colloids)
-
*GLOBAL CONSTANT HEAD PH
0
*GLOBAL CONSTANT HEAD PE
0
*LOCAL CONSTANT HEAD CONCENTRATIONS
-
*LOCAL CONSTANT HEAD PH
0
*LOCAL CONSTANT HEAD PE
0
```

C Input File grm.bug

```
*CARBOXYLIC ACID CARBON NUMBERS
3.3125          NBAR - carbon number of average VFA
7.0             MBAR - carbon number of average FFA
*CELLULOSE HYDROLYSIS DATA
2.93061e-11     V(1,1) - neutral, aerobic, type 1
2.93061e-11     V(1,2) - neutral, anaerobic, type 1
7.32651e-12     V(3,1) - neutral, aerobic, type 2
7.32651e-12     V(2,2) - neutral, anaerobic, type 2
2.93061e-11     V(3,1) - neutral, aerobic, type 3
2.93061e-11     V(3,2) - neutral, anaerobic, type 3
7.0             OPH1 - optimum pH for neutral hydrolysis
1.33            PF1 - pH factor for neutral hydrolysis
4.25            PCO - pH cut-off for neutral hydrolysis
2.93061e-11     VISA(1,1) - alkaline, aerobic, type 1
2.93061e-11     VISA(1,2) - alkaline, anaerobic, type 1
7.32651e-12     VISA(3,1) - alkaline, aerobic, type 2
7.32651e-12     VISA(2,2) - alkaline, anaerobic, type 2
2.93061e-11     VISA(3,1) - alkaline, aerobic, type 3
2.93061e-11     VISA(3,2) - alkaline, anaerobic, type 3
11.0            OPHISA - optimum pH of alkaline hydrolysis
1.33            PF1ISA - pH factor for alkaline hydrolysis
4.25            PCOISA - pH cut-off for alkaline hydrolysis
1.0             SW3 -  excess glucose recycled back into cellulose if > 1
0.0             VCU(1) - unsaturated hydrolysis rate for type 1 cellulose
0.0             VCU(2) - unsaturated hydrolysis rate for type 2 cellulose
0.0             VCU(3) - unsaturated hydrolysis rate for type 3 cellulose
*PROTEIN HYDROLYSIS DATA
2.93061e-11     VP(1,1) - aerobic type 1 protein hydrolysis
2.93061e-11     VP(1,2) - anaerobic type 1 protein hydrolysis
7.32651e-12     VP(2,1) - aerobic type 2 protein hydrolysis
7.32651e-12     VP(2,2) - anaerobic type 2 protein hydrolysis
2.93061e-11     VP(3,1) - aerobic type 3 protein hydrolysis
2.93061e-11     VP(3,2) - anaerobic type 3 protein hydrolysis
7.0             OPH10 - optimum pH for protein hydrolysis
1.33            PF10 - pH factor
4.25            PCP - pH cut-off
0.0             VPU(1) - unsaturated hydrolysis rate for type 1 proteins
0.0             VPU(2) - unsaturated hydrolysis rate for type 2 proteins
0.0             VPU(3) - unsaturated hydrolysis rate for type 3 proteins
```

```
*FAT HYDROLYSIS DATA
2.93061e-11     VF(1,1) - aerobic type 1 fat hydrolysis
2.93061e-11     VF(1,2) - anaerobic type 1 fat hydrolysis
7.32651e-12     VF(2,1) - aerobic type 2 fat hydrolysis
7.32651e-12     VF(2,2) - anaerobic type 2 fat hydrolysis
2.93061e-11     VF(3,1) - aerobic type 3 fat hydrolysis
2.93061e-11     VF(3,2) - anaerobic type 3 fat hydrolysis
7.0             OPH11 - optimum pH for fat hydrolysis
1.33            PF11 - pH factor
4.25            PCF - pH cut-off
0.5             FRATIO - ratio of glycerol to FFAs from fat hodrolysis
0.0             VFU(1) - unsaturated hydrolysis rate for type 1 fats
0.0             VFU(2) - unsaturated hydrolysis rate for type 2 fats
0.0             VFU(3) - unsaturated hydrolysis rate for type 3 fats
*AEROBIC BACTERIA DATA
1e-8            XB(1) - concentration of neutraphiles
1.0             AERMAX(1) - maximum substrate utilisation rate for neutraphiles
0.0             AERKM(1) - half-saturation constant for neutraphiles
0.58            YB(1) - neutraphilc microbe yield coeff
4.8e-6          KB(1) - neutraphilic microbe specific death rate
7.0             OPH2(1) - optimum pH for neutraphiles
1.33            PF2(1) - pH factor for neutraphiles
1e-8            XB(2) - concentration of alkalophiles
1.0             AERMAX(2) - maximum substrate utilisation rate for alkaliphiles
0.0             AERKM(2) - half-saturation constant for alkaliphiles
0.58            YB(2) - alkaliphilic microbe yield
4.8e-6          KB(2) - alkaliphilic microbe specific death rate
9.5             OPH2(2) - optimum pH for alkaliphiles
1.0             PF2(2) - pH factor for alkaliphiles
-0.1            SW1 - instantaneous aerobic degradation if <= 0.0
*DENITRIFYING BACTERIA DATA
1e-3            xno(1) - conc. of non-alkaliphilic organic denitrifiers
7e-4            dfomax(1) - maximum substrate utilisation rate for denitrifiers
0.0             dfokm(1) - half-saturation constant for denitrifiers
0.37            yno(1) - microbe yield coeff
5.3e-7          kno(1) - microbe specific death rate
1e-8            xno(2) - conc. of alkaliphilic organic denitrifiers
7e-4            dfomax(2)  - maximum substrate utilisation rate for alk. denitrifiers
0.0             dfokm(2) - half-saturation constant for alk. denitrifiers
0.37            yno(2) - microbe yield coeff
5.3e-7          kno(2) - microbe specific death rate
```

```
-1.0            sw2 glucose consumed if <= 0.0
1e-3            xna(1) - conc. of non-alkaliphilic autotrophic denits.
7.0e-7          dfamax(1) - maximum substrate utilisation rate for aut. denits
0.0             dfakm(1) -  half-saturation constant for aut. denits.
1.25            yna(1) - microbe yield coeff
5.3e-7          kna(1) - microbe specific death rate
1e-8            xna(2) - conc. of alkaliphilic autotrophic denitrifiers
7.0e-7          dfamax(2) - maximum substrate utilisation rate for alk. aut. denits.
0.0             dfakm(2) -  half-saturation constant for alk. aut. denits.
1.25            yna(2) - microbe yield coeff
5.3e-7          kna(2) - microbe specific death rate
7.0             oph3(1) - optimum pH for non-alkaliphilic denitrifiers
1.33            pf3(1) - pH factor for non-alkaliphilic denitrifiers
9.5             oph3(2) - optimum pH for alkaliphilic denitrifiers
1.33            pf3(2) - pH factor for alkaliphilic denitrifiers
*GLUCOSE ACIDOGEN DATA
0.0             XA3(1) - conc. of glucose fermenters
5.0e-4          acdmax(1) - max. rate of glucose fermentation
0.0             acdkm(1)  - glucose fermentation half-saturation const
0.17            ya1(1)    - microbe yield from glucose fermentation
6e-7            ka1(1)    - glucose acidogen death rate
7.0             oph5(1) - optimum pH for non-alkal. glucose ferment.
1.33            pf5(1)    - pH factor in glucose fermentation
1e-8            xa1(2) - conc. of alkaliphilic glucose acidogens
0.0             XA3(2) - conc. of alkaliphilic ISA acidogens
5.0e-4          acdmax(2) - max. rate of glucose fermentation
0.0             acdkm(2)  - glucose fermentation half-saturation const
0.17            ya1(2)    - microbe yield from glucose fermentation
6e-7            ka1(2)    - glucose acidogen death rate
9.5             oph5(2) - optimum pH for alkaliphilic glucose ferment.
1.33            pf5(2)    - pH factor in glucose fermentation
*PEPTIDE ACIDOGEN DATA
1e-3            xap(1) - conc. of non-alkaliphilic peptide acidogens
5.0e-4          acpmax(1) - max. rate of peptide fermentation
0.0             acdkp(1)  - peptide fermentation half-saturation const
0.17            yap(1)    - microbe yield from peptide fermentation
6e-7            kap(1)    - peptide acidogen death rate
7.0             oph12(1) - optimum pH for non-alkal. peptide ferment.
1.33            pf12(1)   - pH factor in peptide fermentation
1e-8            xap(2) - conc. of alkaliphilic peptide acidogens
5.0e-4          acpmax(2) - max. rate of peptide fermentation
```

```
0.0             acdkp(2)  - peptide fermentation half-saturation const
0.17            yap(2)    - microbe yield from peptide fermentation
6e-7            kap(2)    - peptide acidogen death rate
9.5             oph12(2) - optimum pH for alkaliphilic peptide ferment.
1.33            pf12(2)   - pH factor in peptide fermentation
2.0             fpept  - molar ratio of acetic to VFA in peptide ferm.
*GLYCEROL ACIDOGEN DATA
1e-3            xag(1) - conc. of non-alkaliphilic glycerol acidogens
5.0e-4          acgmax(1) - max. rate of glycerol fermentation
0.0             acdkg(1)  - glycerol fermentation half-saturation const.
0.17            yag(1)    - microbe yield from glycerol fermentation
6e-7            kag(1)    - glycerol acidogen death rate
7.0             oph13(1) - optimum pH for non-alkal. glycerol ferment.
1.33            pf13(1)   - pH factor in glycerol fermentation
1e-8            xag(2) - conc. of alkaliphilic glycerol acidogens
5.0e-4          acgmax(2) - max. rate of glycerol fermentation
0.0             acdkg(2)  - glycerol fermentation half-saturation const.
0.17            yag(2)    - microbe yield from glycerol fermentation
6e-7            kag(2)    - glycerol acidogen death rate
9.5             oph13(2) - optimum pH for alkaliphilic glyc. ferment.
1.33            pf13(2)   - pH factor in glycerol fermentation
2.0             fglyc  - molar ratio of acetic to VFA in glycerol ferm.
*IRON REDUCING BACTERIA DATA
1e-3            xfo(1) - conc. of non-alkaliphilic organic iron reducs.
1e-4            fromax(1) - max. rate of substrate utilisation
0.0             frokm(1) - half-saturation const.
0.25            yfo(1) - microbe yield coeff
6.0e-7          kfo(1) - microbe death rate
1e-8            xfo(2) - conc. of alkaliphilic organic iron reducers
1e-4            fromax(2) - max. rate of substrate utilisation
0.0             frokm(2) - half-saturation const.
0.25            yfo(2) - microbe yield coeff
6.0e-7          kfo(2) - microbe death rate
1e-3            xfa(1) - conc. of non-alkaliphilic auto. iron reducs.
1.9e-6          framax(1) - max. rate of substrate utilisation
0.0             frakm(1) - half-saturation const.
1.25            yfa(1) - microbe yield coeff
1.6e-7          kfa(1) - microbe death rate
1e-8            xfa(2) - conc. of alkaliphilic auto. iron reducers
1.9e-6          framax(2) - max. rate of substrate utilisation
0.0             frakm(2) - half-saturation const.
```

```
1.25            yfa(2) - microbe yield coeff
1.6e-7          kfa(2) - microbe death rate
7.0             oph4(1) - optimum pH for non-alkaliphilic iron reducs.
1.33            pf4(1) - pH factor for non-alkaliphilic iron reducs.
9.5             oph4(2) - optimum pH for alkaliphilic iron reducers
1.33            pf4(2) - pH factor for alkaliphilic iron reducs.
*SULPHATE REDUCING BACTERIA DATA
1e-3            xso(1) - conc. of non-alkaliphilic org. sulph. reducs.
8.e-5           somax(1) - max. rate of substrate utilisation
0.0             sokm(1) - half-saturation const.
0.06            yso(1) - microbe yield coeff
3.5e-7          kso(1) - microbe death rate
1e-8            xso(2) - conc. of alkaliphilic org. sulph. reducers
8.e-5           somax(2) - max. rate of substrate utilisation
0.0             sokm(2) - half-saturation const.
0.06            yso(2) - microbe yield coeff
3.5e-7          kso(2) - microbe death rate
1e-3            xsa(1) - conc. of non-alkaliphilic auto. sulph. reducs.
1.9e-6          samax(1) - max. rate of substrate utilisation
0.0             sakm(1) - half-saturation const.
1.25            ysa(1) - microbe yield coeff
1.6e-7          ksa(1) - microbe death rate
1e-8            xsa(2) - conc. of alkaliphilic auto. sulph. reducers
1.9e-6          samax(2) - max. rate of substrate utilisation
0.0             sakm(2) - half-saturation const.
1.25            ysa(2) - microbe yield coeff
1.6e-7          ksa(2) - microbe death rate
7.0             oph6(1) - optimum pH for non-alkal. sulph. reducs.
1.33            pf6(1) - pH factor for non-alkaliphilic sulph. reducs.
9.5             oph6(2) - optimum pH for alkaliphilic sulph. reducs.
1.33            pf6(2) - pH factor for alkaliphilic sulph. reducs.
*ACETOGENIC BACTERIA DATA
1e-3            xa2(1) - conc. of non-alkaliphilic acetogens
5.2e-5          actmax(1) - max. rate of substrate utilisation
0.0             actkm(1) - half-saturation const.
0.085           ya2(1) - microbe yield coeff
5.9e-7          ka2(1) - microbe death rate
7.0             oph7(1) - optimum pH for non-alkaliphilic acetogens
4.0             pf7(1) - pH factor for non-alkaliphilic acetogens
1e-8            xa2(2) - conc. of alkaliphilic acetogens
5.2e-5          actmax(2) - max. rate of substrate utilisation
```

```
0.0             actkm(2) - half-saturation const.
0.085           ya2(2) - microbe yield coeff
5.9e-7          ka2(2) - microbe death rate
9.5             oph7(2) - optimum pH for alkaliphilic acetogens
4.0             pf7(2) - pH factor for alkaliphilic acetogens
*METHANOGENIC BACTERIA DATA
1.e-3           xm1(1) - conc. of non-alkal. organo. methanogens
1.6e-4          em1max(1) - max. rate of substrate utilisation
0.019           ym1(1) - microbe yield coeff
2.9e-7          km1(1) - microbe death rate
7.0             oph8(1) - optimum pH for non-alkal. org. methanogens
4.0             pf8(1) - pH factor for non-alkal. org. methanogens
1.e-8           xm1(2) - conc. of alkaliphilic organo. methanogens
1.6e-4          em1max(2) - max. rate of substrate utilisation
0.019           ym1(2) - microbe yield coeff
2.9e-7          km1(2) - microbe death rate
9.5             oph8(2) - optimum pH for alkal. org. methanogens
4.0             pf8(2) - pH factor for alkal. org. methanogens
1.e-3           xm2(1) - conc. of non-alkal. auto. methanogens
1e-4            em2max(1) - max. rate of substrate utilisation
0.34            ym2(1) - microbe yield coeff
1.6e-7          km2(1) - microbe death rate
7.0             oph9(1) - optimum pH for non-alkal. auto. methanogens
4.0             pf9(1) - pH factor for non-alkal. auto. methanogens
1.e-8           xm2(2) - conc. of alkaliphilic auto. methanogens
1e-4            em2max(2) - max. rate of substrate utilisation
0.34            ym2(2) - microbe yield coeff
1.6e-7          km2(2) - microbe death rate
9.5             oph9(2) - optimum pH for alkal. auto. methanogens
4.0             pf9(2) - pH factor for alkal. auto. methanogens
*OXYGEN REOXIDISER DATA
1e-8            xr(1) - concentration of non-alkaliphilic reoxidisers
1.0             roxmax(1) - max. rate of substrate utilisation
0.0             roxkm(1) - half saturation constant
0.58            yr(1) - microbe yield coeff
4.8e-6          kr(1) - microbe death rate
7.0             ophrox(1) - optimum pH for non-alkaliphic reoxidisers
1.33            pfrox(1) - pH factor for non-alkaliphic reoxidisers
3.45E-7         maintenance factor for non-alkaliphic reoxidisers
1e-8            xr(2) - concentration of alkaliphilic reoxidisers
1.0             roxmax(2) - max. rate of substrate utilisation
```

```
0.0             roxkm(2) - half saturation constant
0.58            yr(2) - microbe yield coeff
4.8e-6          kr(2) - microbe death rate
9.5             ophrox(2) - optimum pH for alkaliphilic reoxidisers
1.33            pfrox(2) - pH factor for alkaliphic reoxidisers
3.45E-7         maintenance factor for alkaliphic reoxidisers
-1.0            sw4 instantaneous reoxidation if <= 0.0
*NITRATE REOXIDISER DATA
1e-8            xrn(1) - concentration of non-alk. nitrate reoxidisers
1.0             rnxmax(1) - max. rate of substrate utilisation
0.0             rnxkm(1) - half saturation constant
0.58            yrn(1) - microbe yield coeff
4.8e-6          krn(1) - microbe death rate
7.0             ophrnx(1) - optimum pH for non-alk. nitrate reoxidisers
1.33            pfrnx(1) - pH factor for non-alkaliphic reoxidisers
3.45E-7         maintenance factor for non-alkaliphic reoxidisers
1e-8            xrn(2) - concentration of alk. nitrate reoxidisers
1.0             rnxmax(2) - max. rate of substrate utilisation
0.0             rnxkm(2) - half saturation constant
0.58            yrn(2) - microbe yield coeff
4.8e-6          krn(2) - microbe death rate
9.5             ophrnx(2) - optimum pH for alkaliphilic reoxidisers
1.33            pfrnx(2) - pH factor for alkaliphic reoxidisers
3.45E-7         maintenance factor for alkaliphic reoxidisers
-1.0            sw5 instantaneous reoxidation if <= 0.0
*AMMONIA REOXIDISER DATA
1e-8            xrn(1) - concentration of non-alk. ammonia reoxidisers
1.0             rnxmax(1) - max. rate of substrate utilisation
0.0             rnxkm(1) - half saturation constant
0.58            yrn(1) - microbe yield coeff
4.8e-6          krn(1) - microbe death rate
7.0             ophrnx(1) - optimum pH for non-alk. ammonia reoxidisers
1.33            pfrnx(1) - pH factor for non-alkaliphic reoxidisers
3.45E-7         maintenance factor for non-alkaliphic reoxidisers
1e-8            xrn(2) - concentration of alk. ammonia reoxidisers
1.0             rnxmax(2) - max. rate of substrate utilisation
0.0             rnxkm(2) - half saturation constant
0.58            yrn(2) - microbe yield coeff
4.8e-6          krn(2) - microbe death rate
9.5             ophrnx(2) - optimum pH for alkaliphilic reoxidisers
1.33            pfrnx(2) - pH factor for alkaliphic reoxidisers
```

```
3.45E-7          maintenance factor for alkaliphic reoxidisers
-1.0             sw5 instantaneous reoxidation if <= 0.0
*TIME DATA
100  TENDBUG
2                NO. OF DTBUG
1455.    1.261e5 ENDTIME THIS DTBUG  DTBUG 1
10000.   3.153e5 ENDTIME THIS DTBUG  DTBUG 2
*OTHER DATA
1e-20            MINIMUM AMOUNT OF A BUG PRESENT
0.0493           IONIC STRENGTH
0.8              DEGRADABLE FRACTION OF DEAD BIOMASS
7.42             MOLAR RATIO OF FFAs TO PROTEIN IN RECYCLED BIOMASS
2.0              MOLAR RATIO OF ACETIC/VFAs IN FFA DECOMP. PRODUCTS
0.0              CONCENTRATION OF EXISTING INERT MATERIAL (g/m3).
-2.96            LOG DISSOCIATION CONSTANT FOR O2 GAS INTO LIQUID
-1.844           DH FOR O2 GAS USED IN VAN'T HOFF CALC
-3.26            LOG DISSOCIATION CONSTANT FOR N2 GAS INTO LIQUID
-1.358           DH FOR N2 GAS USED IN VAN'T HOFF CALC
-2.86            LOG DISSOCIATION CONSTANT FOR CH4 GAS INTO LIQUID
-3.373           DH FOR CH4 GAS USED IN VAN'T HOFF CALC
0.790184         FRACTION OF AR+N2 GASES IN AIR
0.2095           FRACTION OF O2 GASES IN AIR
0.000316         FRACTION OF CO2 GASES IN AIR
0                SWITCH FOR DISSOLUTION OF O2 (O2 SOLUBLE IF =1)
0                SWITCH FOR DISSOLUTION OF N2 (N2 SOLUBLE IF =1)
0                SWITCH FOR DISSOLUTION OF CH4 (CH4 SOLUBLE IF =1)
1                SWITCH FOR TEMP-DEPENDENCE OF HYDROLYSIS (ON IF =1)
1                SWITCH FOR TEMP-DEPENDENCE OF METHANOGENESIS (ON IF =1)
1                SWITCH FOR USE OF O2 IN PE CALCULATION (USED IF =1)
1                SWITCH FOR USE OF NO3 IN PE CALCULATION (USED IF =1)
1.0              PERMEABILITY OF HEADSPACE CAP (m3/s/atm)
*TEMPERATURE ARRAY
15. 15. 15. 15. 15. 15. 15. 15. 15. 15.
*MOISTURE CONTENT IN SATURATED ZONE
1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0
*MOISTURE CONTENT IN UNSATURATED ZONE
0.  0.  0.  0.  0.  0.  0.  0.  0.  0.
*SLUMPING FLAGS
0 0 0 0 0 0 0 0 0 0
*SLUMPING DENSITIES
1800. 1800. 1800.                CELLULOSE (1-3)
```

```
1900. 1900. 1900.          PROTEINS (1-3)
1700. 1730. 1720.          FATS (1-3)
1600.                      MINERALS
1500.                      IRON
1400.                      FE2O3
1300.                      FE3O4
```

D Input File grm.cem

```
CEMENT DISSOLUTION DATA (example file)
2
NAMES OF CEMENT MINERALS
Bill
Fred
Ca/Si RATIOS
0.1 0.2 0.5 0.6
0.2 0.3 0.1 0.8
CSH CONCENTRATIONS (mol/l of porewater)
1.0E-04 4.0E-04 7.0E-04 1.0E-04
6.0E-04 1.0E-04 9.0E-04 3.0E-04
```

E Input File grm.cor

```
mild steel density [kg/m3]
7800
initial saturated aerobic corrosion rate [m/s]
7.927e-13
initial saturated anaerobic corrosion rate [m/s]
9.513e-14
initial unsaturated aerobic corrosion rate [m/s]
5.708e-13
initial unsaturated anaerobic corrosion rate [m/s]
9.513e-14
aerobic minimum corrosion rate [m/s]
9.513e-14
anaerobic minimum corrosion rate [m/s]
9.513e-14
passivity rate [yr]
0.15
molecular weight of iron [g/mol]
55.847
average initial sphere radius [m]
0.0012
average initial plate thickness [m]
0.0044
average rod radius [m]
1.0
average rod length [m]
1.0
weight of spheres for each cell
 0.0000E+00 0.3259E+07 0.0000E+00
 0.3231E+07 0.3259E+07 0.1867E+07
weight of plates for each cell
 0.0000E+00 0.1660E+07 0.3439E+07
 0.3439E+07 0.3988E+07 0.4022E+07
weight of rods for each cell
 0.2304E+07 0.0000E+00 0.2701E+07
 0.2701E+07 0.2701E+07 0.2701E+07
MOLES of FE2O3 for each cell
0.0 0.0 0.0
0.0 0.0 0.0
MOLES of FE3O4 for each cell
```

```
0.0 0.0 0.0
0.0 0.0 0.0
proportion of Fe(OH)3 forming colloids under suitable conditions COLPER
0.0
pH threshold for formation of passivity layer
9.0
```

F Input File grm.dat

F.1 PHREEQE option YESPC =0

```
*TITLE
Run with chemistry
*RUN TIME OPTIONS
1       1       1       0       YESCHM  YESBUG  YESCOR  YESX
0       1       0       0       IMDFLW  ITDBCS  IFKD    ISLVBK
1       0       0       0       YESPE   PEO2    PEHELD  IHSRDX
1       1       1       1       ISORCP  IH2NRM  ISPWRN  IFE2CR
1       0       0       1       IREOX   INLIM   ICEM    IMSBAL
1       1       1       0       ICHAIN  C14SWT  IFLGH3  IFLGRN
1       0       0       0       IDROP   YESPC   YESSCM  YESPPC
*INTEGER PARAMETERS
12      22                      NE      NC
3 10 14 2                       NME     (NMSP(i) i=1,NME)
0       0                       NEMIC   (NBLKMIC(i) i=1,NEMIC)
4       0       0       3       MACROM  MICROM  NKIN    NCOL
*MICROSPECIES ID NUMBERS (with isotope flags)
30201 1 0 0 0 0 0
30202 1 0 0 0 0 0
30203 1 0 0 0 0 0
31001 1 1 1 0 0 0
31002 1 1 1 0 0 0
31401 1 0 0 0 0 0
*MACROELEMENT PHREEQE ID NUMBERS
 8  9 10 11 12 13 14 15 16 17 18 19
*MACROSPECIES PHREEQE ID NUMBERS
 8  9 10 11 12 13 14 15 16 17 18 19 32 34 36 37 38 39 42 113 117 120
*SPECIES SPECIFIC PHREEQE NUMBERS
11 34 36 130                    CO3-2   HCO3-   H2CO3   CO2GAS
17 117                          CH3COO- CH3COOH
15 39 38 131 12                 HS-     H2S(AQ) S-2     H2SGAS  SO4-2
32 13 10                        O2(AQ)  NO3-  CL-
18 120                          RCOO-   RCOOH
14 8                            FE3+    FE2+
16 42 112 114 43 132            NH4+    NH3(AQ) NH4CL   NH4NO3  NH4SO4- NH3GAS
*MICROMINERALS IN INITIAL INVENTORY
*MACROMINERALS IN INITIAL INVENTORY
CALCITE
```

```
FE(OH)3A
CEMSIO
CEMCSH
*TIME DATA
10000.0          ENDTIME
1                NO. OF DTO
10000.0 0.2      ENDTIME THIS DTO        DTO #1
10000.1   TENDCHEM
3                NO. OF DTSPEC
950.0   0.2      ENDTIME THIS DTSPEC     DTSPEC #1
1950.0  0.2      ENDTIME THIS DTSPEC     DTSPEC #2
10000.0 1.0      ENDTIME THIS DTSPEC     DTSPEC #3
3                NO. OF PRINT FREQUENCIES
20       5       ENDTIME THIS PERIOD     PRINTS IN PERIOD #1
1000.0   49      ENDTIME THIS PERIOD     PRINTS IN PERIOD #2
10000.0  45      ENDTIME THIS PERIOD     PRINTS IN PERIOD #3
2                NO. DIFFERENT OF PH PRINT FREQUENCIES
100.0    1.0     ENDTIME                 PH PRINT FREQUENCY #1
10000.0  10.0    ENDTIME                 PH PRINT FREQUENCY #2
*RESTART DATA
11000.0  11000.0
*PHREEQE CONVERGENCE TOLERANCE
1.0E-10
*BACKWARD-DIFFERENCE TRANSPORT SOLVER DATA
200      1.0E-3  0.5      NITSOR  TOLSOR  OMEGA
*PRINT DATA
0        2       NOUT     MASSOUT
0                (NSOUT(i) i=1,NOUT)
0                NPRNS
0                NPRNE
2                NPRNC
3 5              CELL POSITION FOR NPRNC #1
3 6              CELL POSITION FOR NPRNC #2
20               NPRNT
0                IPREXT
```

F.2 PHREEQC option YESPC =1

```
*TITLE
PHREEQC DEVELOPMENT
*RUN TIME OPTIONS
1 0 0 0 YESCHM YESBUG YESCOR YESX
0 0 0 0 IMDFLW ITDBCS IFKD ISLVBK
0 0 1 0 YESPE PE02 PEHELD IHSRDX
0 0 0 0 ISORCP IH2NRM ISPWRN IFE2CR
0 0 0 0 IREOX INLIM   ICEM    UMSBAL
0 0 0 0 ICHAIN  C14SWT  IFLGH3  IFLGRN
0 1 1 0 IDROP  YESPC YESSCM YESPPC
*INTEGER PARAMETERS
4 7 NE NC
0 0  NME (NMSP(i) i=1,NME)
0 0 NEMIC (NBLKMIC(i) i=1,NEMIC)
0 0 0 0 MACROM MICROM NKIN NCOL
0       0 0 NUMIN NUMIC NIEX
1 2 NSURF NSCM(i) I=1 , NSURF)
*MICROSPECIES NAMES
*MACROSPECIES NAMES
Ca+2        Na+         K+          Cl-         CaOH+       NaOH
KOH
*MACROMINERAL NAMES
*SURFACE SITES
Hfo_sOH     Hfo_wOH
*MICROMINERALS IN INITIAL INVENTORY
*MACROMINERALS IN INITIAL INVENTORY
*TIME DATA
2.0 Endtime
1 No. of transport timesteps
2.0 .1
10000. TENDCHEM
1 No. of speciation timesteps
2.0 .1
1 No. of print frequencies
2.0 10
1 No. of pH print frequencies
2.0 0.1
*RESTART DATA
200.    300.
```

```
*PHREEQE CONVERGENCE TOLERANCE
1E-10
*BACKWARD-DIFFERENCE TRANSPORT SOLVER DATA
200 1.E-3 0.5 NITSOR TOLSOR OMEGA
*PRINT DATA
7 2 NOUT MASSOUT
1,2,3,4,5,6,7      ,NOUT)
0 NPRNS
0 NPRNE
1 NPRNC
1 1
0                                NPRNT
1                                IPREXT
```

G Input File grm.dcy

```
3       total number of master decay chains
6       number of members in master decay chain 1
Cm-245
306     3       8.499e3
Pu-241
304     4       1.440e1
Am-241
305     1       4.329e2
Np-237
301     1       2.140e6
U-233
302     1       1.593e5
Th-229
312     2       7.339e3
1       number of members in master decay chain 2
Tc-99
302     1       2.128e5
1       number of members in master decay chain 3
I-129
303     1       1.569e7
```

H Input File grm.flw

```
*NUMBER OF FLOWFIELD PERIODS
          2

*ENDTIME FOR FLOWFIELD PERIOD  1
 0.1000000E+03
*FLOWS THROUGH RIGHT FACES (m3/day)
 0.1877726E+01   0.2547056E+01   0.0000000E+00
-0.8749643E-05  -0.4332573E-02   0.0000000E+00
*FLOWS THROUGH FRONT FACES (m3/day)
-0.1681179E-03  -0.1681179E-03   0.1001341E-03
 0.0000000E+00   0.0000000E+00   0.0000000E+00
*FLOWS INTO WELL CELLS (m3/day) - non-vertical external flows
 0.1184974E+01   0.0000000E+00   0.8870637E+00
-0.4117013E-03  -0.3125361E-03  -0.9012186E-04
*FLOWS INTO RECHARGE CELLS (m3/day) - infiltration through cap
 0.1591786E+01   0.1591786E+01   0.1591786E+01
 0.2731006E+01   0.2731006E+01   0.9582480E+00
*FLOWS INTO CONSTANT HEAD CELLS (m3/day) - seepage through vault base
-0.8953696E+00  -0.8953696E+00  -0.1668281E+01
-0.2737159E+01  -0.2737159E+01  -0.9584235E+00
*POROSITIES
 0.4000000E+00   0.4000000E+00   0.4000000E+00
 0.3000000E+00   0.3000000E+00   0.3000000E+00
*LONGITUDINAL DISPERSIVITIES (m)
 0.0000000E+00   0.0000000E+00   0.0000000E+00
 0.0000000E+00   0.0000000E+00   0.0000000E+00
*TRANSVERSE DISPERSIVITIES (m)
 0.0000000E+00   0.0000000E+00   0.0000000E+00
 0.0000000E+00   0.0000000E+00   0.0000000E+00

*ENDTIME FOR FLOWFIELD PERIOD  2
 0.1500000E+03
*FLOWS THROUGH RIGHT FACES (m3/day)
 0.7358030E+01   0.1011415E+02   0.0000000E+00
 0.1470908E-03  -0.3810953E-02   0.0000000E+00
*FLOWS THROUGH FRONT FACES (m3/day)
-0.1567399E-02  -0.1567399E-02  -0.2210731E-03
 0.0000000E+00   0.0000000E+00   0.0000000E+00
*FLOWS INTO WELL CELLS (m3/day) - non-vertical external flows
```

```
 0.1553658E+01   0.0000000E+00   0.1149897E+01
-0.3558450E-02  -0.2108075E-02  -0.9285637E-03
*FLOWS INTO RECHARGE CELLS (m3/day) - infiltration through cap
 0.3993429E+01   0.3993429E+01   0.3993429E+01
 0.3545517E+01   0.3545517E+01   0.1245722E+01
*FLOWS INTO CONSTANT HEAD CELLS (m3/day) - seepage through vault base
-0.2055782E+01  -0.2055782E+01  -0.3830794E+01
-0.3540324E+01  -0.3540324E+01  -0.1245291E+01
*POROSITIES
 0.4000000E+00   0.4000000E+00   0.4000000E+00
 0.3000000E+00   0.3000000E+00   0.3000000E+00
*LONGITUDINAL DISPERSIVITIES (m)
 0.0000000E+00   0.0000000E+00   0.0000000E+00
 0.0000000E+00   0.0000000E+00   0.0000000E+00
*TRANSVERSE DISPERSIVITIES (m)
 0.0000000E+00   0.0000000E+00   0.0000000E+00
 0.0000000E+00   0.0000000E+00   0.0000000E+00
```

I Input File grm.grd

```
*NUMBER OF COLUMNS
4
*COLUMN GRID LINE CO-ORDINATES (m)
10.0    20.0    30.0    40.0
*NUMBER OF ROWS
3
*ROW GRID LINE CO-ORDINATES (m)
5.0     10.0    15.0
*ELEVATION OF CELL TOPS (m)
4.2     4.2     4.2     4.2
4.7     4.7     4.7     4.7
5.0     6.7     7.9     7.8
*ELEVATION OF CELL BOTTOMS (m)
0.0     0.0     0.0     0.0
0.0     0.0     0.0     0.0
0.0     0.0     0.0     0.0
*HYDRAULIC HEADS (m)   ( = 999.99 for inactive cells)
999.99  2.1     3.6     3.6
3.2     3.2     2.7     2.7
1.0     1.0     1.7     2.8
```

J Input File grm.iex

J.1 PHREEQE option YESPC =0

```
Types of ionic exchange sites
1
X-
Bulk ionic exchange species
3
NAX
KX
CAX2
Micro ionic exchange species
0
CEC for ion exchange type X- (mol/l)
1.1e-3 1.1e-3 1.1e-3
1.1e-3 1.1e-3 1.1e-3
0.0  0.0  0.0  0.0
Bulk ionic exchange species to be printed
2
NAX
CAX2
Micro ionic exchange species to be printed
0
```

J.2 PHREEQC option YESPC =1

```
CEC for ion exchange type x- in mole/l
1.1e-3 1.1e-3 1.1e-3 1.1e-3 1.1e-3 1.1e-3 1.1e-3 1.1e-3 1.1e-3 1.1e-3 1.1e-3 1.1e-3
```

K Input File grm.inv

```
*SITE TEMPERATURE (oC)
15.0
*SOLID ISO=1 U-238 (mol/l)
0.000e+00 9.154e-03 9.154e-03
9.154e-03 3.624e-03 3.624e-03
*SOLID ISO=2 U-234 (mol/l)
0.000e+00 5.370e-07 5.370e-07
5.370e-07 4.730e-07 4.730e-07
*SOLID ISO=3 U-235 (mol/l)
0.000e+00 7.880e-05 7.880e-05
7.880e-05 9.030e-05 9.030e-05
*SOLID ISO=4 U-233 (mol/l)
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
*SOLID ISO=5 U-236 (mol/l)
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
*LIQUID ISO U (mol/l)
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
*COLLOID 1 U (kmol)
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
*ADSORB U (kmol)
0.000e+00 1.080e-08 1.080e-08
1.080e-08 9.980e-09 9.980e-09
*SOLID ISO=1 NP (mol/l)
0.000e+00 5.120e-08 5.120e-08
5.120e-08 3.940e-08 3.940e-08
*LIQUID NP (mol/l)
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
*COLLOID 1 NP (kmol)
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
*ADSORB NP (kmol)
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
*LIQUID MACROSPECIES 1 - CA (mol/l)
```

```
4.43e-4 4.43e-4 4.43e-4
4.43e-4 4.43e-4 4.43e-4
*LIQUID MACROSPECIES 2 - MG (mol/l)
1.87e-4 1.87e-4 1.87e-4
1.87e-4 1.87e-4 1.87e-4
*LIQUID MACROSPECIES 3 - CL (mol/l)
5.97e-4 5.97e-4 5.97e-4
5.97e-4 5.97e-4 5.97e-4
*LIQUID MACROSPECIES 4 - SO4-2 (mol/l)
1.17e-4 1.17e-4 1.17e-4
1.17e-4 1.17e-4 1.17e-4
*LIQUID MACROSPECIES 5 - O2 (mol/l)
3.15e-5 3.15e-5 3.15e-5
3.15e-5 3.15e-5 3.15e-5
*TRITIUM LIQUID CONCENTRATION (mol/l)
1.0e-3 1.0e-3 1.0e-3
1.0e-3 1.0e-3 1.0e-3
*COLLOID 1 - amount present in each cell (kg/m3)
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
*RELEASE COEFFICIENT FOR COLLOID 1
0.100e+00 0.010e+00 0.120e+00
0.000e+00 0.000e+00 0.000e+00
*PARTIAL PRESSURE CO2
3.160e-04 3.160e-04 3.160e-04
3.160e-04 3.160e-04 3.160e-04
*PARTIAL PRESSURE CH4
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
*PARTIAL PRESSURE H2
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
*PARTIAL PRESSURE N2
7.902e-01 7.902e-01 7.902e-01
7.902e-01 7.902e-01 7.902e-01
*PARTIAL PRESSURE O2
2.095e-01 2.095e-01 2.095e-01
2.095e-01 2.095e-01 2.095e-01
*PARTIAL PRESSURE H2S
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
```

```
*PARTIAL PRESSURE NH3
0.000e+00 0.000e+00 0.000e+00
0.000e+00 0.000e+00 0.000e+00
*CELLULOSE TYPE 1 (kg)
1.0e3 1.0e3 1.0e3
1.0e3 1.0e3 1.0e3
*CELLULOSE TYPE 2 (kg)
1.0e3 1.0e3 1.0e3
1.0e3 1.0e3 1.0e3
*CELLULOSE TYPE 3 (kg)
1.0e3 1.0e3 1.0e3
1.0e3 1.0e3 1.0e3
*PROTEINS TYPE 1 (kg)
1.0e3 1.0e3 1.0e3
1.0e3 1.0e3 1.0e3
*PROTEINS TYPE 2 (kg)
1.0e3 1.0e3 1.0e3
1.0e3 1.0e3 1.0e3
*PROTEINS TYPE 3 (kg)
1.0e3 1.0e3 1.0e3
1.0e3 1.0e3 1.0e3
*FATS TYPE 1 (kg)
1.0e3 1.0e3 1.0e3
1.0e3 1.0e3 1.0e3
*FATS TYPE 2 (kg)
1.0e3 1.0e3 1.0e3
1.0e3 1.0e3 1.0e3
*FATS TYPE 3 (kg)
1.0e3 1.0e3 1.0e3
1.0e3 1.0e3 1.0e3
*PH ARRAY FOR SITE
7.48 8.183 8.183
8.183 8.183 8.183
*PE ARRAY FOR SITE
2.400 2.400 2.400 2.400
2.400 2.400 2.400 2.400
*CALCITE (mol/l)
0.0 5.462 5.462
5.462 5.462 5.462
*DENSITY OF WASTE (kg/m3)
2200.0 2200.0 2200.0
```

```
2200.0 2200.0 2200.0
```

2					
1					
Orig	JG+	06/2003	AP	AP	**ISSUE 2**
	By	Date	Chkd.	Appr.	Description of Issue or Revision

K.1 Input File grm.inv Surface Complexation Example

```
*SITE TEMPERATURE
25
*LIQUID MACROSPECIES 1 - CA
1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4
1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4 1.00e-4
*LIQUID MACROSPECIES 2 - NA
1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1
1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1
*LIQUID MACROSPECIES 3 - K
1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1
1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1 1.e-1
*LIQUID MACROSPECIES 4 - CL
2.002e-1 2.002e-1 2.002e-1 2.002e-1 2.002e-1 2.002e-1 2.002e-1 2.002e-1 2.002e-1
2.002e-1 2.002e-1 2.002e-1 2.002e-1 2.002e-1 2.002e-1 2.002e-1 2.002e-1 2.002e-1
2.002e-1 2.002e-1
*LIQUID MACROSPECIES 8 - O2(AQ)
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*PARTIAL PRESSURE co2
3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4
3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4 3.16e-4
*PARTIAL PRESSURE ch4
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*PARTIAL PRESSURE h2
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*PARTIAL PRESSURE n2
7.902e-1 7.902e-1 7.902e-1 7.902e-1 7.902e-1 7.902e-1 7.902e-1 7.902e-1 7.902e-1
7.902e-1 7.902e-1 7.902e-1 7.902e-1 7.902e-1 7.902e-1 7.902e-1 7.902e-1 7.902e-1
7.902e-1 7.902e-1
*PARTIAL PRESSURE o2
2.095e-01 2.095e-01 2.095e-01 2.095e-01 2.095e-01 2.095e-01 2.095e-01 2.095e-01
2.095e-01 2.095e-01 2.095e-01 2.095e-01 2.095e-01 2.095e-01 2.095e-01 2.095e-01
2.095e-01 2.095e-01 2.095e-01 2.095e-01
*PARTIAL PRESSURE h2s
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*PARTIAL PRESSURE nh3
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*CELLULOSE TYPE 1 (kg)
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*CELLULOSE TYPE 2 (kg)
```

```
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*CELLULOSE TYPE 3 (kg)
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*PROTEINS TYPE 1 (kg)
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*PROTEINS TYPE 2 (kg)
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*PROTEINS TYPE 3 (kg)
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*FATS TYPE 1 (kg)
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*FATS TYPE 2 (kg)
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*FATS TYPE 3 (kg)
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
*PH ARRAY
8.053 8.053 8.053 8.053 8.053 8.053 8.053 8.053 8.053 8.053 8.053 8.053 8.053
8.053 8.053 8.053 8.053 8.053 8.053 8.053
*PE ARRAY
4.00 4.00 4.00 4.00 4.00 4.00 4.00 4.00 4.00 4.00 4.00 4.00 4.00 4.00 4.00
4.00 4.00 4.00 4.00
*SURFACE AREA
1.e+02 1.e+02 1.e+02 1.e+02 1.e+02 1.e+02 1.e+02 1.e+02 1.e+02 1.e+02 1.e+02
1.e+02 1.e+02 1.e+02 1.e+02 1.e+02 1.e+02 1.e+02 1.e+02 1.e+02
*SURFACE MASS
1.e+01 1.e+01 1.e+01 1.e+01 1.e+01 1.e+01 1.e+01 1.e+01 1.e+01 1.e+01 1.e+01
1.e+01 1.e+01 1.e+01 1.e+01 1.e+01 1.e+01 1.e+01 1.e+01 1.e+01
*Hfo_sOH
1.e-02 1.e-02 1.e-02 1.e-02 1.e-02 1.e-02 1.e-02 1.e-02 1.e-02 1.e-02 1.e-02
1.e-02 1.e-02 1.e-02 1.e-02 1.e-02 1.e-02 1.e-02 1.e-02 1.e-02
*Hfo_wOH
1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.  1.
*DENSITY OF WASTE
2200.0 2200.0 2200.0 2200.0 2200.0 2200.0 2200.0 2200.0 2200.0 2200.0
2200.0 2200.0 2200.0 2200.0 2200.0 2200.0 2200.0 2200.0 2200.0 2200.0
```

L Input File grm.kds

L.1 Species–dependent form

```
*SORPTION TYPE IN EACH CELL
1 1 1
1 1 1

*DEFAULT MACROSPECIES SORPTION DATA
1  1.0e-20 1.0e-14 0.03 1.0e-29 1.0e-14  1.0e-9 1.0e-9 1.0e-9 1.0e-9
2  1.0e-20 1.0e-14 0.03 1.0e-29 1.0e-14  1.0e-9 1.0e-9 1.0e-9 1.0e-9
3  1.0e-20 1.0e-14 0.03 1.0e-29 1.0e-14  1.0e-9 1.0e-9 1.0e-9 1.0e-9
4  1.0e-20 1.0e-14 0.03 1.0e-29 1.0e-14  1.0e-9 1.0e-9 1.0e-9 1.0e-9
5  1.0e-20 1.0e-14 0.03 1.0e-29 1.0e-14  1.0e-9 1.0e-9 1.0e-9 1.0e-9
6  1.0e-20 1.0e-14 0.03 1.0e-29 1.0e-14  1.0e-9 1.0e-9 1.0e-9 1.0e-9

*INDIVIDUAL MACROSPECIES SORPTION DATA
11 C
1   0.05   1.0e-14 0.03 1.0e-29 1.0e-14 1.0e-9 1.0e-9 1.0e-9 1.0e-9
2   0.02   1.0e-14 0.03 1.0e-29 1.0e-14 1.0e-9 1.0e-9 1.0e-9 1.0e-9
3   1.0e-9 1.0e-14 0.03 1.0e-29 1.0e-14 1.0e-9 1.0e-9 1.0e-9 1.0e-9
4   1.0e-9 1.0e-14 0.03 1.0e-29 1.0e-14 1.0e-9 1.0e-9 1.0e-9 1.0e-9
5   1.0e-9 1.0e-14 0.03 1.0e-29 1.0e-14 1.0e-9 1.0e-9 1.0e-9 1.0e-9
6   1.0e-9 1.0e-14 0.03 1.0e-29 1.0e-14 1.0e-9 1.0e-9 1.0e-9 1.0e-9
0 (no more)

*DEFAULT MICROSPECIES SORPTION DATA
1 1.0e-3 1.0e-6 0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
2 1.0e-3 1.0e-6 0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
3 1.0e-3 1.0e-6 0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
4 1.0e-3 1.0e-6 0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
5 1.0e-3 1.0e-6 0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
6 1.0e-3 1.0e-6 0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1

*DEFAULT MICROELEMENT SORPTION DATA
303
1 3.0e-3 1.0e-6 0.042553 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
2 3.0e-3 1.0e-6 0.042553 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
3 3.0e-3 1.0e-6 0.042553 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
4 3.0e-3 1.0e-6 0.042553 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
5 3.0e-3 1.0e-6 0.042553 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
```

```
6 3.0e-3 1.0e-6 0.042553 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
306
1 2.0e-5 1.0e-6 0.1961 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
2 2.0e-5 1.0e-6 0.1961 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
3 2.0e-5 1.0e-6 0.1961 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
4 2.0e-5 1.0e-6 0.1961 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
5 2.0e-5 1.0e-6 0.1961 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
6 2.0e-5 1.0e-6 0.1961 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
0 (no more)

*INDIVIDUAL MICROSPECIES SORPTION DATA
0 (no more)
```

L.2 pH–dependent form

```
*SORPTION TYPE IN EACH CELL
1 1 1 1 1 1
2 2 2 2 3 3

*DEFAULT MACROSPECIES SORPTION DATA
1  0.0     0.0      0.0  0.0      0.0       0.0     0.0     0.0     0.0
2  1.0e-9 1.0e-14 0.03 1.0e-29 1.0e-14  1.0e-9 1.0e-9 1.0e-9 1.0e-9
3  1.0e-9 1.0e-14 0.03 1.0e-29 1.0e-14  1.0e-9 1.0e-9 1.0e-9 1.0e-9
4  1.0e-9 1.0e-14 0.03 1.0e-29 1.0e-14  1.0e-9 1.0e-9 1.0e-9 1.0e-9
5  1.0e-9 1.0e-14 0.03 1.0e-29 1.0e-14  1.0e-9 1.0e-9 1.0e-9 1.0e-9
6  1.0e-9 1.0e-14 0.03 1.0e-29 1.0e-14  1.0e-9 1.0e-9 1.0e-9 1.0e-9

*INDIVIDUAL MACROSPECIES SORPTION DATA
0 (no more)

*DEFAULT MICROELEMENT SORPTION DATA
1 0.0     0.0 0.0 0.0 0.0    0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
2 4.75e-6 0.0 0.0 0.0 1.0e-6 0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
3 4.75e-6 0.0 0.0 0.0 1.0e-6 0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
4 4.75e-6 0.0 0.0 0.0 1.0e-6 0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
5 4.75e-6 0.0 0.0 0.0 1.0e-6 0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1
6 4.75e-6 0.0 0.0 0.0 1.0e-6 0.3571 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1 1.0e1

*INDIVIDUAL MICROELEMENT SORPTION DATA
0 (no more)
```

M Input File grm.kin

```
KIN_MIN_1        0.0469      0.0432      0.0181
KIN_MIN_2        0.0219      0.0467      0.0024
```

N Input File grm.rel

```
3       number of microelements
301     1.91E-11        0.001           0.04    Sr
0 0 0 0
0 0 0 0
1 1 1 1
302     3.79E-8         0.0             0.008   Tc
0 0 0 0
0 0 0 0
1 1 1 1
303     1.45E-8         0.0             0.012   I
0 0 0 0
0 0 0 0
1 1 1 1
```

O PHREEQC OPTIONS

The compatibility of the PHREEQC speciation option with other runtime options and integer parameters within GRM V4.1 are described below.

RUN TIME OPTIONS

YES means that the relevant runtime option may be set or unset (i.e. equal to 1 or 0) if PHREEQC speciation is chosen. NO means that the option must be unset. IRRELEVANT means that the particular option has no effect on the simulation, but it is recommended that it be set to 0.

YESCHM
* YES - This flag must be set for speciation (either PHREEQE or PHREEQC) to be an issue.

YESBUG
* NO - Gases are not handled correctly within PHREEQC at present.

YESCOR
* NO - Gases are not handled correctly within PHREEQC at present.

YESX
* YES

IMDFLW
* YES

ITDBCS
* YES

IFKD
* YES

ISLVBK
* IRRELEVANT - This solver is currently disabled for other reasons.

YESPE
* IRRELEVANT - Pe calculations are controlled by entries in input file.

PEO2

```
* IRRELEVANT - Only used if microbiology included.

PEHELD
* IRRELEVANT - Only used if microbiology included.

IHSRDX
* IRRELEVANT - Only used if microbiology included.

ISORCP
* NO - No separate micro-speciation within PHREEQC.

IH2NRM
* IRRELEVANT - Only used if microbiology included.

ISPWRN
* NO - Facility not implemented with PHREEQC.

IFE2CR
* IRRELEVANT - Only used if corrosion included.

IREOX
* IRRELEVANT - Only used if microbiology included.

INLIM
* IRRELEVANT - Only used if microbiology included.

ICEM
* NO - Facility not implemented within PHREEQC.

IMSBAL
* YES

ICHAIN
* NO - NLAPA not updated after PHREEQC speciation.

C14SWT
* NO - Facility not implemented with PHREEQC

IFLGH3
* NO - Gases not handled correctly within PHREEQC at present
```

IFLGRN
* NO - Gases not handled correctly within PHREEQC at present

IDROP
* NO - Mineral molecular weights not calculated for slumping calculations with PHREEQC

YESSCM
* YES

YESPPC
* YES

INTEGER PARAMETERS

YES means that the relevant parameter may be non-zero. NO means that it must be set to zero.

NME
* YES - Microelements can be included, but speciated identically to bulk elements

NEMIC
* NO - This facility is unnecessary as all microelements are included in the bulk chemistry

NKIN
* NO - Kinetic mineral precipitation/dissolution is not included in PHREEQC at present

NCOL
* YES

NIEX
* YES

NSURF
* YES