LEACHATE MIGRATION THROUGH THE TRIASSIC SANDSTONES AT BURNTSTUMP LANDFILL AND ELSEWHERE

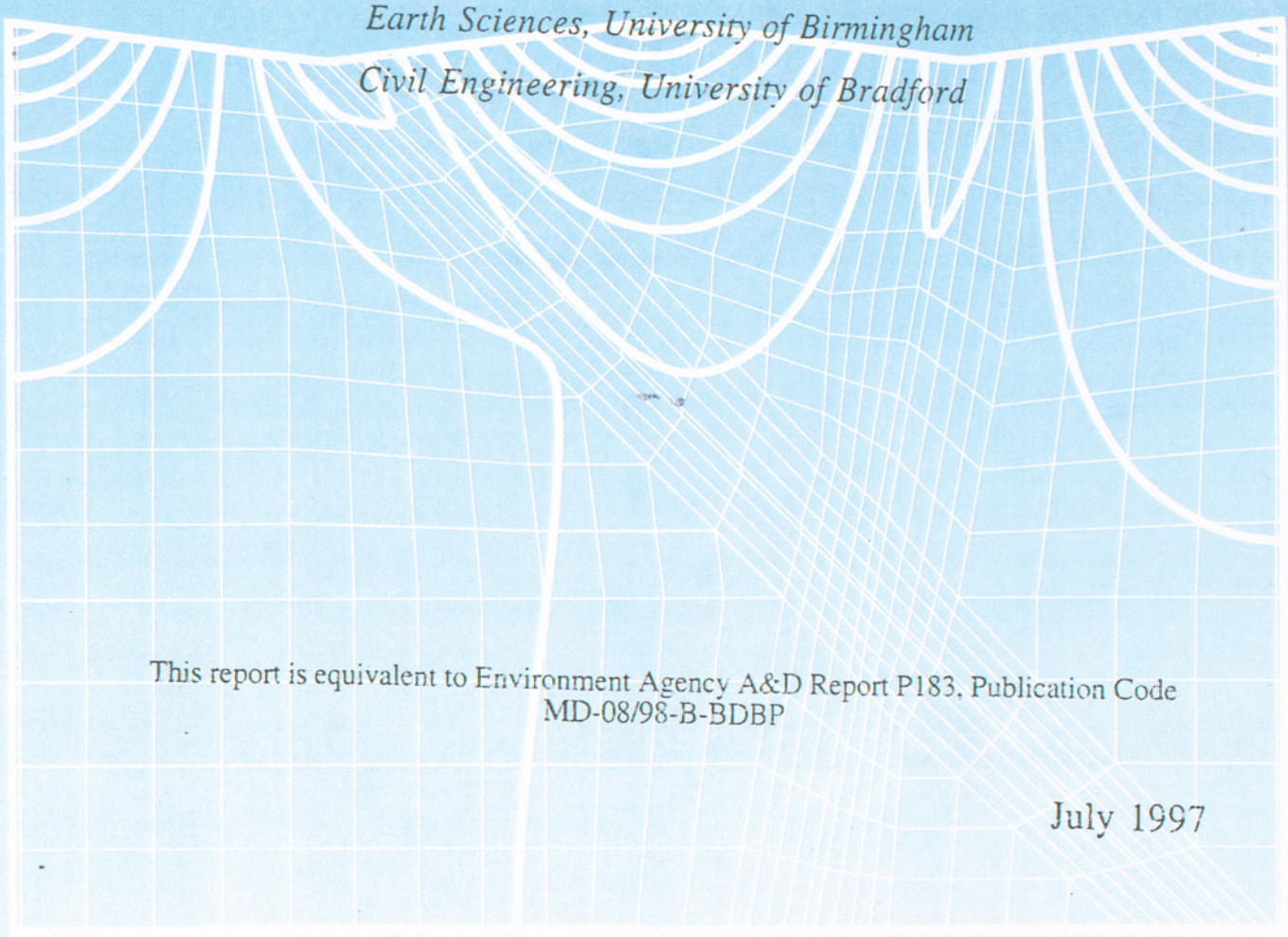
Model to Predict the Attenuation of Leachate from Existing Landfills, for Evaluating Risks Following Liner Failure, and for Designing Attenuating Liners

A Collaborative Research Project

The Environment Agency

Earth Sciences, University of Birmingham

Civil Engineering, University of Bradford



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Summary

LEACHATE MIGRATION THROUGH THE TRIASSIC SANDSTONES AT BURNTSTUMP LANDFILL AND ELSEWHERE

Models to Predict the Attenuation of Leachate

Background This project follows two previous laboratory studies which examined the interaction of landfill leachate and Triassic Sandstone at the Burntstump landfill site, Nottinghamshire. During the previous investigations, preliminary geochemical modelling indicated that the code used - Appelo and co-workers' PHREEQM - may have great potential in interpreting laboratory and field data, and in risk assessment. This project was initiated to evaluate this possibility.

Aims (a) To evaluate PHREEQM in the context of landfill leachate/Triassic Sandstone interactions;
(b) To produce a detailed users' guide for PHREEQM.

Approach Modelling of laboratory data on leachate interactions with Nottinghamshire and West Midlands Triassic sandstone; modelling of field data from the Burntstump site; production of a guide to the modelling package; evaluation of the package; collation of default values for model chemical parameters.

Guide The guide brings together existing material from several sources, and adds further details based on the experience gained during the project. (Section 2 of this report.)

Modelling Seven cases, or "problems" are considered. Problems 1 and 2 were concerned with modelling laboratory data on acetogenic leachate/Nottinghamshire Triassic sandstone interactions; problems 3 to 5 were concerned with the modelling of laboratory data on methanogenic leachate/Nottinghamshire sandstone interactions; problem 6 was concerned with the modelling of laboratory data on methanogenic leachate/West Midlands sandstone; and problem 7 concerned the modelling of field data on leachate migration at the Burntstump landfill, Nottinghamshire. (Section 3 of this report.)

Evaluation PHREEQM is a model capable of dealing with one-dimensional groundwater flow with dispersion and reaction. It is excellent for exchange reaction calculations, and represents a major improvement on the conventional use of partition coefficients for NH_4 risk assessment. It can successfully describe leachate/MnO_2 interactions and acid-base reactions observed in the laboratory, though modelling the field systems is more difficult given that longer time scales mean that organic reactions become more important. The model does not include organic species, though in principle these can either be added (if appropriate thermodynamic data are available), or can be taken account of indirectly. The code has been extremely useful in linking laboratory and field results, and should prove very useful in risk assessment for existing or proposed systems. It has potential application to problems other than those connected with landfill leachate migration, for example to sea water intrusion, regional chemical distribution, sampling, and aquifer storage and recovery problems.

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1. Introduction

1.1 Previous Study

During the past two years, the interactions between landfill leachate and Triassic sandstone have been investigated using laboratory experiments. The work has been carried out in Earth Sciences, University of Birmingham (Thornton et al., 1995), and sponsored by the (then) NRA, the Department of the Environment, and the Water Research Centre.

In Phase 1 of the study, acetogenic-phase (A-phase), methanogenic-phase (M-phase), and A-phase followed by M-phase leachates were passed through columns of Sherwood Sandstone Group sand, the latter from the Burntstump landfill site, Nottinghamshire (Harris and Parry, 1982; Lewin et al., 1994). Samples of elutants were analysed for a wide range of inorganic and organic species. It was found that the general behaviour of the laboratory breakthrough patterns was very similar to that observed in the field. As expected, the main chemical processes involved appear to be ion exchange, acid-base reactions, and sorption. In addition, MnO_2/Fe^{2-} reactions were shown to be important in controlling redox conditions,under which some enhanced xenobiotic organic matter (XOM) degradation occurred.

In Phase 2 of the study, the effect of oxidised groundwater flushing of the systems was investigated by switching the flushing solution from leachate to groundwater in each column. The experiments indicated that most of the contaminants sorbed during the leachate flush could be remobilised during the oxidised water flush, albeit rather slowly. The MnO_2 poising capacity was shown to be large, though certainly finite in the context of landfill lifetime.

During Phase 2, the reactive transport code PHREEQM (Appelo and Postma, 1993), in combination with the "static" model MINTEQA2 (Alison et al., 1990), was used to carry out some first-pass modelling of the inorganic breakthroughs during the leachate flushes. Despite the complexity of the leachate solution and the rock, the model results were encouraging enough to suggest that PHREEQM might be a useful tool in risk assessment in landfill leachate / Triassic Sandstone systems.

1.2 Aims of Present Study

The previous studies demonstrated that the laboratory results are similar to the field results, and suggested that a reactive transport model may be a useful means of quantitative interpretation of the data obtained. The implication of these conclusions is that the model should be able to be used in interpreting / forecasting chemical behaviour in field systems. If the model, calibrated and tested against laboratory data, can be used to predict water chemistry in the field

situation, a very useful evaluation and design tool will have become available. For example, the model could be used: in assessing the risk from leachate migration from old, unlined landfills, in assessing the risk from liner failure in new landfills, or in designing alternative liners for new landfills. It might even be used in designing chemical remediation methods. If the complex Triassic sandstone aquifer can be modelled, perhaps other aquifers could be modelled too.

The aims, therefore, of the present project are:

(i) to validate the code's ability to describe the inorganic chemistry during leachate migration in Triassic sandstone;

(ii) to produce a fully documented guide to the use of the model.

1.3 Approach

To achieve Aim (i), the following tasks were undertaken:

(a) mobilisation (familiarisation with the code, assembling and assessing data);
(b) detailed modelling of the Burntstump laboratory column data from Thornton et al. (1995);
(c) modelling of the Burntstump field data summarised by Lewin et al. (1994); and
(d) modelling of laboratory data from the experiments on West Midlands Triassic sandstone described by Thornton et al. (1995).

The results from these investigations were intended to enable the following to be determined: the viability and shortcomings of the PHREEQM code; the ways that the code might be improved; the problems with up-scaling in space and time; the values/value ranges for important thermodynamic parameters; the relative importance of each variable and hence which needs to be measured, at what accuracy; and the situations in which PHREEQM might not be able to provide reliable interpolations/extrapolations.
Achieving Aim (ii), the production of a guide to the use of the code, was also undertaken.
Very good descriptions PHREEQM already exist. However, none have been written with the intention of drawing the details together in one place for the new user: Appelo and Postma's (1993) intention is didactic, Nienhuis et al.'s (1994) intention is to outline certain modifications made to the PHREEQM package, and Parkhurst et al. (1980) deal only with PHREEQE. The intention of the guide presented here is to draw the information in these publications together, and to add further comments arising from experience gained during the project.

1.4 Report Structure

Section 2 of this report comprises a user's guide for PHREEQM. Section 3 gives examples of the use of PHREEQM in modelling landfill leachate/Triassic sandstone interactions, using laboratory data from the Burntstump Landfill, laboratory data for sandstone from the West Midlands, and field data for the Burntstump site. Section 4 is a discussion of the modelling results and their implications, and the limitations and potential uses of the PHREEQM package. Section 5 presents a summary of the main conclusions of the project, and suggests further work.

A USER GUIDE FOR APPELO AND COWORKERS' CODE PHREEQM, AND ITS ASSOCIATED PREPROCESSOR PIP

This guide is intended to draw together information provided by Appelo and Postma (1993), Nienhuis et al. (1994), and Parkhurst et al. (1980) in a form convenient for workers new to the code.

2. PHREEQM and PIP

2.1 Introduction

PHREEQM is a reasonably sophisticated tool for reactive transport groundwater modelling. Because of this, there are many different types of calculations which can be performed using it, and many data which need to be input. As a result it takes some time and practice to become familiar with operating it. It is hoped that the following description of the code operations will ease this process. The early sections deal with overviews; the last, large section deals with the detail of setting up a run. Of necessity, there is some repetition. The structure of the description is as follows.

Section 2.2 An overview of the PHREEQM code

- 2.2.1 General description
- 2.2.2 PHREEQM's dispersive flow model
- 2.2.3 Overview of the geochemical code PHREEQE
- 2.2.4 The numerical schemes used in PHREEQE
- 2.2.5 Ion exchange in PHREEQM

Section 2.3 An overview of the preprocessor PIP

Section 2.4 An overview of how various types of problems can be tackled using PHREEQM

Section 2.5 A detailed description of the inputs necessary to run PHREEQM.

The descriptions rely heavily on those provided by Appelo and Postma (1993), Nienhuis et al. (1994), and Parkhurst et al. (1980), but are supplemented by additional material.
For those unfamiliar with the code, it is suggested that the overview sections are read together with appropriate sections of Chapter 10 of Appelo and Postma (1993), and that then the final detailed section is read whilst running PHREEQM using one of the data files from later sections in this report (or from Appelo and Postma, 1993).

2.2 An Overview of the PHREEQM Code

2.2.1 General Description

PHREEQM is a reactive transport groundwater flow code developed by Appelo and coworkers (Appelo and Postma, 1993; Nienhuis et al.,

1994). Flow is described using a one dimensional linear or radial mixing cell approach, where packets of water are moved on one cell every time step (ie flow rate = cell pore volume/time step), and dispersion (or diffusion where velocity = 0) is accounted for using a mixing formula. At every time step, chemical calculations are performed using the geochemical code PHREEQE (Parkhurst et al., 1980). This code can take into account complexation, activity corrections, mineral equilibria, temperature variations, and certain types of reaction: default values are provided for all thermodynamic parameters. In addition, Appelo and coworkers have extended PHREEQE's ability to calculate ion exchange equilibria, providing a choice of either the Gaines-Thomas or the Gapon conventions (Appelo and Postma, 1993, Chapter 5). The region through which the groundwater passes can be split into up to ten sub regions, each of which can have its own geochemical properties (minerals, exchange constants) and initial water chemistry. In the terminology used by Appelo and coworkers, the flow region is often referred to as the column (because of their extensive application of the code to laboratory experiments), and each sub region is referred to as a layer: flow crosses layer boundaries at 90° (ie flow is not parallel with layering).
The code has been verified against analytical solutions, where these are available, by Appelo and coworkers, and against column experiment data (Appelo and Postma, 1993). It has been compared with other numerical models, such as IEMODEL (Carlyle, 1990), and a modification of the NAMMU code (Arthur, in progress), and again produces very similar results.

2.2.2 PHREEQM's Dispersive Flow Model

PHREEQM uses a simple mixing cell model to simulate dispersive flow. It is described in some detail in Appelo and Willensen (1987) and Appelo and Postma (1993; sections 9.5 and 10.2.2).
The flow region (or *column*) is divided into a set of up to 10 layers, flow passing through each layer in turn. Each layer consists of a user-defined number of cells. All cells (and therefore all layers) have the same porosity, dispersivity, and average linear velocity: however, each layer may have different geochemical properties.
Water is moved through the "column" of layers as indicated in Figure 2.1 (Appelo and Postma, 1993; Figure 9.36, page 37). A time step (Δt) is defined by:

Δt = Pore volume/Flow rate.

For linear flow systems, this is equivalent to:

$$\Delta t = \Delta x / \bar{v}$$

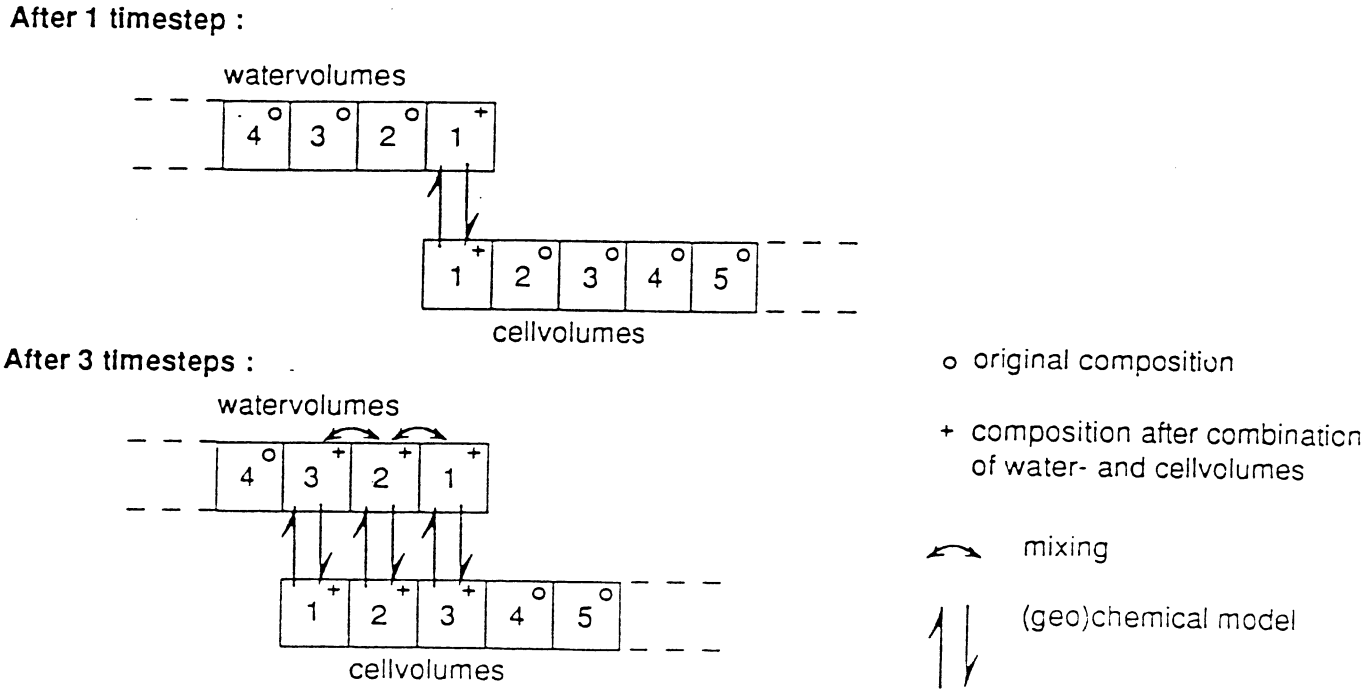


Figure 2.1 The concept of the mixing cell model used by PHREEQM (from Appelo and Postma, 1993).

where Δx is cell size, and $\bar{v}$ is average linear velocity. Hence in each time step the entire dissolved mass in a cell is moved one cell downstream. For radial flow systems, which are also considered by PHREEQM, the cell lengths are changed so that the cell volume remains constant (*length of cell n = length of first cell x* ($\sqrt{n}$ - $\sqrt{(n-1)}$). In this way the time step, ie cell volume/flow rate, is kept constant. The reason that the contents of the whole cell is transferred to the next cell in each time step is that the concentration in the cell in the new time step would be a weighted average of new and old concentrations in that cell: ie a mixing or dispersion would have occurred in the calculation scheme. This numerical dispersion is sometimes used to model physical dispersion (van Ommen, 1985), but it is usually simpler to avoid numerical dispersion and to model physical dispersion using some form of "mixing factor", and this is what PHREEQM does, as explained below. However, this places restrictions on the choice of time step and cell size.
Returning to Figure 2.1, a cell volume of water is moved downflow by one cell every time step. The mixing necessary to take into account dispersion is then calculated using a mixing factor mixf:

$$\text{mixf} = \frac{D_L \Delta t}{(\Delta x)^2}$$

where D_L is the longitudinal dispersion coefficient. mixf is used to move mass between cells as indicated schematically in Figure 2.1: the theoretical development (from the finite difference form of the differential equation) is described by Appelo and Postma (1993; p. 374-375).
At each time step, once mixing has been performed, PHREEQE (and other routines) is called and the geochemical calculations are carried out. It is always good practice to vary the discretisation to check that the solution is independent of the way the model is set up, though this is not necessarily always easy to do.

2.2.3 An overview of the Geochemical Code PHREEQE

PHREEQE (Parkhurst et al., 1980) is a powerful geochemical code capable of dealing with a very large number of chemical species. It can be used for the following types of problem:

(a) calculating the aqueous speciation of a given solution, and the state of saturation of the solution with respect to given mineral phases;

(b) calculating the aqueous speciation and states of saturation of a given solution following a temperature change;

(c) calculating the aqueous speciation and states of saturation of a given solution following equilibration (dissolution or precipitation) with specified mineral phases;

(d) calculating the aqueous speciation and states of saturation of a given solution following a specified set of reactions;

(e) calculating the aqueous speciation and states of saturation of a given solution following mixing with a second solution; and

(f) calculating the aqueous speciation and states of saturation of a given solution following any combination of reactant addition, temperature change, mineral equilibrium, and mixing.

To reduce the number of equations to solved, PHREEQE, as most other geochemical models, works in terms of master species. These are listed in Table 2.1. All other species presently in PHREEQE can be expressed in terms of these master species using association reactions. If required, PHREEQE allows the addition of more master (and non-master) species, and this is very useful when considering heavy metals and metalloids (and organics) which are not in the standard data base (Table 2.1). The thermodynamics data base is satisfactory for most purposes, but can be altered. New minerals can be added to the list for saturation index calculation and new minerals defined for equilibration calculations. Temperatures can be changed, and reactants added in a series of steps, so that reaction progress towards equilibrium can be followed.
PHREEQE does not consider the sorbed phase explicitly, but, as described in Section 2.2.5, it can be used in calculating ion exchange processes if a fictitious sorbed phase is introduced. Redox calculations are monitored using an electron balance: as with most codes, it is assumed that all species are in redox equilibrium. Sometimes the program will crash. There are many potential causes, some chemical, some numerical. Sometimes these are clearly flagged by the program (eg phase rule violation). Numerical problems can often be avoided by adjusting the convergence parameters of the numerical solver or by modifying the description of the problem (eg by changing redox conditions to avoid situations where there are steep concentration / pe gradients). The numerical schemes used in PHREEQE are described in outline in the next section (Section 2.2.4).

Table 2.1 Master species in the standard PHREEQE database as used by PHREEQM, and their index numbers and redox status of redox-sensitive species.

Index No.	Species	Redox Status
1	H^+	
2	e-	
3	H_2O	
4	Ca^{2+}	
5	Mg^{2+}	
6	Na^+	
7	K^+	
8	Fe^{2+}	Fe II
9	Mn^{2+}	Mn II
10	Al^{3+}	
11	Ba^{2+}	
12	Sr^{2+}	
13	H_4SiO_4	
14	Cl^-	
15	CO_3^{2-}	C IV
16	SO_4^{2-}	S VI
17	NO_3^-	N V
18	H_3BO_3	
19	PO_4^{3-}	
20	F^-	
21	Li^+	
22	Br^-	
23	NH_4^+	N -III
30	X^-	

2.2.4 The Basis of the Calculations Undertaken by PHREEQE. The Numerical Schemes Used in PHREEQE.

Parkhurst et al. (1980) provide an outline description of the numerical solvers used in PHREEQE (pages 12-18). The equations PHREEQE needs to solve are based on the following principles:

(i) electroneutrality*;
(ii) electron balance;
(iii) mass balance for each element other than H and O@;
(iv) the law of mass action; and
(v) Debye-Hückel or other activity theory.

[* Because the electroneutrality principle is used a decision has to be made as to the assumptions necessary when dealing with real, imperfect data. This problem is discussed in Section 2.5 under the headings OPTIONS (IOPT[2]) and NEUTRAL.]

[@ No mass balance is undertaken for H and O because of the presence of H_2O: the problem is dealt with by considering the electroneutrality and electron balance equations.]
The independent variables are:

(a) activity of H^+ and e^-;

(b) the total concentration for each element, expressed as an arbitrarily chosen species (the master species)*; and

(c) the amounts of mass *added* to the aqueous phase.

[* All equations involving a given element are written in terms of an arbitrarily chosen species of that element - the master species, also referred to as a component in the context of, for example, reactant addition options in PHREEQE. The master species are listed in Table 2.1: for many elements, the species chosen is the free ion (eg Ca^{2+} for Ca); for C it is CO_3^{2-}. The mass of any other species of the element is calculated when required using an association reaction, eg:

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$
$$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3$$
$$CO_3^{2-} + 2H^+ - H_2O \rightarrow CO_2$$

See also Section 2.2.3, and SUMS in Section 2.5.]
The set of non-linear equations resulting from principles (i) to (v) is solved using a continued fraction approach (Wigley, 1977) for the mass balance equations, and a modified Newton-Raphson procedure for all the other equations. There are some time saving procedures incorporated in the solvers which allow certain equations to be missed out in , for example, early iterations: Parkhurst et al. (1980) provide further detail on these procedures.
If numerical problems occur in PHREEQE, the parameters controlling the numerical solver can be altered using the preprocessor PIP (see KNOBS, Section 2.5). As Parkhurst et al. (1980) point out, most problems are likely to arise in redox calculations, as small changes of pe can bring about huge changes in concentrations (100 orders of magnitude is not unrealistic) which are then very difficult for the solving scheme to deal with. When a problem does arise, it is worth considering the chemistry before altering the solver parameters. For example, before the numerical solver parameters are altered, it is worth considering setting the pH and pe close to their estimated final values; or checking to see whether the problem is really one which involves redox calculations. The example Parkhurst et al. (1980) give here concerns NH_4 - if no oxidation is expected, NH_4 can be redefined as a master species, thus avoiding potentially troublesome redox calculations (in fact, in the PHREEQM preprocessor PIP, Smit and Appelo (1994) do define NH_4 as a master species, and if NH_4 is likely to be oxidised, NH_4 or NO_3 need removing from the list of master species).
Some comment is necessary on the manner in which PHREEQE deals with inorganic carbon species. Normally, inorganic carbon is determined by measurement of alkalinity, with the assumption that non-carbonate species contribute only negligibly to the alkalinity in normal pH ranges. PHREEQE allows input of alkalinity as a means of specifying inorganic carbon. It calculates the alkalinity using:

$$Alk = \Sigma A_i.m_i$$

where A_i is the number of equivalents contributed to the total alkalinity by a mole of the i^{th} aqueous species and m_i is the molality of species I (Parkhurst et al., 1980). Values of A are assigned to each species. Many species have A set to zero as they do not react with added acid. Parkhurst et al. (1980) chose a pH of 4.5 as their assumed alkalinity titration end point, as this is the standard analytical practice: any species with an H+ dissociation reaction pK greater than 4.5 is taken to contribute to the alkalinity, even though for some species fitting this criterion only partial dissociation would have taken place at a pH of 4.5. Values for A for each species can be changed in PHREEQE (see Section 2.5, under heading SPECIES (ALKSP)). Parkhurst et al. (1980) warn that the approach used for dealing with alkalinity, although satisfactory when carbonate reactions dominate, is less satisfactory when other species dominate the measured alkalinity.

2.2.5 Ion Exchange in PHREEQE/M

[The following account relies heavily on that given by Appelo and Postma (1993) on p.403-405, but also includes material from Nienhius et al. (1994)].

Appelo and coworkers recognised the basic ability of PHREEQE to carry out ion exchange calculations and used this in PHREEQM. They also provide additional refinements in PHREEQM related to sorption activity coefficients and exchange equation conventions. No allowance is made for changes in selectivity coefficients with site occupancy, with ionic strength, or with pH.
In common with most geochemical models, PHREEQE uses an ion-association model to calculate complexes in solution. To avoid changing the basic code algorithm, ion exchange reactions are dealt with as association reactions rather than in the conventional formats. For example, the reaction

$$2Na^+ + CaX \rightarrow 2NaX + Ca^{2+} \qquad (K_{Na/Ca})^2$$

(where MX is the sorbed species) is rewritten as two half reactions:

$$2Na^+ + 2X^- \rightarrow 2NaX \qquad (K_{NaX})^2$$

$$CaX_2 \rightarrow 2X^- + Ca^{2+} \qquad (K_{CaX_2})^{-1}$$

where X^- is a (fictitious) ion representing the sorption substrate. The convention used is that K values refer to reactions involving one reactant ion, ie the stoichiometric coefficient is 1 (see the note at the end of this section). It is clear that adding the half reactions produces the full reaction, and that

$(K_{Na/Ca})^2 = (K_{NaX})^2/(K_{CaX_2})$

ie $K_{Na/Ca} = (K_{NaX})/(K_{CaX_2})^{0.5}$.

There are two problems in implementing this scheme using the standard ion association algorithm. Firstly, free X^- does not exist, and introducing it would not only be physically unrealistic, it would also have implications for the solution electroneutrality and associated ionic strength and activity calculations. This problem is circumvented by setting the association constants (K_{MX}) at very high values: this results in free X^- concentrations being very low. For example, if K_{NaX} = 10, total cation exchange capacity is 0.01 mol/kg H_2O, and total Na = 0.02 mol/kg H_2O, X^- is found to be 10^{-20} mol/kg H_2O - a negligibly low concentration. Hence in PHREEQM, K_{NaX} has been set at 10^{20} (though this can be altered by the user), and numerical values for other association constants can be calculated from this value for K_{NaX}. For example, for

$Ca^{2+} + 2X^- \rightarrow CaX_2$,

$K_{CaX_2} = (K_{NaX})^2/(K_{Na/Ca})^2$

$K_{Na/Ca}$ is the standard selectivity coefficient which will either be chosen based on laboratory measurement, or used as a calibration variable in the model.
The second problem with treating ion exchange reactions as association reactions is that PHREEQM will calculate the sorbed activities in mol/kg H_2O whereas it is usual to calculate these as equivalent fractions(Gaines-Thomas convention) or molar fractions (Vanselow convention). However, this problem is solved in PHREEQM as follows. Taking the Gaines-Thomas convention, equivalent fractions can be calculated from:

Equivalent fraction = Concentration x Activity Coefficient * Charge/CEC

where CEC is total cation exchange capacity (TOT(30) in PHREEQM). Recognising that for a given cation in a given system, Activity Coefficient * Charge/CEC is a constant, the association constant can be altered to include Activity Coefficient * Charge/CEC. Thus, for example, for Ca, the true K_{CaX_2} is

$$K_{CaX_2} = \left[2.(CaX2)/[\gamma_{CaX2}.CEC]\right]/(Ca^{2+})\ (X^-)^2$$

(where round brackets are activities, and γ_{CaX2} is the CaX_2 activity coefficient). The PHREEQM algorithm requires the form

$$^{c}K_{CaX_2} = \frac{(CaX_2)}{(Ca^{2+})\,(X^{-})^2}$$

and hence

$$^{c}K_{CaX_2} = K_{CaX_2}\,\frac{CEC}{2}\,\gamma_{CaX2}.$$

PHREEQM uses the K_{MX} values in its database PHREEDA (either input or, for K_{NaX}, = 10^{20} unless altered by the user) and calculates the $^{c}K_{MX}$ values which it then uses in its calculations. Three options for calculating γ_{MX} are available:

(a) $\gamma_{MX} = \gamma_{M^+}$
ie the activity coefficient of the sorbed cation is the same as the activity of the cation in solution;

(b) $\gamma_{MX} = \gamma_{M^+} * 10\text{^}[a(1 - MX)]$
ie the "active fraction model" where a is an empirical factor dervied from the constant capacitance model; and

(c) $\gamma_{MX} = 1.0$.

Changing the activity assumption from (a) to (c) usually has little effect compared with changing selectivity coefficients within their likely ranges.

The Vanselow convention (molar fractions) cannot be implemented directly in PHREEQM as the code stands. The Gapon convention (where X^- is always single eg $0.5\ Ca^{2+} + X^- \rightarrow Ca_{0.5}\ X$) can be implemented by choosing this as an option in the input data file, and changing the database PHREEDA as indicated in Appendix V of Nienhuis et al. (1994) reproduced here as Figure 2.2.

A Note on Exchange Equation Nomenclature Used in PHREEQM

Care needs to be taken with the conventions used for K values for the exchange equations. In PHREEQM and in this report, KM/N is taken to mean an equilibrium type expression written for a reaction involving one reactant ion, ie the stoichiometric coefficient for the dissolved reactant is 1. This leads to the following equation forms:

$M^+ + NX \rightarrow N^+ + MX$	$K_{M/N}=(N^+)(MX)/[M^+)(NX)]$
$M^+ + 0.5\ NX_2 \rightarrow 0.5N^{2+} + MX$	$K_{M/N} = (N^{2+})^{0.5}(MX)/[(M^+)(NX_2)^{0.5}]$
$M^{2+} + 2NX \rightarrow 2N^+ + MX_2$	$K_{M/N} = (N^+)^2(MX_2)/[(M^{2+})(NX)^2]$
$M^{2+} + NX_2 \rightarrow N^{2+} + MX_2$	$K_{M/N} = (N^{2+})(MX_2)/[(M^{2+})(NX_2)]$
$M^{3+} + 3NX \rightarrow 3N^+ + MX_3$	$K_{M/N} = (N^+)^3(MX_3)/[(M^{3+})(NX)^3]$
etc	

In the symbol $K_{M/N}$, M and N refer to the reactant cations. It is important to note the conventions used in these equations: they lead to the simple relationships listed in Table 2.2. To use this table,

APPENDIX V

Gapon convention for exchangeable cations

Earlier versions of PHREEQM used Gapon convention for calculating activities of exchangeable ions. This convention considers the exchanger site X as basis for calculating the activity of the exchangeable cation. It can be introduced in an ion-association model by simply writing the "half reactions" as an association reaction with a single X-, and a fraction of the cation which balances the charge. Recalculation of the value of the association constant for each value of CEC (or TOT(30)) as is performed with the Gaines Thomas convention is not necessary. Set IOPT(10) = 2, and replace the species which define exchangeable cations in PHREEDA from Table V-1 below.

TABLE V-1. Adsorbed species in PHREEDA for Gapon convention.

```
181     $ START OF BLOCK OF ADSORBED SPECIES. IBEGX=181; UP TO 200
NAX       200 0.0     0.0      0.0                  0.0
14.00     0.0
 6 1.0    30 1.0
182
KX        200 0.0     0.0      0.0                  0.0
14.70     0.0
 7 1.0    30 1.0
183
CA.5X     200 0.0     0.0      0.0                  0.0
14.30     0.0
 4 0.5    30 1.0
184
MG.5X     200 0.0     0.0      0.0                  0.0
14.20     0.0
 5 0.5    30 1.0
185
AL.3X     200 0.0     0.0      0.0                  0.0
14.10     0.0
 10 0.33  30 0.99
186
MN.5X     200 0.0     1.0      0.0                  0.0
14.20     0.0
 9 0.5    30 1.0
187
FE.2X     200 0.0     1.0      0.0                  0.0
14.20     0.0
 8 0.5    30 1.0
188
FE.3X     300 0.0     0.99     0.0                  0.0
9.80      3.3
 8 0.33   30 0.99   2 -0.33
200     $ LAST OF BLOCK OF ADSORBED SPECIES. ILASX=200.
BA.5X     200 0.0     0.0      0.0                  0.0
14.60     0.0
11 0.5    30 1.0
```

Figure 2.2 Carrying out Gapon convention ion exchange reactions using PHRREQM. (From Nienhuis et al., 1994.)

decide on which species M, N, and O refer to, and use the appropriate equation: it may be necessary to use more than one equation. Two examples are:
(i) want $K_{Na/Mg}$ given $K_{K/Na}$ and $K_{K/Mg}$. In this case, M=Na, N=Mg, and O=K. Hence choose case from Table 2.2 where M=U (univalent), N=D (divalent), and O=U, and use the equation for this case [$K_{Na/Mg} = (K_{K/Mg}/K_{K/Na})$].
(ii) want $K_{Ca/K}$ given $K_{K/Na}$ and $K_{Ca/Na}$. Here, M=Ca, N=K, and O=Na. Hence choose from Table 2.2 the case where M=D, K=U, and O=U. The equation is $K_{M/N} = (K_{O/N}/K_{O/M})^2$, ie $K_{Ca/K} = (K_{Na/K}/K_{Na/Ca})^2$. A conversion is now required from $K_{K/Na}$ to $K_{Na/K}$ and from $K_{Ca/Na}$ to $K_{Na/Ca}$: these are given in Table 2.2 under the cases M=U, N=U, and M=D, N=U.

Table 2.2. A quick reference to the relationships involving selectivity coefficients for full reactions (U = univalent; D = divalent; T = trivalent).

Cation			Relationship	
M	**N**	**O**	**$K_{M/N}$=**	**$K_{N/M}$=**
U	U	-	$(K_{N/M})^{-1}$	$(K_{M/N})^{-1}$
U	D	-	$(K_{N/M})^{-0.5}$	$(K_{M/N})^{-0.5}$
D	U	-	$(K_{N/M})^{-2}$	$(K_{M/N})^{-2}$
D	D	-	$(K_{N/M})^{-1}$	$(K_{M/N})^{-1}$
U	U	U	$(K_{O/N}/K_{O/M})$	$(K_{O/M}/K_{O/N})$
D	U	U	$(K_{O/N}/K_{O/M})^2$	$(K_{O/M}/K_{O/N})$
U	D	U	$(K_{O/N}/K_{O/M})$	$(K_{O/M}/K_{O/N})^2$
U	U	D	$(K_{O/N}/K_{O/M})^{0.5}$	$(K_{O/M}/K_{O/N})^{0.5}$
D	D	U	$(K_{O/N}/K_{O/M})^2$	$(K_{O/M}/K_{O/N})^2$
U	D	D	$(K_{O/N}/K_{O/M})^{0.5}$	$(K_{O/M}/K_{O/N})$
D	U	D	$(K_{O/N}/K_{O/M})$	$(K_{O/M}/K_{O/N})^{0.5}$
D	D	D	$(K_{O/N}/K_{O/M})$	$(K_{O/M}/K_{O/N})$
T	U	U	$(K_{O/N}/K_{O/M})^3$	$(K_{O/M}/K_{O/N})$
U	T	U	$(K_{O/M}/K_{O/M})$	$(K_{O/M}/K_{O/N})^3$
etc				

In PHREEQM, ion exchange "1/2 reactions" are also written in terms of one reactant cation for the purposes of calculating K_{MX}:

$M^+ + X^- \rightarrow MX$ $\quad K_{MX} = (MX)/[(M^+)(X^-)]$

$M^{2+} + 2X^- \rightarrow MX_2$ $\quad K_{MX2} = (MX_2)/[(M^{2+})(X^-)^2]$

$M^{3+} + 3X^- \rightarrow MX_3$ $\quad K_{MX3} = (MX_3)/[(M^{3+})(X^-)^3]$.

The relationships between K_{MX} and $K_{M/N}$ are given in Table 2.3 for ease of reference. Use of Tables 2.2 and 2.3 in combination should allow calculation of any of the desired relationships.

Table 2.3 A quick reference to the relationships involving selectivity coefficients for half reactions (U = univalent; D = divalent; T = trivalent).

Cation		Relationship	
M	**N**	$K_{M/N}$ =	$K_{N/M}$ =
U	U	K_{MX}/K_{NX}	K_{NX}/K_{MX}
U	D	$K_{MX}/(K_{NX2})^{0.5}$	$(K_{MX2})^{0.5}/K_{NX}$
D	U	$(K_{MX2})^{0.5}/K_{NX}$	$K_{MX}/(K_{NX2})^{0.5}$
D	D	K_{MX2}/K_{NX2}	K_{NX2}/K_{MX2}
U	T	$K_{MX}/(K_{NX3})^{0.33'}$	$(K_{NX3})^{0.33'}/K_{MX}$
etc			

2.3 An Overview of the Preprocessor PIP

Setting up a model in PHREEQM (or PHREEQE) is facilitated using the preprocessor PIP (PHREEQM Input Procurer) (Smit and Appelo, 1993). The use of PIP will be covered in detail in Section 2.5, and only an outline will be provided here.

PIP allows input files for PHREEQM (or PHREEQE) to be constructed and modified rapidly. It also allows the user to export the output files in the degree of detail required, either in text or spreadsheet formats. PIP operates using eighteen "keywords" as listed below. Each keyword refers to a type of data which can be included in the PHREEQM input file by PIP, indicated below. Those keywords starred are only applicable when running PHREEQE.

TITLE Allows a title to be input. Useful for providing information on ouput files.

OPTIONS Basic information informing PHREEQM what type of calculation it is to do, and how it is to report the results and any problems:

IOPT[1]	Form of "printout" (ie output file contents)
IOPT[2]	Choice of procedure for enforcing, if desired, electroneutrality of initial solutions
IOPT[3]	Type of geochemical calculation (mixing/titration/ reaction/mineral equlibration)
IOPT[4]	Temperature control (constant, stepped change)
IOPT[5]	pe
IOPT[6]	Equations for activity coefficient calculation
IOPT[7]	Saving the solution for future runs
IOPT(8, 9)	Debugging options
IOPT[10]	Choice of PHREEQE (ie static, no flow calculation) or PHREEQM: and ion exchange option (see Section 2.2.4).

ELEMENTS Elements incorporated in PHREEQM: allows more elements to be added if required. Most elements are listed in their master species form: the exceptions are (master species in brackets): HCO_3^- (CO_3^{2-}), SiO_2 (H_4SiO_4), and B (H_3BO_3). The reason for these species not being in their master species form is given in Section 2.5.7 (ELEMENTS) and in Section 2.5.10 (SOLUTION (see IALK)).

SPECIES Lists elements in their "master species" forms, and all species incorporated in the geochemical model (these latter will be made up from combinations of the master species). Allows new species to be incorporated, the thermodynamic data associated with any species to be altered, and is needed to tell PHREEQM that ion exchange reactions are to be modelled.

LOOK MIN Allows thermodynamic properties of minerals to be changed, and allows new minerals to be defined. Resulting data are used only in calculation of saturation indices.

SOLUTION Defines the chemistry of the solution to be used. When using PHREEQE, the solution (or solutions if mixing or titrating) is simply the solution which will be the subject of the calculations: when using PHREEQM, the solution defined here is the solution which will be injected into the "column".

MINERALS Allows thermodynamic properties of minerals to be changed, and allows new minerals to be defined. Resulting data are used in calculations of water/rock equilibrium.

NEUTRAL Defines which species are to be used to enforce electroneutrality in the initial solution (not used unless the appropriate IOPT[2] choice is made - see OPTIONS).

REACTIONS* Defines the types and total amount of reactants to be added.

STEPS* Defines how many steps there are to be in the addition of the reactants or steps in the change of temperature.

KNOBS Convergence tweakers for the numerical solver.

SUMS Defines groups of species for output files. Useful for water quality parameters (eg hardness = Ca + Mg + Sr) and, very importantly, for outputting species which are not master species (eg S^{2-}) (see Section 2.5).

TEMP* Defining temperatures if they are to be controlled (OPTION(4), see OPTIONS). Possibilities are - fixed temperature or temperature changed in steps.

LAYERSOL Defines cell numbers and dimensions, layer dimensions, some transport parameters (eg dispersivity), initial solutions in each layer, and reactions/mineral equilibrations required.

MEDIUM Defines diffusion coefficient.

TRANSPRT Defines some transport parameters (eg porosity), printout detail, export of results to spreadsheets.

Files File management.

Quit Quitting PIP, with option to return to Files to save current work.

Hence to set up a PHREEQE model to simply examine the aqueous chemistry based on a chemical analysis, the following Keywords must be used:

OPTIONS, SOLUTION, and Files.

Additionally, TITLE might be useful, and ELEMENTS, SPECIES, LOOK MIN, NEUTRAL, and SUMS might be used if elements or species or minerals not in PHREEQE's data base are to be used (Table 2.1), thermodynamic data are to be altered, or some adjustment to the analysis is required to obtain electroneutrality, or the type of output requires modification from the default. KNOBS may be required if numerical convergence problems arise.
For a more complex PHREEQE calculation, MINERALS and/or REACTIONS or TEMP and STEPS may also be required. In this case, for example, calcite addition to the water could be modelled: or changes in water chemistry could be modelled as temperature was increased.
For a PHREEQM model of flow along a flow path in an aquifer, the following keywords may be needed:

OPTIONS, SOLUTION, LAYERSOL, MEDIUM, TRANSPT and Files.

Additionally, TITLE might be useful. ELEMENTS, SPECIES, and MINERALS would be used if new elements, species or minerals (including gases) are required or if thermodynamic constants associated with existing species or minerals (including gases) are to be changed. SPECIES is also required to initiate ion exchange reactions. LOOK MIN would allow new mineral saturation indices to be defined. NEUTRAL, KNOBS, and SUMS might also be used.
Once PIP has been used to set up the data file, PHREEQE or PHREEQM is run; these packages prompt the user for data and output file names.

2.4 Tackling Various Problems Using PHREEQE and PHREEQM

2.4.1 Setting Up the Input File Using PIP

Table 2.4 indicates the use of the PIP keywords when examining a range of problems using PHREEQE and PHREEQM.
The thermodynamic data necessary for adding new species to the PHREEQM data base may be available from a range of research papers and text books (eg Stumm and Morgan, 1996). However, internal consistency of research paper results should be assessed, and text books often only have data compilations for the more commonly investigated species. Other sources of data include special research programmes such as the CEC CHEMVAL study, and, perhaps most conveniently, the data bases in other geochemical models such as MINTEQA2 (Alison et al., 1990) and EQ3NR/6 (originally Wolery, 1983 and 1989, though considerably updated since). MINTEQA2 is available from the US EPA.

2.4.2 General Approaches

There are several types of problems which may be tackled using the PHREEQM package:

(a) if field data exist, then a model can be developed such that it adequately represents the data; developing the model will usually involve refinement in the understanding of the system, and the final solution may be used, with great care, in forecasting;
(b) if laboratory data are available, the modelling might be used to improve the conceptual understanding of the water/rock interactions, or to interpret the concentrations in terms of chemical parameters (eg CEC, selectivity coefficients (eg El-Ghonemy, 1997)); the results might then be used in attempting to predict at the field scale, though this can be dangerous;
(c) if no chemical data are available, models can be used to explore, tentatively, various possible scenarios.

A general approach to modelling with PHREEQM for cases where data exist ((a) and (b) above) might be summarised as follows:

(i) examine the problem and develop a conceptual chemical/flow model;
(ii) if necessary, test out chemical ideas using PHREEQE "static" calculations (eg saturation states, redox states);
(iii) set up the basic flow parameters (average linear velocity, porosity, dispersivity), using estimates or by fitting a breakthrough curve for a conservative species;
(iv) starting with a simple PHREEQM model (fewer cells, fewer chemical processes), gradually build up the complexity until the

conceptual model is being adequately represented; in some cases this final stage will never be reached, it being clear that the original conceptual model is wrong; style of results is more important that getting precise reproduction of experimental data;

(v) carry out sensitivity analysis of the final, preferred solutions; ie vary chemical and flow parameters to see which are the most sensitive, and check whether changing cell size or time step or convergence criteria has any effect on the predicted result.

Sensitivity analysis is very important in that it provides an indication of which parameters are the most important, and hence which to concentrate on when considering other conceptual models and/or more precise field or laboratory measurements. An important problem, as with all environmental modelling, is that of equivalence - the available data may be explained by more than one set of processes. A rapidly found solution (ie set or processes) which satisfies the available data may indicate that equivalence is a problem: if a solution is difficult to find, it may be because there are few possible solutions.

Where data do not exist the range of processes investigated and constants used needs to be much broader: the results are inevitably even less certain, though often better than simple calculations using partition coefficients.

2.5 Setting Up a PHREEQM Model Run

2.5.1 Introduction

As described above, a preprocessor, PIP (PHREEQM Input Procurer), is available for constructing input files for PHREEQE and PHREEQM (Smit and Appelo, 1994). Once the data file has been prepared, PHREEQM can be run. Figure 2.3 is a excerpt from Appelo and Postma (1993) (pages 426-427), and describes the computer requirement for running PHREEQM. On a 100MHz Pentium machine, fairly complex PHREEQM models such as those described in Section 3 take no more than a couple of minutes to run.

In the following sections, the inputs required for PHREEQM are described in some detail, taking material from Appelo and Postma (1993), Nienhuis et al. (1994), and Parkhurst et al. (1980), and incorporating additional comments arising from experience when using PIP.

2.5.2 Input Files

An input file defines the compositions of solutions, characterises the rock and where appropriate specifies chemical reactions, mineral equilibria, and mixing. Each input file has a title line and a second line where options are set. These are followed by data blocks under specific headers (keywords) which define the solutions, minerals, and reactions.

Input files are created using PIP. When this program is activated, a screen appears prompting the user to press the space bar. When this is done another screen appears, showing the keywords at the top (see Section 2.3). Each keyword refers to a type of data which can be included in the PHREEQM input file. Below the keyword list at the top of the screen, information is displayed about which keywords have to be included according to the choices made under OPTIONS (see below). Unless all these keywords have been included, the program will not run. Keywords which have been included are highlighted on the screen menu. The TITLE and OPTIONS keywords are always highlighted as they always have to be included: both these keywords are associated with data with default values, so that forgetting to alter these data will not necessarily prevent the model from running. The user may move around the keywords by using the arrow keys. The keyword which the cursor is presently on is highlighted. To select a keyword, move the cursor to the keyword and press ENTER.
In the following sections each of the keywords are described in turn.

2.5.3 Files

"Files" deals with file management. It is used to open existing data files for editing and to store completed data files. Thus it is the first keyword to be used when editing, and, except for Quit, the last (so that the prepared data file can be stored). If a data file is to be created from scratch, Files will only be needed for storing the data file. When the Files keyword is selected, four options are given at the top of the screen: quit, store data, read data and close. "Quit" returns to the main screen showing the keywords. "Read data" allows existing data files to be opened. To open a data file, select "read data" and press ENTER. The next screen displays the current directory. Use the arrow keys to select the file to be opened and press ENTER. To change drive, press the TAB key and select the drive in the box in the top right hand corner of the screen. Selecting the file and pressing ENTER returns to the Files screen. The screen space allocated to file names is limited, and PIP allows access only to the first 73. The file which is currently open is displayed at the bottom of the screen.
If a file consists of several appended files (see below), each one of the appended files can be edited, one at a time. When "Read data" is chosen, PIP will give the option of opening a new file or another one of the appended files. However, when storing the files they need to be saved in a new file and appended again, as PIP will only save the last part of the appended file when the "overwrite" command is used.
The F5 key allows the input file to be viewed at any time. Press ESCAPE to get back to the previous screen.

TABLE 2.4 The PIP keyword usage for various PHREEQE and PHREEQM problems (**Y** - necessary: Y = can be used: **X** = cannot be used: X = can be used, but not appropriate: *Y* = one or more of the marked keywords must be used: * see Section 2.2.3)

Keyword in PIP	Conditions for Use			PHREEQE Calculation Types*						PHREEQM		
				(a)	(b)	(c)	(d)	(e)	(f)			
TITLE	If title required		Y	Y	Y	Y	Y	Y			Y	
OPTIONS				**Y**	**Y**	**Y**	**Y**	**Y**	**Y**			**Y**
ELEMENTS	If adding new elements		Y	Y	Y	Y	Y	Y			Y	
SPECIES	If adding new species, altering thermodynamic data, or calculating ion exchange			Y	Y	Y	Y	Y	Y			Y
LOOK MIN	If adding new minerals for saturation index calculation			Y	Y	Y	Y	Y	Y			Y
SOLUTION				**Y**	**Y**	**Y**	**Y**	**Y**	**Y**			**Y**
MINERALS				X	X	**Y**	X	X	*Y*			Y
NEUTRAL	If require specific ions to be altered to achieve electroneutrality			Y	Y	Y	Y	Y	Y			Y
REACTION				X	X	X	**Y**	X	*Y*			**X**
STEPS	If require stepwise reaction			X	Y	Y	Y	**Y**	*Y*			**X**
KNOBS	If numerical problems	Y	Y	Y	Y	Y	Y			Y		
SUMS	If non-standard ouput is required			Y	Y	Y	Y	Y	Y			Y
TEMP				X	**Y**	X	X	X	*Y*			**X**
LAYERSOL				X	X	X	X	X	X			**Y**
MEDIUM				X	X	X	X	X	X			**Y**
TRANSPRT				X	X	X	X	X	X			**Y**
Files				**Y**	**Y**	**Y**	**Y**	**Y**	**Y**			**Y**
Quit				**Y**	**Y**	**Y**	**Y**	**Y**	**Y**			**Y**

"Store data" is concerned with saving created data files. It has a similar screen to "Read data". If the data file is to be stored as a new file, the question marks ["???"] should be selected and ENTER pressed. PIP will then ask for a file name which should be typed in in the format FILE.DAT, ie without specifying the drive: the drive is that indicated at the top right of the screen, and can be changed using the tabs key (in the same way as described for "Read data"). The file will then be saved in the current directory. If it is to be saved in a different directory, [...] should be selected. This will move up one level in the directory and the required directory can be found.

If an existing data file is to be overwritten, that file should be selected by moving the highlight to the appropriate file name in the list on the screen. PIP will recognize that the file already exists and give the options to overwrite [O], append [A] or cancel [C] at the top of the screen. To overwrite, type O and press return. The changes will then be saved in the file and PIP returns to the Files screen. If "append" is chosen, the edited file will be appended to the original file. The files will then be run one after the other and output data will be given for both simulations in the same output file. This option can be used to either run several simulations sequentially in the same model run, or to simulate different steps in an experiment such as flushing different solutions through a column of aquifer material. The first file needs to contain all the information needed for the basic simulation, for example the aquifer properties, while the appended files only contain information which is to be changed in the steps contained in the appended files. An example where three files have been appended to each other is given on page 438 in Appelo and Postma (1993). The "cancel" option returns the user to the previous page.
The file into which the edited file or new file has been saved is given as the "current output file" at the bottom of the Files page. This is an actual output file for PIP, not an output (ie results) file for PHREEQM. PHREEQM output files cannot be viewed in PIP.

2.5.4 Quit

The keyword QUIT will exit PIP. Before exiting it gives the option to either save the current file first or to exit. Type q and press ENTER to exit, or type s and press ENTER to save. If s is chosen, PIP will display the Files screen.
It is recommended that backup copies of input files be made, as sometimes the program does not run due to incompatibilities in the chosen options, and sometimes it is then not possible to access that file again (an error message appears when trying to open the file). This also happens when a file is closed before all recommended keywords have been included, eg if the user would like to preview another file before continuing. It is therefore recommended that an input file be finished before closing it for the first time. (If previewing of another file is necessary, open PIP again so that now there are two versions opened simultaneously, examine the second file, close the second

version of PIP, and continue with the editing using the original version.)

2.5.5 TITLE

Select the TITLE keyword and press ENTER to open it. In the next screen a title can be entered for the input file. The word "Example" which is given as a default title has to be deleted first (by using the backspace or delete key). The title will appear on top of the input file when it is viewed using the F5 key and in the top part of the PHREEQM output file. Press F10 when the desired title has been typed. As with all the keywords, if ESCAPE is pressed, the title will not be saved in the input file.
The top of the screen shows that there are also functions for the F9, INSERT and DELETE keys on this screen. The F9 key will return to the title which was saved the last time the F10 key was pressed. INSERT and DELETE insert or delete one character when the cursor is moved to the desired position.

2.5.6 OPTIONS

When this is selected, a screen shows a line of zeros. These correspond to 10 options (IOPT[1] - [10]), NSTEPS, NCOMPS and V0 which are listed in the bottom part of the screen and will be discussed in turn. Use the RIGHT and LEFT arrow keys to move around these options, or use the HOME, END, CTRL→ and CTRL← as explained at the top of the screen.

IOPT[1]: If set to 1 this gives a line by line "printout" (actually an output file) of the database as it is being used by PHREEQE in the output file. If set to zero, this printout is suppressed. As the printout is very large, this option can often be set to zero to suppress the printout. It must be set to zero when using PHREEQM: printout options for PHREEQM are defined under TRANSPRT (IPREX).

IOPT[2]: This option defines how electroneutrality is achieved in the initial solution. As discussed in Section 2.2.4, PHREEQE uses an electroneutrality equation in its calculations. Analyses will not be perfectly electrically neutral in general because of analytical error and unanalysed species. Hence some choice has to be made concerning how electroneutrality is to be achieved in the initial solution (all other solutions are calculated relative to the initial solutions, and hence it is only the first solutions which need to be considered). If IOPT[2] is set to zero, electroneutrality is not adjusted in the initial solution, ie any initial charge imbalance is maintained all the way through the calculation. This might be the preferred option if there is no reason to doubt the analysis. If IOPT[2] is set to 1, the pH is altered by the program to achieve electroneutrality: this cannot be done if carbon is input as alkalinity, because by fixing alkalinity, any change in pH will be unable to convert carbonate and bicarbonate to dissolved carbon

dioxide. This option is useful where the pH measurement is doubtful. If IOPT[2] is set to 2, electroneutrality is obtained by increasing the concentration of an anion or cation, each of which is defined by the user in NEUTRAL (see below): electroneutrality is achieved by addition of a charged species only, as subtraction would allow the possibility of negative concentrations occurring. This option can also be used to assign all errors to an individual species: for example, if sulphate were not analysed for, or the data were doubtful, sulphate could effectively be calculated by difference in the initial solution using IOPT[2]=2 and listing sulphate in NEUTRAL. In landfill leachates, apparent inorganic analysis charge imbalances will often be found due to the presence of acidic organic anions. In such cases, setting IOPT[2] to 0 is probably most frequently the best option.

IOPT[3]: This can have values between zero and 6, instructing the code as follows (square brackets indicate necessary parameters/keywords, and curved brackets indicate optional keywords):

= 0 calculates aqueous model only;

= 1 SOLUTION 1 is mixed with SOLUTION 2 in NSTEPS steps [STEPS and NSTEPS] (MINERALS);

= 2 SOLUTION 1 is titrated with SOLUTION 2 in NSTEPS steps [STEPS, NSTEPS, and VO] (MINERALS);

= 3 reagents added in NSTEPS reaction steps, each step involving a different specified amount of reactants [REACTION, STEPS, NSTEPS, and NCOMPS] (MINERALS);

= 4 reagents added in NSTEPS equal increments [REACTION, STEPS, NSTEPS, and NCOMPS] (MINERALS);

= 5 equilibration of SOLUTION 1 with minerals [MINERALS]; and

= 6 reagents added until equilibrium with first mineral in MINERALS [NCOMPS, MINERALS, and REACTION].

Options 1 - 6 are used only with PHREEQE. In PHREEQM reactions and mineral equilibration are defined in LAYERSOL where IOPT[3] occurs under NCELL. If it is attempted to define them here, the model will not calculate them. It may appear that option 5 can be used if the solution which is to be flushed into the column is to be equilibrated with minerals. However, option IOPT[3] = 5 deals with SOLUTION 1 which is reserved in PHREEQM for the initial water in the first layer in the column. The solution to be flushed into the column is numbered with the next higher number after the "LAYERSOLS", ie the solutions initially in each layer in the column. For example, if there are two layers in the column, the solution will be SOLUTION 3 (see also keywords SOLUTION and LAYERSOL). SOLUTION 1 is therefore not possible in PHREEQM as there will always be LAYERSOL 1.

IOPT[4]: This gives options concerning temperature. There are 4 options (square brackets indicate necessary parameters/keywords):

= 0 temperature is constant or calculated (as a linear function) when mixing / titrating;

= 1 temperature is constant, but is listed under TEMP [TEMP]; used, only in PHREEQE calculations, when the temperature of the solution for which the calculation is being carried out is different from the initial solution temperature;

= 2 temperature is changed from T0 to Tf in NSTEPS increments [NSTEPS and TEMP]; used in PHREEQE calculations only; and

= 3 temperature is varied NSTEPS times, temperature values being listed under TEMP [NSTEPS and TEMP]; used in PHREEQE only. For PHREEQM calculations where the temperature is constant, IOPT[4] = 0 is the appropriate choice, the temperature being input under LAYERSOL. IOPT[4] = 1 or 2 or 3 are only used when modelling with PHREEQE.

IOPT[5]: IOPT[5] concerns pe:

= 0 pe is constant; and
= 1 pe is determined by the reactions.

If this option is set to zero, the concentrations of redox-sensitive species such as Fe, Mn, and S^{2-} will be adjusted to keep the pe constant. If set to 1, the pe will change when redox-sensitive species are present. Setting IOPT[5] to 0 can be used if there are no redox-sensitive species present, and will speed up the calculations and reduce the chance of numerical instability problems.

IOPT[6]: This option allows the user to choose how activity coefficients are calculated:

= 0 the Debije-Hückel formula is to be used; and
= 1 the Davies formula is to be used.

Parameters for the WATEQ Debije-Hückel formula (Plummer et al., 1976) can be input or accessed under SPECIES (the WATEQ Debije-Hückel formula is the same as the standard extended Debije-Hückel formula except that the ion size parameter takes different values, and there is a second term $b_i I$, where I is the ionic strength, and b a constant dependent on species i). The extended Debije-Hückel equation is valid for ionic strengths to about 0.1 M, the Davies equation to about 0.5M (Stumm and Morgan, 1996, page 103).

IOPT[7]: This option allows a solution to be saved for another simulation:

= 0 Do not save the solution at the end of the simulation.
= i Save at the end in SOLUTION i (i in 1 - 9).

This should be set to 0 when using PHREEQM. In PHREEQE the solution composition can be saved and another simulation performed on the saved solution. However, in PHREEQM this is not applicable and when this option is set to anything other than 0 the program simply ignores the value. If another solution is to be put through the

same column, appended files have to be used as described under File Management. The appended file then contains the information on the second solution.

IOPT[8,9]: These options are only used if there are convergence problems and can be set to 0 or 1. If set to 0 there will no debugging printout in the output file, while a long printout of the iteration process will be given if set to 1. It is suggested to set them to 0 until numerical problems occur.

IOPT[10]: This option allows the user to choose which part of the code is to be used for the modelling (square brackets indicate necessary keywords, curved brackets optional keywords):

= 0 PHREEQE;
= 1 PHREEQM - transport calculations in a flowtube [TRNSPRT] (LAYERSOL, SOLUTION);
= 2 PHREEQM - Gapon exchange convention.

Setting IOPT[10] = 1 results in the use of the Gaines-Thomas convention when calculating the exchanger compositon in ion exchange calculations while setting IOPT[10] = 2 results in the use of the Gapon convention. The Gapon convention was originally used in PHREEQM, but was later replaced with the Gaines-Thomas convention. If the Gapon convention is to be used, the data in the thermodynamic database PHREEDA should be replaced using the SPECIES keyword with the data in Appendix V in the manual which comes on disk with the program (Nienhuis et al., 1994) and reproduced here as Figure 2.2 (see Section 2.2.4). An explanation of these conventions is given in Appelo and Postma (1993) pages 155 - 159, and in Section 2.2.4 above.

NSTEPS: This is the number of reaction steps. A value is needed when IOPT[3] = 1 - 4 or IOPT[4] = 2 or 3. This option is only used in PHREEQE. Reactions in PHREEQM are added under the LAYERSOL keyword.

NCOMPS: The number of reagents added in a reaction when using PHREEQE. When using PHREEQM, NCOMPS should be set here to zero: the NCOMPS option is available in LAYERSOL for each layer in the column, thus allowing different reactions to be added in different layers.

V0: The initial volume of SOLUTION 1 when titrating. Again, this is only applicable for PHREEQE as titrations are not part of transport calculations. Therefore when using PHREEQM this option needs to be set to 0.0.

When the input file is viewed using the F5 key, all these options appear as one line of numbers at the top of the input file below the title. To save the options in the input file, press F10. ESCAPE will not save the options. An example of the options line is shown in Table 2.5.

Table 2.5 Example of the OPTIONS line in an input file

Options example *Title line*		
0000110001 0 0	0.00000	*Options Line*
IOPT(1-10) NSTEPS NCOMPS VO		

2.5.7 ELEMENTS

ELEMENTS defines the elements in the model data base, their associated index numbers, and their associated (total) gramme formula weights (TGFWs). ELEMENTS can be used to make certain changes in units employed when inputting analytical data (see TNAME below), and to define new elements for consideration in the calculations. There are two headings, Include and New Elem.. To include ELEMENTS, move the highlight to Include, and press ENTER. In response to the question "Include this Keyword in Data-file? (Y/N)" type Y: the screen returns to the main ELEMENTS menu. New Elem. contains a table listing values for NELT (index number),TNAME (name), and TGFW (total gramme formula weight).

NELT NELT is the index number associated with the element. It lies between 4 and 30 inclusive. PHREEQM has the indices 4-23 and 30 preassigned, and PIP allows 24 -29 to be used for any new elements. To add a new element, move the cursor to the desired NELT line (24-29), and press F2. The TNAME and TGFW columns then become assessable.

TNAME TNAME is the name of the "element". In the case of the preassigned elements, the element is usually, but not always, named after its master species (Section 2.2.3): thus Ca appears as Ca^{2+}. Three species do not appear as their master species in the standard PHREEQM package: C appears as HCO_3^- (instead of the master species CO_3^{2+}), Si as SiO_2 (H_4SiO_4), and B as B (H_3BO_3). This is because PHREEQM is arranged so that input for carbon, when as alkalinity, will be expressed as *units* as HCO_3 (eg mg/L as HCO_3). If input for carbon were required in the form *units* as $CaCO_3$, a $CaCO_3$ entry in ELEMENTS would be necessary (with the appropriate gramme formula weight: see TGFW below). This could be achieved by changing species 15 to $CaCO_3$ using an editor (PIP does not allow access to existing species listed in the New Elem. table). Alternatively, $CaCO_3$ can be defined as a new "element" with a new NELT. In this case when C is requested in SOLUTION or LAYERSOL, the new NELT must be used in place of 15 (HCO_3^-) to indicate alkalinity. Using this approach also necessitates linking the new C species to species 15 (use SPECIES, setting logK = 0 for the association reaction for the formation of $CaCO_3$ from HCO_3). The same explanation is valid for Si and B, and it is vital that the elements are expressed in their appropriate forms, with the correct TGFWs, unless IUNTS (in SOLUTIONS) = 0 (in which case input is in mol/kg H_2O, and a correction for TGFW is not needed).

TGFW TGFW is the total gramme formula weight of the species used to represent the analytical data.

2.5.8 SPECIES

The SPECIES keyword allows new chemical species to be incorporated in the model, the thermodynamic data associated with any species to be altered, allows choice of species to be excluded from particular calculations, and is used in instructing PHREEQM which ion exchange reactions are to be considered. (There is no need to use SPECIES to list all the species required in a particular model. All the species in the data base relevant to the problem in hand will automatically be considered: in fact, as indicated above, SPECIES is used to exclude unwanted species rather than to include wanted species.) Altering the database is always *specific* to a particular input file. For any new input file which is created after the input file for which the database has been altered, PIP will go back to default values.
When the SPECIES keyword is selected a screen shows with the following headings: Include, Selection, SP-Index, SNAME, LKTOSP, LSP, Remove and Quit.

Include As described for ELEMENTS, this allows the keyword to be "included" (in the data file). The heading "Include" is selected by using the arrow keys and pressing ENTER. The next screen asks whether the user wants to include the keyword (SPECIES). Type y to include it or n not to include it. The program then returns to the previous screen. To remove a keyword from an input file, go to Include and type n.

Selection This heading shows 5 pages of species. To select a species, move the cursor to the species using the arrow keys and type y. The species will then be highlighted and "no" replaced with "yes" to indicate that the species is selected. Use the Page up and Page down keys to change page. A maximum of 30 species can be included. Each species in the database has a reference number which the program uses to identify the species. The first 30 species are reserved for the master species. The rest are species which can be formed from the master species. There are a considerable number of reference numbers with empty spaces. Here new species can be added. To do this move the cursor to an empty reference number and press the F2 key. Type the name of the new species and press ENTER. If the new species is to be included type y. It needs to be included to add the data for it to the data base which will be described in the following sections.
Species 181-190 are required for modelling ion exchange reactions. Each species is labelled MX_n, where M is the sorbed species and n its charge (see Section 2.2.4). The species "H_2CO_3" is really $H_2CO_3^*$ (ie $CO_2(aq) + H_2CO_3$ (Stumm and Morgan, 1996)), and not true H_2CO_3.

SP-Index This gives a list of the species which have been selected. This is done by moving the highlight to the appropriate species and pressing ENTER. In order to work on a species it has to be selected. Then all the headings which are described below can be edited for that species. To work on the next species go back to the SP-index and select the next species. Repeat until all selected species have been edited.

SNAME There are 9 parameters included in this heading: NSP, KFLAG, GFLAG, ZSP, THSP, DHA, ADHSP(1), ADHSP(2) and ALKSP. These are all recorded in one line in the input file produced by PIP under the heading SPECIES. The name of the species (SNAME) is recorded at the beginning of the line, and the reference number in a line of its own above this line. If new species are added, data for these parameters have to be input.

NSP This is the number of master species in the association reaction in which the species in question is formed from the appropriate master species, ie the number of species with reference numbers 1 - 30 of which the species under consideration is made up. For example, NaX is made up of Na^+ and X^- and NSP is therefore 2: or HCO_3^- is made up of CO_3^{2-} (the master species) and H^+ (master species), and NSP is therefore again 2.

KFLAG This option determines how the equilibrium (association) constant is calculated if temperatures other than the standard condition of 25°C are specified. If set to 0 the Van't Hoff equation is used, if set to 1 a power series is used. Usually the Van't Hoff equation is specified and this option set to 0: power series data only exist for a relatively small number of reactions, but are a more accurate way of representing the effects of temperature change when available. Details about the thermodynamics and application of the Van't Hoff equation can be found in Appelo and Postma (1993), pp. 59 - 62.

GFLAG This option allows the user to choose how activity is calculated for each species:

= 0 activity will be calculated as specified in IOPT[6], using either the Debije-Hückel formula or the Davies formula.

= 1 the WATEQ-Debije-Hückel formula is used (Appelo and Postma, 1993, p.413; see Section 2.5.6);

= 2 the active fraction model is used (see Nienhuis et al., 1994) in the form:

$$\gamma_{iX} = \gamma_i \times 10^{\alpha(1 - Xi)}$$

where γ_I = the activity coefficient for cation I;
iX = exchangeable cation;
α = a factor derived from the constant capacitance model;
Xi = the equivalent fraction of iX; and

= 3 activity coefficient = 1, ie activity equals concentration.

The GFLAG = 2 and 3 options are only applicable for the calculation of activity coefficients for exchangeable species (ie MX species). Often GFLAG will be set equal to 0, except for exchangeable species.

ZSP This is the charge of the species, eg it is 2.0 for Mg^{2+}, -2.0 for SO_4^{2-} and 0.0 for neutral species such as NaX.

THSP THSP is the "operational valency" or "operational oxidation state" of a species (Parkhurst et al., 1980). It is the valency or oxidation state relevant in the natural environment. In many cases, THSP is equal to the "true" valency or oxidation state of the species; however, as explained below, to increase the mathematical efficiency of the calculations, THSP is sometimes set to a value which differs from the "true" valency. The THSP of any species can be calculated by summing the THSPs of its component species, appropriately adjusted by multiplying by stoichiometric coefficients (see below).

For elements sensitive to redox conditions in the natural environment, the THSP of the elemental form is often set to zero. For elements not sensitive to redox conditions in the natural environment, it is mathematically convenient to choose another species to have a zero THSP. For example, the following species all have zero THSPs assigned to them: H^+, O^{2-}, Ca^{2+}, Mg^{2+}, Na^+, K^+, Ba^{2+}, Sr^{2+}, Al^{3+}, Li^+, Cl^-, F^-, Br^-, H_4SiO_4, H_3BO_4, PO_4^{3-}, X^- (see Section 2.2.5), and H_2O. The THSP for an electron e^- is given a value of -1.

For a redox-sensitive species, the THSP is calculated from the THSP values of its components, as indicated below:

Species	*THSP*	*Reaction*	*THSP calculation*
Fe2+	+2.0	$Fe - 2e^- \rightarrow Fe^{2+}$	0 - 2(-1) = 2
H_2	-2.0	$2H^+ + 2e^- \rightarrow H_2$	2(0) + 2(-1) = -2.0
Fe^{3+}	+3.0	$Fe^{2+} - e^- \rightarrow Fe^{3+}$	(2) - (-1) = 3.0
O_2	+4.0	$2O^{2-} - 4e^- \rightarrow O_2$	2(0) - 4(-1) = 4.0
Mn^{2+}	+2.0	$Mn - 2e^- \rightarrow Mn^{2+}$	(0) - 2(-1) = 2
CO_3^{2-}	+4.0	$C + 3O^{2-} - 4e^- \rightarrow CO_3^{2-}$	(0) + 3(0) - 4(-1) = 4.0
NO_3^-	+5.0	$N + 3O^{2-} - 5e^- \rightarrow NO_3^-$	0 + 3(0) -5(-1) = 5.0
NH_4^+	-3.0	$N + 4H^+ + 3e^- \rightarrow NH_4^+$	0 + 4(0) + 3(-1) = -3.0
SO_4^{2-}	+6.0	$S + 4O^{2-} - 6e^- \rightarrow SO_4^{2-}$	0 + 4(0) - 6(-1) = 6.0
CH_2O	0.0	$CO_3^{2-} + 6\,H^+ + 4\,e^- \rightarrow CH_2O + 2\,H_2O$	4 + 6(0) + 4(-1) = **0** + 2(0)

DHA This is the ion size parameter a_i in the extended Debije-Hückel formula for the calculation of activity coefficients. If the Davies formula is used, for example when modelling higher strength solutions, DHA is not needed, but can be left as it is - it will simply be ignored by the model. When inputting a new species this parameter can be left out unless the Debije-Hückel formula is to be used.

ADHSP(1) This is the ion size parameter a_i in the WATEQ-Debije-Hückel formula (see IOPT[6] in Section 2.5.6). Again it is not needed if the Davies equation is used, and can in such cases be ignored or left out when defining a new species.

ADHSP(2) This is the parameter b_i in the WATEQ-Debije-Hückel formula (see IOPT[6] in Section 2.5.6). Again it is not needed if the

Davies formula is used, and can in such cases be ignored or left out when defining a new species.

ALKSP This is the factor A as described in the discussion of alkalinity in Section 2.2.3. It is "the alkalinity of the species", ie the equivalents of H^+ which the species can react with when titrated with acid to an end point of pH = 4.5.

LKTOSP There are three parameters under this heading: LKTOSP, DHSP and ASP(1...5). They are the inputs needed to calculate the equilibrium constant at temperatures other than 25°C. The method of calculation to be used was specified under KFLAG (above, this section). In the input file produced by PIP, these form the second line under SPECIES.

LKTOSP This is the log K of the association reaction at 25°C. Usually these values will be determined from measured thermodynamic data, but in the case of the ion exchange "half reactions" (see Section 2.2.4), these values may be the subject of calibration against field or laboratory data.

DHSP This is the reaction enthalpy, ΔH_r^o (kcal/mole: 1 cal = 4.186 J), of the association reaction which is used in the Van't Hoff equation to recalculate log K if the temperature differs from 25°C. [Reaction enthalpies can be calculated from formation enthalpy values ΔH_f^o which are listed in thermodynamic tables (eg those in Stumm and Morgan, 1996). For example, in the following reaction to form (true) H_2CO_3, each component has the enthalpies of formation as listed:

Reaction:	CO_3^{2-}	+	$2\ H^+$	$\Rightarrow$	H_2CO_3
ΔH_f^o:	-161.84		2(0)		-167.22 kcal/mol.

To calculate the reaction enthalpy, the formation enthalpies of the reactants are to be subtracted from the formation enthalpies of the products, ie

Enthalpy: $\Delta H_r^o = -167.22 - (-161.84 + 2(0)) = -5.38$ (kcal / mole).]

ASP(1..5) If KFLAG is set to 1, a power series will be used to calculate the variation of the K of the association reaction with temperature. The power series is a function which has been obtained by fitting to experimentally determined ΔH values at different temperatures. The following equation is used by PHREEQM:

$\log K_{ass} = ASP(1) + ASP(2) \times T + ASP(3)/T + ASP(4) \times \log T + ASP(5)/T2.$

ASP(1...) are the parameters needed for this equation and there are 5 spaces where they can be entered. Values for specific reactions may be found in the literature: however, in many cases the experimental

data do not exist, and recourse has to be made to the Van't Hoff equation.

LSP There are three parameters under this heading, NSP, LSP and CSP. They define the stoichiometry of the association reaction forming the species. For reference, at the right of the screen a box shows the numbers of the master species from which the association reaction is constructed. NSP, the number of master species in the association reaction was already set in SNAME. This input is displayed in the third line under SPECIES in the input file produced by PIP.

NSP Number of species in the association reaction: eg, if there are two master species in the reaction, NSP will have values of 1 and 2. A line for the LSP and CSP entries is provided for each master species.

LSP Species index as listed in the box on the right of the screen.

CSP Stoichiometric coefficient of the LSP species in the association reaction. Eg NaX has two components, Na^+ and X^-. Each component is present once. Hence the CSP for both Na^+ and X^- is 1. For MgX_2 the components are Mg^{2+} and X^-, but this time two X^- are needed for each Mg^{2+} and the CSP is 1 for Mg^{2+} and 2 for X^-. [In fact, neither NaX or MgX_2 need defining as they are both already in the data base.]

Remove This option allows certain species to be excluded from the calculations. The data for this species are then effectively removed from the database for the current simulation only. In the input file produced by PIP the index number is shown followed by an empty line. The screen is the same as that described under "Selection" and operated in exactly the same way. Put Y against the species which are to be removed.
Remove can be used to switch between inclusion and exclusion of a new species, thus avoiding repeated editing of data or the use of two separate input files. Alternatively, Remove may be used to prevent reactions or equilibria with a particular species, eg if NO_2 and N_2 are removed from the database, NO_3 becomes a conservative ion (eg Appelo and Postma, 1993, p. 432). A further use is in the exploration of the role played by a particular species (eg in the case where thermodynamic data are uncertain, or kinetics are slow).

Use F10, not Escape, to exit any of the heading screens. Escape will not save the changes. Exiting any of the heading screens will return to the main SPECIES screen. The parameters which can be edited under each heading are shown in the bottom part of the screen. To exit SPECIES go to Quit, and the keyword screen will appear. An example of the SPECIES input in the input file is shown in Table 2.6.

Table 2.6 Example of the SPECIES data in an input file.

```
Species example                                    Title Line
0000110001 0 0        0.00000                          Options Line
SPECIES                                        Heading for SPECIES section
 48                                    )
                                       }       Species removed from
                                       }       the database using
 49                                    )       "Remove"

181                                            Index Number of species below
NAX       200 0.0       0.0       4.0       4.0       0.075     0.0          )
      SNAME
20.00     0.0                                                               }
      LKTOSP
 6  1.000 30  1.000                                          )      LSP
182  NSP KFLAG GFLAG  ZSP  THSP  DHA  ADHSP(1)  ADHSP(2)  ALKSP
KX        200 0.0       0.0       3.0       3.5       0.015     0.0
20.70     0.0          (LKTOSP and DHSP)
 7  1.000 30  1.000  (LSP and CSP for species No.7, LSP and CSP for species No.30)
189  Species Name
NH4X      200 0.0      -3.0       2.5                           0.0
20.60     0.0
 23 1.000 30  1.000
END
```

2.5.9 LOOK MIN

LOOK MIN allows control of which saturation index values are printed in output files: it has no influence over the aqueous model calculations, and can be omitted from any model run without affecting the model calculations. Hence LOOK MIN is used to add or remove minerals from the solution index output, and to alter thermodynamic data for saturation index calculations *only*. Standard PHREEQE/M output files contain many saturation indices of interest, and often it is unnecessary to use LOOK MIN. In the context of LOOK MIN, and elsewhere in the context of the PHREEQM package, "minerals" include gases, as solid and gas phases are dealt with in the same way by PHREEQM. Six headings are given: Quit, Include, Selection, NAMELK, LLOOK and AMIN. Include works in the same way as for other keywords (Y to include LOOK MIN, N to not include LOOK MIN).

Selection Provides the means to choose which mineral to work on (34 minerals, three gases) and the means to define new minerals.

NAMELK NAMELK contains the thermodynamic data for the minerals chosen using Selection. The operation of NAMELK is exactly as for SIMIN in MINERALS.

LLOOK LLOOK defines the mineral in terms of its *dissolution* reaction. The operation of LLOOK is exactly as for LMIN&CMIN in MINERALS.

AMIN AMIN defines the power series for calculating the equilibrium constant variation with temperature (see ASP in SPECIES, Section 2.5.8). Access to AMIN is only allowed if LOOKFL = 1 in NAMELK, ie a power series is chosen. The operation of AMIN is exactly as for AMIN in MINERALS.
It is possible to have different thermodynamic data in MINERALS and LOOK MIN, which might just be of use when investigating the effect of varying thermodynamic parameters, but obviously great care needs to be taken to keep track of such modifications.

2.5.10 SOLUTION

In PHREEQE, the keyword SOLUTION defines the solution composition which is to be used: if mixing or titration is to be modelled, two solutions (solutions 1 and 2) are defined using this keyword (mineral equilibrations are always done on solution 1). In PHREEQM, SOLUTION is used to define the solution which will be injected into the "column" of aquifer material; the composition of the solutions already in the column are defined under the LAYERSOL keyword.
SOLUTION can be used to instruct *PHREEQE* to carry out ion exchange reactions on a solution: X^- is input under the heading DTOT, and appropriate exchanging species (eg NaX, CaX_2) must be input in SPECIES. The calculation assumes the exchanger is initially "empty", and therefore great care needs to be taken in doing ion exchange calculations using SOLUTION: enough equivalents of cations need to be added to the initial solution in order that the exchange sites can be filled up, or else an initially unplanned apparent electrical imbalance results.
There are 6 headings in the SOLUTION keyword: Quit which is self-explanatory, Include which works in exactly the same way as explained under SPECIES (type Y to include the keyword), Sol. Index, Head, NTOTS and DTOT. F5 allows the input file to be viewed at any time, and the parameters which can be edited under each heading are again shown in the bottom half of the screen. Use the right and left arrow keys to move from keyword to keyword.

Sol. Index This screen has two functions. The first is to select the solutions which are to be used, by using the up and down arrow keys to move the cursor to the solution in question, and typing Y for yes or N for no. The second function is to select the solution which is to be worked on by moving the cursor to that solution and pressing ENTER. Only that solution will be edited after leaving "Sol.Index" and working on the other headings. If a second solution is to be edited it has to be selected in the "Sol.Index" first.

When using the PHREEQE component of PHREEQM up to two solutions can be used (eg one solution and one titrating solution), and these are assigned the names Solution 1 and Solution 2. However, in PHREEQM only one solution can be used, ie the solution which is to be injected into the aquifer material. Which solution index number is used for this solution depends on how many layers are defined in the "column". Each layer in the column already contains a solution. These are called LAYERSOLs when they are being defined in the LAYERSOL keyword, though they are referred to here as SOLUTIONS. Under the SOLUTION keyword, the LAYERSOLs are counted as the first solutions, and the flushing solution defined in SOLUTION has an index number one greater than the last LAYERSOL. For example, if two layers are present in the column (LAYERSOL 1 and LAYERSOL 2), the flushing solution will be Solution 3. As up to ten layers (meaning ten LAYERSOLs) can be used, eleven solutions are shown on the "Sol.Index". Solution 1 in SOLUTION is never used with PHREEQM. When modelling continuous injection of a solution into homogeneous (ie unlayered) aquifer material, the injection fluid will be labelled SOLUTION 2, and the water which is to be displaced, SOLUTION1. When modelling a pulse injection, two layers can be used, the upflow one having an initial water composition of the injection fluid: in this case the initial waters will be labelled SOLUTION1 and SOLUTION2 (and LAYERSOL1 and LAYERSOL2 in keyword LAYERSOL), and the flow will result from injection of SOLUTION3 at the upstream end of the flow tube. Note that if Sol.Index is ignored, PIP allows input of the solution details, highlights SOLUTION in the main menu, and allows the data file to be stored. However, it will have ignored the solution when it constructed the final input data file, thus leading usually to failure when running the PHREEQM package.

Head This allows a title for the solution to be entered. This will then be displayed in the input file produced by PIP under the heading of the solution under consideration. The screen operates in an identical manner to that described for the TITLE screen.

NTOTS There are 7 parameters under this heading: NTOTS, IALK, IUNITS, PH, PE, TEMP(°C) and SDENS.

NTOTS Number of element concentrations to be input under DTOT.

IALK This specifies the way inorganic carbon is input. Two main options are available: as total inorganic carbon (TIC) or as alkalinity.

If the inorganic carbon is to be input (under DTOT) as TIC, IALK is set to 0. The units of TIC are *units* as HCO_3 , where *units* (eg mg/L) are specified under IUNTS (see immediately below). If it is required to input TIC as *units* as C, for example, species 15 in ELEMENTS would have to be altered from HCO_3 to C with the appropriate TGFW (total gramme formula weight): PIP does not allow this to be carried out, and hence it would need to be done by direct editing of the input file produced by PIP. If the inorganic carbon is to be

input (under DTOT) as alkalinity, IALK is set to 15 or to a value between 24 and 29 inclusive. These values of IALK relate to the index number of the carbon species as listed under ELEMENTS. Species 15 in ELEMENTS is HCO_3, so that if IALK = 15, alkalinity values should then be input in DTOT as *units* as HCO3 (where *units* are defined in IUNTS, see immediately below). If alkalinity is to be input in terms of some other unit, such as units as $CaCO_3$, a slot between 24 and 29 inclusive would be chosen in ELEMENTS to define $CaCO_3$ with its appropriate TGFW. Setting IALK to this slot number would then allow input of inorganic carbon in the appropriate units. In addition, if this route is chosen, the new carbon species would need to be linked, using SPECIES, to the carbon master species (CO_3) (see Section 2.5.7). The easiest way to alter the input units is probably to replace CO_3 and its TGFW in ELEMENTS using a separate editor (ie the first method described above). See Section 2.2.3 for a discussion of the way PHREEQM calculates alkalinity.

IUNTS IUNTS is used to inform PHREEQM which units are to be used when inputting the concentration data. The options are:
= 0 mol / kg H_2O, alkalinity or total inorganic carbon (TIC) (see DTOT) in eq/kg H_2O;
= 1 mmol / L, alkalinity or TIC (see DTOT) in meq/L;
= 2 mg / L for the species as listed (with their appropriate TGFWs (total gramme formula weights)) in ELEMENTS; alkalinity or TIC (see DTOT) in mg/L as *species*, where *species* is as specified by IALK (see immediately above) (in PHREEQM as supplied, setting IALK to 15 will indicate carbon species are to be input in mg/L as HCO_3, as species 15 in ELEMENTS is HCO_3);
= 3 ppm for the species as listed in ELEMENTS (see IUNTS=2), hence alkalinity or TIC (see DTOT) will be in ppm as HCO_3; and
= 4 mmol / kg solution, alkalinity or TIC (see DTOT) in meq/kg solution.

Note that for IUNTS = 2 or 3, the input concentrations will be in terms of *units* (mg/L for 2, ppm for 3) as species (where species is as defined in ELEMENTS). Care needs to be taken, especially in the cases of N species, Si, B, and P, where frequently analytical data are presented in varying forms (eg NO_3 as NO_3, and NO_3 as N). Units for X^- (the exchange capacity, see under DTOT below) are always meq/kg H_2O (see DTOT below).

[Measured alkalinity is usually expressed as mg/L as $CaCO_3$ and has to be converted to mg/L as HCO_3^- unless the species used to represent carbon is changed in ELEMENTS as explained above. Alkalinity is measured by titration with acid such as sulphuric acid, and is therefore a measure of how much H^+ can be neutralized by the solution. To convert from mg/L as $CaCO_3$ to mg/L as HCO_3^-, one has to consider that CO_3^{2-} can neutralize two H^+ per molecule while HCO_3^- can neutralize only one. Therefore the correction factor which has to be applied to the measured alkalinity in mg/L as $CaCO_3$ to express it in mg/L as HCO_3^- can be calculated as follows:

$$\frac{2\,HCO_3^-}{CaCO_3} = \frac{2\,(61)}{100} = 1.22$$

ie *multiply measured alkalinity in mg/L as* $CaCO_3$ *by 1.22 to express it as mg/L as* HCO_3^-. *For TIC of X mg/L as C, proportion using X x 61/12 mg/L as* HCO_3.]

PH This is the pH of the solution. The default is set at 7.00.

PE This is the pe of the solution. The default is set to a pe of 8.0. pe and E_H are related by:

$$Eh = \frac{2.303\,RT}{F} pe$$

where R = gas constant (1.987 cal / K.mol (= 8.314 x 10^{-3} kJ / K.mol))
T = absolute temperature (K)
F = Faraday constant (23.06 kcal / V (=96.42 kJ/V))
2.303 is the conversion from natural to base 10 logarithms.
Substituting for the constants gives:

$$E_H = 0.059\ pe$$

TEMP The temperature of the solution needs to be input in °C.

SDENS Solution density in kg/L. The default is set to 1.0 kg/L. This is reasonable for most groundwaters. It may be appropriate to change this parameter when modelling interactions with highly saline waters, eg concentrated wastes or seawater. However, at high concentrations, activity coefficient calculation using the standard equations becomes increasingly less valid, and flow patterns will also be affected. There is a version of PHREEQE available which includes the Pitzer equations (Crowe and Longstaffe, 1987), capable of describing the behaviour of a limited range of elements in aqueous systems up to brine strength, but the Pitzer option is not available in the PHREEQM package.

DTOT Under this heading the concentrations are input using the units which were specified under IUNITS, each component being entered in the form of the species listed in ELEMENTS. Move around the species using the arrow keys. Press ENTER after entering each concentration, or it will not be saved. To deselect a species, move the cursor to the species and press the DELETE key. Only the number of species specified under NTOTS can be entered. If a different number has been entered, PHREEQM does not allow exiting from the screen. Some fluids, such as landfill leachates, contain high concentrations of organic acids which contribute to the measured alkalinity. In this case the measured alkalinity may be a significant overestimate of the inorganic C content of the water. There are several ways to circumvent this problem, including defining new organic species with appropriate ALKSP values (see SPECIES, Section 2.5.8). Sometimes the assumption of calcite saturation can be used with measured pH to calculate solution alkalinity (due to carbon sources)(using PHREEQE

prior to the main modelling work). In other cases, measured CO_2 gas phase concentrations and pH may be available to define alkalinity. In other cases a value for TIC may be available, and this may be input by setting IALK to zero and entering TIC (in *units* as HCO_3) under species 15.

X^- represents the exchange capacity of a solid in contact with the solution (see Section 2.2.5). Its units are meq/L H_2O, whatever the choice made using IUNITS. It can be calculated from the usual units of cation exchange capacity (meq/100g dry solid) using:

$$[X^-](mg/L\ H_2O) = 10\ \rho\ CEC/\phi,$$

where ρ is dry bulk density, CEC is cation exchange capacity in meq/100g, and ϕ is porosity (for more detail see DTOT under LAYERSOL (Section2.5.6)).

Once all concentrations have been entered correctly press F10 to return to the SOLUTION screen. Again, the input file can be previewed using F5. An example of the input under SOLUTION is shown in Table 2.7.

Table 2.7 Example of SOLUTION data in an input file

```
Solution Example                                          Title Line
0000110001 0 0        0.00000                             Options Line
SOLUTION 2                                                Solution Index
Column Flush                                              Solution Head
11 15 2        7.85       8.0       10.0       1.0       NTOTS
  4 5.7000E+01   5 2.7000E+01   6 1.5000E+01   7 1.3000E+01   8
1.0000E-02        )    DTOT:Species
  9 1.0000E-02  14 7.0000E+01  15 1.8540E+02  16 7.3000E+01  19
2.0000E-02 }     Index Numbers
  23 1.2900E-01                                        ]    and
Concentrations
END
```

2.5.11 MINERALS

The MINERALS keyword is used to define minerals which solutions are to be kept in equilibrium with during PHREEQE calculations. A solution can be kept in equilibrium with up to 10 minerals (although this may not be chemically possible). Alternatively, reactants can be added until equilibrium is achieved with respect to the first mineral listed under MINERALS. MINERALS is also used to define up to three new minerals which will then be used in either PHREEQE or PHREEQM calculations. MINERALS may be used when IOPT[3] (in OPTIONS) = 1,2,3,or 4, and is required when IOPT[3] = 5 and 6: all these are PHREEQE options. When using PHREEQM, IOPT[3] = 0, and mineral equilibria are defined in LAYERSOL: however, MINERALS is needed if new minerals are to be defined for use in PHREEQM, or if the thermodynamic properties of the minerals are to altered. There are six headings: Quit, Include, Selection, SIMIN, LMIN&CMIN, AMIN.

Include operates as for other keywords (cursor to Include (or type I), ENTER, reply Y if this keyword is to be used).
Selection Selection allows choice of minerals for the water to be kept in equilibrium with, including choice (and naming) of new minerals. Once chosen, access is allowed to the thermodynamic data for each mineral. Selection displays a screen containing 34 mineral names and three gas names ("PCO2", "O2 gas", and "H2 gas"). Moving the cursor to the appropriate mineral name and typing Y includes the mineral in further calculations. Up to three new minerals can be added: move the cursor to a slot marked <new> and press F2. A box will appear in the right of the screen with space to type a name: on pressing ENTER, the mineral name will replace <new>, and the new mineral can then be selected. Gases are treated as minerals in that equilibrium with a gas phase is dealt with in a very similar way to equilibrium with a mineral phase. One of the minerals to be included in the calculations must be chosen for further work. This is achieved by moving the cursor to one of the mineral names marked Yes and pressing ENTER. This returns the user to the menu.

SIMINSIMIN displays the following details of the mineral phase chosen in Selection, and allows access in most cases to change these details: name (not changeable), the number of species in the dissolution reaction (NMINO), the sum of the operational valencies (ie sum of THSP values; see SPECIES, Section 2.5.8) of the constituent species (THMIN)(see below), the log(K) of the dissolution reaction at 25°C (LKTOM), the enthalpy of the dissolution reaction (DHMIN) (kcal/mol), a flag to indicate whether the Van't Hoff equation (MFLAG = 0) or a power series equation (MFLAG = 1) is to be used to calculate K temperature dependence, and the saturation index (= log10([ion activity product]/[K]) value which is to be used to control concentrations in the aqueous phase (SIMIN)(see below).

THMIN represents the sum of the operational valencies (THSP, see SPECIES, Section 2.5.8) for the species in the association reaction under consideration (including H^+, e^-, and H_2O)(Parkhurst et al., 1980, page 23). For example,

Ca^{2+}	+	CO_3^{2-}	$\rightarrow$	$CaCO_3$
$THSP(Ca^{2+})$	+	$THSP(CO_3^{2-})$	=	$THMIN(CaCO_3)$
=1(0)	+	1(+4)	=	4.0

THSP is explained in Section 2.5.8.

SIMIN allows a mineral phase to maintain some degree of oversaturation before precipitation can occur, and is also useful when controlling gas phase/water phase interactions (enter the partial pressure for SIMIN)(see below under LAYERSOL, Section 2.5.18 (SIMEX)).
F10 stores the newly created input data, and returns the user to the main menu: ESCape ignores changes to the input data and returns the user to the main menu.

LMIN&CMIN The screen associated with LMIN&CMIN provides the dissociation reaction details for the mineral phase chosen using

Selection. There are three columns displayed, and a box containing the full list of the aqueous species together with the species indices, for ease of reference (page up and page down allows examination of all the pages of species). When defining new minerals there is no need to use just the master species. The first column, headed NMINO, contains the numbers of the species involved in the reaction. The second column, headed LMIN, contains the index numbers of the species involved in the dissociation reaction. The CMIN column contains the stoichiometric coefficients of the species in the dissociation reaction: products of the dissociation reaction are written as positive, eg for

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$

NMINO	LMIN	CMIN
1	4	+1.0
2	15	+1.0.

F10 stores the newly created data, and returns the user to the main menu; ESC ignores changes to the data, and returns the user to the main menu.

AMIN AMIN displays and allows alteration to the power series constants for the temperature dependence of the dissociation reaction for the mineral. Few minerals have such data, and normally access to AMIN will be denied (MFLAG in SIMIN = 0, ie Van't Hoff equation is chosen). AMIN does not allow a power series parameter to remain unentered (ie blank), even if it is missing in the default value set provided: exit AMIN using ESCape, or, if the parameters have been altered, by entering zero in the place of the blanks.

2.5.12 NEUTRAL

If IOPT 2 was chosen to be 2, ie electroneutrality is to be obtained by the addition of positive or negative ions, the ions to be used for this purpose has to be entered here. A maximum of two ions can be used: one cation to add positive charge and one anion to add negative charge. Subtraction of ions is not allowed in order to prevent the possibility of negative total concentrations being calculated. There are two headings under this keyword: Include and Selection. Include works as described previously: the keyword has to be included before an ion can be selected by typing Y for yes or N for no if it is not to be included.

Selection There are two subheadings under this heading: LPOS and LNEG. A list of ions which can be entered is given in the box on the right of the screen. Only master species are allowed and H^+ and e^- cannot be used. Enter the index number of the cation-forming master species under LPOS and the index number of the anion-forming master species under LNEG. A discussion of electroneutrality is given in Section 2.5.6 (OPTIONS), under IOPT[2].

Table 2.8 shows an example of how the entries under NEUTRAL are represented in the input file produced by PIP. Under the heading NEUTRAL the index numbers of the cations used to obtain electroneutrality are shown, in this case Ba^{2+} and Br^-.

Table 2.8 Example of data under NEUTRAL in an input file

NEUTRAL	*Keyword*
11 22	*Index numbers of cation and anion used for electroneutrality*

2.5.13 REACTION

REACTION allows reactions to be carried out using PHREEQE. Reagents are: added in steps (IOPT[3] (in OPTIONS) = 3); added in steps of equal increment (IOPT[3]=4); or added until equilibrium with the first mineral listed under MINERALS (IOPT[3]=6). REACTION defines the stoichiometry and valence of the species to be added as a reaction to a solution defined under SOLUTION. The maximum number of reagent species is 30. The amount of reaction - the "reaction progress" - is defined using XSTEP in the keyword STEPS: REACTION changes the total aqueous mass by the stoichiometric coefficient (CREAC in REACTION) multiplied by the total moles of reaction (XSTEP) (although, subsequently, in a calculation, PHREEQE may further change the mass in order to bring the water into equilibrium with a mineral phase).
When adding reactants it is necessary to be careful to balance charges. Adding SO_4 without a cation is equivalent to adding H_2SO_4, which may or may not be the intention.
It is possible to add an inert electrical charge using REACTION. This may be useful if PHREEQE is being used to model the chemical pathways from one known solution with an electrical imbalance to a second with a different electrical imbalance. The procedure, which must be carried out by direct editing of the data file as PIP does not appear to allow the access necessary, is to assign LREAC(I) (the index number of reaction component I) to zero, CREAC(I) (the stoichiometric coefficient for the reaction component) to the difference in charge imbalance in eq/kg H_2O, and THMEAN(I) (the summed operational valency) to zero. In this way, the implicit addition of acid or base is avoided. Care needs to be taken to use the correct formats, as PHREEQE is format sensitive (4I for LREAC, F8.3 for CREAC and THMEAN, one line containing a maximum of four reagents: add as many lines as appropriate for NCOMPS (OPTIONS)).
To use REACTION, IOPT[3] in OPTIONS needs to be set to 3 (reagents added in steps of specified increments), 4 (reagents added in steps of equal increments), or 6 (reagents added until equilibrium with first mineral in MINERAL). In addition, NCOMPS also in OPTIONS, needs to be set to the appropriate number of components which are to be added in the reaction.
REACTION has four headings: Quit, Include, Selection, and CREAC. Include is used in the same way as in other keywords (Y = inclusion of REACTION; N = no inclusion of REACTION).

Selection Selection allows the selection of the reaction components. The choice is from the list of master species, though H^+, e^-, and H_2O are excluded, and O_2 (aq) and H_2 (aq) are included. Move the cursor to the appropriate location and press Y for yes. F10 returns the user to the REACTION menu.

CREAC CREAC allows the stoichiometric coefficients of the reaction components (CREAC(I)) and the component operational valencies (THMEAN(I)) to be input. The idea of operational valency is discussed under THSP in SPECIES (Section 2.5.8). THMEAN is the THSP assigned to the master species for the reaction being modelled: it does not necessarily have to be equal to the value of THSP. For example, input of organic (ie reduced) carbon might be modelled using master species 15 (CO_3^{2-}) but with the usual THSP of 4.0 replaced by (a THMEAN) of 0.0. (See Appelo and Postma, 1993, example 10.7, page 418).

There are four columns on the CREAC screen. The first has the index numbers of the species chosen in Selection, the second their names. The third column is to allow values for CREAC to be entered. The fourth column is to allow the input of THMEAN. F10 retains the amendments and returns the user to the main REACTION menu: ESC looses the amendments and returns the user to the main menu.

2.5.14 STEPS

STEPS allows the progress of a reaction to occur in steps when using PHREEQE. Thus, for example, calcite might be added to a solution in small increments, or steps, until calcite solution is achieved. NSTEPS in OPTIONS defines the number of steps ($\leq$50): if NSTEPS = 0, PIP will not allow access to STEPS. There are three headings: Quit, Include, and XSTEP. Include works as for all other keywords (Y for inclusion, N for no inclusion of the keyword).

XSTEP This has different meanings depending upon the value for IOPT[3] in OPTIONS:

for IOPT[3]=0, the aqueous model only is calculated, and hence XSTEP is not required; PIP denies access to XSTEP;

for IOPT[3]=1 (mixing of solutions), XSTEP is the fraction of solution 1 to be mixed with solution 2. NSTEPS values are read, with each XSTEP value representing the absolute fraction; inputting 0.5, 0.5 will cause the model to carry out the same calculation twice;

for IOPT[3]=2, XSTEP is the value of solution 2 to be titrated into solution 1. The volume must have the same units as V0 (OPTIONS); again, NSTEPS values are required;

for IOPT[3]=3 (addition of reactants in specified amounts), XSTEP is the "number of moles of reaction" to occur (for explanation, see REACTION); again, NSTEPS values are required;

for IOPT[3]=4 (addition of reactants in NSTEPS equal amounts), XSTEP is the total "number of moles of reaction" to be added in NSTEPS steps; hence in this case, only one XSTEP value should be input; each step will allow XSTEP/NSTEPS moles of reaction;
for IOPT[3]=5, as mineral equilibrium only occurs, XSTEP is not required and PIP denies access to XSTEP;
for IOPT[3]=6, as reactants are added until equilibration with the first listed mineral, XSTEP is not required and PIP denies access to XSTEP.

2.5.15 KNOBS

The input under this keyword varies the parameters which are used in the numerical procedure. Being able to vary these parameters is useful in the case of convergence problems. The numerical procedure is very briefly outlined in Section 2.2.4. There are two headings, Include and DMAX. Include operates as described before for other keywords (Y for inclusion of the keyword, N for no inclusion). There are 9 parameters under DMAX, none of which have been described in detail by either Parkhurst et al. (1980) or by Appelo and Postma (1993). Unfortunately there has been insufficient time in the current project to investigate these parameters in detail, but Table 2.9 summarises some useful information. Section 2.2.4 provides some suggestions for solving convergence problems.

2.5.16 SUMS

This keyword can be used to define sums of up to 50 species. A maximum of 10 sums can be defined. The total concentrations of the species defined in each sum are reported in the spreadsheet file named under SSNAM3 (TRANSPRT, Section 2.5.20) in mol/L. SUMS is used most frequently for two main reasons. Firstly, to allow the output of water quality parameters (eg hardness is the sum of Ca, Mg, ...). Secondly, and more importantly, the concentrations of individual species or a group of species which are not routinely reported on can be obtained. For example, in modelling landfill leachates it may be useful to output concentrations for different sulphur species (SO_4^{2-}, HS^-, H_2S) and methane (CH_4aq) as these are components of sulphate reduction and organic matter degradation reactions: as only master species (SO4 = sum of all S-bearing species, and CO3 = sum of all C-bearing species) are output in the other spreadsheets, SUMS provides the only way of conveniently outputting the concentrations of the individual species of interest.
Apart from Include and Quit which are as described above there are two other headings under this keyword: SUNAME AND LSUM.

Table 2.9 Values for KNOBS parameters.

Parameter	PHREEQE Default	PHREEQM Default	PHREEQM Expected Range
DMAX	10.0	17.0	0.4 - 20.0
DMIN	0.7	0.4	0.1 - 0.9
FUDGE	1.0	1.0	
RMAX	20.0	17.0	0.4 - 20.0
RMIN	0.9	0.8	0.1 - 0.9
CNVRG1	0.1	0.1	
CNVRG2	10000.0	10000.0	
ITMAX*	200	400	
CHKMU	1000.0	1000.0	

** Maximum number of iterations*

SUNAME Under this heading the sums are named and the number of species which each sum is to contain is entered. Enter the name of the sum under SUNAME and the number of species under NSUM. Press ENTER after each entry and use the arrow keys to move between SUNAME and NSUM. A reference number is given for each sum. Up to 10 sums are possible. The sums will appear in the spreadsheet file in this order. To leave the screen select one of the defined sums and press ENTER. It will then be possible to work on the selected sum. If no sum is to be worked on press ESCape.

LSUM The species in each sum are defined under this heading. The name of the sum which is being worked on and the number of species which it is to consist of are given at the bottom of the screen. A reference number list for the species which are to be added is given, corresponding to the chosen number of species. A table of species index numbers is given on the right. Use the "Page Up" and "Page Down" keys for further pages in this table. Enter one species index number against each of the reference numbers given. When finished, press F10. If more than one sum is to be defined, go back to SUNAME, select the next sum and repeat the procedure.
If a species for which a sum is to be made is contained in a molecular formula more than once, the index number of that species has to be listed in the sum as many times as it occurs in the molecular formula. For example, if a sum of species containing HS^- is to be made, the index number of the species $Fe(HS)_3^-$ has to be listed three times in the sum as each mole of $Fe(HS)_3^-$ contains three moles of HS^-; obviously, one might require only to consider HS^-, in which case $Fe(HS)_3$- will be ignored.
As it is necessary to know how many species each sum is to consist of before the table of species can be accessed in LSUM, a table of all species already in the database and their reference numbers is given in Table 2.10. The most common redox status of redox sensitive species is also shown. An example of SUMS in an input file is shown in Table 2.11.

Table 2.10 Species contained in the PHREEQE database and their index numbers and redox status of redox-sensitive species.

Index No.	Species	Redox Status	Index No.	Species	Redox Status
1	H^+		106	$FeCO_3$	Fe II, C IV
2	e-		107	$FeHCO_3^+$	Fe II, C IV
3	H_2O		108	$FeSO_4$	Fe II, S VI
4	Ca^{2+}		109	$FeHSO_4^+$	Fe II, S VI
5	Mg^{2+}		110	$Fe(HS)_2$	Fe II, S -II
6	Na^+		111	$Fe(HS)_3^-$	Fe II, S -II
7	K^+		112	$FeHPO_4$	Fe II
8	Fe^{2+}	Fe II	113	$FeH_2PO_4^+$	Fe II
9	Mn^{2+}	Mn II	114	FeF^+	Fe II
10	Al^{3+}		115	Fe^{3+}	Fe III
11	Ba^{2+}		117	$FeOH^{2+}$	Fe III
12	Sr^{2+}		118	$FeOH_2^+$	Fe III
13	H_4SiO_4		119	$FeOH_3$	Fe III
14	Cl^-		120	$FeOH_4^-$	Fe III
15	CO_3^{2-}	C IV	121	$Fe_2OH_2^{4+}$	Fe III
16	SO_4^{2-}	S VI	122	$Fe_3OH_4^{5+}$	Fe III
17	NO_3^-	N V	123	$FeCl^{2+}$	Fe III
18	H_3BO_3		124	$FeCl_2^+$	Fe III
19	PO_4^{3-}		125	$FeCl_3$	Fe III
20	F^-		126	$FeSO_4^+$	Fe III, S VI
21	Li^+		127	$FeHSO_4^{2+}$	Fe III, S VI
22	Br^-		128	$Fe(SO4)_2^-$	Fe III, S VI
23	NH_4^+	N -III	129	$FeHPO_4^+$	Fe III
30	X^-		130	FeH_2P^{2+}	Fe III
31	OH^-		131	FeF^{2+}	Fe III
32	O_2aq		132	FeF_2^+	Fe III
33	H_2aq		133	FeF_3	Fe III
34	HCO_3^-	C IV	134	$MnOH^+$	Mn II
35	H_2CO_3	C IV	136	$MnCl^+$	Mn II
36	CH_4aq	C -IV	137	$MnCl_2$	Mn II
40	HSO_4^-	S VI	138	$MnCl_3^-$	Mn II
41	S^{2-}	S -II	139	$MnCO_3$	Mn II, C IV
42	HS^-	S -II	140	$MnHCO_3^+$	Mn II, C IV
43	H_2S	S -II	141	$MnSO_4$	Mn II, S VI
48	NO_2^-	N III	142	$Mn(NO_3)_2$	Mn II, N V
49	N_2aq	N 0	143	MnF^+	Mn II
50	NH_3aq	N -III	144	Mn^{3+}	Mn III
52	$NH_4SO_4^-$	N -III, S VI	150	$AlOH^{2+}$	
57	$H_2BO_3^-$		151	$AlOH_2^+$	
58	$BFOH_3^-$		152	$AlOH_3$	
59	$BF_2OH_2^-$		153	$AlOH_4^-$	
60	BF_3OH^-		154	$AlSO_4^+$	S VI
61	BF_4^-		155	$Al(SO_4)_2^-$	S VI
65	HPO_4^{2-}		156	$AlHSO_4^{2+}$	S VI
66	$H_2PO_4^-$		157	AlF^{2+}	
69	HFaq		158	AlF_2^+	
70	HF_2^-		159	AlF_3	
75	$CaOH^+$		160	AlF_4^-	
76	$CaCO_3$	C IV	161	AlF_5^{2-}	
77	$CaHCO_3^+$	C IV	162	AlF_6^{3-}	
78	$CaSO_4$	S VI	164	$H_3SiO_4^-$	
80	$CaPO_4^-$		165	$H_2SiO_4^{2-}$	
81	$CaHPO_4$		166	SiF_6^{2-}	
82	$CaH_2PO_4^+$		167	LiOH	
83	CaF^+		168	$LiSO_4^-$	S VI
85	$MgOH^+$		170	$BaOH^+$	
86	$MgCO_3$	C IV	171	$BaCO_3$	C IV
87	$MgHCO_3^+$	C IV	172	$BaHCO_3^+$	C IV
88	$MgSO_4$	S VI	173	$BaSO_4$	S VI
89	$MgPO_4^-$		176	$SrOH^+$	
90	$MgHPO_4$		177	$SrHCO_3^+$	C IV
91	$MgH_2PO_4^+$		178	$SrCO_3$	C IV
92	MgF^+		179	$SrSO_4$	S VI

93	NaOH		181	NaX	
94	$NaCO_3^-$	C IV	182	KX	
95	$NaHCO_3$	C IV	183	CaX_2	
96	$NaSO_4^-$	S VI	184	MgX_2	
97	$NaHPO_4^-$		185	AlX_3	
98	NaFaq		186	MnX_2	Mn II
99	KOH		187	FeX_2	Fe II
100	KSO_4^-	S VI	188	FeX_3	FeIII
101	$KHPO_4^-$		189	NH_4X	
102	$FeOH^+$	Fe II	190	SrX_2	
105	$FeCl^+$	Fe II	200	BaX_2	

2.5.17 TEMP

TEMP allows the temperature of the reactions to be changed. Three headings are given: Quit, Include, and XTEMP. Include is as for other keywords (Y = inclusion of TEMP, N = no inclusion of TEMP). XTEMP is the temperature in celsius. When modelling with PHREEQE, four options for defining temperatures are allowed. The choice is made using IOPT[4] under the keyword OPTIONS:

for IOPT[4]=0, the temperature is held constant or calculated when mixing or titrating; in this case the temperature of the solution is entered in SOLUTION and the XTEMP value is not required (PIP, infact, does not allow access to XTEMP if IOPT[4]=0);

for IOPT[4]=1, the temperature is kept constant, but is specified under TEMP (this allows the effects of step changes in temperature to be modelled);

for IOPT[4]=2, the temperature is changed from T_o to T_f in NSTEPS increments; in this case, two XTEMP values are required (in the order T_o, T_f), and a value for NSTEPS must be included under OPTIONS;

for IOPT[4]=3, the temperature is changed NSTEPS times; the NSTEPS temperature values required are entered here using XTEMP; NSTEPS must be included under OPTIONS.

2.5.18 LAYERSOL

This keyword defines the chemistry of the water in the *column* (the one dimensional region being modelled), the chemistry of the aquifer materials, and the flow parameters of the column. The column is divided into layers which can have different properties (see Section 2.2). Up to 10 layers are allowed. Each layer contains a solution which is equilibrated with that part of the column. Different cation exchange, mineral equilibration, and reactions can be specified for each layer (though in the case of ion exchange, only the exchange capacity can be varied between layers, not the selectivity coefficients). The water chemistry input for each layer is used to initialise the cation exchange equations: the rock chemistry is changed to fit the water chemistry input (unlike the case in PHREEQE ion exchange calculations where the water chemistry input using SOLUTION *and*

the rock chemistry change). Flow parameters are, however, the same for the whole column. There are 12 headings under this keyword: Quit, Include, Column, Lay.Index, Head, NTOTS, DTOT, NCELL, MNAME, SIMEX, LEXREA and EXCREA. Quit and Include are as described previously for other keywords (eg ELEMENTS, Section 2.5.7).

Column Under this heading flow parameters are defined. There are 4 parameters: NCOL, TOTX, Flow and DISP. These parameters are the same for all layers and cannot be changed for individual LAYERSOLs. Do not enter numbers omitting the initial zero (eg .0X) as PIP interprets this as X, not XE-2.

NCOL The total number of cells in all layers, up to a maximum of 100 cells. Layers are subdivided into cells. Each layer can contain a different number of cells, ie have a different thickness.

TOTX Total column length (m). For linear (as opposed to radial) flow modelling, all cells have an equal length in the column, and the length of each cell is determined by the total column length. For example, if the total column length is 100m and there are 50 cells in the column (contained in up to 10 layers), the length of each cell is 2 m. Flow direction (low numbered cells to high numbered cells or vice versa) is defined under TRANSPRT (ISHIFT under NSHIFT, see Section 2.5.20).
In radial flow mode, flow can be either from the centre outwards or from the periphery into the centre (see ISHIFT and NSHIFT in TRANSPRT, Section 2.5.20). Cells are arranged in rings around the centre. Cell lengths are modified by PHREEQM in such a way that each cell has an equal volume. Successive cells have the size:

$$\text{Length}(n) = \text{Length}(1) \times (\sqrt{n} - \sqrt{n-1})$$

where Length (1) is the size of the first cell, adjacent to the centre, and n is the number of the cell. The volume of solution which is moved per shift (ie time step, see Sections 2.2 and 2.5.8) is

$$\pi\,(\text{Length}(1))^2 \times \text{porosity}$$

PHREEQM uses the total flow path length (TOTX) and the number of cells (NCOL) to calculate Length(1) (=TOTX/$\sqrt{}$NCOL), and hence can calculate each value of Length(n).

Flow Flow allows definition of the flow type - linear or radial. Type L for linear and R for radial.

DISP Dispersivity of the column (m). When modelling existing field or laboratory data, this parameter will often be estimated by fitting the breakthrough for a conservative species.

There is no separate line for this heading in the input file produced by PIP. Instead, PIP uses the information provided under Column to list values of cell length and dispersivity for each cell as indicated in Table 2.12.

Table 2.11 Example of input under SUMS. For each sum, the name of the sum, number of species in the sum and species index numbers for the species in the sum are shown. The first two sums separate sulphate species (S VI) from sulphide species (S -II). The third sum gives the concentration of methane which is not routinely reported on. The fourth and fifth sums separate Fe II and Fe III, and the sixth and seventh sum Mn II and Mn III. The eighth and ninth sums give sums of all positive and negative ions respectively whereby each ion is counted as many times as it has charges. This allows the electrical balance to be assessed rapidly (although electroneutrality is enforced for all PHREEQE calculations). The last sum is a sum for the cation exchange capacity, adding up all species on the exchanger. Each species is counted as many times as X^- appears in the molecular formula, ie once for each site which it can take up on the exchanger. (Values for MX- are usually reported using a separate spreadsheet: see TRANSPRT, Section 2.5.20.)

```
SUMS
SO4-2    21
  16  40  52  78  88  96 100 108 109 126 127 128 128 141 154 155
155 156 168 173
 179
S-2       8
  41  42  43 110 110 111 111 111
CH4aq     1
  36
Fe+2     12
   8 102 105 106 107 108 109 110 111 112 113 114
Fe+3     21
 115 117 118 119 120 121 121 122 122 122 123 124 125 126 127
128 129 130 131 132
 133
Mn+2     10
   9 134 136 137 138 139 140 141 142 143
Mn+3      1
 144
Pos(t)   11
   4   4   5   5   6   7   8   8   9   9  23
Neg(t)    8
  14  15  15  16  16  19  19  19
CEC      14
 181 182 183 183 184 184 186 186 187 187 188 188 188 189
```

Lay.Index This screen operates in the same way as the Sol.Index screen under SOLUTION. Select one Layersol for each layer in the column which is to be modelled. Up to 10 layers can be selected. Press ENTER to work on one of the selected layers. Except for Head, all the following headings have to be completed for each layer.
Head A title for each layer can be entered. The screen operates the same as described under SOLUTION.

NTOTS The parameters NTOTS, IALK, IUNITS, PH, PE, TEMP and SDENS are contained under this heading. These are the same as those described under NTOTS under the SOLUTION keyword and will not be described again here. They refer to the water which is initially contained in that particular layer of the *column.*
DTOT DTOT allows data for the solution contained in the layer of the column under consideration to be input. The only difference between DTOT usage here and that in SOLUTION is that when the solutions defined here will be used in initialising ion exchange equilibria, they will remain unchanged, ie the rock chemistry will change so that it is in equilibrium with the input water chemistry. In SOLUTION, when carrying out calculations using PHREEQE, the solution and the sorbed concentrations will both be changed: the sorbed phase is initially assumed to be "empty".
X^- is the amount of exchange complex which is present in each cell of the layer. It has index number 30 and is expressed in meq/L of water. Exchangeable cations which associate with X^- have reserved species numbers between 181 and 200 and must be selected under SPECIES (Section 2.5.8). The log K values in LKTOSP under SPECIES determine the ratios of exchangeable cations on the exchanger. PHREEQM divides the concentration of X^- by 10^{10} before the initial solution is calculated. Afterwards, when the cations complexed to this small amount of X^- have been calculated, the amounts of cations on the exchanger (NaX, CaX_2, etc.) are multiplied again by 10^{10} (see Section 2.2.5). For this reason, X^- must be larger than about 10^{-6} mol/kg H_2O since PHREEQM only includes elements with concentrations above typical machine precision of around 10^{-16} mol/kg H_2O. If, in any layer, cation exchange is not expected to take place, a small number such as 10^{-3} should be entered for X^-.
X^- represents the cation exchange capacity of a layer and is calculated from it in the following way:

$$[X^-](\text{meq/L of water}) = 10\ \rho.CEC/\phi$$

where ϕ = porosity, expressed as a fraction;
CEC = cation exchange capacity (CEC) in meq/100g of dry soil
ρ = dry bulk density of the soil (kg/L).

NCELL There are 5 parameters under this heading which define the size of the layer, mineral equilibration and reactions which take place in the layer: NCELL, IOPT[3], NMINEX, NCMPEX and EXSTEP.

NCELL Number of cells in this layer. The total number of cells in all layers must add up to the number input under NCOL (Column; see above, this section).

Table 2.12. Example of the LAYERSOL input in an input file.

```
LAYERSOL 1                                                    Layer Index: Layersol 1 data below
Leachate in Landfill                                          Head for Layersol 1
12 15 2      6.21     2.0     10.0     1.0                    NTOTS
  4 4.0000E+03  5 1.2250E+03  6 3.4380E+03  7 3.4140E+03  8 4.5000E+02   }   DTOT: as
  9 1.1900E+02 14 4.3980E+03 15 3.8000E+01 16 1.7470E+03 19 5.3000E-01   }   in Figure 3
 23 2.3670E+03 30 1.0000E-03                                              }
 3 3 2 1  0.140                                               NCELL
2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02  cell size (m) and dispersivity (m) for 3 cells
PYRITE   0.000E+00 -1.000E+00          SIMEX and AMTMIN for Pyrite
FES ppt  0.000E+00 -1.000E+00          SIMEX and      AMTMIN for FES ppt
 15  2.000  0.000                          Index Number for reaction component and CREAC
                                           and THMEAN
LAYERSOL 2                                                    as above for Layersol 2
Groundwater in Triassic Sandstone, mineral equilibration (cc,Feam,O2)
12 15 2      7.85     8.0     10.0     1.0
  4 5.7000E+01  5 2.7000E+01  6 1.5000E+01  7 1.3000E+01  8 1.0000E-02
  9 1.0000E-02 14 7.0000E+01 15 1.8544E+02 16 7.3000E+01 19 2.0000E-02
 23 1.2900E-01 30 3.3500E+02
37 5 6 0  0.0
2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02   }
2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02   |
2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02   | cell sizes
2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02   | and
2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02   | α values
2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02   } for
2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02   | 37 cells
2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02   |
2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02 2.10E+00  5.00E-02   |
2.10E+00  5.00E-02                                                           }
CALCITE   0.000E+00 1.000E+01    |
FE(OH)3a  0.000E+00-1.000E+00    |
PYRITE    0.000E+00-1.000E+00    } mineral equilibrations in Layersol 2
FES ppt   0.000E+00-1.000E+00    |
BIRNESSI  0.000E+00 5.000E-05    |
O2 gas   -7.000E-01 1.000E-20    }
```

IOPT[3] This is equivalent to IOPT[3] under OPTIONS and can be input for each layer. However, only values of 0, 3, 4 or 5 can be used: values 1, 2, and 6 refer to mixing and titrating of solutions under OPTIONS and are therefore only possible with PHREEQE. Values 0,3,4,and 5 have the following meanings here:

= 0 calculates aqueous model only (no reactions or mineral equilibrations);

= 3, 4 these are equivalent since NSTEPS = 1 in PHREEQM (see OPTIONS): both indicate reaction input and / or mineral equilibration; and

= 5 indicates mineral equilibrations only.

NMINEX The number of minerals (maximum 10) with which equilibrium is to be maintained in this layer. In this context, "minerals" includes gases. Equilibrium includes the options: equilibrium at all times, precipitation only, and equilibrium at all times until a finite stock of the "mineral" is used up (if equilibrium is required for the solution only at time zero, this finite stock can be set at a very small value). See MNAME (naming the mineral(s)) and SIMEX (choosing the option), both under NCELL below.

NCMPEX The number of reaction components (maximum 10) to be input in each cell in this layer. Reaction components are species which need to be added to the water so that reactions can be initiated. For example, consider sulphate reduction of the form:

$$SO_4^{2-} + 2CH_2O \rightarrow HS^- + 2HCO_3^- + H^+.$$

The SO_4^{2-} is already in the water, and should not be added as a reaction component, and as the program will calculate the products, these also should not be added. Hence for this form of SO_4 reduction, only one component - CH_2O - needs selecting under NCMPEX. Components are identified under LEXREA (see below). They are limited to master species 4-30 (see SPECIES, Section 2.5.8), plus species 32 and 33 (O_2(aq) and H_2(aq)). Master species 1-3, H^+, E^-, and H_2O are not included: H^+ and H_2O are replaced by species 32 and 33, and half reactions are not relevant here. Species 24-29 are available for adding new "elements" (see ELEMENTS, Section 2.5.7). Hence in the sulphate reduction example above, CH_2O might be defined as a new "element" (and linked to the carbon master species CO_3 using SPECIES): alternatively, and more easily, it could be defined using CO_3 with an operational valency (THSP) of 0.0 rather than 4.0 (see SPECIES, Section 2.5.8 (THSP), EXCREA below, and Appelo and Postma (1993) page 418, example 10.7). In all cases, the number of components imported (+) or exported (-) from the solution should be considered rather than the number of reactants and products in the desired reaction: ie the net importation of species is required. Further guidance on this can be found in Appelo and Postma (1993), pages 399-401.

EXSTEP The amount of reaction, expressed as the number of mol/kg H_2O added per cell per time step or shift (shifts are described under TRANSPRT). The amount of reaction can be determined from the stoichiometry of the reaction. Take the sulphate reduction reaction considered above:

$$SO_4^{2-} + 2\ CH_2O \Rightarrow HS^- + 2\ HCO_3^- + H^+.$$

The amount of sulphate which needs to be reduced in each step is first decided and recalculated as mol/L. The species which is specified as the reaction component, however, is organic matter (represented here by CH_2O), and therefore 2X mol/L of CH_2O are required.

MNAME Under this heading the minerals for which equilibrium has to be maintained are selected: "mineral" in this context includes gases, ie MNAME allows specification of gases as well as minerals with which the solution is to be kept in equilibrium. "Equilibrium" in this context includes the options: equilibrium at all times, precipitation only, and equilibrium at all times until a finite stock of the "mineral" is used up. If equilibrium is required for the solution only at time zero, this finite stock can be set at an extremely small value (see SIMEX immediately below): the initial solution will be equilibrated with the mineral no matter how much mineral is required to do this, but in subsequent calculations only a negligibly small amount of mineral is available for dissolution. Note that any precipitated

mineral (even when using the precipitation only option) will be available for later redissolution. Type Y against each mineral to be selected, choosing as many as were specified under NMINEX (NCELL). If no minerals were selected for equilibration, it will not be possible to access this screen: a message appears that no minerals have been selected, and pressing the space bar returns the user to the main NCELL screen.
Which minerals are included will depend on the composition of the aquifer material which is to be modelled. For the Triassic sandstone, for example, calcite is often present, as is ferric and manganese oxyhydroxide phases (eg hematite, goethite, MnO_2 (eg birnessite)). For a given problem, calcite or hematite might be present in effectively infinite amounts, MnO_2 at finite amounts. The latter often takes part in redox reactions involving dissolved Fe^{2+}, and hence it can be dangerous to incorporate one of these species in a model without the other. If sulphate reduction is to be modelled, a solid sulphide phase may be appropriate to allow sulphide precipitation where appropriate. If a water was initially in equilibrium with the atmosphere but is now isolated from it, it may be appropriate to allow an initial equilibrium with the "mineral" O_2: this is done by defining the O_2 to be present at extremely small concentrations (see SIMEX, immediately below).

SIMEX The SIMEX screen shows three columns: the first contains the names of the minerals listed in MNAME, the second leaves a space for the values for SIMEX, the third space for values for AMTMIN. The parameters SIMEX and AMTMIN have to be set for each mineral by moving the cursor to the space provided, entering a value and pressing ENTER. Using the arrow keys instead of ENTER to enter a value and move to the next space does not save the entered value. Note that SIMEX interprets .4 as 4, not as 0.4: if 0.4 is required, type 0.4.

SIMEX is the saturation index (defined in the form $\log_{10}$(ion activity product / solubility product)). If set to zero, equilibrium will be maintained. If set to a positive number, the solution is allowed to become supersaturated before any precipitation occurs: if set to a negative number, the solution will start to precipitate before saturation is reached. It may be necessary to experiment with these numbers and conditions, especially where time for precipitation is limited (eg in column experiments), or where the effects of organic/inorganic complexation are being crudely investigated, or where other types of thermodynamic data are uncertain. For gases, the solubility product is defined by the Henry's law constant, ie K = (activity in water/gas partial pressure). Hence for equilibrium, the "saturation index" for the gas = $\log_{10}$ [(activity in water) / (activity in water / gas partial pressure)] = $\log_{10}$ [gas partial pressure]. Therefore the SIMEX value for gases should be set to the gas partial pressure of any gas phase in contact with the solution. For example, SIMEX for water in equilibrium with the above ground atmosphere would be -0.7 [$\log_{10}$ (0.2 atmos.) = -0.7].

AMTMIN is the initial amount of the mineral present in each cell, expressed in mol/kg H_2O. If an estimate of the amount is available from the mineralogy, it needs to be recalculated and a correction made for the porosity as done for X^-. The measured amount of mineral present is often expressed in wt per unit dry wt % of sediment. Thus

AMTMIN (mol/kg H_2O) = $[(wt\ \%/100)(\rho)]/[(TGFW \times 10^{-3})(\phi)]$

where TGFW is the total gramme formula weight of the mineral expressed in g/mol;

ρ is the dry bulk density in kg/L; and

ϕ is the porosity expressed as a fraction.

Setting AMTMIN at zero results in PHREEQM resetting the initial concentration to 10 mol/kg H_2O, effectively meaning that an effectively infinite amount of the mineral is available in the aquifer for dissolution and reaction. If AMTMIN is set at <0 mol/kg H_2O, the mineral is initially not present in the aquifer, but can precipitate if conditions permit. PHREEQM keeps a record of the precipitated amounts of minerals, and allows dissolution to occur at some later stage if the conditions permit. If only initial equilibration is required without a substantial amount of the mineral being available for dissolution, AMTMIN can be set to a small positive amount (eg 10^{-20} mol/kg H_2O). A common example is where it is required to set the initial state of the redox system by equilibration with atmospheric oxygen: putting a small value in AMTMIN will allow initial equilibration which will determine the initial pe with only a negligibly small buffering gas phase which would almost immediately be exhausted by any subsequent reduction reactions. In effect, O_2 is dissolved to saturation in the water, and the gas phase then reduced to negligible volume. It is important to note that the amount entered as AMTMIN is not depleted to set up the initial water composition: if 10^{-20} mol/kg H_2O O_2 gas is entered under AMTMIN, this will not be used up in setting up the initial water chemistry.

LEXREA This screen allows the components in a reaction to be selected. See NCMPEX for a further explanation. Type Y against the species which are to be selected. The allowed number is that specified in NCMPEX. Press F10 to exit the screen and save the changes.

EXCREA This screen lists the reaction components which were selected on the previous screen, listing firstly the index number and species name and then two further parameters: CREAC and THMEAN.

CREAC This is used to specify the relative proportions of reaction components added to solution. The absolute amounts added are calculated by PHREEQM using CREAC*EXSTEP. For reactions involving single components, the coefficient can conveniently be set to 1. If the reactions involve more than one added component, the coefficients might be conveniently set so that one of the added species has a coefficient of 1. Hence the coefficients are stoichiometric coefficients, but there is freedom in defining how

many moles of specific species are added per mole/kg H2O of reaction (ie EXSTEP).

THMEAN This is the redox status of the master species and has to be entered for each component of the reaction. PHREEQM uses this parameter to recognize redox reactions. THMEAN is analogous to THSP described under the SPECIES keyword (Section 2.5.8) and can be calculated in exactly the same way. However, the value of THMEAN does not have to be the same as the THSP for the master species being considered. For example, in the case of SO_4 reduction described under NCMPEX above, it was suggested that organic matter ("CH_2O") could be represented by the master species CO_3^{2-}. CO_3^{2-} has a THSP of 4 but in using it to represent CH_2O, a THMEAN of 0 is used, thus inducing the required redox reaction to occur. The value 0 is chosen in this case because $THSPCO_3^{2-}(=4)$ + $THSPH_2O(=0)$ + $4THSPE^-(4 \times -1)$ - $3THSPO^{2-}(=3 \times 0) = 0$; by having a THSP of 0, the charge balance for the sulphate reduction reaction is correct. See Appelo and Postma (1993, page 418, example 10.7) for more detail. After all values have been entered as desired, press F10 to save and return to the LAYERSOL screen.
If more than one Layersol was selected under Lay.Index, enter data for the remaining Layersols. An example of the data in the Layersol data block as it appears in the input file is shown in Table 2.12.

2.5.19 MEDIUM

This keyword is used for inputting the diffusion coefficient. It firstly needs to be included in the same way as the keywords described previously (Include: Y for yes, N for no). There is only one parameter under this keyword, namely DM, the effective molecular diffusion coefficient (m^2/s). If set to zero, diffusion is "switched off" and the mixing between adjacent cells is determined by mechanical dispersion only. Table 2.13 shows the representation of the MEDIUM keyword in the input file.

Table 2.13 Example of the MEDIUM input in an input file

MEDIUM	*Medium title line*
0.00000000E+00	*DM: diffusion set to zero*

2.5.20 TRANSPRT

This keyword is used for defining both transport parameters (eg flow direction and dispersivity), and the use of spreadsheet files. There are 6 headings: Quit, Include, NSHIFT, SS-files, SSNAM, ISSDMP. Quit and Include are as previously described for other keywords, NSHIFT defines the flow parameters, and SS-files, SSNAM and ISSDMP specify

whether or not spreadsheet files are to be produced as well as the output file, and what is to be sent to the spreadsheet files.
First it is necessary to explain the concept of shifts as used by PHREEQM. It has already been explained that a region to be modelled, or a "column" is divided into up to 10 layers, and that layers are subdivided into varying numbers of cells, the total of which cannot be more than 100. The transport takes place by shifts. The solutions stay in a cell for a specified amount of time, Δt (the timestep). During this time all specified reactions and mineral equilibrations take place, and solutions also mix with adjacent cells (dispersion). The time step is defined as pore volume/flow rate (or cell size/average linear velocity for linear as opposed to radial flow) (see Section 2.2). At the end of each time step the solutions in each cell shift to the next cell, exchange and react within the new cells and mix with their new neighbour cells. This simulates dispersion (and diffusion, but when only diffusion is being modelled, the water is not moved between cells). From the above it follows that:

number of pore volumes = number of shifts/number of cells.

The velocity of pore water is:

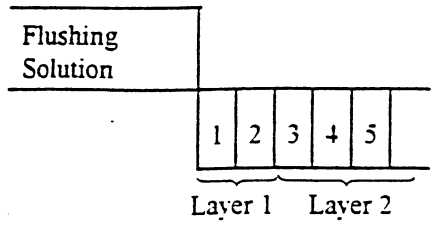
$$v = \Delta x/\Delta t$$

where Δx = cell length, Δt = time step, and v = pore water velocity.
At one end of the column is a flushing solution (entered under SOLUTION) which keeps a constant composition. It can be specified in TRANSPRT (ISHIFT under NSHIFT) whether the solutions in the cells move up (to higher numbered cells) or down (to lower numbered cells) in the column. Figure 2.4 shows the mixing during three shifts.

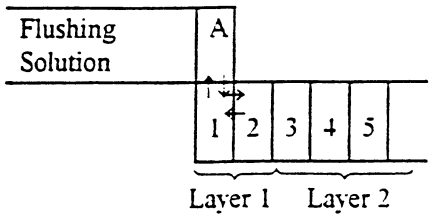
NSHIFT There are 8 parameters under this heading: NSHIFT, ISHIFT, IFRIX, IPREX, POR, DELTAT, SOLTOL and TMPTOL

NSHIFT Number of shifts of the aqueous solution in the column. A set of data for compositions in each cell will be produced for each shift and recorded in output / spreadsheet files as requested (see below).

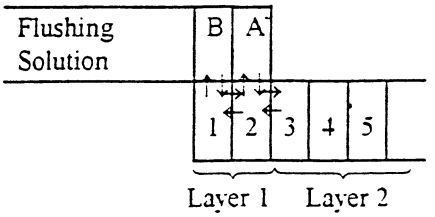
ISHIFT This is the shifting direction. Three settings are possible:
1 advective transport into higher numbered cells
0 only diffusion, no advective transport
-1 advective transport into lower numbered cells.
The choice has no effect on the hydraulics or chemistry of the problem.
IFRIX This parameter determines how mixing is calculated at the boundaries of the column, either in the case of diffusion only (ISHIFT = 0), or in the case of dispersive transport (ISHIFT = 1, -1). The available options are as follows.
For diffusion (ISHIFT = 0):
1 first cell mixes with upper solution;
0 closed column, no mixing with outer solutions;



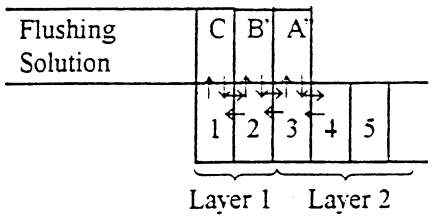
Shift 0:
Cells in the respective layers contain their respective solutions and are reacting / equilibrating. Flushing solution has not entered the cells yet.



Shift 1:
The flushing solution has been shifted into cell 1 where equilibrations and reactions are taking place, as well as exchange with cell 2. The solution in cell 1 now aquires a new composition A.



Shift 2:
The solution with composition A has been shifted into cell 2, and more flushing solution has been shifted into cell 1. Reactions and equilibrations with the original solutions in cells 1 and 2 are taking place as well as exchange with neighbouring cells. The composition of cell 2 is now A' and that of cell 1 is B.



Shift 3:
All solutions have again been moved one cell, and more flushing solution has been moved into cell 1. Reactions, equilibrations and exchanges are taking place. The front of the flushing solution has now been moved into Layer 2. Compositions in cells 1-3 have again changed.

Figure 2.4 The mixing of solutions during three shifts/time steps in PHREEQM.

-1 last cell mixes with end solution.

For dispersive flow (ISHIFT = 1, -1):

0 mixing factor will be multiplied by (1 + 2/NCOL); where NCOL is the total number of cells in the column; and

<>0 mixing factor will not be corrected.

For dispersive flow a mixing factor is calculated by PHREEQM by combining the following equations:

$$mixf = \frac{D_L \times \Delta t}{(\Delta x)^2}$$

where mixf is the mixing factor, D_L is the hydrodynamic dispersion coefficient (m^2/s), Δt is the length of the timestep (s) and Δx is the cell length (m);

$$D_L = \alpha_L v + D^*$$

where D^* is the effective diffusion coefficient (m^2/s), α_L is the longitudinal dispersivity (m) and v is the average linear velocity; and

$$v \times \Delta t = \Delta x,$$

which gives

$$mixf = \frac{a_L}{Dx} + \frac{D^* Dt}{(Dx)^2}.$$

Expressed in PHREEQM input parameters:

$$mixf = \frac{DISP(i)}{LENGTH(i)} + \frac{DM \times DELTAT}{((LENGTH(i))^2}$$

where DISP is the dispersivity input under Column in LAYERSOL, LENGTH is the cell length calculated by PHREEQM from total column length and total number of cells input under Column in LAYERSOL, DM is the diffusion coefficient input under MEDIUM and DELTAT is the time step input under NSHIFT in TRANSPRT as described below.

If transport is modelled and IFRIX is set to zero, the mixing factor is multiplied by (1 + 2/NCOL) to correct for not mixing the end cells. If IFRIX is set to <> 0, this correction is not performed. The correction term is necessary when modelling laboratory columns as mixing of the end cells is not done to preserve mass balance in the column. When modelling transport in an "infinite" medium such as an aquifer, it is better to add a few additional cells to prevent end-cell problems. In this case IFRIX should not be set to 0.

IPREX This option determines the level of detail for the "printout" for the output file. The output file can be accessed using either a spreadsheet such as EXCEL or a word processor such as WORD. If a printout is required it is most conveniently made through the spreadsheet or word processor. The output file defined using IPREX is not a spreadsheet file: however, PHREEQM can create spreadsheet files to make data processing easier (see SS-files? below). The options which are available for the IPREX, non spreadsheet printout detail are:

= 1 extended printout of species concentrations and activities is provided after each model calculation;
= 0 prints only total molalities;
= -1 prints minimal information about calculations only; and
= -2 prints minimal information about end cell only.

For PHREEQM the printout options have to be set here. IOPT[1] (options, Section 2.5.6) has to be set to zero if PHREEQM is used. If IOPT1 is set to 1 with PHREEQM the program will not run. Setting printout details using IOPT[1] is only appropriate for PHREEQE. When IPREX = 1 is chosen the output file gives first a list of the PHREEQE data files which were used for the simulation and a copy of the input file. This is followed by a characterization of the starting solutions, ie the solutions entered under LAYERSOL and SOLUTION after any equilibrations have taken place. The solutions entered under LAYERSOL are listed first, starting with Layersol 1.
For each solution first the total molalities of elements are listed, and then the logarithm of this value. Then, under the heading "Description of Solution", values for the following are given: pH, pe, activity of water, ionic strength, temperature, electrical balance, THOR, total alkalinity and the number of iterations which were performed to arrive at the results. [The THOR of PHREEQE is the THSP of PHREEQM (see SPECIES). PHREEQE also uses the term OVP (operational valence) for THOR, and defines THOR (or OVP) as the valence of a species that can change valence under naturally occurring conditions. The OVP or THOR state of a solution is defined by Parkhurst et al. (1980, page 7) as the sum over all the species of the product molality x OVP.] This is followed by a section "Distribution of Species" which gives data on all species which were considered in the calculations, ie species related to the input under DTOT, specified under SPECIES, or formed during reactions and equilibrations. The data listed are: index number of the species, name of the species, charge, molality (mol/kg H_2O), log of the molality, activity, log of the activity, the activity coefficient γ and the logarithm of the activity coefficient. The next section gives data on mineral equilibria under the heading "LOOK MIN IAP". The data include the name of the phase, the log of the ion activity product (IAP), log K of the dissociation reaction of the mineral at the temperature specified for the simulation (log KT) and the log of the ratio IAP/KT (ie the saturation index). This is repeated for each solution.
Next, data on the compositions of solutions in each cell for each shift is listed, starting with shift 1. First, data on the solutions in the first cell in each LAYERSOL at the beginning of the shift is shown, followed by data on every cell in the column at the end of the shift. There are three data sections with the following headings: "Description of Solution", "Summed Concentrations" and "Look Min IAP". "Description of Solution" and "Look Min IAP" are as described above for the initial solutions. "Summed Concentrations" gives a summary of the species information and each species listed represents the sum of concentrations of *all* species listed under

"Distribution of Species" containing the element under consideration, eg SO_4^{2-} represents the sum of the concentrations for all species containing sulphur, including ion pairs and sulphide species. For each species the index number, species name, charge, total molality (mol/kg H_2O), logarithm of total molality, activity and logarithm of activity are listed.
Apart from the information described above for every cell in every shift, messages about any processes which are occurring also appear, such as dissolution and exhaustion of phases for which equilibrium was specified, information on reactions and whether phase boundaries have been reached and minerals are dissolving or precipitating. Cells for which no changes have taken place during a shift, e.g. because a solution of a different composition has not reached that part of the column, are skipped and no data are given for these cells. SUMS, as defined using SUMS (Section 2.5.16) are also given.
If IPREX = 0, the information on the initial solutions (Layersols and flushing solution) is as for IPREX = 1. For the cells during each shift only the information under the heading "Description of Solution" as described above is given, as well as the messages about the calculations and sums mentioned above. The spreadsheet files produced are identical to those produced if option 1 is chosen.
If IPREX = -1, the information for the initial solutions is again the same as that described for option 1. For the cells during the shifts only the messages about the calculations are given. No information on chemistry is given. The spreadsheet files produces are the same as for option 1.
If IPREX =-2, the output file is the same as that for option -1. The only difference is in the spreadsheet files. Instead of giving data for each cell in each shift, data for each cell for the initial equilibration and for the end cell in each shift is given.

POR The porosity of the column material has to be entered here, expressed as a fraction. All cells have the same porosity. It is not possible to have different porosities in different layers.

DELTAT DELTAT is the time step in seconds and represents the time it takes to complete each shift. The default is set at 3600 s. DELTAT is equal to *cell pore volume/flow rate* (see Section 2.2.2). For linear flow, where cell length is constant, this is conveniently expressed as *cell length/average linear velocity*. For radial flow, where cell length decreases outwards in order that cell pore volume remains constant, the time step can be calculated from *length of cell n/average linear velocity in cell n*, or directly from *cell pore volume/flow rate*. Cell lengths can be calculated using the relationships given in Section 2.5.18 (LAYERSOL, Column).

SOLTOL In the interests of conserving computer time, PHREEQM will "skip" calling PHREEQE if differences in concentrations between time steps are very small (eg ahead of an advancing pollution plume). SOLTOL is the concentration tolerance level used by PHREEQM to decide when to skip calculations. If, for any master

species the summed, normalised differences in absolute concentrations between the last and current time steps after dispersion has been accounted for are greater than this level, the geochemical model is called. Differences in concentrations in a cell are summed over successive shifts until the geochemical model is called for that cell. This means that concentrations may vary around some average during several shifts before the tolerance is exceeded. Another check is performed to see whether concentrations have changed after a calculation. When the concentrations of all elements in a cell changed less than SOLTOL relative units, a message appears: 'COLUMN CELL NR nr. FLUSHED'. The default value for SOLTOL is 5×10^{-5}. Figure 2.5 shows the iron curve of a simulation where SOLTOL was changed but all other parameters kept the same. Figure 2.5a) shows the simulation with the default value for SOLTOL of 5×10^{-5}. Figure 2.5b) shows that decreasing the value to 5×10^{-20} does not improve the simulation. However, when SOLTOL is decreased to 5×10^{-1} it can be seen that iron concentrations go back to equilibrium values at a depth of 25m instead of 33 m in simulations with lower values for SOLTOL. This means that calculations for cells in this depth range were skipped in this simulation and the predicted concentration profile is incorrect.

TMPTOL This is the tolerance level for temperature changes. It works in the same way as SOLTOL, except that it is for temperature. The present version of PHREEQM works for isothermal cases only. The default value for TMPTOL is 10.

SS-files? This heading asks whether spreadsheet files are to be used. Spreadsheets can only be used for PHREEQM output, not for PHREEQE output. Type Y for yes and N for no. If Y is typed, the next two headings will become available. If N is typed it will not be possible to access them.

SSNAM The types of spreadsheet files to be used (SSNAM), the number of species to be reported in them (NSSDMP) and the names of the spreadsheet files (SSNAM2 and SSNAM3) are defined under this heading.

SSNAM This is the file for (total) aqueous concentrations in each cell of the column. Only master species, ie the summed concentrations as explained under IPREX can be reported here. Type a name for the spreadsheet file. The format file.s is suggested in the program text, the s standing for solution to distinguish it from other spreadsheet files containing other types of data (see below): however, any file name can be used.
The spreadsheet contains seven columns with standard information and columns of concentrations for the specified elements in mol/L (strictly, mol/kg H_2O). The seven columns which occur in all spreadsheet output files give the following information: "Run" gives information on which run the data is for. If only one run is contained in the input file, this will be 1 throughout the file, but if files are

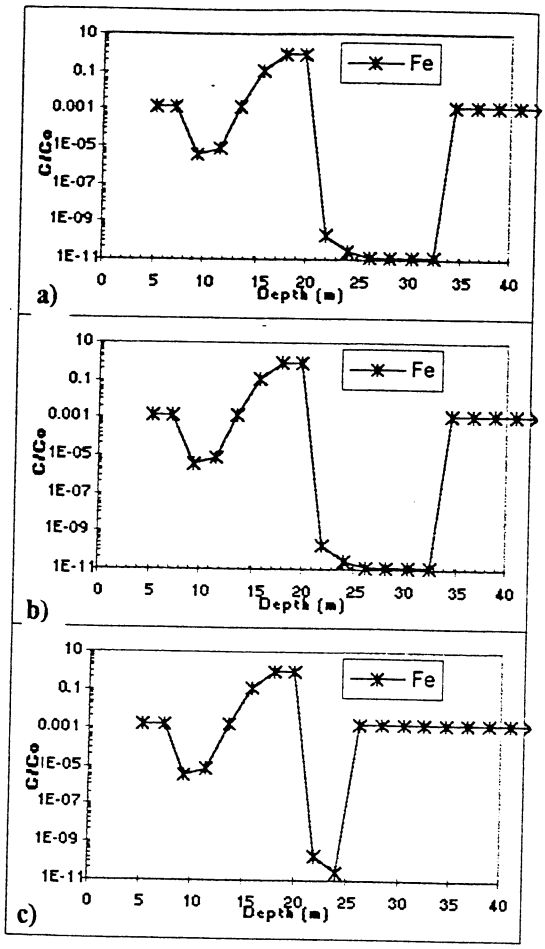


Figure 2.5 The iron curve of a simulation with values for SOLTOL of a) 5×10^{-5} (default), b) 5×10^{-20} and c) 5×10^{-1}.

appended, each run gives information for one appended file. "X" gives the position which the centre of each cell occupies in the column in m, the top of the column having position 0.0. The first cell has a value of $\frac{1}{2}$ cell length, the second cell of $\frac{1}{2}$ - 1 cell lengths, etc. The third column gives the cell number for each shift and the fourth column the number of the shift. The first shift which is listed is shift 0. This is data on the composition of solutions after equilibrations have taken place but before the flushing solution has been shifted into the column. For shift 0 there are two more cells specified than there are in the column. The first cell is cell 0 which gives data on the flushing solution which was entered under SOLUTION. The last cell is cell NCOL+1 (total number of cells + 1) and gives the concentration of the solution in the LAYERSOL at the end of the column, usually the same as the concentrations in the cells in the lowermost LAYERSOL. However, this cell does not have a position in the column and represents the column effluent. After shift zero data for each cell in each shift is listed when the printout option is 1, 0 or -1 or data for the end cell of each shift if printout option is -2. The next three columns give data on pe, pH and temperature (°C) for all cells and shifts which are listed. Then follow up to 9 columns with species concentrations in mol/L. Care needs to be taken to check the output: the results may not always be given for all cells in all time steps, with output starting with cell X instead of cell 1, and ending where cells start to be "skipped" (see SOLTOL, above).

NSSDMP This is the number of master species to be reported on in the spreadsheet files. The maximum is 9. These species will be reported on in the spreadsheet files entered under SSNAM and SSNAM2.

SSNAM2 This is the spreadsheet file for the concentrations of exchangeable cations and the amounts of minerals precipitated or dissolved. It is a vital source of information when trying to determine what reactions are occurring. Again, enter the name. It is suggested by the program text that the format file.x is used, where the x stands for exchangeable cations. The first 4 columns in this spreadsheet file are the same as for SSNAM, ie "Run", "X", "Cell" and "Shift". Data for the zero shift is also given, but only for the number of cells specified in NCOL. Then follows data for the number of species specified in NSSDMP and for minerals. If any species has been specified which were not included in the exchange reactions under SPECIES, these are listed but zero concentrations given. Ion exchange sorbed concentrations are given in mol/L; hence the summed values will vary even though the ion exchange capacity, in meq/kg H_2O, is fixed. The values for the minerals are cumulative balances up to the end of the current time step in the particular cell. As noted in SSNAM, care needs to be taken to check which cells the data refer to, as not all data are always displayed.

SSNAM3 This is a spreadsheet file for summed species. The sums are specified under the keyword SUMS. The program text suggested format for the file name is file.su where su stands for summed

species. There are columns for "Run", "Cell" and "Shift" and the sums which were specified under SUMS. This spreadsheet is usually the most convenient means of getting access to non master species concentration data (eg separating sulphate and suphides from total sulphate (the master species)) (see SUMS, Section 2.5.16).

ISSDMP This heading allows the master species to be reported on in the SSNAM1 and SSNAM2 spreadsheet files to be selected. Two columns are displayed, headed NSSDMP and ISSDMP.

NSSDMP NSSDMP will already have been entered under SSNAM, and is the number of master species to be listed in the spreadsheet file. Here, the column headed NSSDMP contains the numbers 1 to NSSDMP (eg if NSSDMP = 3, the column contains 1,2,3). In PIP, this column cannot be altered except by altering NSSDMP in SSNAM.

ISSDMP The index numbers of the master species to be included in the spreadsheet files have to be entered here. The data for the species will appear in the spreadsheet files in the order in which they are entered here. The box on the right shows the master species and their index numbers which can be entered. Press ENTER each time an index number is entered and F10 to leave the screen and save the information. If data on more than 9 master species is required the program has to be run more than once, changing the species in ISSDMP as needed. The data which are listed in the spreadsheet for the solution are for summed concentrations of species as described under IPREX.

The information entered under TRANSPRT can be previewed from the main TRANSPRT screen using the F5 key. An example of data entered under TRANSPRT is shown in Table 2.14.

Table 2.14 Example of TRANSPRT keyword in an input file.

```
TRANSPRT                                                    TRANSPRT title line
   8   1   0   1   0.24   63072000      5.e-5      10.0
       NSHIFT: NSHIFT,ISHIFT,IPRIX,IPREX,POR,DELTAT,SOLTOL,TMPTOL
example2.s  9  example2.x  example2.su                    SSNAM: names of
spreadsheet files and no. of species in NSSDMP
   4   5   6   7   8   9  14  16  23                      ISSDMP: species index numbers of
species to be entered in spreadsheet
```

2.5.21 Running PHREEQE/PHREEQM

Once the input data file has been created, it should be stored using Files, and PIP exited using Quit. The PHREEQM package can then be run: the OPTIONS line (IOPT[10]) in the input file created using PIP tells the PHREEQM package whether PHREEQE or PHREEQM is to be

run. To run the PHREEQM package, simply use the executable version supplied either using a platform such as Windows or by typing PHREEQM at the Dos prompt.

3. Modelling Landfill Leachate/Triassic Sandstone Interactions Using PHREEQM

3.1 Introduction

Section 3 contains a summary of modelling work performed when attempting to simulate the interactions between landfill leachate and Triassic Sandstone. The experimental data were obtained from previous laboratory studies, and from full-scale field investigations. The laboratory data, in the form of column breakthrough curves, were obtained from the study of Thornton et al.(1995) which used uncemented Triassic Sandstone from the Burntstump Landfill site in Nottinghamshire (Harris and Parry, 1982; Lewin et al., 1994) and acetogenic and methanogenic phase leachate. Additional laboratory data were extracted from column experiments undertaken by Thornton et al. (1994) using uncemented Triassic Sandstone from the West Midlands, and a methanogenic phase leachate. The field data were obtained from field work carried out at the Burntstump landfill, as summarised in Lewin et al. (1994). The data comprise porewater profiles obtained from cored boreholes drilled at intervals of a few years.

The emphasis of the modelling has been on interpretative, rather than predictive modelling. In each case, it has been the intention to reproduce the laboratory data using realistic processes, and then to compare the interpretations in order to assess the most important processes affecting leachate attenuation in the Triassic sandstones. This latter task is attempted in Section 4.

In most cases, only the final models are presented: these may represent the last in a series of tens of runs. The model inputs are described in detail, and are intended to act as examples for the code description presented in Section 2. Because the examples are intended to be read in conjunction with Section 2 rather than straight through, there is necessarily some repetition in the descriptions of the input files.

3.2 Modelling of Triassic Sandstone / Landfill Leachate Interactions

3.2.1 Problem 1: Laboratory Flushing of Burntstump Triassic Sandstone Columns With Acetogenic Phase Landfill Leachate

Problem 1: Simulating transport of acetogenic (A-phase) landfill leachate through laboratory columns of Triassic Sandstone aquifer material taken from Burntstump landfill site, Nottinghamshire.

Laboratory experimental results: The aquifer sandstone was found to contain around 1.22% $CaCO_3$ and has a CEC of about 1.63meq/100g, based on solid phase analysis. The experimental results are presented in terms of normalised solute concentrations (C/C_o) against pore

volumes of leachate passed through the aquifer column, where C and C_o represent the concentration of a solute in the column effluent and A-phase leachate, respectively. The aquifer column is initially saturated with groundwater prior to flushing with leachate. Examples of breakthrough curves for selected solutes in A-phase leachate are presented in Figure 3.1.

Conceptual model used in simulation: Native Ca and Mg are desorbed from the aquifer sandstone in response to sorption of Na, K and NH_4 from the leachate. This results in the elution of Ca and Mg at relative high concentrations as a pulse at the leachate front during breakthrough but relative retardation of the Na, K and NH_4 fronts. Despite the presence of native calcite in the aquifer material, the porewater pH is buffered at that of the leachate (pH5.9) during leachate flushing, due to the presence of high concentrations of organic acids in the leachate (up to 30,000mg/L).
A redox front is formed during leachate flushing in this experiment by the reduction of solid phase manganese oxyhydroxides on the aquifer sandstone by ferrous iron in the leachate. This results in the elution of a pulse of Mn at high concentrations and simultaneous complete removal of the leachate Fe^{2+} load. The masses of Mn and Fe involved are consistent with the following reaction stoichiometry:

$$2Fe^{2+} + MnO_2 + 4H_2O \rightarrow 2Fe(OH)_3 + Mn^{2+} + 2H^+$$

where leachate Fe^{2+} is oxidised and precipitated as insoluble Fe oxyhydroxide. This feature lasts for approximately 4 pore volumes of the leachate flush, after which concentrations of Mn and Fe returned to input levels (Figure 3.1). The system redox status, represented by Eh, is also poised at a higher level during the Mn flush, suggesting that the former is influenced by the reduction of Mn oxyhydroxide fractions. Sulphate remains a conservative species in this system and the concentration increase in the column effluent reflects the breakthrough of the leachate.

Model input file: The input file for this problem is listed in Table 3.1. The parameters used in the construction of the input file are described below for the relevant option blocks. These are described in the order that they appear in the file.
OPTIONS: Option 5 is set to 1, allowing pe to be determined from the reactions simulated. This is useful when modelling redox reactions for following changes in the system Eh due to changes in the concentrations of the redox sensitive species responsible. Option 6 is set to 1, where the Davies formula is used to make the appropriate activity corrections for solute concentrations and Option 10 is set to 1 to select the flow tube modelling option in PHREEQM.

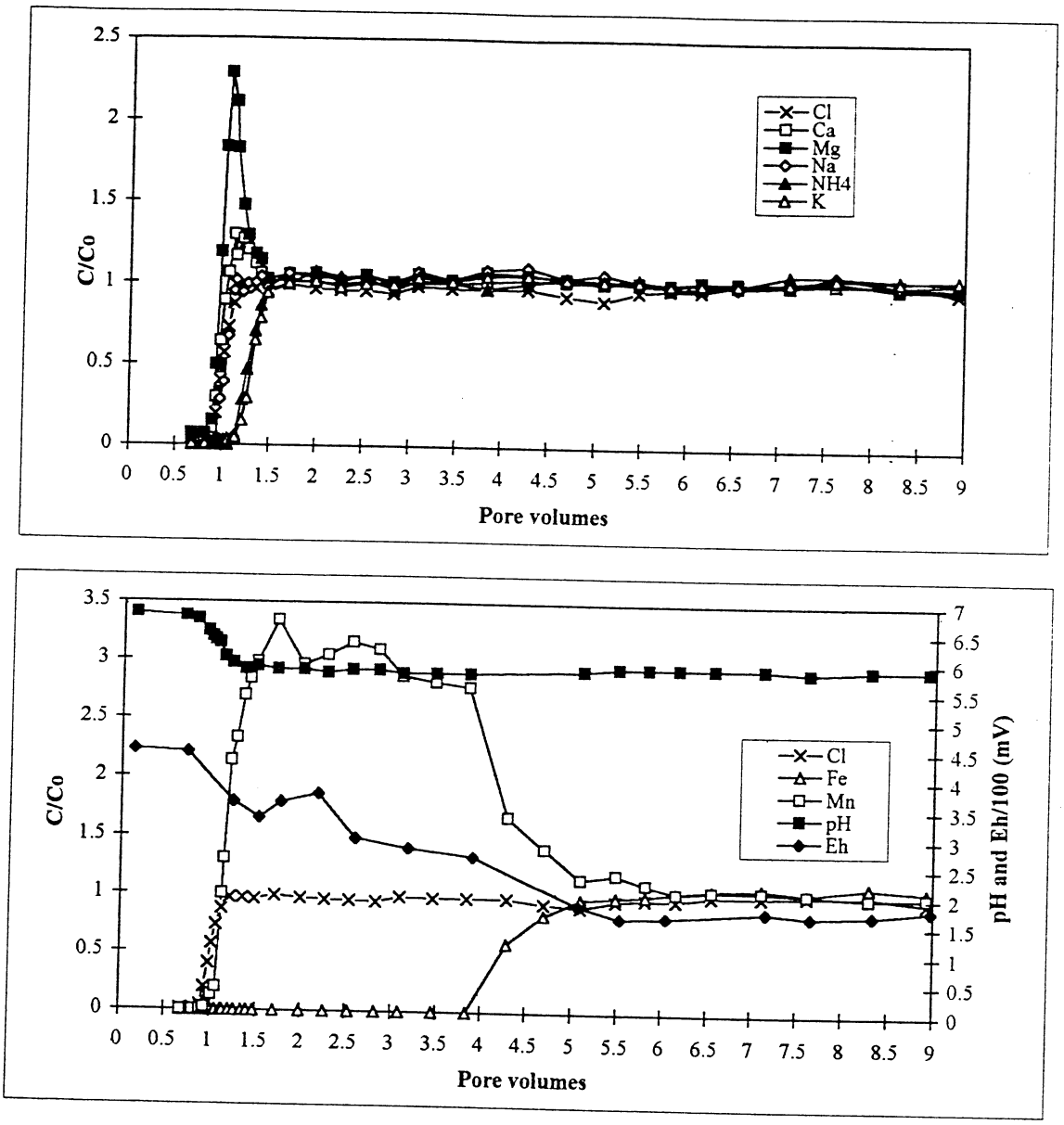


Figure 3.1. Experimental breakthrough curves for problem 1.

Table 3.1 PHREEQM input file for problem 1.

```
col 1:g/water equilib/a-phase leachate flush+exch/redox reactions+CaCO3 eq
0000110001 0 0     0.0
SPECIES
181
NAX       200 0.0     0.0     4.0     4.0     0.075    0.0
20.00    0.0
 6  1.000 30  1.000
182
KX        200 0.0     0.0     3.0     3.5     0.015    0.0
21.02    0.0
 7  1.000 30  1.000
183
CAX2      200  0.0    0.0     6.0     5.0     0.165    0.0
40.80    0.0
 4  1.000 30  2.000
184
MGX2      200 0.0     0.0     8.0     5.5     0.20     0.0
41.20    0.0
 5  1.000 30  2.000
186
MNX2      200 0.0     2.0     6.0                 0.0
40.70    0.0
 9  1.000 30  2.000
187
FEX2      200 0.0     2.0     6.0                 0.0
40.95    0.0
 8  1.000 30  2.000
188
FEX3      300 0.0     3.0     9.0                 0.0
47.28    9.68
 8  1.000 30  3.000  2 -1.000
189
NH4X      200 0.0    -3.0     2.5                 0.0
20.55    0.0
 23  1.000 30  1.000

SOLUTION 2
A-phase leachate
10 00 2  5.90     2.61    25.0     1.000
  4 3.8320E+03  5 5.6400E+02  6 2.0080E+03  7 1.1430E+03  8 4.4800E+02
  9 9.8100E+01  14 2.8600E+03  15 3.2700E+02  16 1.2760E+03  23 1.4630E+03
NEUTRAL
   0  14
LAYERSOL 1
FILLS COLUMN WITH GROUNDWATER
10 15 2  6.75     7.496    25.0     1.000
  4 1.7600E+02  5 3.9400E+01  6 1.1500E+01  7 7.9000E+00  8 2.1000E-02



  9 1.2000E-01  14 3.0900E+01  15 5.8600E+02  23 1.0000E-02  30 6.0180E+01
 10  5  4  0  0
 1.00E-01  3.70E-03 1.00E-01  3.70E-03 1.00E-01  3.70E-03 1.00E-01  3.70E-03
 1.00E-01  3.70E-03 1.00E-01  3.70E-03 1.00E-01  3.70E-03 1.00E-01  3.70E-03
 1.00E-01  3.70E-03 1.00E-01  3.70E-03
CALCITE  0.000E+00 1.000E+01
FE(OH)3a 0.000E+00-1.000E+00
BIRNESSI 0.000E+00 1.160E-02
O2 gas  -7.000E-01 1.000E-20
MEDIUM
 0.00000000E+00
TRANSPRT
  50   1   0  -2     0.39   185806.   5.E-05      10.0
A:CA1XCR1    9
  4  6  7  14  5  15  23  8  9
END
```

NEUTRAL: The presence of a high concentration of organic acids in the acetogenic leachate results in a marked deficit in negative charge and the solution is electrically unbalanced. Selection of this option allows corrections to be made for this and in this case a non-reactive species (Cl) is added to the leachate composition to balance the positive charge. [The use of NEUTRAL is not strictly necessary in the present case.]
SPECIES: All species which, based on the experimental results, participate in ion-exchange reactions with the aquifer column are specified in this block. This includes the major ions (Ca, Mg, Na, K, NH_4) and also reduced species of Mn and Fe which may be involved in these reactions.
SOLUTION: The composition of the acetogenic leachate (designated as solution 2) which displaces the groundwater from the aquifer column is specified in this block. In NTOTS the total number of species concentrations to be input is specified as 10 and IALK is set to 0 as a value for TIC is used to represent the inorganic alkalinity in this system. This is because the conventional method of determining alkalinity by titration (e.g. to a pH4.5 end-point) does not provide an accurate measure of inorganic alkalinity in acetogenic leachate due to interference from dissociated organic acids (Thornton et al., 1995). The use of alkalinity values determined by the conventional titration method is likely to result in the overestimation of alkalinity contributed by inorganic species in this type of leachate. An estimate of inorganic alkalinity (or, infact, TIC) may be obtained from measured pH, Ca concentration and carbonate equilibria, but only if a specific saturation state can be assumed for a specific carbonate mineral. (Of course, if using this approach for estimating inorganic carbon, alkalinity or TIC can be estimated, and inorganic carbon can be entered into the model in either form.) An input value of pe for this problem is calculated from the measured Eh of the leachate using the relationship: pe=Eh(mV)/59.1 and the temperature is set to that of the laboratory (25°C). The concentrations of the 10 species indicated in NTOTS are input in DTOTS in mg/L. Alkalinity (solute index number 15) is input in DTOTS as the measured TIC concentration, as specified in IALK.
LAYERSOL: This block specifies the properties of the aquifer column, the composition of the groundwater saturating the column and the chemical reactions to be simulated between the column and pore fluid. A single layer model of 1m length and divided into 10 cells is set up in COLUMN. Flow is set to linear with a dispersivity of 0.37cm. The latter has been estimated from fitting the leachate Cl breakthrough curve from the experimental data to an analytical solution of the advection-dispersion transport equation (Ogata and Banks, 1961). It is important to note that the concentrations of species input in this block are those of the groundwater in equilibrium with the column and not those of the groundwater prior to contact with the aquifer material. This distinction is important when modelling the results of column studies but is usually not applicable to analysis of field data where the composition of the uncontaminated porewater in the aquifer is used. The number of species concentrations in the groundwater to

be input is set to 10 in NTOTS. This number must include the aqueous species of interest and also X^-, the equivalent CEC of the column on a per volume basis. The IALK input for the groundwater is defined as the total alkalinity and set to 15 (rather than 0 for TIC): the measured alkalinity in this case accurately reflects the inorganic species present. The measured pH of the groundwater is used and a pe calculated from the measured Eh is also included. The concentrations of the species specified in NTOTS are input in mg/L in DTOTS. Although NH_4 is not present above detection limits in the groundwater a very small concentration is included in DTOTS to set up the exchange equilibria between aqueous and sorbed NH_4 fractions in the column. If this is not done, NH_4 will be treated as a conservative species during the model simulations. The value of alkalinity required for input as element 15 in DTOTS was calculated from the measured alkalinity (required alkalinity in mg/L as HCO_3^- = measured alkalinity in mg/L as $CaCO_3$ x 1.22). The measured alkalinity of the groundwater in equilibrium with the aquifer column was 480 mg/L as $CaCO_3$, providing a corresponding alkalinity of 586 mg/L as HCO_3^-. A value for the column CEC, expressed in meq/L of H_2O, is included in X^-. The latter is calculated from the measured CEC of the aquifer material (1.63 meq/100g), column dry bulk density (1.44 kg/L) and column effective porosity (0.39) using the following relationship:

X^- = 10 x (1.44/0.39) x 1.63 = 60.18 meq/L of H_2O

[In this case the bulk density and porosity values are inconsistent in that they imply an unrealistically low solid density: the porosity, obtained from breakthrough curve matching is a kinematic interpretation-dependent value, and not ideal for the present purpose. However, in the absence of grain densities and other porosity measurements, and given the other uncertainties, the above X- value has been used as the starting point for the simulation.]

The 1m long column is split into 10 cells, each of 0.1m thickness in NCELLS. In this example NCELLS = NCOL because only 1 layer is being modelled. For simulations using multiple layers, each configured separately, NCELLS < NCOL. Mineral equilibration is also specified in this block (IOPT 3 set to 5) rather than in the OPTIONS block. This is the normal exception when modelling equilibration with mineral phases using the LAYERSOL option. Four mineral phases are selected for equilibration in this layer. The minerals and equilibrium conditions concerned are:

Mineral	SIMEX	AMTMIN (moles/kg H_2O)
Calcite	0.0	10.0
$Fe(OH)_3am$	0.0	-1.0
Birnessite (MnO_2)	0.0	1.16×10^{-2}
O_2 gas	-0.7	1×10^{-20}

Calcite is naturally present in the sandstone and equilibrium is maintained (SIMEX = 0) with an infinite amount of this mineral (AMTMIN = 10.0 moles/kg H_2O). The remaining minerals in this table are set up to simulate the redox front formed by the reductive

dissolution of Mn oxyhydroxides by Fe^{2+} in the leachate. The column pore water is equilibrated with MnO_2 at a pO_2 of 0.2 atm. The amount of "O_2 gas" is set very small at 10^{-20} mole/kg H_2O, so that although there is an initial O_2 control on Eh, the buffering capacity once the dissolved O_2 has been used up is negligible. Amorphous iron hydroxide is set to a negative quantity (AMTMIN = -1.0), that is, this phase is not originally present in the column, although it will precipitate when saturated conditions are obtained in the column (SIMEX = 0). The amount of MnO_2 available for reduction by ferrous iron is obtained from the experimental data by determining a mass balance for the net quantity of Mn mobilised from the column during the Mn flush. For the present problem, an additional 33.2 mmoles of Mn was mobilised from the column and the corresponding amount of MnO_2 in moles/kg H_2O available for reduction is calculated from the column mass (10.55kg), bulk density (1.44kg/L) and effective porosity (0.39) using the following relationship:

$$MnO_2 \text{ (moles/kg } H_2O) = [(33.2/1000) / (10.55)] \times (1.44/0.39) = 0.0116.$$

The calculation could, alternatively, have been performed using PHREEQM.

MEDIUM: This block is included in order to set the diffusion coefficient. In the simulations carried out, the coefficient was set at zero in all cases.

TRANSPORT: In this block the number of shifts (NSHIFT) is set to 50, that is all solutions are transported ("shifted") 50 times into the next cell. This means that 50 (= NSHIFT)/10 (= NCOL, the number of cells in all layers, in this case, 1) = 5 pore volumes are injected and eluted. Solutions are shifted into higher numbered cells (ISHIFT = 1) and by setting IFRIX to 0.0, mixing between adjacent cells is determined by dispersivity only. IPREX is set to -2 to provide a printout of information about the end cell only (which is flushed by 5 pore volumes of solution). A porosity of 0.39 is input for each cell in the column. This value represents the effective porosity determined for the column by transport modelling of the Cl breakthrough curve (see explanation in LAYERSOL, above). A time step of approximately 185,800 seconds is also used for DELTAT (Δt) and is calculated from $\Delta t = \Delta x/ALV$ where Δx is the cell length (0.1m) and ALV is the (average) linear velocity, in this case determined from transport modelling of the leachate Cl breakthrough curve (4.65 cm/day). In contrast a time step is normally required for modelling transport through aquifers at the field scale. The output from these simulations is sent to a spreadsheet file on a floppy drive in the form of aqueous concentrations of species only. A maximum of 9 species (Ca, Na, K, Cl, Mg, CO_3^{2-}, NH_4, Fe^{2+}, Mn^{2+}) are sent to this file for output and these are specified using the index number for each species. Other species modelled (e.g. SO_4) can be included for output by reselection from the default list provided.

Results: Simulated breakthrough curves for inorganic solutes in A-phase leachate for this column experiment are presented in Figure 3.2. There is good agreement in the style and timing of contaminant breakthrough between the simulated data and experimental results (cf

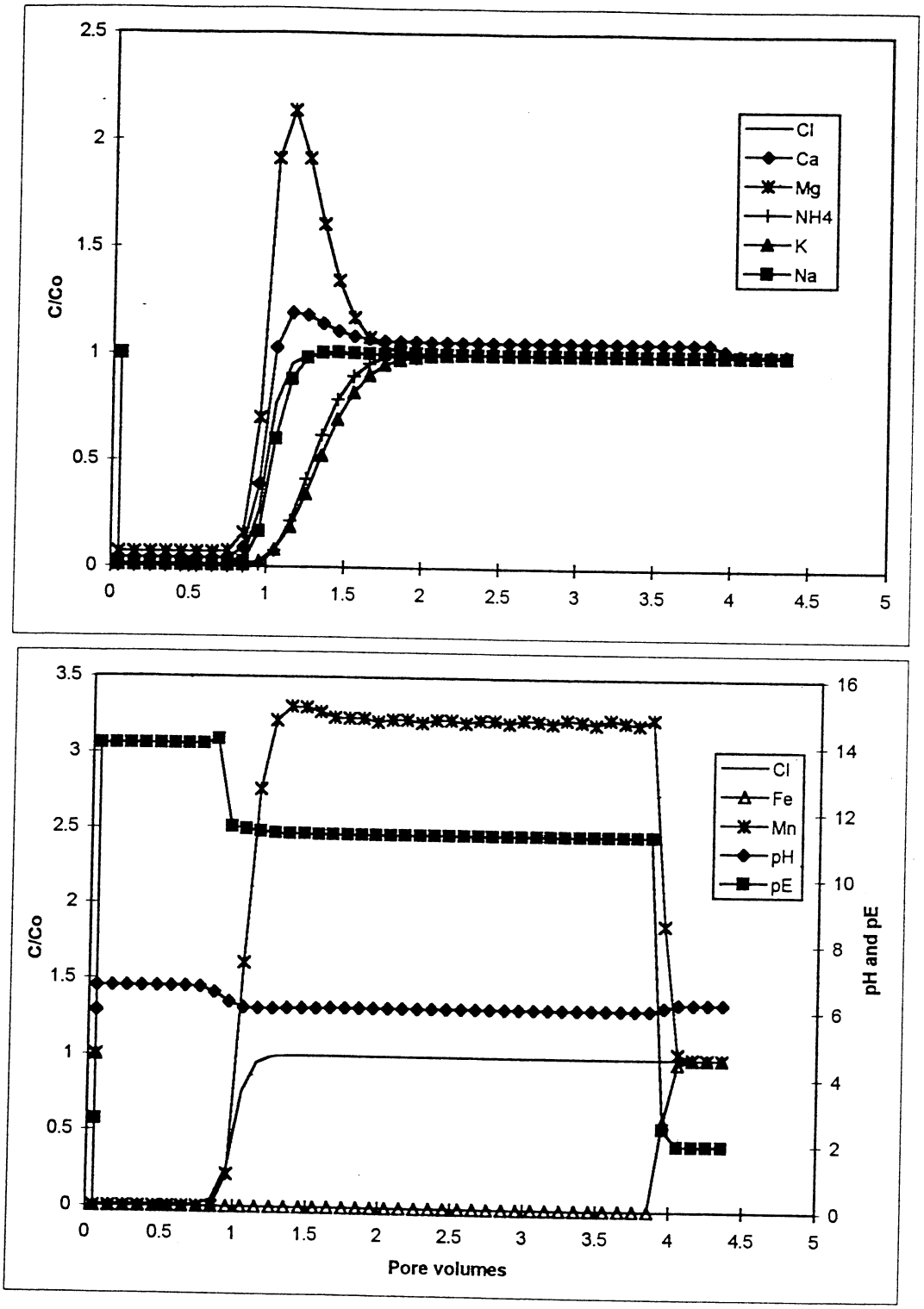


Figure 3.2. Simulated breakthrough curves for problem 1.

Figure 3.1). The simulated breakthrough curves for the major cations have been fitted to the experimental results by adjustment of the LKTOSP values for each exchangeable species (e.g. CaX, NH4X etc.) in the SPECIES block of the input file. This enables a conventional selectivity coefficient to be obtained for each cation involved in the ion-exchange reactions observed within the aquifer column. Both the duration and peak concentration of the Mn flush, removal of leachate Fe^{2+} and qualitative change in system redox status following its termination are adequately reproduced by the model for this experiment.

Conclusion: This simulation shows that all of the key features observed during flushing of this aquifer column with A-phase leachate can be qualitatively replicated using the code. The modelled results suggest that the 3 processes simulated (ion-exchange reactions between the major cations (Ca, Mg, K, Na, NH_4, Mn^{2+}, Fe^{2+}), carbonate equilibria and reductive dissolution of MnO_2 by Fe^{2+}) adequately characterise the chemical interactions of these species in this leachate and with this aquifer material. Several important observations can be made. Firstly, the model is sufficiently robust as to be able to simulate the main inorganic reactions controlling contaminant transport in this system, despite the very high organic load found in this type of leachate. This suggests that either complexation between inorganic species and organic fractions in the leachate is not significant or that this has only a minor impact on chemical interactions with the aquifer material. A interesting feature successfully modelled by the code is the development of a Mn flush caused by the reduction of Mn oxyhydroxides on the sandstone by ferrous iron in the leachate. In many leachate plumes this feature is attributed to the reduction of metal oxides coupled to the microbial oxidation of dissolved organic matter in leachate (e.g. Christensen *et al.*, 1994). However, the Mn flush simulated in this column experiment is not microbially catalysed but results from an abiotic reaction. This suggests that environmental conditions in the experimental column were unsuitable for microbially mediated reduction of Mn oxyhydroxides or that reaction kinetics are important in determining the mechanism of solid phase Mn mobilisation. The latter cause is plausible given that oxidation of organic matter coupled to Mn oxyhroxide reduction involves the transfer of 4 electrons whereas the abiotic reaction requires the transfer of only 2 electrons and should therefore be faster. The wider significance of this reaction in producing zones of high Mn concentrations in leachate plumes within this aquifer requires confirmation.

3.2.2 Problem 2: Laboratory Flushing of Burntstump Triassic Sandstone Columns With Acetogenic Phase Landfill Leachate

Problem 2: Simulating transport of acetogenic landfill leachate through columns of Triassic Sandstone aquifer material taken from Burntstump landfill site, Nottinghamshire. This problem further evaluates the chemical interactions in the column experiment used to

illustrate problem 1. In particular the current problem examines whether precipitation of rhodochrosite ($MnCO_3$) is likely to reduce the high Mn concentrations produced by reduction of Mn oxyhydroxides during flushing of this aquifer sandstone with A-phase leachate.

Laboratory experimental results: The experimental results for this problem are the same as those for problem 1 (Figure 3.1).

Conceptual model used in simulation: As for problem 1, but with rhodochrosite equilibrium.

Model input file: The input file for this problem is listed in Table 3.2. The parameters used in the construction of the input file are identical to those described above for problem 1 and only the changes necessary to modify the simulation for this problem are discussed here.
LAYERSOL: The number of mineral phases to be equilibrated in the column is increased from 4 to 5 in NCELLS and rhodochrosite is selected in MNAME. Values of SIMEX and AMTMIN for this phase are set to 0.0 and -1.0, respectively in the SIMEX option. This means that $MnCO_3$ is not initially in equilibrium with the pore fluid although precipitation of this phase may occur if conditions permit.

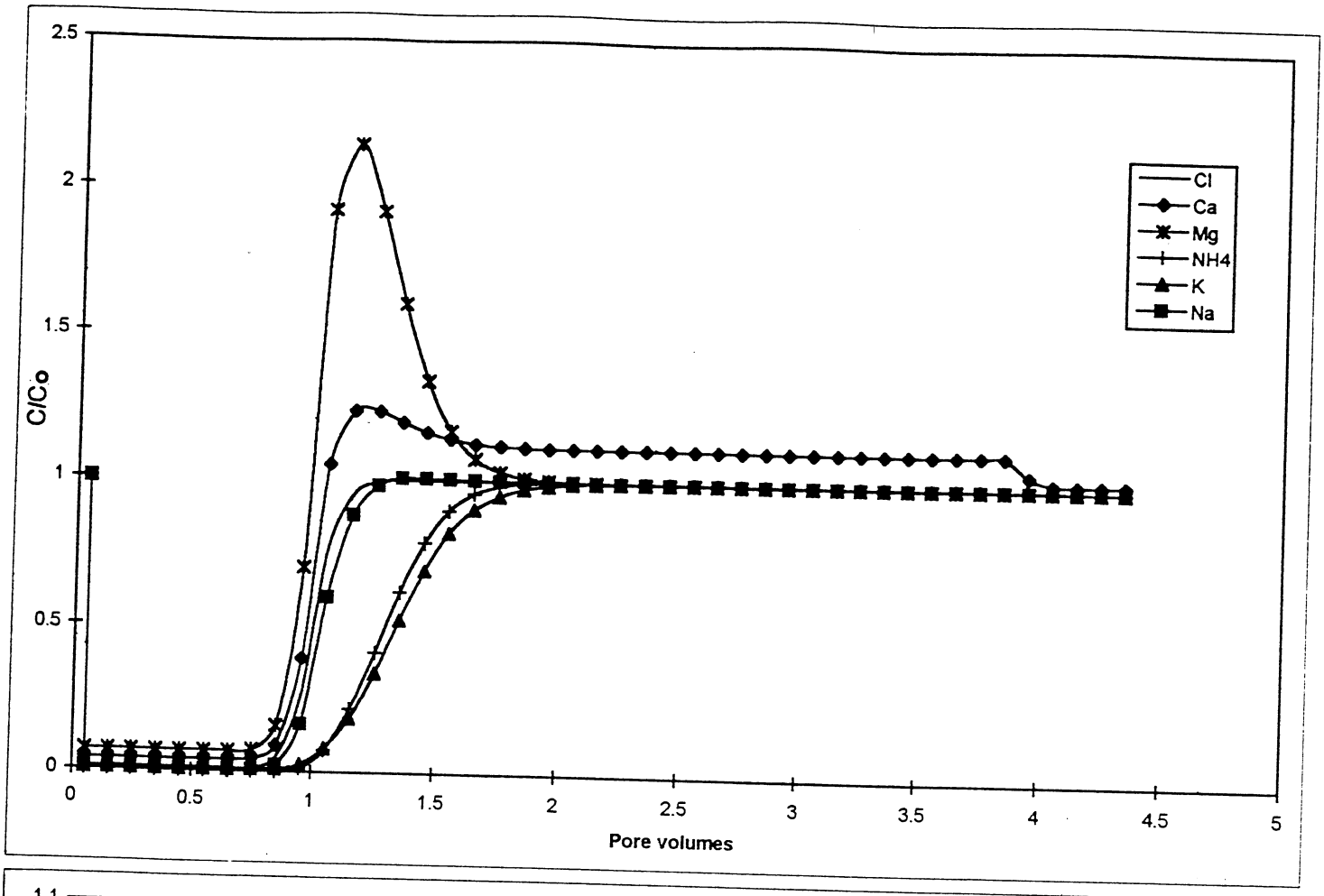
Results: Simulated breakthrough curves for inorganic solutes in A-phase leachate for this column experiment under the new conditions modelled are presented in Figure 3.3. There is no change in the style and timing of breakthrough for contaminants, with the exception of Mn and pe. The effluent Mn concentration is predicted by PHREEQM to reach a maximum of 0.15 input leachate values, that is 14mg/L, as opposed to peak values of 300mg/L produced in the absence of $MnCO_3$ equlibrium (Figure 3.2). The Mn concentrations also remain invariant of changes in eluted Fe^{2+} under these new conditions. Simulated changes in the system redox status are qualitatively similar under these conditions to those observed in problem 1, although the absolute values of pe are slightly lower (cf Figure 3.2).

Conclusion: The results of this simulation suggest that $MnCO_3$ precipitation is unlikely to reduce the high dissolved Mn load produced in this leachate by contact with the sandstone, despite the presence of native carbonate in the aquifer material. This feature may result from slow reaction kinetics which mean that precipitation of $MnCO_3$ occurs over a time scale which is greater than the residence time of the laboratory column. With the longer residence time expected in the field system conditions will tend towards equilibrium. Therefore, precipitation of $MnCO_3$ may be more important and exert a greater control on Mn concentrations in the aquifer than in the column experiments shown here.

Table 3.2 PHREEQM input file for problem 2.

```
g/w equilib/a-phase leachate flush+ion exch/redox reactions+CaCO3/rhodoch eq
0000110001 0 0      0.0
SPECIES
181
NAX        200 0.0      0.0      4.0      4.0      0.075     0.0
20.00     0.0
 6  1.000 30  1.000
182
KX         200 0.0      0.0      3.0      3.5      0.015     0.0
21.02     0.0
 7  1.000 30  1.000
183
CAX2       200  0.0     0.0      6.0      5.0      0.165     0.0
40.80     0.0
 4  1.000 30  2.000
184
MGX2       200 0.0      0.0      8.0      5.5      0.20      0.0
41.20     0.0
 5  1.000 30  2.000
186
MNX2       200 0.0      2.0      6.0                 0.0
40.70     0.0
 9  1.000 30  2.000
187
FEX2       200 0.0      2.0      6.0                 0.0
40.95     0.0
 8  1.000 30  2.000
188
FEX3       300 0.0      3.0      9.0                 0.0
47.28     9.68
 8  1.000 30  3.000  2 -1.000
189
NH4X       200 0.0      -3.0     2.5                 0.0
20.55     0.0
 23  1.000 30  1.000

SOLUTION 2
A-phase leachate
10 00 2   5.90      2.61     25.0      1.000
  4 3.8320E+03   5 5.6400E+02   6 2.0080E+03   7 1.1430E+03   8 4.4800E+02
  9 9.8100E+01  14 2.8600E+03  15 3.2700E+02  16 1.2760E+03  23 1.4630E+03
NEUTRAL
   0   14
LAYERSOL 1
FILLS COLUMN WITH GROUNDWATER
10 15 2   6.75      7.496     25.0      1.000
  4 1.7600E+02   5 3.9400E+01   6 1.1500E+01   7 7.9000E+00   8 2.1000E-02
  9 1.2000E-01  14 3.0900E+01  15 5.8600E+02  23 1.0000E-02  30 6.0180E+01
 10  5  5  0  0
 1.00E-01   3.70E-03 1.00E-01   3.70E-03 1.00E-01   3.70E-03 1.00E-01   3.70E-03
 1.00E-01   3.70E-03 1.00E-01   3.70E-03 1.00E-01   3.70E-03 1.00E-01   3.70E-03
 1.00E-01   3.70E-03 1.00E-01   3.70E-03
CALCITE   0.000E+00 1.000E+01
RHODOCHR  0.000E+00-1.000E+00
FE(OH)3a  0.000E+00-1.000E+00
BIRNESSI  0.000E+00 1.160E-02
O2 gas   -7.000E-01 1.000E-20
MEDIUM
 0.00000000E+00
TRANSPRT
  50    1   0   -2     0.39   185806.   5.E-05       10.0
A:CA1XCR2     9
  4   6   7  14   5  15  23   8   9
END
```



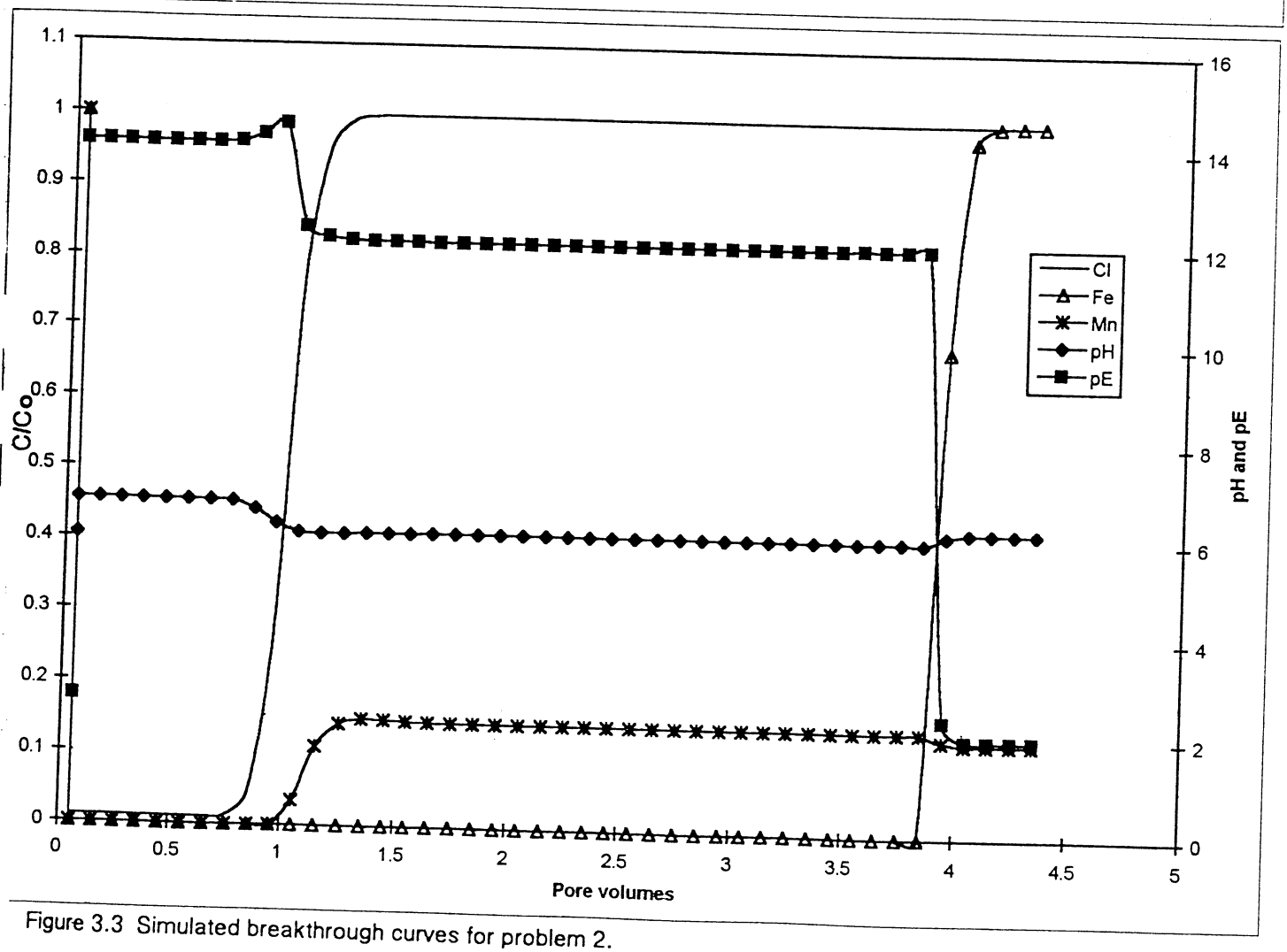


Figure 3.3 Simulated breakthrough curves for problem 2.

3.2.3 Problem 3: Laboratory Flushing of Burntstump Triassic Sandstone Columns With Methanogenic Phase Landfill Leachate

Problem 3: Simulating transport of methanogenic (M-phase) landfill leachate through laboratory columns of Triassic Sandstone aquifer material taken from Burntstump landfill site, Nottinghamshire. This forms part of a study assessing the chemical impact of leachate migration from landfills on the Triassic Sandstone aquifer.

Laboratory experimental results: The aquifer sandstone contains around 1.22% $CaCO_3$ and has a CEC of about 1.63meq/100g, based on solid phase analysis. The experimental results are presented in terms of normalised solute concentrations (C/C_o) against pore volumes of leachate passed through the aquifer column, where C and C_o represent the concentration of a solute in the column effluent and M-phase leachate, respectively. The aquifer column is initially saturated with groundwater prior to flushing with leachate. Examples of breakthrough curves for selected solutes in M-phase leachate are presented in Figure 3.4.

Conceptual model used in simulation: Native Ca and Mg are desorbed from the aquifer sandstone in response to sorption of Na, K and NH_4 from the leachate. This results in the elution of Ca and Mg at relative high concentrations as a pulse at the leachate front during breakthrough but relative retardation of the Na, K and NH_4 fronts. The front of desorbed Mg is eluted from the column slightly later than the front of desorbed Ca.
The porewater pH decreases slightly during leachate breakthrough but subsequently recovers to that of the leachate (pH 7.4) for the remainder of the experiment. Breakthrough of the leachate alkalinity front is retarded slightly but this parameter achieves final breakthrough when effluent pH values have stabilised at those of the leachate. Manganese is eluted in high concentrations (up to 20 times that of the leachate) from this column for the duration of the experiment. This also coincides with the removal of the leachate Fe load and buffering of the system redox status (represented by Eh) to values which are higher than that of the leachate (-76mV).

Model input file: The input file for this problem is listed in Table 3.3. The parameters used in the construction of the input file are described below for the relevant option blocks. These are described in the order that they appear in the file.
OPTIONS: Option 5 is set to 1, allowing pe to be determined from the reactions simulated. This is useful when modelling redox reactions for following changes in the system Eh due to changes in the concentrations of the redox sensitive species responsible. Option 6 is set to 1, where the Davies formula is used to make the appropriate activity corrections for solute concentrations and Option 10 is set to 1 to select the flow tube modelling option in PHREEQM.

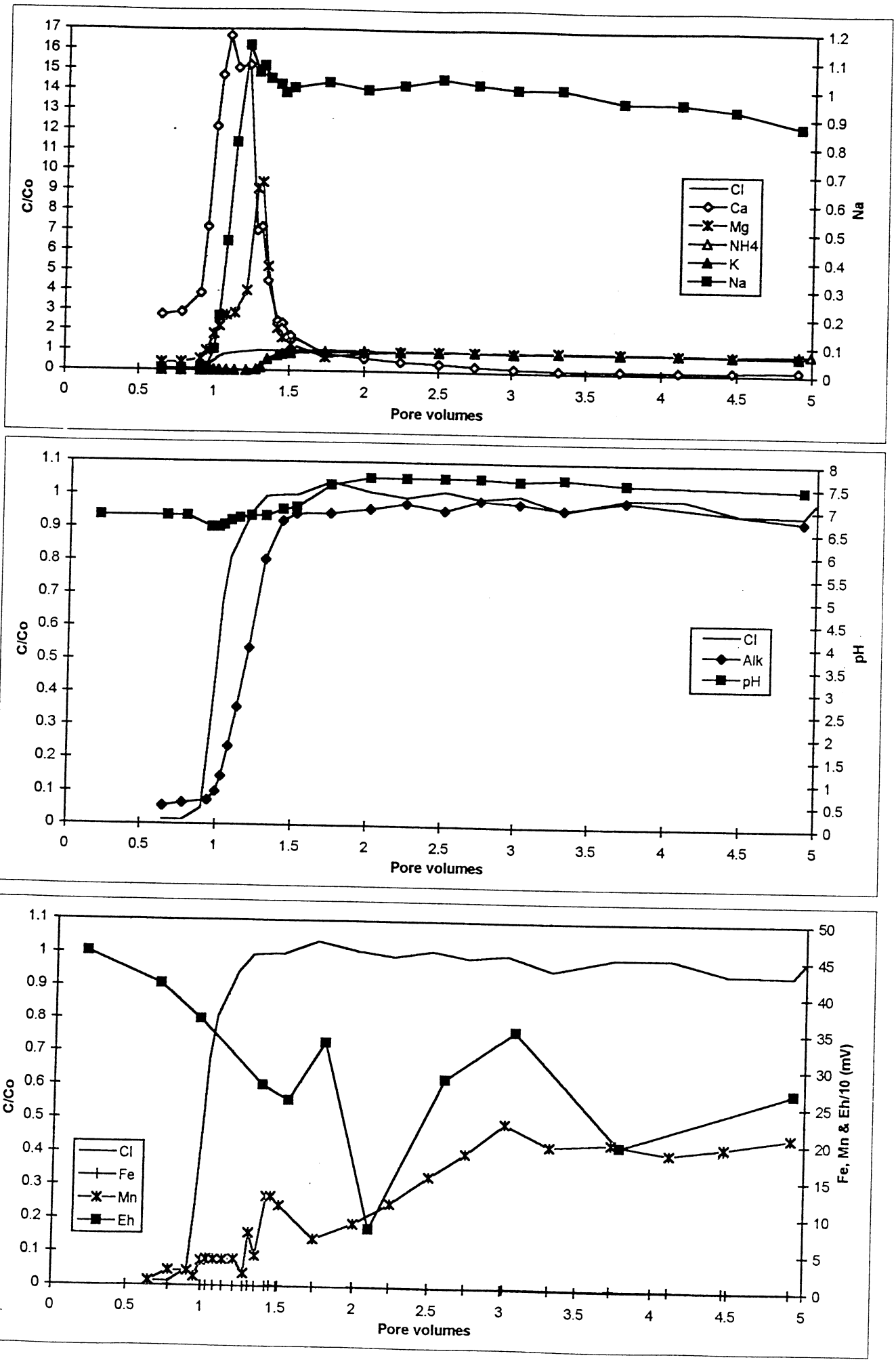


Figure 3.4. Experimental breakthrough curves for problem 3.

Table 3.3 PHREEQM input file for problem 3.

```
col 4:g/water equilib/M-phase leachate flush+exch/redox reactions+CaCO3 equilib
0000110001 0 0    0.0
SPECIES
181
NAX      200 0.0     0.0     4.0     4.0     0.075   0.0
20.00    0.0
 6  1.000 30  1.000
182
KX       200 0.0     0.0     3.0     3.5     0.015   0.0
21.10    0.0
 7  1.000 30  1.000
183
CAX2     200  0.0    0.0     6.0     5.0     0.165   0.0
40.43    0.0
 4  1.000 30  2.000
184
MGX2     200 0.0     0.0     8.0     5.5     0.20    0.0
40.47    0.0
 5  1.000 30  2.000
186
MNX2     200 0.0     2.0     6.0                     0.0
40.50    0.0
 9  1.000 30  2.000
187
FEX2     200 0.0     2.0     6.0                     0.0
40.45    0.0
 8  1.000 30  2.000
188
FEX3     300 0.0     3.0     9.0                     0.0
47.28    9.68
 8  1.000 30  3.000  2 -1.000
189
NH4X     200 0.0     -3.0    2.5                     0.0
20.73    0.0
 23  1.000 30  1.000

SOLUTION 2
M-phase leachate
9  15 2  7.80     -1.43     25.0      1.000
  4 6.2000E+01   5 9.2000E+01   6 1.8960E+03   7 1.1390E+03   8 2.6000E+00
  9 1.0000E-01   14 2.5000E+03   15 9.0770E+03   23 1.9290E-03
LAYERSOL 1
FILLS COLUMN WITH GROUNDWATER
10 15 2   6.80      6.980     25.0      1.000
  4 1.6300E+02   5 3.5200E+01   6 1.1100E+01   7 7.9000E+00   8 2.1000E-02
  9 7.3000E-02   14 3.1000E+01   15 5.0500E+02   23 1.0000E-02   30 5.7248E+01
 10  5  4  0  0
 1.00E-01   3.10E-03 1.00E-01   3.10E-03 1.00E-01   3.10E-03 1.00E-01   3.10E-03
 1.00E-01   3.10E-03 1.00E-01   3.10E-03 1.00E-01   3.10E-03 1.00E-01   3.10E-03
 1.00E-01   3.10E-03 1.00E-01   3.10E-03
CALCITE   0.000E+00 1.000E+01
FE(OH)3a  0.000E+00-1.000E+00
BIRNESSI  0.000E+00 1.295E-04
O2 gas    -7.000E-01 1.000E-20
MEDIUM
 0.00000000E+00
TRANSPRT
  50    1    0   -2     0.41   193722.   5.E-05      10.0
A:CM4XCR1     9
  4   6   7  14   5  15  23   8   9
END
```

SPECIES: All species which, based on the experimental results, participate in ion-exchange reactions with the aquifer column are specified in this block. This includes the major ions (Ca, Mg, Na, K,

NH_4) and also reduced species of Mn and Fe which may be involved in these reactions.
SOLUTION: The composition of the methanogenic leachate (designated as solution 2) which displaces the groundwater from the aquifer column is specified in this block. In NTOTS the total number of species concentrations to be input is specified as 9 and IALK is set to 15 to denote that measured alkalinity, rather than total inorganic carbon, will be input to represent the inorganic carbon in the leachate. In M-phase leachate, as opposed to A-phase leachate (problem 1), alkalinity is predominantly derived from inorganic species, rather than dissolved organic matter fractions, and is accurately measured using the conventional method of titration to a pH4.5 end-point (Thornton et al., 1995). An input value of pe for this problem is calculated from the measured Eh of the leachate using the relationship: pe=Eh(mV)/59.1 and the temperature is set to that of the laboratory (25°C). The concentrations of the 9 species indicated in NTOTS are input in DTOTS in mg/L. Alkalinity (solute index number 15) is input in DTOTS expressed as mg/L as HCO_3^-, re-calculated from the measured alkalinity (expressed as mg/L as $CaCO_3$).
LAYERSOL: This block specifies the properties of the aquifer column, the composition of the groundwater saturating the column and the chemical reactions to be simulated between the column and pore fluid. A single layer model of 1m length and divided into 10 cells is set up in COLUMN. Flow is set to linear with a dispersivity of 0.31cm. The latter has been estimated from fitting the leachate Cl breakthrough curve of the experimental data to an analytical solution of the advection-dispersion transport equation (Ogata and Banks, 1961). It is important to note that the concentrations of species input in this block are those of the groundwater in equilibrium with the column and not those of the groundwater prior to contact with the aquifer material. This distinction is important when modelling the results of column studies but is usually not applicable to analysis of field data where the composition of the uncontaminated porewater in the aquifer is used. The number of species concentrations in the groundwater to be input is set to 10 in NTOTS. This number must include the aqueous species of interest and also X^-, the equivalent CEC of the column on a per volume of water basis. The IALK input for the groundwater can be defined as the total alkalinity and set to 15 (rather than 0 for TIC), since no dissolved organic fractions are present and the measured alkalinity accurately reflects the inorganic species present. The measured pH of the groundwater is used and a pe calculated from the measured Eh is also included. The concentrations of the species specified in NTOTS are input in mg/L in DTOTS. Although NH_4 is not present above detection limits in the groundwater a very small concentration is included in DTOTS to set up the exchange equilibria between aqueous and sorbed NH_4 fractions in the column. If this is not done, NH_4 will be treated as a conservative species during the model simulations. The value of alkalinity required for input as element 15 in DTOTS is calculated from the measured alkalinity, expressed in mg/L as $CaCO_3$, using mg/L as HCO_3^- = mg/L as $CaCO_3$ x 1.22. The measured alkalinity of the groundwater in equilibrium with the aquifer column was 414 mg/L as $CaCO_3$,

providing a corresponding alkalinity of 505 mg/L as HCO_3. A value for the column CEC, expressed in meq/L of water, is included in X^-. The latter is calculated from the measured CEC of the aquifer material (1.63 meq/100g), column bulk density (1.44 kg/L) and column effective porosity (0.41) using $X^- = 10 \times (1.44/0.41) \times 1.63 = 57.24$ meq/L. The 1m long column is split into 10 cells, each of 0.1m thickness in NCELLS. In this example NCELLS = NCOL because only 1 layer is being modelled. For simulations using multiple layers, each configured separately, NCELLS < NCOL. Mineral equilibration is also specified in this block (IOPT 3 set to 5) rather than in the OPTIONS block. This is the normal exception when modelling equilibration with mineral phases using the LAYERSOL option. Four mineral phases are selected for equilibration in this layer. The minerals and equilibrium conditions concerned are:

Mineral	SIMEX	AMTMIN (moles/kg H_2O)
Calcite	0.0	10.0
$Fe(OH)_3a$	0.0	-1.0
Birnessite (MnO_2)	0.0	1.295×10^{-4}
O_2 gas	-0.7	1×10^{-20}

Calcite is naturally present in the sandstone and equilibrium is maintained (SIMEX = 0) with an infinite amount of this mineral (AMTMIN = 10.0 moles/kg H_2O). The remaining minerals in this table are set up to simulate a redox front formed by the reductive dissolution of Mn oxyhydroxide coatings on the sandstone by Fe^{2+} in the leachate. This redox reaction is comparable to that simulated for this aquifer material during flushing with A-phase leachate (see problem 1) and is undertaken to evaluate whether the high Mn concentrations and Fe attenuation observed during flushing with this M-phase leachate could be produced by the same mechanism. The column pore water is equilibrated with MnO_2 at a pO_2 of 0.2 atm. The amount of "O_2 gas" is set very small at 10^{-20} mole/kg H_2O, so that only aqueous O_2 provides redox buffering. Amorphous iron hydroxide is set to a negative quantity (AMTMIN = -1.0), that is, this phase is not originally present in the column, although it will precipitate when saturated conditions are obtained in the column (SIMEX = 0). The amount of MnO_2 available for reduction by ferrous iron is obtained from the experimental data by determining a mass balance for the net quantity of Mn mobilised from the column during the Mn flush. For the present problem, an additional 0.388 mmoles of Mn was mobilised from the column and the corresponding amount of MnO_2 in moles/kg H_2O available for reduction is calculated from the column mass (10.52kg), bulk density (1.44kg/L) and effective porosity (0.41) using the following relationship:

MnO_2 (moles/kg H_2O) = $[(0.388/1000) / (10.52)] \times (1.44/0.41)$ = 1.295×10^{-4}

MEDIUM: This block is included in order to set the diffusion coefficient. In the present case, all runs used a zero diffusion coefficient.

TRANSPORT: In this block the number of shifts (NSHIFT) is set to 50, that is all solutions are transported ("shifted") 50 times into the next cell. This means that 50 (= NSHIFT)/10 (= NCOL, the number of cells in all layers, in this case, 1) = 5 pore volumes are injected and eluted. Solutions are shifted into higher numbered cells (ISHIFT = 1) and by setting IFRIX to 0.0, mixing between adjacent cells is determined by dispersivity only. IPREX is set to -2 to provide a printout of information about the end cell only (which is flushed by 5 pore volumes of solution). A porosity of 0.41 is input for each cell in the column. This value represents the effective porosity determined for the column by transport modelling of the Cl breakthrough curve (see explanation in LAYERSOL, above). A time step of approximately 194,000 seconds is also used for DELTAT (Δt) and is calculated from $\Delta t = \Delta x/ALV$ where Δx is the cell length (0.1m) and ALV is the (average) linear velocity, in this case determined from transport modelling of the leachate Cl breakthrough curve (4.46 cm/day). The output from these simulations is sent to a spreadsheet file on a floppy drive in the form of aqueous concentrations of species only. A maximum of 9 species (Ca, Na, K, Cl, Mg, CO_3^{2-}, NH_4, Fe^{2+}, Mn^{2+}) are sent to this file for output and these are specified using the index number for each species. Other species modelled (e.g. SO_4) can be included for output by reselection from the default list provided.

Results: Simulated breakthrough curves for inorganic solutes in M-phase leachate for this column experiment are presented in Figure 3.5. There is good agreement in the style and timing of contaminant breakthrough between the simulated data and experimental results, but with some notable exceptions (cf Figure 3.4). The model effectively describes the transport of the major cations (including some desorption of sorbed Na during leachate breakthrough), together with the contrasting styles of desorption of native Ca and Mg. However, the amount of expected Ca desorption is slightly underestimated, reaching a relative concentration of 13 compared with an experimentally observed value of 17 (cf Figure 3.4). The simulated breakthrough curves for the major cations have been fitted to the experimental results by adjustment of the LKTOSP values for each exchangeable species (e.g. CaX, NH_4X etc.) in the SPECIES block of the input file. The simulated breakthrough profiles for pH and alkalinity are in good agreement with the experimental results. The apparent retardation of the alkalinity front in this experiment is explained by precipitation of $CaCO_3$ during leachate breakthrough. This precipitation is caused by the high Ca concentrations produced as a result of desorption of this cation from the sandstone. This reaction also induces a drop in porewater pH during leachate breakthrough. Although the duration of the Mn flush and removal of leachate Fe^{2+} in this column experiment are accurately simulated by the model, the style and magnitude of the Mn flush is less effectively simulated (Figure 3.5). Similarly, the simulated changes in system redox status during leachate flushing are qualitatively consistent with those in the experimental data, but the detailed style of these changes is not predicted.

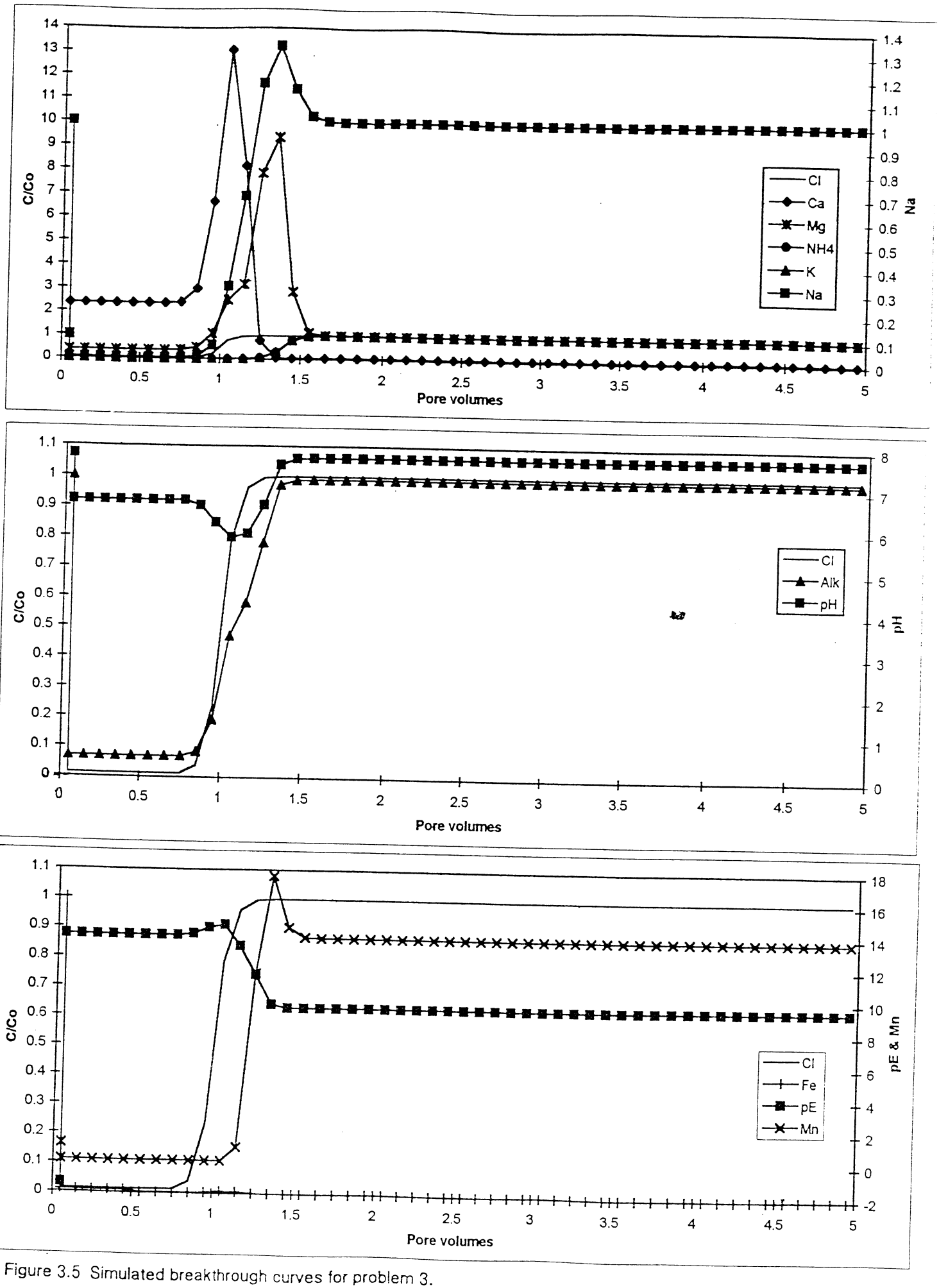


Figure 3.5 Simulated breakthrough curves for problem 3.

Conclusion: This simulation shows that most of the key features observed during flushing of this aquifer column with M-phase leachate can be qualitatively replicated using the code. The modelled results suggest that the 3 processes simulated (ion-exchange reactions between the major cations (Ca, Mg, K, Na, NH_4, Mn^{2+}, Fe^{2+}), carbonate equilibria and reductive dissolution of MnO_2 by Fe^{2+}) adequately characterise the chemical interactions of these species in this leachate and with this aquifer material. The model was, however, unable to accurately describe the detailed form of the Mn flush and redox poising in this experiment, although the maintenance of the Mn flush for up to 5 pore volumes was predicted. It is possible that the evolution of the Mn flush in this system is not simply related to the reduction of one Mn oyxhydroxide phase by ferrous iron. Nevertheless, the general behaviour of Mn in this experiment appears to be broadly explained by a reaction of this type. If it is assumed that the total amount of Mn oxyhydroxide on this aquifer material that is available for reduction is that mobilised by the A-phase leachate, and that the same reaction is consistent to both systems, then the duration of the Mn flush and redox buffering produced by contact with M-phase leachate would be considerable. This period may be predictable for this aquifer material, based on the results from these experiments and model simulations.

3.2.4 Problem 4: Laboratory Flushing of Burntstump Triassic Sandstone Columns With Methanogenic Phase Landfill Leachate

Problem 4: Simulating transport of methanogenic landfill leachate through columns of Triassic Sandstone aquifer material taken from Burntstump landfill site, Nottinghamshire. This problem further evaluates the chemical interactions in the column experiment used to illustrate problem 3. The current problem examines whether precipitation of rhodochrosite ($MnCO_3$) is likely to lower the Mn concentrations produced by reduction of Mn oxyhydroxides during flushing of this aquifer sandstone with M-phase leachate.

Laboratory experimental results: The experimental results for this problem are the same as those for problem 3 (Figure 3.4).

Conceptual model used in simulation: As for problem 3, but with rhodochrosite equilibrium.

Model input file: The input file for this problem (CM4XCR2.DAT) is listed in Table 3.4. The parameters used in the construction of the input file are identical to those described above for problem 3 and only the changes necessary to modify the simulation for this problem are discussed here.

Table 3.4 PHREEQM input file for problem 4.

```
col 4:g/water equilib/M-phase leachate flush+exch/redox reactions+CaCO3 equilib
0000110001 0 0     0.0
SPECIES
 181
NAX       200 0.0     0.0     4.0     4.0     0.075    0.0
20.00    0.0
  6  1.000 30  1.000
 182
KX        200 0.0     0.0     3.0     3.5     0.015    0.0
20.97    0.0
  7  1.000 30  1.000
 183
CAX2      200  0.0    0.0     6.0     5.0     0.165    0.0
40.08    0.0
  4  1.000 30  2.000
 184
MGX2      200 0.0     0.0     8.0     5.5     0.20     0.0
40.30    0.0
  5  1.000 30  2.000
 186
MNX2      200 0.0     2.0     6.0                 0.0
40.50    0.0
  9  1.000 30  2.000
 187
FEX2      200 0.0     2.0     6.0                 0.0
40.45    0.0
  8  1.000 30  2.000
 188
FEX3      300 0.0     3.0     9.0                 0.0
47.28    9.68
  8  1.000 30  3.000  2 -1.000
 189
NH4X      200 0.0     -3.0    2.5                 0.0
20.57    0.0
 23  1.000 30  1.000

 SOLUTION 2
 M-phase leachate
 9  15 2  7.80     -1.43    25.0      1.000
   4 6.2000E+01  5 9.2000E+01  6 1.8960E+03  7 1.1390E+03  8 2.6000E+00
   9 1.0000E-01  14 2.5000E+03  15 9.0770E+03  23 1.9290E+03
 LAYERSOL 1
 FILLS COLUMN WITH GROUNDWATER
 10 15 2  6.80     6.980    25.0      1.000
   4 1.6300E+02  5 3.5200E+01  6 1.1100E+01  7 7.9000E+00  8 2.1000E-02
   9 7.3000E-02  14 3.1000E+01  15 5.0500E+02  23 1.0000E-02  30 5.7248E+01
 10  5  5  0  0
 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03
 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03
 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03
CALCITE  0.000E+00 1.000E+01
RHODOCHR 0.000E+00-1.000E+00
FE(OH)3a 0.000E+00-1.000E+00
BIRNESSI 0.000E+00 1.295E-04
O2 gas  -7.000E-01 1.000E-20
MEDIUM
 0.00000000E+00
TRANSPRT
   50    1   0  -2     0.41   193722   5.E-05      10.0
A:CM4XCR2    9
   4  6  7  14  5  15  23  8  9
END
```

LAYERSOL: The number of mineral phases to be equilibrated in the column is increased from 4 to 5 in NCELLS and rhodochrosite is selected in MNAME. Values of SIMEX and AMTMIN for this phase are set to 0.0 and -1.0, respectively in the SIMEX option. This means that $MnCO_3$ is not initially in equilibrium with the pore fluid although precipitation of this phase may occur if conditions permit.

Results: Simulated breakthrough curves for inorganic solutes in M-phase leachate for this column experiment under the new conditions modelled are presented in Figure 3.6. There is no change in the style and timing of breakthrough for contaminants, with the exception of Mn and pe. The effluent Mn concentration is predicted by PHREEQM to attain relative concentrations no higher than 0.5 input leachate values, that is 0.05mg/L, as opposed to peak values of 2mg/L produced in the absence of $MnCO_3$ equlibrium (Figure 3.5). The Mn concentrations also remain invariant of changes in eluted Fe^{2+} under these new conditions. Simulated changes in the system redox status are qualitatively similar under these conditions to those observed in problem 3, although the absolute values of pe are slightly higher (cf Figure 3.5).

Conclusion: The results of this simulation suggest that $MnCO_3$ precipitation is unlikely to have occurred to equilibrium in the laboratory experiments. This may be due to slow reaction kinetics which mean that precipitation of $MnCO_3$ occurs over a time scale which is greater than the residence time of the laboratory column. With the longer residence time expected in the field system conditions will tend towards equilibrium. Therefore, precipitation of $MnCO_3$ may be more important and exert a greater control on Mn concentrations in the aquifer than in the column experiments shown here. Complexation of Mn with different organic ligands in the leachate may also limit the precipitation of $MnCO_3$ under conditions in which the leachate appears to be supersaturated with respect to this phase.

3.2.5 Problem 5: Laboratory Flushing of Burntstump Triassic Sandstone Columns With Methanogenic Phase Landfill Leachate

Problem 5: Simulating transport of methanogenic landfill leachate through columns of Triassic Sandstone aquifer material taken from Burntstump landfill site, Nottinghamshire. This problem further evaluates the chemical interactions in the column experiment used to illustrate problem 3. The current problem examines the effect calcite precipitation on the concentrations of major cations. This is assessed by removing calcite equilibrium from the simulation and comparing the results with those in which this condition is maintained (problem 3).

Laboratory experimental results: The experimental results for this problem are the same as those for problem 3 (Figure 3.4).

Conceptual model used in simulation: As for problem 3, but with calcite equilibrium.

Model input file: The input file for this problem is listed in Table 3.5. The parameters used in the construction of the input file are identical to those described below for problem 3 and only the changes necessary to modify the simulation for this problem are discussed here.
LAYERSOL: The number of mineral phases to be equilibrated in the column is reduced from 4 to 3 in NCELLS. Equilibrium with calcite is deleted from MNAME and only ion exchange and the redox reaction between MnO_2 and ferrous iron is included in the simulation. No other changes are necessary.
Results: Simulated breakthrough curves for inorganic solutes in M-phase leachate for this column experiment under the new conditions modelled are presented in Figure 3.7. There is no change in the style and timing of breakthrough for contaminants, with the exception of Ca, Mg, pH and alkalinity. There is a significant increase in the concentration of desorbed Ca at the leachate front but a slight drop in the predicted amounts of desorbed Mg. Also, these fronts are no longer separated, as in the simulation for problem 3 (Figure 3.5), but elute from the aquifer column at the same time. The alkalinity front is now transported conservatively in this problem and there is no temporary reduction in porewater pH during leachate breakthrough.
Conclusion: The exchange coefficients for the major cations were not changed for this simulation from those in problem 3 and the modelled results are generated for this system in the absence of calcite equilibrium. The disagreement with the experimental data suggests that calcite precipitation is highly likely to occur during leachate breakthrough in this system and is implicated as an important control on the behaviour of pH and leachate alkalinity. Mass balances on the quantity of alkalinity and desorbed Ca removed during leachate breakthrough in this experiment support the attenuation mechanism proposed (Thornton et al., 1995).

3.2.6 Problem 6: Laboratory Flushing of Bromsgrove Triassic Sandstone With Methanogenic Phase Landfill Leachate

Problem 6: Simulating the transport of methanogenic (M-phase) landfill leachate through a laboratory column of Triassic Sandstone aquifer material taken from Bromsgrove, West Midlands.

Laboratory experimental results: This aquifer sandstone contains no measurable $CaCO_3$, has an acidic pH (pH 4.3) and a CEC of about 3.24 meq/100g, based on solid phase analysis. The experimental results are presented in terms of normalised solute concentrations (C/C_o) against pore volumes of leachate passed through the aquifer column, where C and C_o represent the concentration of a solute in the column effluent and M-phase leachate, respectively. The aquifer column is initially saturated with oxygen-rich freshwater prior to flushing with leachate. Examples of breakthrough curves for selected solutes in this leachate are presented in Figure 3.8.

Table 3.5 PHREEQM input file for problem 5.

```
col 4:g/water equilib/M-phase leachate flush+exch/redox reactions+CaCO3 equilib
0000110001 0 0    0.0
SPECIES
181
NAX      200 0.0     0.0     4.0     4.0     0.075    0.0
20.00    0.0
 6  1.000 30  1.000
182
KX       200 0.0     0.0     3.0     3.5     0.015    0.0
20.97    0.0
 7  1.000 30  1.000
183
CAX2     200  0.0    0.0     6.0     5.0     0.165    0.0
40.08    0.0
 4  1.000 30  2.000
184
MGX2     200 0.0     0.0     8.0     5.5     0.20     0.0
40.30    0.0
 5  1.000 30  2.000
186
MNX2     200 0.0     2.0     6.0                0.0
40.50    0.0
 9  1.000 30  2.000
187
FEX2     200 0.0     2.0     6.0                0.0
40.45    0.0
 8  1.000 30  2.000
188
FEX3     300 0.0     3.0     9.0                0.0
47.28    9.68
 8  1.000 30  3.000  2 -1.000
189
NH4X     200 0.0     -3.0    2.5                0.0
20.57    0.0
 23  1.000 30  1.000

SOLUTION 2
M-phase leachate
9  15 2  7.80    -1.43    25.0     1.000
  4 6.2000E+01  5 9.2000E+01  6 1.8960E+03  7 1.1390E+03  8 2.6000E+00
  9 1.0000E-01  14 2.5000E+03  15 9.0770E+03  23 1.9290E+03
LAYERSOL 1
FILLS COLUMN WITH GROUNDWATER
10 15 2  6.80    6.980    25.0     1.000
  4 1.6300E+02  5 3.5200E+01  6 1.1100E+01  7 7.9000E+00  8 2.1000E-02
  9 7.3000E-02  14 3.1000E+01  15 5.0500E+02  23 1.0000E-02  30 5.7248E+01
 10  5  3  0  0
 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03
 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03
 1.00E-01  3.10E-03 1.00E-01  3.10E-03
FE(OH)3a 0.000E+00-1.000E+00
BIRNESSI 0.000E+00 1.295E-04
O2 gas  -7.000E-01 1.000E-20
MEDIUM
 0.00000000E+00
TRANSPRT
  50   1   0  -2    0.41  193722   5.E-05      10.0
A:CM4XCR3    9
  4  6  7  14  5  15  23  8  9
END
```

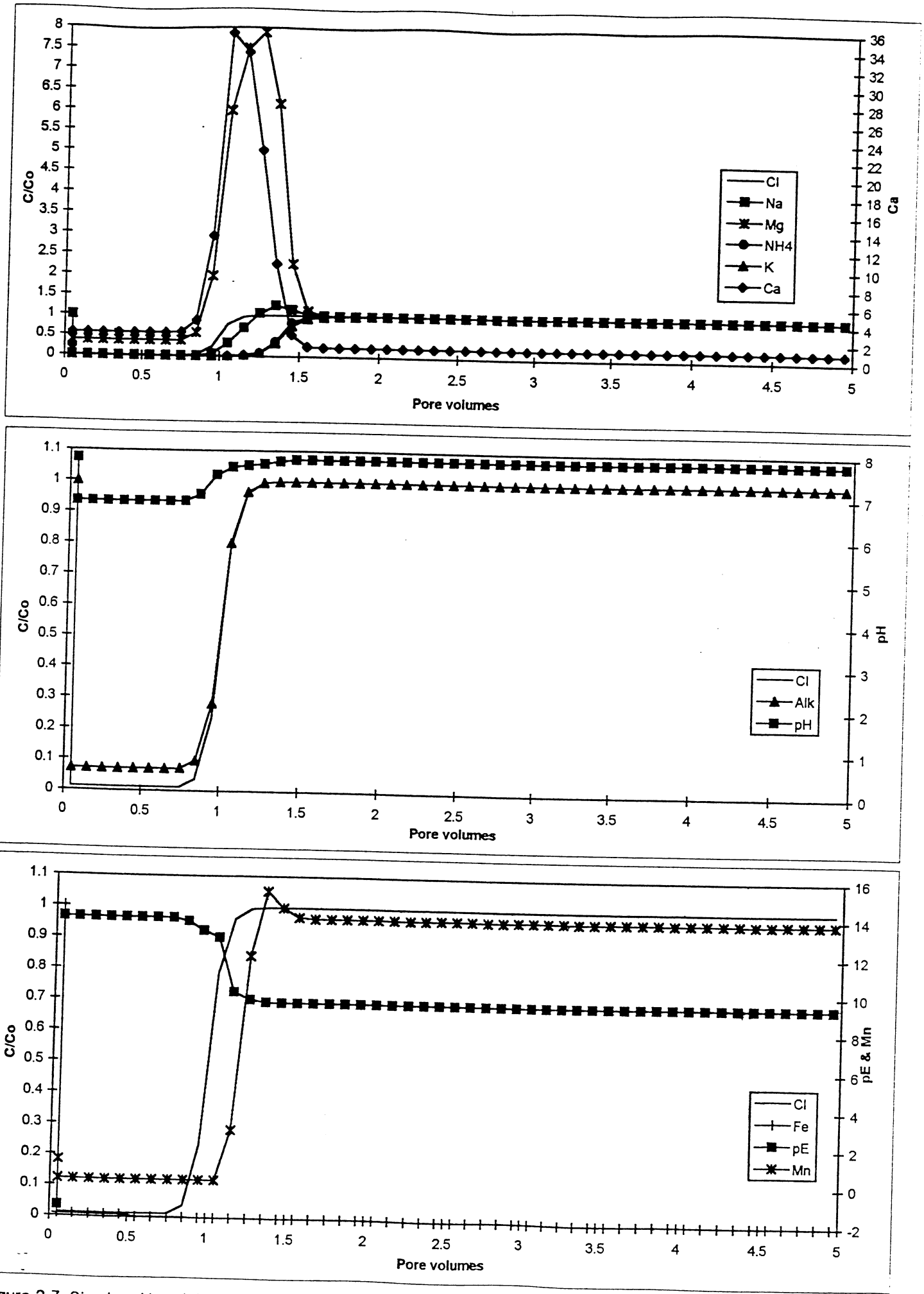


Figure 3.7 Simulated breakthrough curves for problem 5.

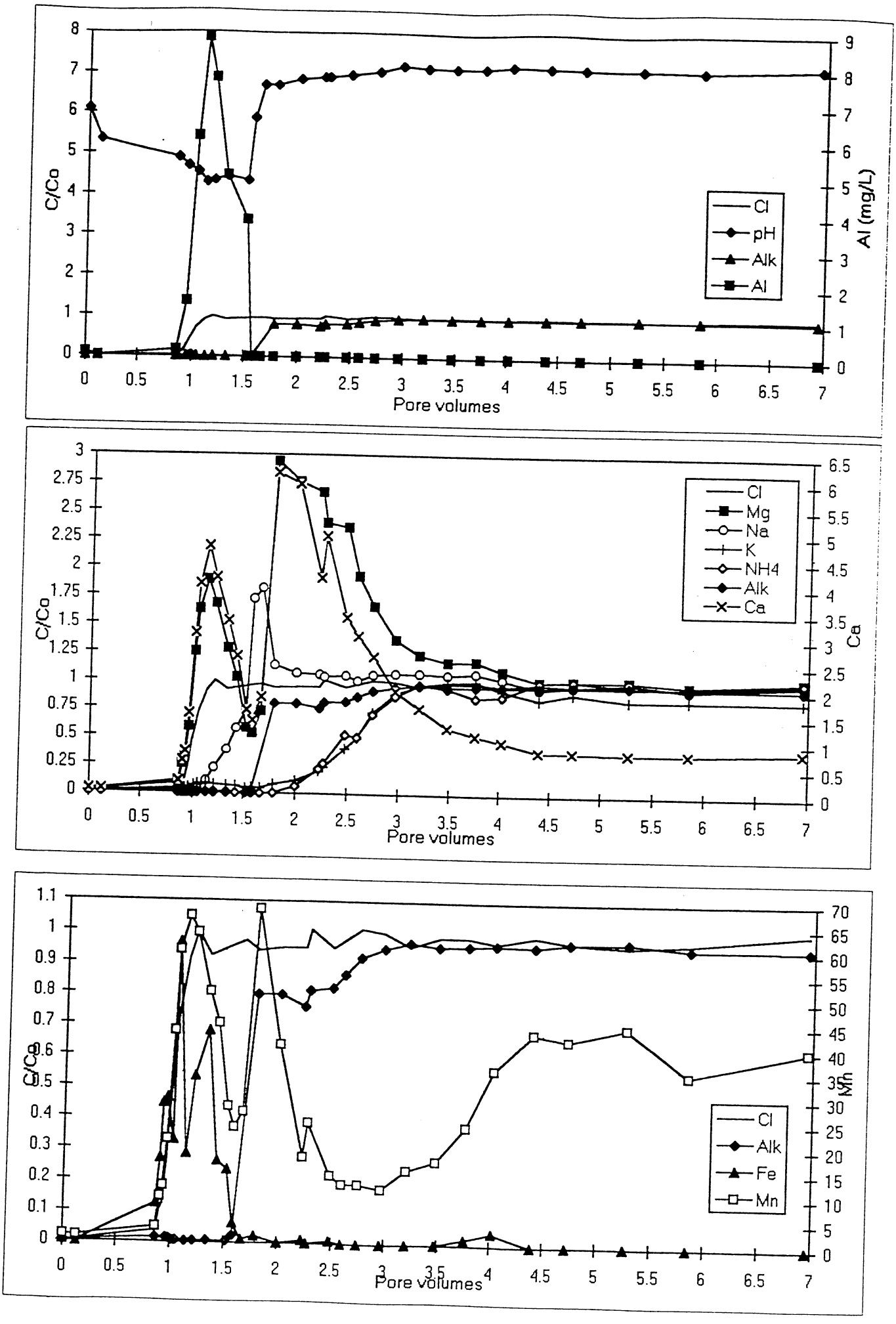


Figure 3.8.Experimental breakthrough curves for problem 6.

Conceptual model used in simulation: Calcium and Mg are desorbed from the aquifer sandstone in response to sorption of Na, K and NH_4 from the leachate. This results in the elution of Ca and Mg at relatively high concentrations in a series of fronts during leachate breakthrough, combined with retardation of the Na, K and NH_4 fronts. The first set of Ca and Mg fronts represents desorption of native fractions of these species whereas the second set of fronts is formed by desorption of fractions sorbed from the leachate. This results from strong sorption of K and NH_4 in the leachate by the aquifer column. There is also some desorption of attenuated Na which forms a separate front.

Porewater pH is buffered at low values (pH 4.3-4.5) for 0.5 pore volumes during leachate breakthrough. This coincides with the removal of most of the alkalinity which decreases from a concentration of 4600mg/L as $CaCO_3$ in the leachate to 21mg/L as $CaCO_3$ over this interval. Both pH and alkalinity rapidly increase to values near those of the leachate after 2 pore volumes have eluted. No Al is present in the freshwater or leachate above detection limits but this metal is eluted from the column during leachate breakthrough in relatively high concentrations (up to 8.5mg/L) as a pulse for 0.5 pore volumes. This coincides with the minima in the pH and alkalinity breakthrough curves and production of CO_2-rich gas in the column (data not shown). The behaviour of pH, alkalinity and Al at this time can be explained by reactions involving the hydrolysis of Al fractions and equilibrium with Al hydroxides (e.g. gibbsite, $Al(OH)_3$). The pH buffering observed during leachate breakthrough results from hydrolysis of available Al according to the general reaction:

$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$$

with the consumption of leachate alkalinity (Figure 3.8) and CO_2 production observed between 1.0-1.5 pore volumes reflecting neutralisation of the generated acidity, as in:

$$H^+ + HCO^-_3 \leftrightarrow H_2O + CO_2.$$

Hence leachate alkalinity is initially consumed, during passage through this aquifer material, by an acid-base reaction and titration with H^+ generated through Al hydrolysis reactions. This mechanism is probably initiated by the mobilisation of native exchangeable Al on the sand, supplemented by contributions released during dissolution of oxide fractions. These reactions effectively buffer leachate pH to low levels until all the dissolved, exchangeable and oxide bound Al is hydrolysed and precipitated as $Al(OH)_3$, as in:

$$Al_{exch} \rightarrow Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \rightarrow H^+ + HCO^-_3 \rightarrow H_2CO_3^*$$

$$H^+ + Al_{oxyhydroxide}$$

A Mn flush is eluted from the column for the duration of the experiment. This is coincident with the removal of the leachate Fe load

after the system pH has reached input levels. Mass balance calculations for these metals indicate that this feature is consistent with the reduction of solid phase manganese oxyhydroxide on the aquifer sandstone by ferrous iron in the leachate, according to the following reaction stoichiometry:

$$2Fe^{2+} + MnO_2 + 4H_2O \rightarrow 2Fe(OH)_3 + Mn^{2+} 2H^-$$

where leachate Fe^{2+} is oxidised and precipitated as insoluble Fe oxyhydroxide. The mechanism producing the Mn flush in this column is identical to that responsible for the redox front in the Nottingham Triassic Sandstone column flushed with A-phase leachate (problem 1).

Model input file: The input file for this problem (LTSDX4.DAT) is listed in Table 3.6. The parameters used in the construction of the input file are described below for the relevant option blocks. These are described in the order that they appear in the file.
OPTIONS: Option 5 is set to 1, allowing pe to be determined from the reactions simulated. This is useful when modelling redox reactions for following changes in the system Eh due to changes in the concentrations of the redox sensitive species responsible. Option 6 is set to 1, where the Davies formula is used to make the appropriate activity corrections for solute concentrations and Option 10 is set to 1 to select the flow tube modelling option in PHREEQM.
SPECIES: All species which, based on the experimental results, participate in ion-exchange reactions with the aquifer column are specified in this block. This includes the major ions (Ca, Mg, Na, K, NH_4), reduced species of Mn and Fe and also different Al hydrolysis products (Al^{3+}, $Al(OH)^{2+}$) which may be involved in these reactions. Species 187 and 188 (FeX2 and FeX3) are subsequently removed from participation in the ion-exchange reactions. This is done to check whether ion-exchange reactions or the simulated redox reaction (see below) have a greater impact on aqueous concentrations of these metals during flushing of the aquifer column with leachate.

SOLUTION: The composition of the methanogenic leachate (designated as solution 2) which displaces the freshwater from the aquifer column is specified in this block. In NTOTS the total number of species concentrations to be input is specified as 11 and IALK is set to 15 to denote that total alkalinity will be input to represent the inorganic carbon in the leachate. In M-phase leachate, as opposed to A-phase leachate (problem 1), alkalinity is predominantly derived from inorganic species, rather than dissolved organic matter fractions, and is accurately measured using the conventional method of titration to a pH4.5 end-point (Thornton et al., 1995). An input value of pe for this problem was calculated from the measured Pt electrode Eh of the leachate using the relationship: pe=Eh(mV)/59.1 and the temperature is set to that of the laboratory (25°C). The concentrations of the 11 species indicated in NTOTS are input in DTOTS in mg/L. Alkalinity (solute index number 15) is input in DTOTS as HCO_3^-, re-calculated from the measured alkalinity which is expressed as mg/L as $CaCO_3$.

Table 3.6 PHREEQM input file for problem 6.

```
Example Liners Triassic sand:exchange and min(no calcite) eq
00001 10001 0 0      0.00000
SPECIES
187

188

181
NAX      200 0.0    0.0    4.0    4.0    0.075   0.0
20.00   0.0
 6  1.000 30  1.000
182
KX       200 0.0    0.0    3.0    3.5    0.015   0.0
21.11   0.0
 7  1.000 30  1.000
183
CAX2     200  0.0    0.0    6.0    5.0    0.165   0.0
40.70   0.0
 4  1.000 30  2.000
184
MGX2     200 0.0    0.0    8.0    5.5    0.20    0.0
40.66   0.0
 5  1.000 30  2.000
185
ALX3     200 0.0    0.0    9.0                  0.0
61.50   0.0
 10  1.000 30  3.000
186
MNX2     200 0.0    2.0    6.0                  0.0
39.00   0.0
 9  1.000 30  2.000
187
FEX2     200 0.0    2.0    6.0                  0.0
39.95   0.0
 8  1.000 30  2.000
188
FEX3     300 0.0    3.0    9.0                  0.0
47.28   9.68
 8  1.000 30  3.000  2 -1.000
189
NH4X     200 0.0    -3.0   2.5                  0.0
20.74   0.0
 23  1.000 30  1.000
191
ALOHX2   400  0.0    0.0    0.0    0.0    0.0    0.0
 38.80    0.0
 10  1.000 30  2.000  3  1.000  1 -1.000

SOLUTION 2
Methanogenic leachate
11 15 2      7.25    1.08    25.0     1.0
  4 1.2500E+02  5 1.3500E+02  6 1.3400E+03  7 4.9000E+02  8 1.3900E+01
  9 1.7000E-01  13 1.7830E+01  14 1.9650E+03  15 5.6120E+03  16 5.2100E+01
 23 1.0290E+03
LAYERSOL 1
Triassic sand column+tapwater
13 15 2      5.35    5.9    25.0     1.0
  4 6.8100E+00  5 2.8500E+00  6 2.6600E+00  7 5.2700E+00  8 8.0000E-02
  9 2.3000E-01  10 1.6500E-02  13 8.3000E+00  14 9.6000E+00  15 2.6840E+01
 16 2.7400E+01  23 1.0000E-03  30 1.2534E+02
 10  5  5  0  0.0000
 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03
 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03 1.00E-01  3.10E-03
 1.00E-01  3.10E-03 1.00E-01  3.10E-03
GIBBSITE  0.000E+00-1.000E+00
FE(OH)3a  0.000E+00-1.000E+00
BIRNESSI  0.000E+00 6.909E-04
PCO2     -8.900E-01-1.000E+00
O2 gas   -7.000E-01 1.000E-20
MEDIUM
 0.00000000E+00
TRANSPRT
  50   1   0  -2   0.38     200000    5.e-5     10.0
a:ltsdx4     9
  4  5  6  8  10  14  15  23  9
END
```

LAYERSOL: This block specifies the properties of the aquifer column, the composition of the freshwater saturating the column and the chemical reactions to be simulated between the column and pore fluid. A single layer model of 1m length and divided into 10 cells is set up in COLUMN. Flow is set to linear with a dispersivity of 0.31cm. The latter has been estimated from fitting the leachate Cl breakthrough curve from the experimental data to an analytical solution of the advection-dispersion transport equation (Ogata and Banks, 1961). It is important to note that the concentrations of species input in this block are those of the freshwater in equilibrium with the column and not those of the freshwater prior to contact with the aquifer material. This distinction is important when modelling the results of column studies but is usually not applicable to analysis of field data where the composition of the uncontaminated porewater in the aquifer is used. The number of species concentrations in the freshwater to be input is set to 13 in NTOTS. This number must include the aqueous species of interest and also X^-, the equivalent CEC of the column on a per volume of water basis. The IALK input for the groundwater is defined as the total alkalinity and set to 15 (rather than 0 for TIC), since no dissolved organic fractions are present and the measured alkalinity accurately reflects the inorganic species present. The measured pH of the freshwater is used and a pe calculated from the measured Pt electrode Eh is also included. The concentrations of the species specified in NTOTS are input in mg/L in DTOTS. Although NH_4 is not present above detection limits in the freshwater a very small concentration (0.001mg/L) is included in DTOTS to set up the exchange equilibria between aqueous and sorbed NH_4 fractions in the column. If this is not done, NH_4 will be treated as a conservative species during the model simulations. No Al was measured in the freshwater and a small concentration (0.0165mg/L) is similarly input in DTOTS to initialise the Al exchange equilibria with the column. The amount of Al required for this purpose can be calculated separately with PHREEQE, using the composition input in DTOTS, to be that in equilibrium with gibbsite (SI=0.0). This is reasonable, given that the pH and Al concentrations in this system are partly controlled by dissolution and precipitation of this mineral. Some Al is likely to exist in exchangeable form on the column and it is desorption of this fraction that initiates the cycle of gibbsite precipitation and pH fall during the first 2 pore volumes of the leachate flush. If Al was only tied up in gibbsite on the column, then no gibbsite dissolution would be expected to occur to increase aqueous Al concentrations under the circumneutral pH of either the freshwater or leachate.
The value of alkalinity required for input as element 15 in DTOTS was calculated from the measured alkalinity, expressed in mg/L as $CaCO_3$, using mg/L as HCO_3^- = mg/L as $CaCO_3$ x 1.22. The measured alkalinity of the freshwater in equilibrium with the aquifer column was 22mg/L as $CaCO_3$, providing a corresponding alkalinity of 26.84 mg/L as HCO_3. A value for the column CEC, expressed in meq/L of H_2O, is included in X^-. The latter is calculated from the measured CEC of the aquifer material (3.24 meq/100g), column bulk density (1.47 kg/L) and column effective porosity (0.38) using X^- = 10 x (1.47/0.38) x 3.24 = 125.34 meq/L of H_2O. The 1m long column is split into 10

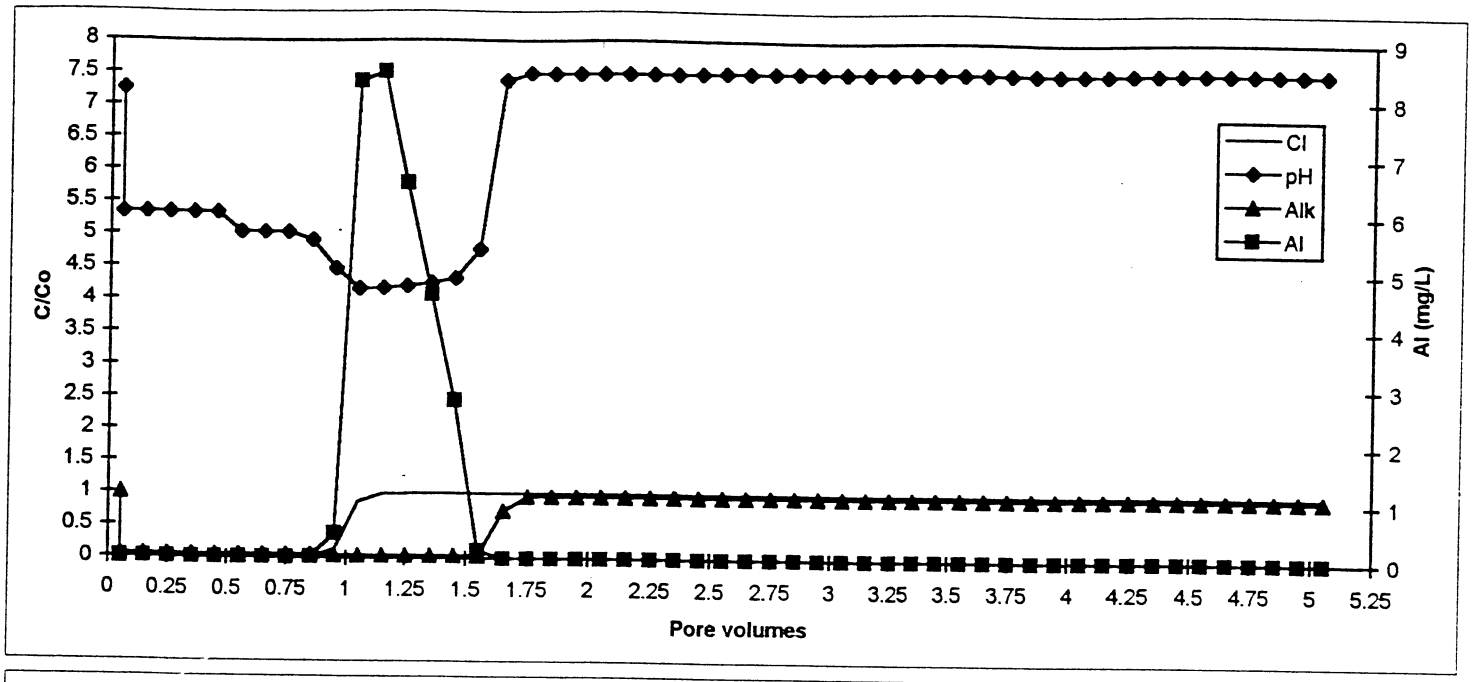
cells, each of 0.1m thickness in NCELLS. In this example NCELLS = NCOL because only 1 layer is being modelled. For simulations using multiple layers, each configured separately, NCELLS < NCOL. Mineral equilibration is also specified in this block (IOPT 3 set to 5) rather than in the OPTIONS block. This is the normal exception when modelling equilibration with mineral phases using the LAYERSOL option. Five mineral phases are selected for equilibration in this layer. The minerals and equilibrium conditions concerned are:

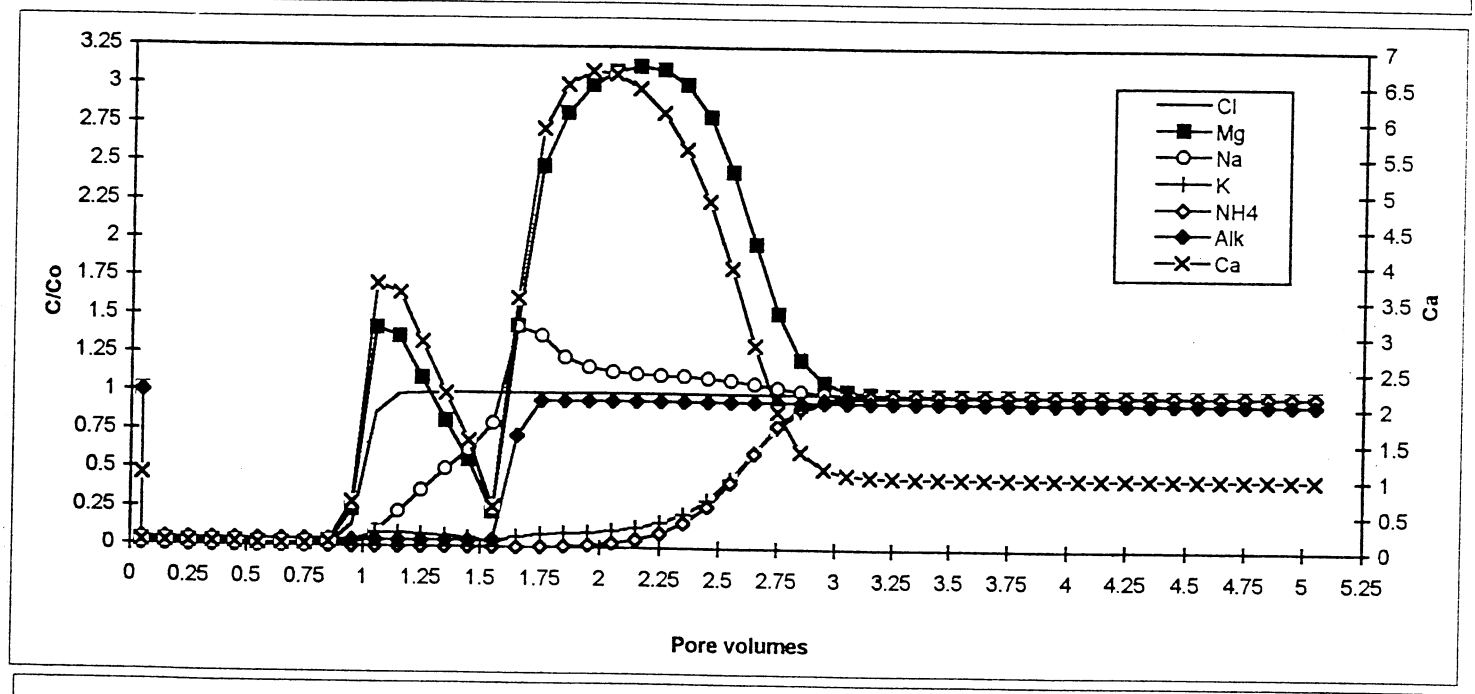
Mineral	SIMEX	AMTMIN (moles/kg H_2O)
Gibbsite	0.0	-1.0
CO_2	-0.89	-1.0
$Fe(OH)_3a$	0.0	-1.0
Birnessite (MnO_2)	0.0	6.909×10^{-4}
O_2 gas	-0.7	1×10^{-20}

There is no initial equilibrium with gibbsite ($Al(OH)_3$) in the column (AMTMIN = -1.0), but this may occur later if conditions permit. This condition ensures that there is no dissolution of gibbsite during flushing with the freshwater but that precipitation of this phase can occur if concentrations of desorbed Al exceed the solubility limit for this mineral during flushing with the leachate.
Dissolved CO_2 is treated as a mineral by PHREEQM, in terms of setting equilibrium conditions according to designated partial pressures of this gas (note dissolved O_2 input). The conditions under which this gas is input in this problem requires care consideration since changes in the CO_2 partial pressure (pCO_2) have a marked impact on the speciation and concentrations of other elements (e.g. Al^{3+}, $Al(OH)^{2+}$). Very high pCO_2 values can be calculated for aqueous compositions between 1-1.6 pore volumes. In many cases these values are greater than 1 atmosphere, indicating aqueous concentrations which are above those in equilibrium with a gas phase at atmospheric pressure and that degassing of CO_2 from the water would therefore occur if permitted. This is consistent with the observations of CO_2 gas production at this time in the column. However, in a practical context it is unlikely that all of the CO_2 produced by the reactions would escape and some will remain trapped in pore spaces within the column. This residual fraction may then slowly "bleed" back into the leachate when the Al hydrolysis reactions have been completed (post 1.6 pore volumes) and no longer have any significant direct effects on the solution PCO_2. Hence the effect of this may be an "averaging" of the $pPCO_2$ values for the period of leachate flushing. A pCO_2 value of -0.89 (0.13atm.), calculated from the pH and alkalinity of the freshwater sample in equilibrium with the column, was used for this purpose. As the phase of CO_2 production is correlated only with the period between 1-1.6 pore volumes, AMTMIN is set to -1.0 so that there is no initial equilibrium with respect to this pCO_2.
The remaining minerals in this table are set up to simulate a redox front formed by the reductive dissolution of Mn oxyhydroxides by Fe^{2+} in the leachate. The column pore water is equilibrated with MnO_2 at a

pO_2 of 0.2 atm. The amount of "O_2 gas" is set very small at 10^{-20} mole/kg H_2O, so that only aqueous O_2 provides redox buffering. Amorphous iron hydroxide is set to a negative quantity (AMTMIN = -1.0); that is, this phase is not originally present in the column, although it will precipitate when saturated conditions are obtained in the column (SIMEX = 0). The amount of MnO_2 available for reduction by ferrous iron is obtained from the experimental data by determining a mass balance for the net quantity of Mn mobilised from the column during the Mn flush. For the present problem, 2.23mmoles of Mn was mobilised from the column and the corresponding amount of MnO_2 in moles/kg H_2O available for reduction is calculated from the column mass (12.486kg), bulk density (1.47kg/L) and effective porosity (0.38) using the following relationship:
MnO_2 (moles/kg H_2O) = [(2.23/1000) / (12.486)] x (1.47/0.38)
= 6.909×10^{-4}
MEDIUM: This block is included in order to set the effective molecular diffusion coefficient to 0.0, since only advective transport through the column is being simulated.
TRANSPORT: In this block the number of shifts (NSHIFT) is set to 50, that is all solutions are transported ("shifted") 50 times into the next cell. This means that 50 (= NSHIFT)/10 (= NCOL, the number of cells in all layers, in this case, 1) = 5 pore volumes are injected and eluted. Solutions are shifted into higher numbered cells (ISHIFT = 1) and by setting IFRIX to 0.0, mixing between adjacent cells is determined by dispersivity only. IPREX is set to -2 to provide a printout of information about the end cell only (which is flushed by 5 pore volumes of solution). A porosity of 0.38 is input for each cell in the column. This value represents the effective porosity determined for the column by transport modelling of the Cl breakthrough curve (see explanation in LAYERSOL, above). A time step of 200,000 seconds is used for DELTAT (Δt) and is calculated from $\Delta t = \Delta x/ALV$ where Δx is the cell length (0.1m) and ALV is the (average) linear velocity, in this case determined from transport modelling of the leachate Cl breakthrough curve (4.32 cm/day). The output from these simulations is sent to a spreadsheet file on a floppy drive (A:LTSDX4) in the form of aqueous concentrations of species only. A maximum of 9 species (Ca, Na, Cl, Mg, CO_3^{2-}, NH_4, Fe^{2+}, Mn^{2+}, Al^{3+}) are sent to this file for output and these are specified using the index number for each species. Other species modelled (e.g. K) can be included for output by re-selection from the default list provided and undertaken an additional simulation.

Results: Simulated breakthrough curves for inorganic solutes in M-phase leachate for this column experiment are presented in Figure 3.9. There is good agreement in the style and timing of contaminant breakthrough between the simulated data and experimental results, but with some exceptions (cf Figure 3.8). The model effectively describes the transport of the major cations, including some desorption of sorbed Na during leachate breakthrough and the double fronts produced by desorption of Ca and Mg. The simulated breakthrough curves for the major cations have been fitted to the experimental results by adjustment of the LKTOSP values for each





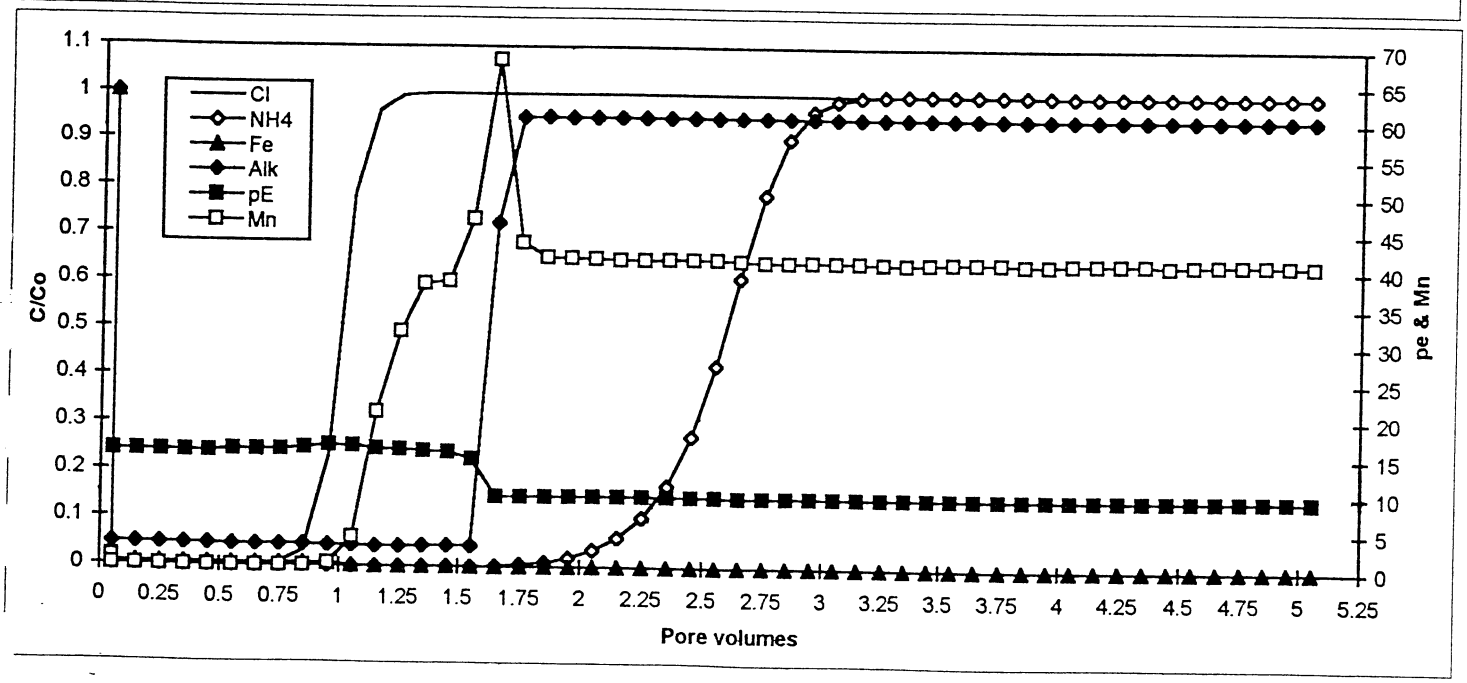


Figure 3.9 Simulated breakthrough curves for problem 6.

exchangeable species (e.g. CaX, NH_4X etc.) in the SPECIES block of the input file. This enables a conventional selectivity coefficient to be obtained for each cation involved in the ion-exchange reactions observed within the aquifer column.
The simulated breakthrough profiles for pH and alkalinity agree very well with the experimental results. Both the minima in the pH profile and apparent retardation of the alkalinity front, together with the joint recovery of these determinands to their values in the leachate, are replicated by the model. There is no precipitation of calcite allowed in the simulation. Additional simulations allowing calcite precipitation (SIMEX = 0, AMTMIN = -1.0) result in the removal of the second Ca desorption front, suggesting that this process does not occur over the time scale of the experiment. The Al flush from this aquifer column, comprising a front lasting for 1.6 pore volumes with peak concentrations of 8.5mg/L, is also reproduced in the simulation. Although the duration of the Mn flush and removal of leachate Fe^{2+} in this column experiment are accurately simulated by the model, the style of the Mn flush is less effectively simulated (Figure 3.9). Only one Mn front eluting at 1.65 pore volumes is reproduced, compared with two observed in the experimental results, but the peak values of this single front (C/C_o=68) and subsequent Mn flush (C/C_o= 41) are consistent with those in the experimental data (Figure 3.8).

Sensitivity analysis: Including the exchangeable species of Fe (FeX2 and FeX3) in the simulations and changing the LKTOSP values (exchange coefficients) of these species over relatively wide limits has no effect on the aqueous concentrations of these metals in this system. This suggests that ion-exchange reactions are less important than the redox reaction involving MnO_2 reduction by ferrous iron in the attenuation of iron species in this system. In the case of Mn, only the peak concentrations during the acidic phase of the leachate breakthrough are sensitive to changes in the LKTOSP value of MnX2. This suggests that both ion exchange processes and the reduction of MnO_2 by ferrous iron influence Mn concentrations during leachate flushing.
The peak height and amount of Al eluted in the Al front during leachate breakthrough are very sensitive to the token quantity of Al included in DTOTS in the LAYERSOL block, all other parameters being equal. This is because this input is responsible for initialising the exchange equilibria for this metal with the aquifer column. Therefore there will be increased desorption of exchangeable Al during leachate flushing, as the concentration of Al in the LAYERSOL block is increased. Conversely there will be less Ca and Mg desorbed in the first set of fronts under the these conditions, since lower amounts of these cations are partitioned into the exchange complex during the initial phase of saturation with freshwater/groundwater. If no Al is included in the LAYERSOL and the column is set in equilibrium with gibbsite at all times (e.g. AMTMIN = 10.0), then peak Al concentrations between 1-1.6 pore volumes only reach 0.95mg/L. This occurs because only dissolution of gibbsite can generate aqueous Al under these conditions and there is only minor dissolution in the mildly acidic groundwater prior to the leachate flush.

The amount of retardation of the leachate alkalinity front is sensitive to changes in the LKTOSP value of $Al(OH)^{2+}$ in this system. Increasing the LKTOSP value for this species results in the displacement of the leachate alkalinity front to higher pore volumes, i.e. producing an apparent increase in the retardation. This arises because this species generates acidity (i.e H^+), through hydrolysis reactions, which is buffered by the alkalinity of the leachate. Increasing the amount of $Al(OH)^{2+}$ that is available for hydrolysis, by increasing the LKTOSP value, generates more acidity and hence consumption of leachate alkalinity.

Conclusion: This simulation shows that all of the key features observed during flushing of this aquifer column with M-phase leachate can be qualitatively replicated using the code. The modelled results suggest that the following processes characterise the chemical interactions between this leachate and aquifer material:

a) ion-exchange reactions (Ca, Mg, K, Na, NH_4, Mn^{2+}, Al^{3+}, $Al(OH)^{2+}$);
b) Al-hydroxide equilibria (pH, gibbsite, Al^{3+}, $Al(OH)^{2+}$);
c) acid base reactions (pH, gibbsite, Al^{3+}, $Al(OH)^{2+}$, HCO^{3-});
d) redox reactions (pe, MnO_2 ,Mn^{2+}, Fe^{2+})

An important feature evident from the experimental data and successfully modelled by the code is the development of acidic conditions at the leachate front, caused by hydrolysis of exchangeable Al which is desorbed from the sandstone during contact with the leachate. This process is significant in generating enough acidity to effectively buffer the leachate inorganic alkalinity and result in a flush of Al from the aquifer material. The Al mobilised by these reactions forms a pulse at environmentally significant concentrations which will migrate with the leachate front through the aquifer. The acid front generated under these conditions also has implications for the mobilisation and transport of other metals present on the aquifer sediments. It is likely that the duration of the acidic conditions and Al flush will be partly determined by the availability of inorganic alkalinity in the leachate which can buffer these reactions, ie neutralise the Al hydrolysis products. It is possible that for M-phase leachates with lower inorganic alkalinity or A-phase leachates which are poor in inorganic alkalinity, the period of low pH conditions and Al mobilisation may be more severe for this aquifer material.

3.2.7 Problem 7: Field Data From the Burntstump Landfill Site

Problem 7: Simulating the movement of landfill leachate through the unsaturated zone below Burntstump Landfill, Nottinghamshire.

Field and laboratory results: The data for this problem are taken from Lewin et al. (1994). The data consist of porewater profiles from boreholes drilled at close but different locations within the site, at

different times, together with laboratory analyses of rock geochemistry (CEC, % $CaCO_3$, and mineralogy). The data set differs from those collected in laboratory studies in that:

(i) the input leachate chemistry is variable in time and space, and this variation is poorly known;

(ii) flow rates may also vary in time and space, and are also poorly known;

(iii) flow is unsaturated, and may not be one dimensional, and some by-pass flow may occur;

(iv) the porewater profiles are from different locations and may not necessarily be directly comparable; and

(v) only concentration/depth profiles for a few dates are available in contrast to a continuous concentration/time profile for the laboratory data.

Hence the data set is not as "clean" as the laboratory data sets, and inevitably compromises need to be made when setting up the model representation and also when comparing model output with observed values.

The aquifer sandstone properties have been described previously: CEC is a few meq/100g, and calcite is present (determined at 0.5wt/wt% by Lewin et al.(1994), and at 1.22wt/wt% by Thornton et al.(1995)). Porosity ranges from 21-27%.

Figure 3.10 shows porewater depth profiles for three cored boreholes drilled in 1985, 1987, and 1991 at locations within the landfilled area and within 20m of each other. The profiles show the downwards movement of a slug of relatively high concentration, low pH leachate. Cation concentrations are very variable, with NH_4 and K being strongly retarded and Ca and Mg elevated. SO_4 is almost completely attenuated in the leachate slug. These features are considered in more detail in the following paragraphs.

Qualitative interpretation of the data: As in the cases of problems 1-6, it is necessary prior to modelling to consider in a qualitative way the possible mechanisms operating. In addition, it is also necessary in the present problem to consider the self-consistency of the data set, what level of agreement between model predictions and field data is to be considered adequate, and what compromises need to be made when using the model. The considerations are discussed under headings relating to each group of determinands. A final sub section summarises the modelling approach. However, any of the conclusions in these subsections are preliminary, and may be altered by the subsequent modelling described in the later sections.

Cl: Figure 3.10 indicates the downward movement of the Cl front from 1985 to 1987 to 1991. The landfill is represented by the top 8m of the profile. The average velocity in the first time interval is around 3 m/y, in the second 2.25 m/y. Lewin et al. (1994) indicate rates of 0.8 m/y in 1978-1981, 3.7 m/y in 1985-1987 (from Williams et al., 1991) and an overall rate of 1.7 m/y over the period 1981-1991. A rate of just over 1m/year fits the 1987 profile data best. As Lewin et al., 1994) point out, the initial slow rate is probably due to a moisture deficit uptake, but it is unclear how much the other variations implied by the data in Figure 3.10 are due to variations in recharge rate in time, or in space. Although, in principle, PHREEQM could be used to

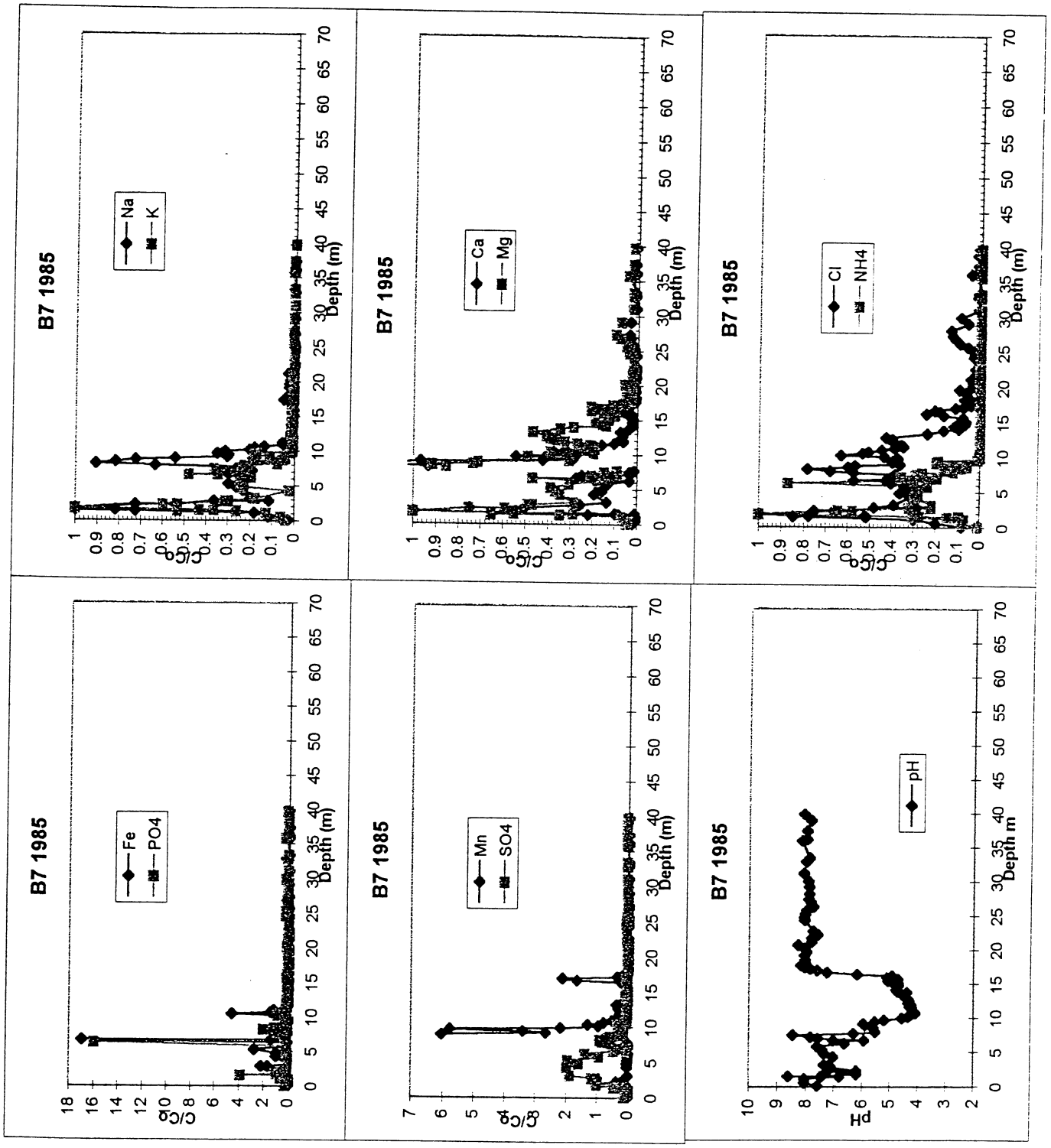


Figure 3.10 Field data for the Burntstump site: 1985 pore water profiles.

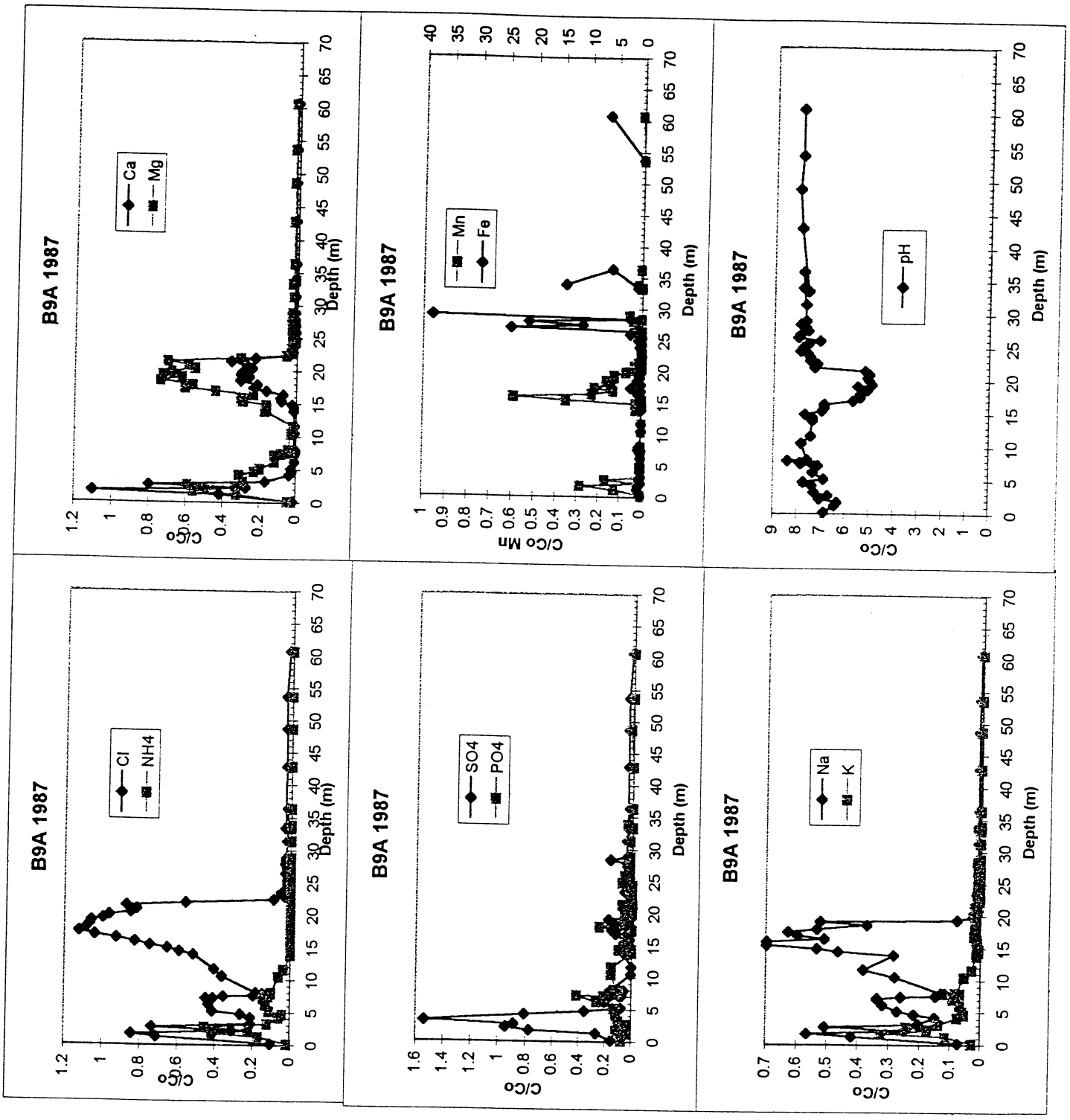


Figure 3.10 Field data for the Burntstump site (continued) :1987 pore water profiles.

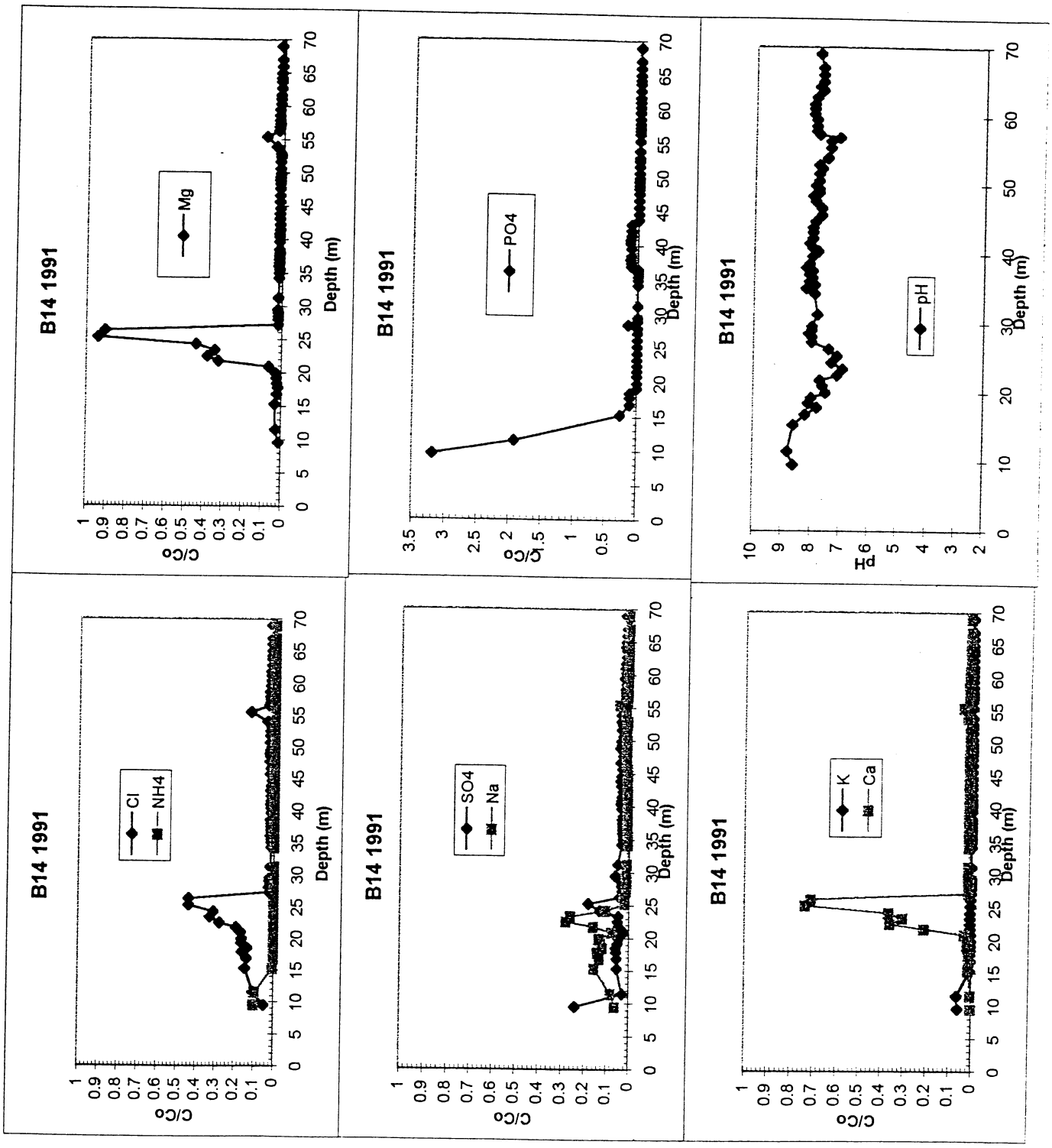


Figure 3.10 Field data for the Burntstump site (continued) :1991 pore water profiles.

represent a system with varying flow rate, this could only be achieved by dovetailing separate models together : this is impracticable when trying to match observed data, given that the latter can involve many tens of runs. Hence one velocity is used in the modelling work, and this immediately introduces a source of uncertainty when comparing field and model values. A rate was chosen to fit the Cl front in 1987; distortion either in time or space cannot be avoided given the model restrictions. It is also clear from Figure 3.10 that the Cl concentration in the leachate varies in time and with location. The Cl concentrations fall with time, indicating that a "slug" of leachate moves down through the profile (Lewin et al., 1994). As the maximum C/C_o value occurs in the 1987 profile, not the 1985 profile, it is also clear that leachate composition varies even over the short distance between the cored boreholes, as might be expected. Given the uncertainties, for modelling purposes it is only practicable to assume that a slug of leachate of constant composition is "pushed" downwards by recharge of good quality water from the top of the profile. The implication is that the absolute values of C/C_o for each species cannot be directly compared : in any model testing, obtaining the correct style of concentration variation must take precedence over obtaining the correct absolute values for C/C_o. (Normalisation by dividing the C/C_o values for other species by the C/C_o for Cl is inappropriate for the reason explained below.) PHREEQM (or any other dispersive model) should be able to investigate Lewin et al.'s (1994) suggestion that the drop in Cl concentration is entirely due to dilution (ie dispersion).

Major cations : Figure 3.10 indicates that the cation/Cl ratio in the leachate has changed in time, the ratios for 1987 being much lower than for 1985 and 1991. Hence normalising cation (or other) concentrations using the Cl concentration is unlikely to be helpful. Again, it is the style of variation which much be considered the most important attribute to replicate using the model.

It is clear that the major cations are affected by ion exchange (as tentatively suggested by Lewin et al., 1994, page 59). NH_4 and K behave very similarly, being very much delayed and breaking through at low concentrations. As NH_4 and K behaviour is so similar, and as this is also the case in laboratory experiments where NH_4 oxidation can be dismissed, it appears likely that little NH_4 attenuation by oxidation has occurred: this accords with Lewin et al.'s (1994) opinion, based on lack of oxidised N species in the waters. Na breakthrough is slightly delayed relative to Cl. Ca, and especially Mg, breakthrough at high concentrations.

Sulphate: Figure 3.10 indicates that in broad terms the behaviour of SO_4 in the three profiles is similar. In each case, SO_4 is removed and also delayed relative to Cl. Sorption can be discounted as a SO_4 removal process, given the pH values. It is thus likely that SO_4 reduction is the main process.

Lewin et al. (1994) report sulphate reducing bacteria at the base of the landfill and in the interval 30-40m bgl, with very few bacteria in the low pH zones (Figure 3.10; see below). The latter might be due to the intolerance of the bacteria to low pHs, or might simply be because little SO_4 is present in these zones as it has been removed higher up the profile. The data thus seem to be consistent with the main zone of

sulphate reduction being in the landfill itself. Examined in more detail, the data from the three profiles indicate that the input and process rates are not constant in terms of time and/or space. However, these features will not be considered when modelling: they would significantly increase the effort involved, without, given only three profiles to test against, increasing the certainty of the result.
Controls on pH : The most likely dominant controls on system pH are interaction with rock carbonates, the disassociation of organic acids, and the production of CO_2 from organic degradation. Other pH-affecting reactions, such as sulphate reduction and Fe/MnO_2 interactions, are assumed to be secondary, and are discussed separately.

Laboratory measurements have indicated that the Burntstump sandstone cations around 0.5 - 1.5 wt/wt % $CaCO_3$ (see above). Lewin et al. (1994) suggest that 0.5 % of carbonate is insufficient to buffer the pH of the leachate total volatile acid (TVA) content. As 0.5% wt/wt $CaCO_3$ is equivalent to around 0.1 mol $CaCO_3$/L water in this aquifer, every litre of groundwater should be able to neutralise of the order of 6000-9000 mg TVA/L (depending on which carboxylic acid is involved), about the same amount as is present in the groundwater. Not all the rock carbonate may be accessible, but there are other buffering reactions in addition to carbonate ones (Moss and Edmunds, 1992; Buss et al., 1997). Using Thornton et al.'s(1995) figure of 1.22 % CaCO3, 14600 - 22000 mg TVA/L could be neutralised, significantly more than is present in the leachate. It is clear that a finite amount of rock carbonate needs to be included within the model system.
The TVAs travel at the same rate as the Cl, and comprised 70% of the TOC in 1987 and 30-45% in 1991 (Lewin et al., 1994). The TVA fraction is dominated by ethanoic, propionic, and butanoic acids. These acids have K_a values of around 4.7-4.9, and are therefore candidates for maintaining the pHs in the main leachate phase at low values provided the rock carbonate buffering capacity has been exceeded. Occasional pH measurements below 4 indicate that other mechanisms may also be operating.
TVA degradation may provide a source of CO_2 which in turn might explain the low pHs associated with the main leachate pulse. However, Lewin et al. (1994) indicate that the main loss of TVAs occurs above the low pH zone, and in addition they cite laboratory evidence that degradation is only likely at pHs of 7.3 and greater. If CO_2 is the cause, rather than the product of, the low pH zone, degradation of other organics must be invoked. The gas content of the unsaturated zone around the migrating leachate consists roughly of 15-25% CO_2, 10-50% N_2 and 30-50% CH_4, the latter suggesting significant degradation.
A further control on pH may be ion exchange induced calcite precipitation: as leachate NH_4 and Na displace Ca and Mg from the rock exchange sites, the wate precipitates calcite, driving the pH down. Unfortunately estimating degrees of calcite saturation from the available data is difficult, measured alkalinity values clearly including

the effects of organic anions. There are several options available for estimating TIC : ionic balance, but this is predicated by the presence of the organic anions; assuming calcite equilibrium; assuming the groundwater to be in equilibrium with the gas phase concentrations measured at the site. Both the latter options were investigated (see below). Organic/cation complexes are not directly taken into account.
Aluminium: There are no Al data available, but when the pH drops to 4, significant amounts of Al are likely to be released into solution.
Fe and Mn: The Fe and Mn concentration patterns are complex, and differ between the two data sets available (1985 and 1987) (Figure 3.10). Hence the two sets of data will be discussed separately. In 1985, Mn concentrations show peaks with C/C_o ratios >>1 at the leading and trailing edges of the low pH pulse. Outside the pH trough, Mn concentrations are extremely low, except for a local peak in the landfill material. Between the peaks, there are two sub unity C/C_o plateau's, the deeper one having a lower value. Assuming that the data are correct, it appears that Mn becomes mobile, as expected when the pH falls at the leading edge of the pH front : as $C/C_o >> 1$, the implication is that aquifer solids are released. In the central part of the low pH zone, Mn C/C_o values are <1, though not zero. There is no obvious pH or Eh control on Mn in this pH range, and the two other obvious possibilities - ion exchange and supply rate limitation - must be considered. In the low pH zone, Mg and Ca are relatively high responding to Na and NH_4 uptake : it could be that Mn is sorbed too. The Mn, Mg, and Ca concentration profiles in this zone are very similar. Another possibility is supply limitation : the pH leading edge Mn peak may represent $MnCO_3$ dissolution, and the lower Mn concentrations later in the pH probe may represent MnO_2 release, the latter slow due to lack of appropriate electron donors or due to slow reactions at the low pHs. The very substantial Mn peak (C/C_o to 6) at the trailing edge of the pH trough suggests release of Mn as the NH_4 front arrives, or possibly quicker reduction of MnO_2 at higher pH. Fe in the 1985 profile only occurs as a peak ($C/C_o = 4$) at the lowest pH zone of the pH trough : a crude estimation indicates that the Eh for Fe_2O_3 reduction in keeping with the observed pH at the Fe peak would be around 200mV (pe $\simeq$ 3.5). Alternatively, FeS_2 stability might limit Fe concentrations (Eh $\simeq$ - 200mV), but only if the sulphide were very rapidly precipitated. In 1987, the low pH zone is accompanied by a zone where Fe rises from C/C_o ratios close to zero, to ones where C/C_o is between 0.5 and 1. This would imply a Fe system Eh slightly lower than for the 1985 profile, again indicating a spatial variation in chemistry. The pattern in the Mn concentrations is similar to that for 1985, though the absolute C/C_o values are lower and the peak at the leading edge of the low pH zone is missing. The lack of a leading edge peak may simply be because of the local lack of an appropriate Mn supply : the rest of the Mn profile can be explained using similar arguments to those used when discussing the 1985 data, though any role of NH_4 can be dismissed.
Fe and Mn are not easy to sample successfully, especially from core material (Spears, 1986), because of their sensitivity to Eh and pH. It is therefore possible that the discussion above is based on an

overinterpretation of the data : indeed, the Fe C/C_o peak rising to 40 in the 1987 data in the zone well beyond the leachate front has been assumed to be an artifact in the above discussion.
The interpretation of the data is of some relevance given the importance of the Fe and Mn systems to the mobility of trace metals, and because of the difference between the laboratory column experiment results (problems 1-6) and the field data. Use of PHREEQM can help tackle the problem quantitatively: however, because of the uncertainties of kinetics, bacterially-mediated reactions, multiple redox states, and the importance of colloidal phases, a unique answer is unlikely to be found.
The rock is represented in terms of ion exchange capacity and interaction with various minerals (calcite, birnessite, hematite, rhodochrosite, pyrite, and gibbsite at various stages) : details are given in the appropriate locations below. The saturated porosity was assumed to be 0.24, bulk density 2100 kg/m^3, and dispersivity was obtained by fitting the Cl breakthrough curves using the Ogata-Banks solution (Ogata and Banks, 1961) (α = 0.05m).
Cation exchange was incorporated using the Gaines-Thomas convention, and involved Na^+, K^+, Ca^{2+}, Mg^{2+}, Mg^{2+}, NH_4^+, Mn^{2+}, Fe^{2+}, Al^{3+}, and $Al(OH)^{2+}$. Cation exchange parameters were treated as a calibration variable, though bearing in mind the laboratory measurements of 1-2 meq/100g for cation exchange capacity and the numerical ranges for selectivity coefficient values (eg Appelo and Postma, 1993, Table 5.5, page 160).
Sulphate reduction is assumed to occur principally at the landfill, and is hence represented simply by adjustment of initial leachate pe. By inputting a low pe, SO_4 is converted to S^{2-}, which is then available for precipitation of metals and as a redox buffering system as the leachate moves down the profile.
Al is assumed to have a very low concentration in the initial leachate. By making gibbsite available in the cells representing the Triassic sandstone, a source of Al is made available to the groundwater. Al is assumed to participate in ion exchange reactions (Al^{3+}, $Al(OH)^{2+}$), but no account is taken of complexing with organics.
Sources and sinks of Fe ad Mn incorporated in the modelling include at various stages MnO_2 (as birnessite), rhodochrosite, haematite, and pyrite. Control of concentrations is also achieved using pe. Separate modelling runs were undertaken to examine the Fe/Mn chemistry.
The representation of the inorganic carbon system also required separate consideration. TIC is estimated using the equilibrium with calcite and fixed CO_2 assumptions.
Modelling approach: Because of the nature of the data, aiming to reproduce the exact patterns depicted on Figure 3.10 is inappropriate. Hence the model will be judged successful if it reproduces the main features of the profiles.
As discussed in the previous sections, because of the limitations of the code and the data, the hydrogeology of the site will be simplified for modelling purposes. The system will be represented by a set of 60 cells. The first two cells at the upflow end of the system represent the landfill, and initially contain landfill leachate of a single composition.

The remaining 58 cells contain the background groundwater. The leachate is then moved down into the cells representing the sandstone by injection of recharge water in the upstream cell. The flow velocity was chosen to allow a best fit to the 1987 data set (1.05 m/year). The leachate composition chosen is listed in Table X (1.6-2.0m porewater analysis, borehole B7, 1985; Lewin et al., 1994).
The chemistry of the preexisting groundwater as used in the modelling is also given in Table 3.7. In the absence of data, the same composition was used for the infiltrating water which pushes the leachate through the profile.
The presence of CH_4 is not explicitly modelled, as the organic degradation from which it arises is itself not explicitly modelled. However, the redox potentials necessary for inducing sulphate reduction result in conversion of some TIC to CH4, thus providing a further Eh buffering mechanism as the leachate moves down the profile.
The approach adopted for the modelling work for problem 7 is as follows:

7a assess the approaches for estimating leachate TIC;
7b attempt to reproduce the main features of the chemical profiles;
7c investigate the possibility of using laboratory-determined parameters to predict the field system;
7d investigate the effect of the amount of calcite in the sandstone on the chemical profiles; and
7e investigate the effect of MnO_2 on the chemical profiles.

Problem 7a: What value for TIC should be used in modelling the leachate chemistry?

Because alkalinity measurements will include contributions from organic species, and no other direct measure of total inorganic carbon is available, TIC needs to be estimated. pH is known, and gas phase measurements indicate 15-25% of the gas in the unsaturated zone is CO_2. Given these data, two approaches were considered:

(i) given measured pH and assuming the leachate is in equilibrium with calcite, and

(ii) given measured pH and assuming P_{CO_2} = 0.2 atmospheres.

Both approaches were modelled using PHREEQE. Approach (i) indicates that TIC = 714 mg/L as HCO_3 and P_{CO_2} = 0.11 atmos. at saturation with calcite. Using approach (ii), the TIC was found to be 1300 mg/L as HCO_3 and the saturation index for calcite to be 0.3. It is therefore concluded that approach (i) should be used. If pe is lowered, some of the TIC might be converted to CH_4, and as a result, more inorganic matter is required to satisfy the conditions of approach (i): this problem was considered as pe was changed during the modelling work.

Table 3.7 Compositions of fluids used in modelling.

Species	Concentration (mg/l)	
	Leachate	Groundwater/Recharge Water
Na	3433	15
K	3414	13
Ca	4000	57
Mg	1225	27
Cl	4398	70
SO_4	1747	73
NH_4	2368	0.129
pH	6.21	7.85
pe	See text	8.0
Fe	6.25	0.01
Mn	119	0.01
Al[1]	0.001	0.001
PO_4	0.53	0.02

1 As data unavailable, 0.001 mg/l is therefore estimated.

Problem 7b Simulating the main features of the leachate migration through the field system at Burntstump.

Problem 7b incorporates a great deal of exploratory modelling work. However, it is not easy to separate individual aspects of the modelling investigations (eg acid-base reactions, Fe/Mn interactions), as obtaining the "final" model required many iterative loops of various sizes. For example, obtaining a representation of the major cation profiles may require returning to reconsider acid base reactions, simply because of the effect of Ca concentrations on calcite equilibria. As a result, the "final", basic, model will be described without chronological details of how it was developed. The model represents over 100 simulations. In the following sections, this "final" model is referred to as the "standard case model".

Model input file: The standard case model input file is listed in Table 3.8. The parameters used in the concentration of the input file are described below for the relevant option blocks. These are described in the order in which they appear in the file.
OPTIONS: As for previous problems.

SPECIES: The assumed ion exchange species NaX, KX, CaX_2, MgX_2, AlX_3, MnX_2, FeX_2, NH_4, and $Al(OH)X_2$ are included. The value for $KAl(OH)X2$ was initially assumed to be of the order of 10^{40}. $CH_4(aq)$ was also included.
SOLUTION: The fresh water analysis of Table 3.7 was input.
SUMS: SUMS was used to output details of non-master species. Although the species listed varied during the simulation, the list included at various times: true SO_4^{2-}, HS^-, H_2S, $H_2S + S^{2-}$, CH_4, an alkalinity estimate (sum of all HCO_3 and CO_3 bearing species, except H_2CO_3), "true" HCO_3^- true CO^{2-}_3, H_2CO_3, total sorbed Al, total dissolved Al, and "true" NH_4.
LAYERSOL: "Column" inputs were: 60 cells, total flow zone 63m, linear flow, dispersivity = 0.05m. LAYERSOL1 contains a representation of the leachate as indicated in Table 3.7. Temperature was set at 10^oC: in comparison with other parameters, temperature has little effect on the reactions as modelled, even if it is raised to the high values sometimes encountered in landfills. After much experimentation, a pe of -2.9 was chosen. This pe resulted in conversion of much of the input SO_4 to sulphide: this is tantamount to assuming that (a) the sulphate reduction occurs below 2m depth, the level to which the analysis in Table 3.7 relates, and (b) that only the zone below the completion of the sulphate reduction has been modelled. A pe of -2.9 also converts around 3.7×10^{-3} mol/L of TIC to CH_4: this is a large amount of CH_4, equivalent to a pP_{CH_4} of -0.46 ($K_H = 1.29 \times 10^{-3}$ M/atmos.; Stumm and Morgan, 1996, page 214). At this pressure, much CH_4 would escape in a real system, and in fact CH_4 does constitute a substantial proportion of the unsaturated zone gases at Burntstump (Lewin et al., 1994). Allowing a large CH_4 content to remain in solution is a crude way of presenting redox poising by organic species. In the real system, different values of pe may be appropriate for the TIC/CH_4 system and the SO_4/sulphide system, but PHREEQM does not allow multiple redox states to be simulated. The production of CH_4 results in a drop in the calcite saturation index, but only to -0.1, and hence in the final version of the standard case model TIC has not been increased from 714 mg/L. No Al data are available, and the small value of 0.01 mg/L was initially included in the input file in case future modelling required detailed explanation of Al concentrations. The negligible value of 10^{-2} meq/L H_2O was used for X^- so that subsequent ion exchange reactions could be incorporated without affecting the input leachate cation ratios. Care must be taken not to input too low a value for X^- (see LAYERSOL, Section 2). NCELL was set to 2 (ie 2 landfill cells - see above), IOPT[3] to 5 (ie equilibration with minerals), NMINEX to 3 (ie 3 minerals involved), and NCMPEX and EXSTEP T to zero, as no reactants were added. The three minerals chosen for equilibration under MNAME were gypsum, gibbsite, and pyrite. Only precipitation was allowed in each case (SIMEX = 0, AMTMIN = -1, in each case under heading SIMEX). Negligible amounts of gypsum and gibbsite

Table 3.8 PHREEQM input file for problem 7b.

```
Burntstump:
0000110001 0 0        0.00000
SPECIES
 36
CH4 AQ     400 0.0      -4.0      0.0                    0.0
 41.071   -61.039
 15  1.000  1 10.000  2  8.000  3 -3.000
181
NAX        201 0.0      0.0       4.0       4.0       0.075     0.0
20.00     0.0
 6  1.000 30  1.000
182
KX         201 0.0      0.0       3.0       3.5       0.015     0.0
21.30     0.0
 7  1.000 30  1.000
183
CAX2       201  0.0     0.0       6.0       5.0       0.165     0.0
40.40     0.0
 4  1.000 30  2.000
184
MGX2       201 0.0      0.0       8.0       5.5       0.20      0.0
41.60     0.0
 5  1.000 30  2.000
185
ALX3       200 0.0      0.0       9.0                    0.0
60.70     0.0
 10  1.000 30  3.000
186
MNX2       200 0.0      2.0       6.0                    0.0
40.40     0.0
 9  1.000 30  2.000
187
FEX2       200 0.0      2.0       6.0                    0.0
42.00     0.0
 8  1.000 30  2.000
189
NH4X       200 0.0     -3.0       2.5                    0.0
21.50     0.0
 23  1.000 30  1.000
191
Al(OH)X2   403  0.0     0.0       0.0       0.0       0.0       0.0
40.00      0.0
 10  1.000  3  1.000  1 -1.000 30  2.000

SOLUTION 3
Groundwater flush
12 15 2        7.85      8.0      10.0      1.0
  4 5.7000E+01   5 2.7000E+01   6 1.5000E+01   7 1.3000E+01   8 1.0000E-02
  9 1.0000E-02  10 1.0000E-02  14 7.0000E+01  15 1.8540E+02  16 7.3000E+01
 19 2.0000E-02  23 1.2900E-01
SUMS
SO4-2     21
 16  40  52  78  88  96 100 108 109 126 127 128 141 154 155 156 168 173 128 155
 179
HS-        5
 42 110 110 111 111
H2S        2
 43  41
CH4aq      1
 36
ALK       18
 15  15  34  76  76  77  86  86  87  94  94  95 106 106 107 139 139 140
AltotX     2
 191 185
CO3-2      6
 15  76  86  94 106 139
Al         8
 10 150 151 152 152 154 155 156
```

Table 3.8 PHREEQM input file for problem 7b, continued.

Continued .....

```
NH4     1
23
pco2    1
 35

LAYERSOL 1
Leachate in Landfill
13  0 2      6.21    -2.90     10.0      1.0
  4 4.0000E+03  5 1.2250E+03  6 3.4380E+03  7 3.4140E+03  8 6.2500E+00
  9 1.1900E+02  10 1.0000E-02  14 4.3980E+03  15 7.1400E+02  16 1.7470E+03
 19 5.3000E-01  23 2.3670E+03  30 1.0000E-02
 2  5  3  0   0.0
 1.05E+00   5.00E-02 1.05E+00   5.00E-02
GYPSUM    0.000E+00-1.000E+00
GIBBSITE  0.000E+00-1.000E+00
PYRITE    0.000E+00-1.000E+00
LAYERSOL 2
Groundwater in Triassic Sandstone
13 15 2       7.85      8.0      10.0      1.0
  4 5.7000E+01   5 2.7000E+01   6 1.5000E+01   7 1.3000E+01   8 1.0000E-02
  9 1.0000E-02  10 1.0000E-02  14 7.0000E+01  15 1.8544E+02  16 7.3000E+01
 19 2.0000E-02  23 1.2900E-01  30 8.0000E+01
58  5  8  0   0.00
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02 1.05E+00   5.00E-02
 1.05E+00   5.00E-02 1.05E+00   5.00E-02
CALCITE   0.000E+00 1.000E+00
RHODOCHR  0.000E+00-1.000E+00
GIBBSITE  0.000E+00 1.000E+01
HEMATITE -1.000E+00 1.000E+01
PYRITE    0.000E+00-1.000E+00
BIRNESSI  0.000E+00 1.000E-03
PCO2     -1.000E+00 5.000E-04
O2 gas   -7.000E-01 1.000E-20
MEDIUM
 0.00000000E+00
TRANSPRT
  25   1   0   0   0.24   31536000    5.e-5     10.0
bsf.s       9    bsf.e        bsf.su
  4   5   6   7   8   9  14  16  23
END
```

were precipitated in the final version of the simulations, and only small amounts of pyrite were precipitated in the layer 1, landfill cells compared with that precipitated in the layer 2, sandstone cells.

LAYERSOL 2 contains the analysis of the sandstone groundwater as in Table 3.7. The X^- value was set initially at 134 meq/L H_2O, equivalent to the laboratory measured value. Subsequently this parameter was altered, and the "final" model used a value of 200 meq/L H_2O. NCELL (under NCELL in LAYERSOL) was set to 58 (ie 58 sandstone cells), IOPT[3] was set to 5 (mineral equilibration) and 8

minerals were equilibrated (NMINEX = 8); no reactions were included (NCMPEX = EXSTEP = 0). The minerals chosen for equilibration were as shown below.
Calcite is known to be present (Lewin et al., 1994; Thornton et al., 1995; see above): 1.0 mol/kg H_2O represents approximately 1.22% (the value Thornton et al. (1995) measured), but using the lower value of 0.5% makes no difference in the case of the simulations described here (see discussion below).

MNAME	SIMEX	AMTMIN (mol/kg H_2O)
Calcite	0.0	1.0
Rhodochrosite	0.0	-1.0
Gibbsite	0.0	10.0
Hematite	-1.0	10.0
Pyrite	0.0	-1.0
Birnessite	0.0	0.001
PCO2	-0.7	0.0005
O2 Gas	-0.7	10^{-20}

Rhodochrosite is allowed to precipitate; it is rarely reported as a phase in Triassic sandstone, but may be a control on Mn concentrations (see problem 2 above). Gibbsite is assumed to be present in effectively infinite amounts, as is hematite. However, it was found necessary to use a value of SIMEX less than zero in the simulations: this suggests that the Fe source is not hematite, or that some process is inhibiting its free oxidation. Pyrite is allowed to precipitate: it is unlikely that pyrite exists in significantly available amounts in the sandstones. Birnessite has been added in an amount equivalent to that used in problem 1: this amount is justified on the basis of the laboratory experiments. In addition to the minerals, the water in the sandstone is assumed to be in equilibrium with a gas phase containing P_{CO_2} at 0.2 atmospheres partial pressure. This is an attempt to simulate the unsaturated zone gas phase below the Burntstump site: Lewin et al. (1994) found this gas phase to contain about 20% CO_2, presumably resulting from organic degradation reactions. Because of the way the code is set up, all of the sandstone waters are equilibrated with a P_{CO_2} of 0.2 atmos. even at the base of the modelled profile: this is unrealistic, the effect of the CO_2-rich zone only preceding the plume by c.10 m in 1987 and 0 m in 1991 (interpretation of figure 36 of Lewin et al. (1994)). The limit of 0.0005 mol CO_2/kg H_2O was determined by matching the point at which the pH rises behind (ie above) the plume in the simulation with the same point in the field data: 0.0005 mol CO_2/kg H_2O corresponds to around 1.5% of pore space being taken up by gas.
An O_2 partial pressure of 0.2 atmosphere is defined for the sandstone cells, but with an AMTMIN value of 10^{-20} mol/kg H_2O in order to insure that only dissolved oxygen in the initial water was available for

redox poising. Having the oxygen in the water is not realistic given the CH_4 in the gas phase around the plume. However, the amount of O_2 present has no significant effect on predicted concentrations, and has the slight advantage of allowing the lower waters to have a pe in equilibrium with atmospheric oxygen.

MEDIUM: The diffusion coefficient was set to zero.

TRANSPORT: Twenty five shifts into higher numbered cells were specified in each run. An end effect correction was incorporated (IFRIX = 0). Porosity was taken as 0.24, and the time step as 31536000 seconds (1 year). SOLTOL was set at 5×10^{-5} and TMPTOL at 10.0.

RESULTS: Figures 3.11 to 3.13 show the modelled chemical profiles for the years 1985, 1987, and 1991 respectively. The data are presented as C/C0 versus depth plots. C0 is taken to be the initial landfill cell concentrations (ie the leachate). The landfill is to a depth of 7m, the first landfill cell being at 5.9m. No attempt was made to represent the profile in the landfill. Most effort was concentrated on reproducing a profile for the period 1985-1991, rather than attempting to reproduce each of the profiles separately: one problem is the faster the average flow rate in the 1985-1991 interval. Figures 3.14 and 3.15 indicate the sorbed, mineral and gas phase variations up until 1987. In the case of the minerals and gases, each plotted point represents the number of moles/L dissolved (positive) or precipitated (negative) in the cell up until 1987. In the case of the sorbed species, each point represents the current number of moles/L associated with the sorbed phase. Comparison of Figures 3.11 to 3.13 with Figure 3.10 indicates general agreement of measured and modelled profiles. The Cl front is where it should be for 1987: the tail is less well represented, but this is because no attempt was made to describe the variation in leachate quality with time. The general styles of the cation profiles are correct, with NH_4 and K being strongly attenuated, Na being slightly attenuated, and Mg being enriched in solution relative to Ca. The pH trough is reproduced. Sulphate is removed in the main plume, as in the field. The Mn and Fe field profiles are complex, and the modelled profiles are discussed in more detail below. The profiles produced represent well over a hundred model runs, which suggests that equivalence is not a major problem.

DISCUSSION: The main control on the major cation concentrations is ion exchange, though calcite equilibrium is also significant. The main characteristics of the field profiles are the retardation and attenuation of NH_4 and K, the slight attenuation and retardation of Na, and the enhancement of Mg and (to a slightly lesser extent) Ca. The representation of these features (Figure 3.12) was not easy, and necessitated using the ion-exchange parameters listed in Table 3.9. Figure 3.14 shows the model exchange site chemistries for 1987. The CEC used is smaller than that measured on laboratory samples (134 meq/kg H_2O) and used in the modelling of the column experiments. A possible reason is that the laboratory samples were disaggregated, and thus any hydraulic/chemical property correlations would be removed: alternatively, the sandstone used in the laboratory

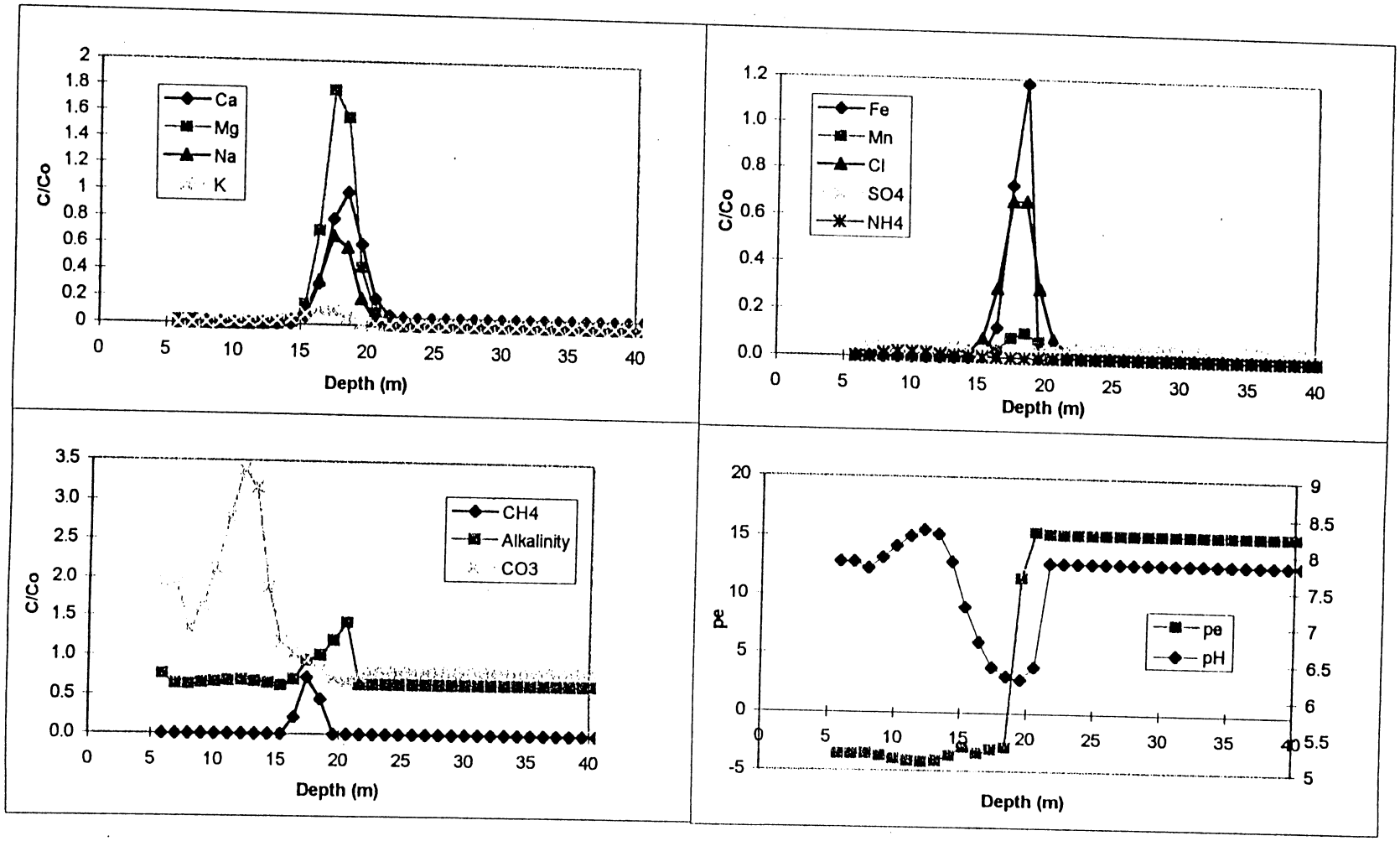


Figure 3.11 Standard simulation of the Burntstump field profiles for 1985 (problem 7b): dissolved concentrations.

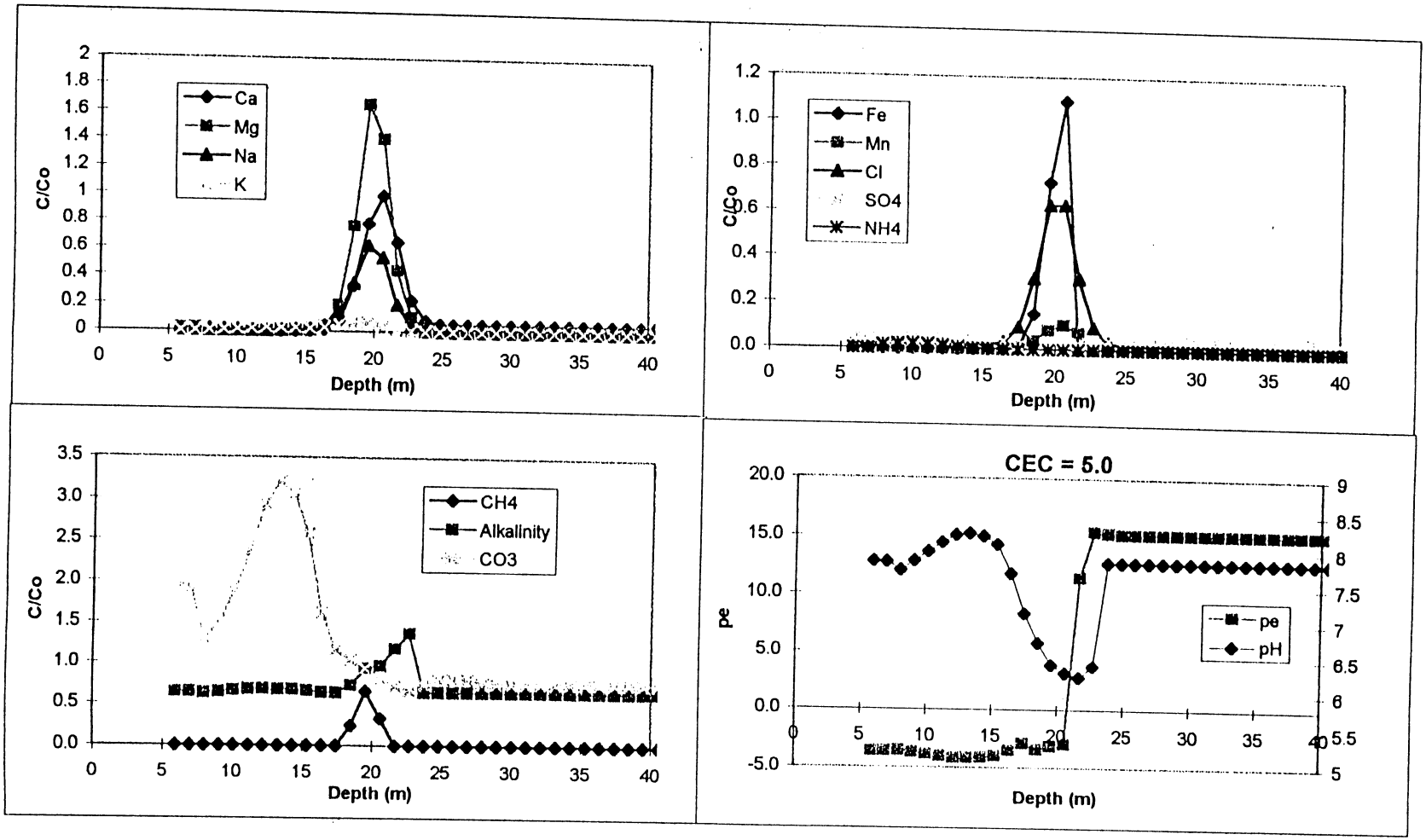


Figure 3.12 Standard simulation of the Burntstump field profiles for 1987 (problem 7b): dissolved concentrations.

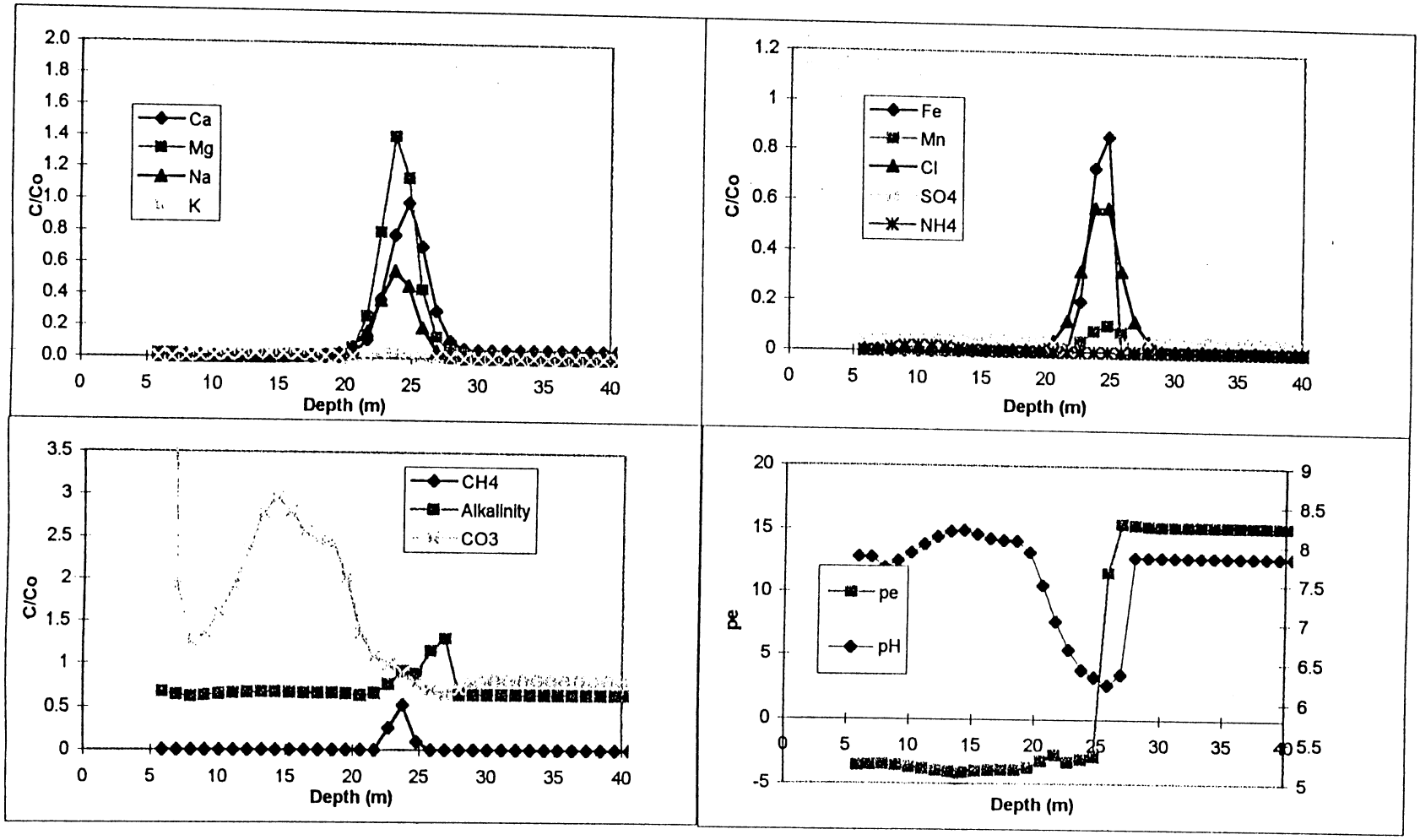


Figure 3.13 Standard simulation of the Burntstump field profiles for 1991 (problem 7b): dissolved concentrations.

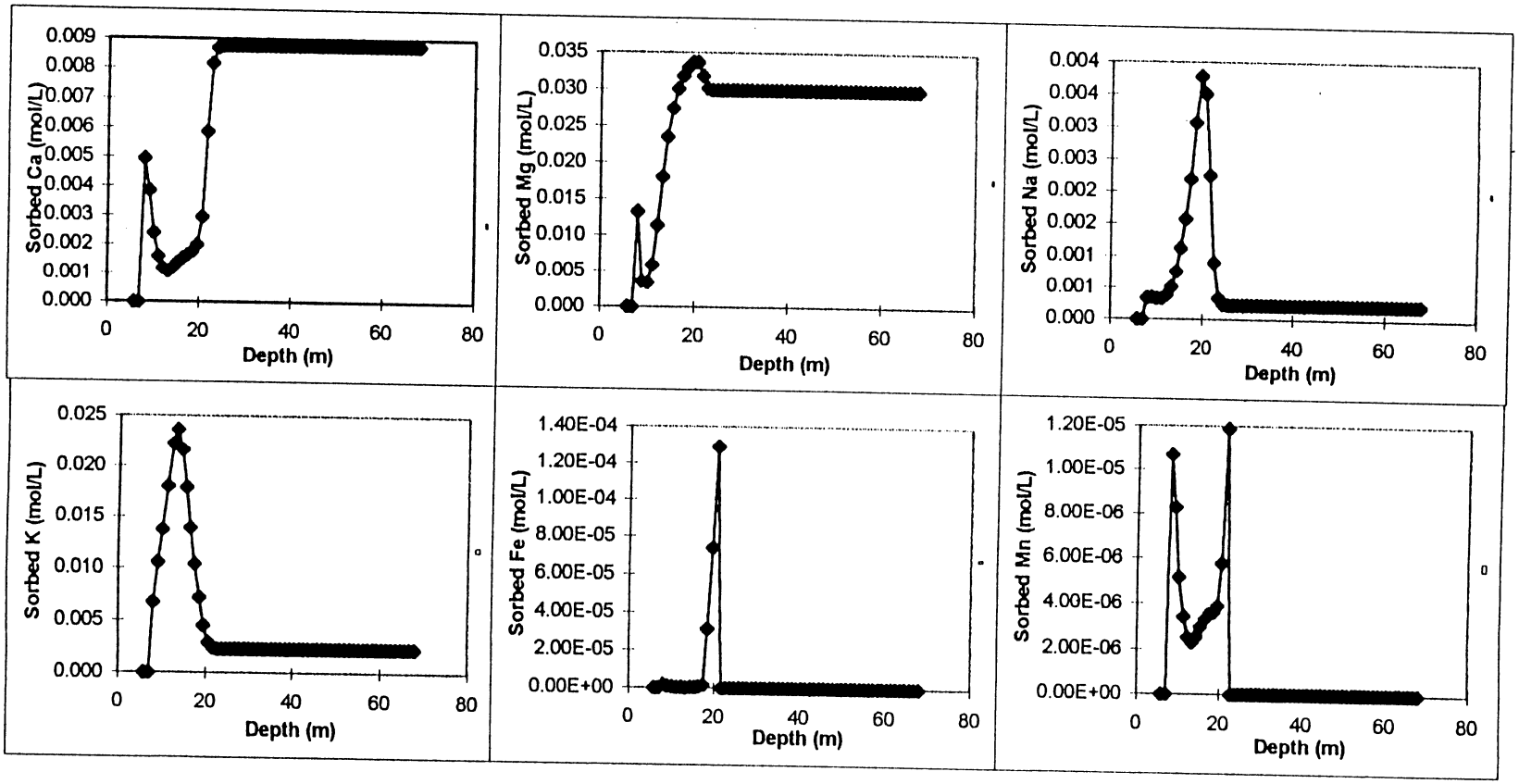


Figure 3.14 Sorbed concentrations for simulation for problem 7b (1987).

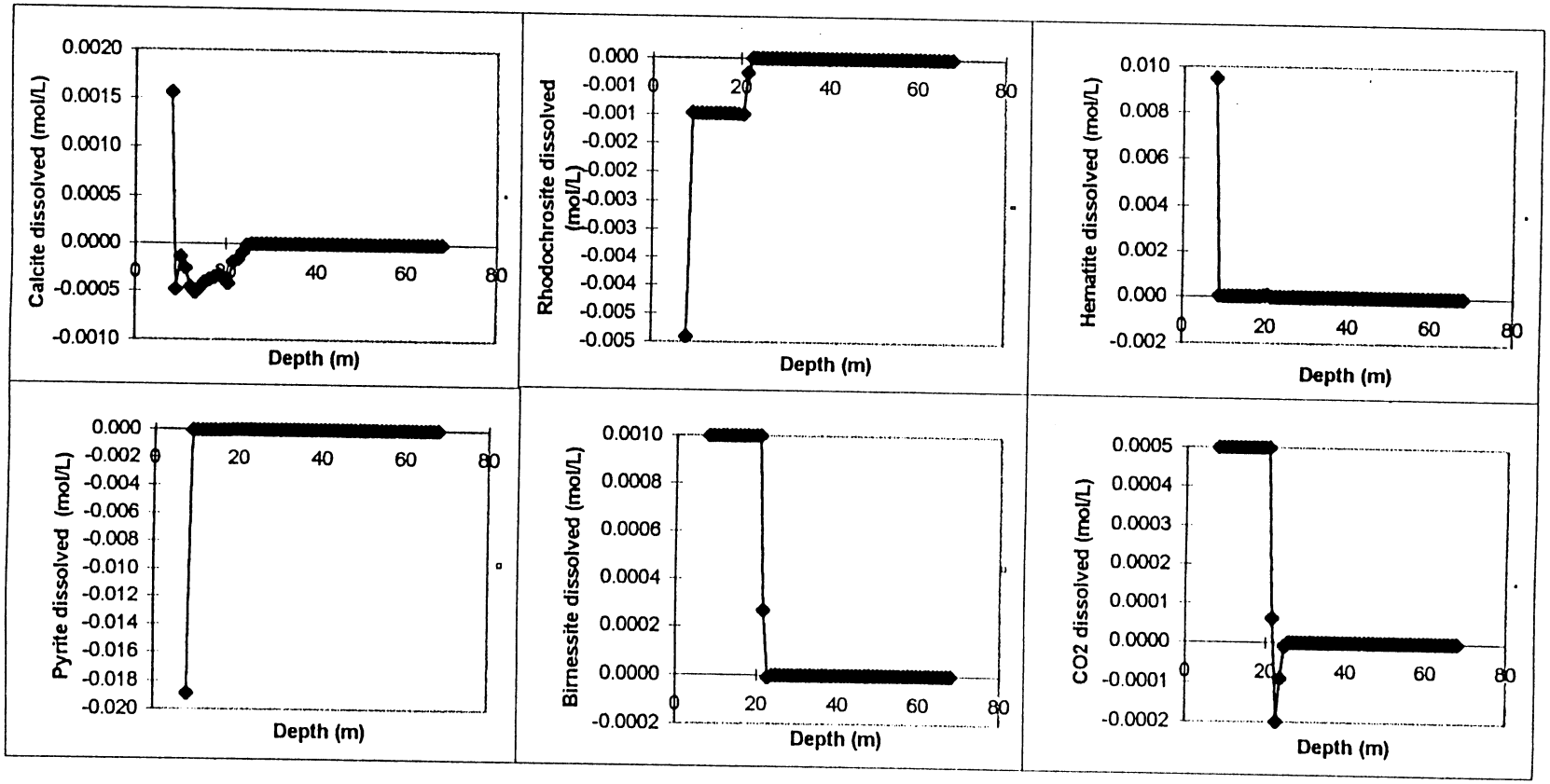


Figure 3.15 Mineral and gas dissolution for simulation for problem 7b (1987).

experimentation was from shallow depths below ground level, and may simply not have been representative of the profile.

The K_{NX} values are also at the extremes of the ranges expected in several cases. Calculations undertaken using MINTEQA2 (Alison et al., 1990) indicate that, assuming organic matter to be represented by acetate, Ca, Mg (and Fe and Mn), are complexed to about the same degree, perhaps around 60%: NH_4, Na, and K are marginally complexed (see Section 4.2). The effect of complexation would be to change the apparent Ca and Mg K_{MX} values by a factor of roughly 1/0.4: this brings the value of K_{MgX2} closer to that expected. Further discussion is given in Section 4.3.2.3. More research is required on ion exchange in systems where organic complexation is important. In the case of NH_4, even at the relatively high pHs above the plume, NH_3 comprised no more than a few percent of total NH_4. No NH_4 oxidation to NO_3 has been considered (see Section 2.2.4). The dissolution of calcite due to the high P_{CO2} injected into the water in the sandstone resulted, in initial runs, in an amount of Ca which could not be removed by changing the ion exchange parameters within a realistic range. As a result the P_{CO2} was reduced from 0.2 to 0.1 atmospheres. This pressure is less than that measured in the field (around 0.2 atmospheres) (Lewin et al., 1994)) : this is discussed below.

Table 3.9 Major ion exchange parameters used in modelling the Burntstump field profiles. Expected means and ranges for K_M values are taken from Appelo and Postma (1993, page 160, Table 5.5). For meaning of "?True values", see text.

	pK_{NaX}	pK_{KX}	pK_{CaX2}	pK_{MgX2}	pK_{NH4X}	CEC (meq/kgH_2O)
Values used	-20.0 80	-21.3	-40.4	-41.6	-21.5	
Expected mean	-20.0	-20.7	-40.8	-40.6	-20.6	
Expected range	-20.0	-20.4 to -21.0	-40.2 to -41.4	-40.0 to -41.2	-20.3 to -20.9	
? True values	-20.0	-21.3	-40.0	-41.2	-21.5	

Sulphate is mostly reduced before the leachate leaves the landfill, and this was simulated simply by using a low pe in the landfill cells. A pe value of -2.9 appeared to work satisfactorily, and resulted in some conversion of alkalinity to CH_4. At maximum, CH_4 reached 4 mmol/L, equivalent to a pP_{CH4} of around -0.19 (K_H = 1.29 x 10^{-3} M/atmos.; Stumm and Morgan, 1996, p. 214). Although this would indicate degassing no account was taken of CH_4 migration in the model: the CH_4 served as a reasonable redox buffer, even if the CH_4 content was itself too high. In the model, the sulphide produced was almost completely removed by pyrite precipitation. There is no indication in Lewin et al. (1994) of H_2S in the sandstone waters.

Pyrite was chosen as the main sulphide phase as it became oversaturated more rapidly than FeS, which was also investigated. The Fe was supplied via hematite reduction (see below).
The drop in pH associated with the plume is caused in the model system by the low pH initially assigned to the leachate, and in this sense represents the effect of the TVAs. The degradation of the organic matter is represented by fixing the P_{CO2}, as discussed above, at 0.1 atmospheres: this also contributes to maintaining the low pH. The presence of 0.1 atmospheres is rather less than measured in the field (Table 3.10), and if the field data correct, it may be that there is limited gas phase/water phase interaction.

Table 3.10 CO2 content (%) of the gas phase at Burntstump (Lewin et al., 1994, page 117 onwards). (N/A - not available; brackets indicate zone of low pH at plume).

Depth (mbgl)	**1985**	**1987**			**1991**		
1-1.2	N/A	N/A	13.5	N/A	N/A	N/A	N/A
4-4.2	4.0	29.9	15.5	N/A	N/A	N/A	N/A
7-7.2	N/A	24.0	2.0	N/A	N/A	N/A	N/A
9.2-9.4	[25.0]	21.6	20.9	N/A	N/A	N/A	N/A
12.3-12.4	[31.9]	26.6	N/A	N/A	N/A	N/A	N/A
15.2-15.4	[29.3]	28.8	29.4	N/A	N/A	N/A	N/A
18.2-18.4	28.4	[30.2	29.8]	32.0	31.7	29.7	20.4
21.2-21.4	21.0	[27.6	23.0]	20.4	13.0	18.2	17.5
27.2-27.4	12.4	12.6	17.0	[11.5	N/A	N/A	0.2]
33.2-33.4	4.7	8.1	12.8	13.4	6.1	11.1	5.3
39.4-39.5	0.3	16.0	12.7	1.8	2.2	1.7	1.0

The predicted minimum pH is greater than that seen in the 1985 and 1987 field data, and less than that in the 1991 field data. To induce lower pHs, several possible mechanisms might be operating: increased CO_2 due to organic degradation, pyrite oxidation, rhodochrosite precipitation, birnessite reduction, or gibbsite reactions. However, it was not possible to simulate the marked decrease in pH in the 1985 and 1987 profiles because of constraints imposed by other measured concentrations, and it is possible that the initial leachate pH at the 1985 and 1987 borehole sites might have been lower than that assumed in the model. Another consideration is variable calcite cement: it is unlikely that the leachate could maintain a pH of 5, as found in the 1985 profile, in contact with calcite-bearing sandstone, suggesting that locally calcite is sparse, or at least poorly accessible. In the simulation, the amount of CO_2 in the gas phase available to the sandstone waters was determined by trial and error fitting of the timing of the pH rise following the passage of the plume. In the real system, the mass of CO_2 available will be determined by a dynamic equilibrium between varying production rates and CO_2 migration rates, and as

such is likely to vary in time. The model is thus rather crude. In the model, the CO_2 becomes exhausted above the plume, resulting in a rise in pH (Figure 3.12). A rise in pH is also seen in the field data (Figure 3.10), yet gas phase measurements indicate that P_{CO_2} values are elevated for some distance above the plume, including where pHs are high. This seems odd, and no attempt has been made to model high pH at high P_{CO_2} using PHREEQM. Calculations using PHREEQE indicate that for the water with the lowest Ca concentration above the plume in the 1987 profile, the measured pH of 8 implies that for P_{CO_2} = 0.2 atmospheres the water would contain a TIC of around 25000 mg/l as HCO_3, and would have a calcite saturation index of about 1.2. It thus appears that either the measurements are incorrect, or the system is far from (physical) equilibrium.

Net dissolution of calcite only occurs in the first cell below the landfill. The amount dissolved is about 1.5 mmol/kg H_2O, much less than the that apparently available in the sandstones (0.4-1 mol/kg H_2O (Lewin et al., 1994; Thornton et al., 1995). The increase in alkalinity caused by the dissolution of calcite moves down the profile as part of the leachate plume (Figure 3.12). In front of the plume in the model system, the injected CO_2 causes an increase in TIC relative to the background groundwater. In the real system, this increase only occurs for a limited distance ahead of the plume - in the zone where the produced CO_2 has moved downward. To represent this, on Figures 3.11 to 3.13 the pH and alkalinity below the plume have been altered to the values present in the native groundwater. This "manual" modification of the model is the only convenient way of representing the effect of a rolling CO_2 front using the code.

Iron is present in only small amounts in the leachate (6 mg/L), but occurs in large amounts in the rock. In the model, an effectively infinite amount of hematite is allowed to equilibrate with the groundwater, most of the dissolution being "in response to" an Fe requirement in order to precipitate pyrite. Thus, most hematite dissolution (c.10 mmol/L) occurs in the first cell below the landfill, where most pyrite precipitation occurs (19 mmol/L) (Figure 3.15). At the leachate plume an Fe peak occurs, largely controlled by ion exchange (Figure 3.12): the peak is clear in the field data for 1987, though less so for the data for 1985 (there are no Fe data for 1991) (Figure 3.10). Hematite was chosen as the main Fe mineral rather than goethite or $Fe(OH)_3$ (am) arbitrarily, though hematitie is certainly an important phase in the rock. Hematite is of intermediate solubility in the present system, with goethtite being the most soluble of the three iron minerals. There is a great deal to be learnt of Fe chemistry in Triassic Sandstone systems (eg Edmunds and Morgan-Jones, 1976; Walton, 1982; Tellam, 1996).

Manganese concentrations in the leachate are relatively high (119 mg/L), and the laboratory experiments have shown there to be a limited amount of MnO_2 in the rock. In the 1985 and 1987 field data sets (the only data sets available for Mn), concentrations are generally low: no attempt has been made to simulate the two very high isolated Mn peaks in the 1985 profile (see above). The 1 mmol/kg H_2O MnO_2, included in the standard case model's representation of the rock is rapidly exhausted by the leachate (Figure 3.14). Mn is precipitated as

rhodochrosite (Figure 3.14) as soon as the leachate enters the sandstone, and precipitation also occurs in the leachate plume where high HCO_3 over compensates for the lower pHs. Ion exchange controls the form of the Mn peak at the plume. The clearly dominant role of MnO_2/Fe interactions in the laboratory experiments is not observed in the field data. This is because of the importance of Fe sulphide and rhodochrosite precipitation: sulphate reduction was not observed in the laboratory experiments, and rhodochrosite oversaturation persisted over the relatively short residence times in the columns.
The pe remains low above the leachate plume in the model system. This seems to be caused by the presence of precipitated pyrite and the relatively low oxidising potential of the recharging fresh groundwater. Aluminium was included in the model, and will be of importance if the ore falls below 5. However, this did not occur in the standard case model system.

Problem 7c: Investigating the possibility of using laboratory-determined parameters for predicting breakthrough at the field scale.

It would be very useful if laboratory-determined parameters could be used when modelling field systems. A simple test of this approach is to use the parameters derived in problems 1-5 (Burntstump laboratory experiments) to predict the chemical profile at the Burntstump site. Averages of the K_{MX} values, measured CEC (134 meq/kg H_2O) and % $CaCO_3$ (1.22%) values, and average mass-balance calculated MnO_2 values (0.001 mol/kg H_2O) were input into the standard case model of the field system. The results (for 1987) are shown in Figure 3.16. Comparison with Figure 3.12 indicates that using the laboratory values increases the predicted Ca concentrations relative to the Mg concentrations, and increases Fe and pH values. However, overall the predicted breakthrough styles are similar, with NH_4 and K being generally retarded, a pH low associated with the plume, and Mn more attenuated than Fe.

Problem 7d: Investigating the effect of the amount of calcite in the sandstone on the breakthrough profiles.

As the amount of calcite included in the basic model of problem 7b has not been exhausted, increase in calcite content will not affect the model system. However, reduction of calcite content may potentially have an effect on the breakthroughs, and is directly relevant to many areas of the UK where the Triassic Sandstone is carbonate-free at shallow levels (Moss and Edmunds, 1992; Tellam, 1996). A first impression of the implications of a carbonate-free sandstone may be obtained by re-running the basic model of problem 7b, but without equlibrium with calcite. Figure 3.17 shows the predicted 1987 profiles. The breakthrough of Mg, Ca, Mn, Fe, and alkalinity are markedly affected, and the pH minimum is lowered by around 0.5. Care must be taken when interpreting this prediction, as processes which can be ignored at higher pHs are not necessarily included in the model: for example, H^+

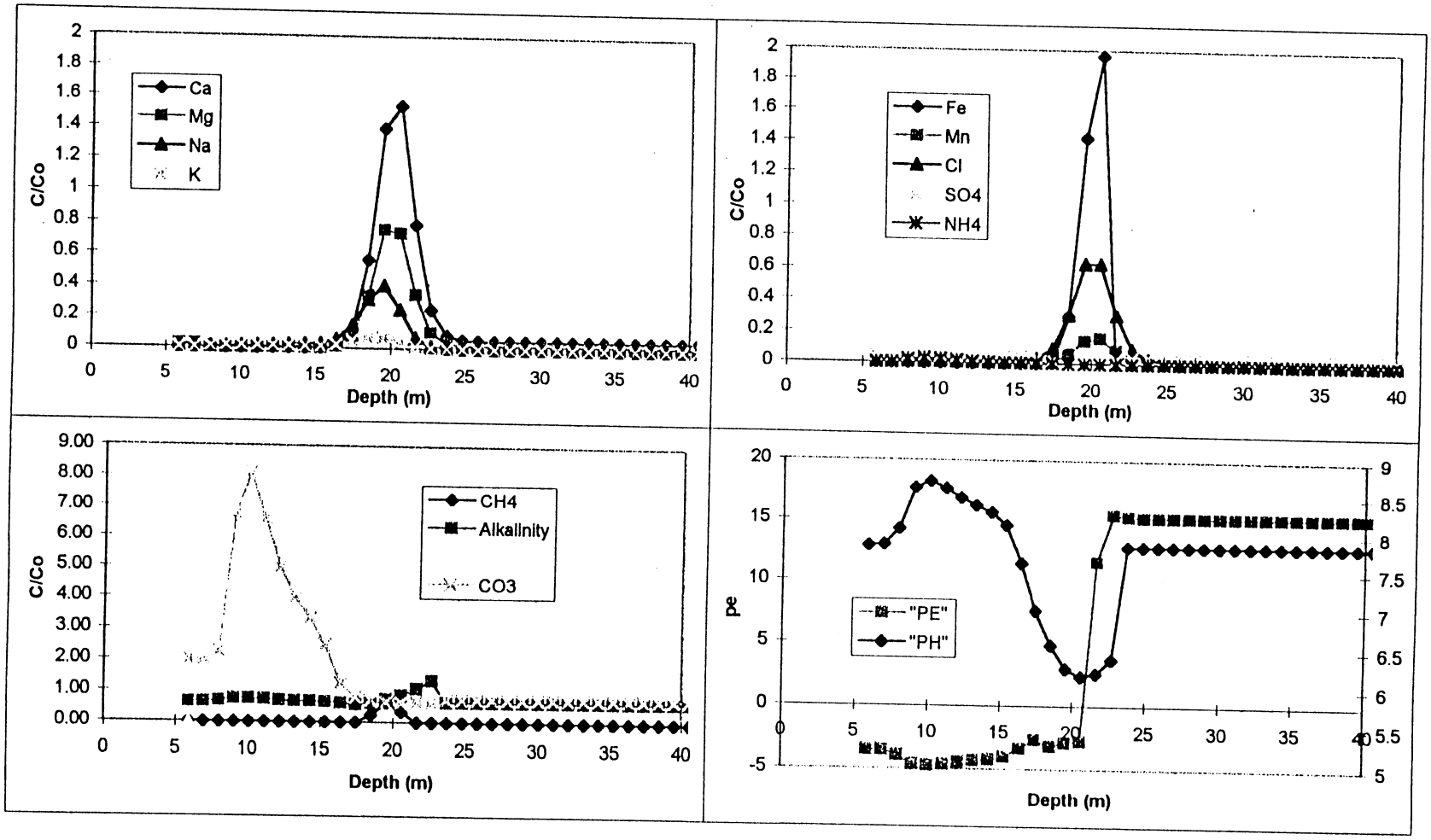


Figure 3.16 Prediction for the Burntstump system using laboratory-determined parameters.

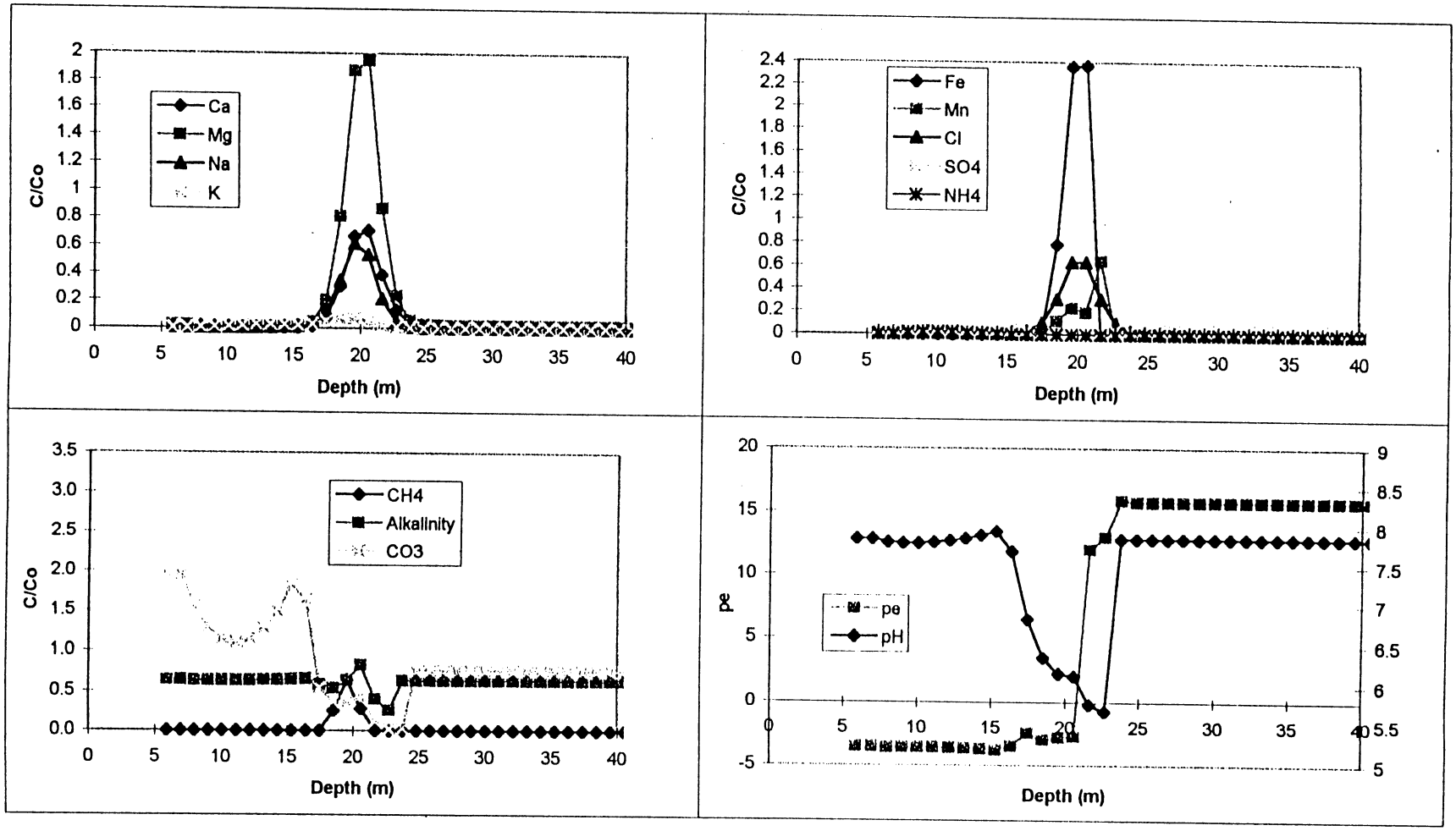


Figure 3.17 Prediction for the Burntstump system when calcite dissolution is not permitted.

exchange. Much has yet to be learnt of acid neutralisation in carbonate-free Triassic Sandstone (Moss and Edmunds, 1992; Buss et al., 1997; Buss, in progress).

Problem 7e: Investigating the effect of MnO_2 on breakthrough profiles.

Usually MnO_2 is present in relatively small amounts in Triassic Sandstone. However, because of its potentially very important role in redox, acid-base, and ion exchange systems, it is worthwhile investigating the sensitivity of the system to changes in MnO_2 content. An extreme case has been chosen - that of excess MnO_2 (as birnessite). The prediction for the 1987 profiles are shown in Figure 3.18. The effect of having excess MnO_2 is profound: the ion exchange system changes to such a degree that NH_4 is no longer delayed; Fe is almost completely removed; pH rises at the plume to very high values, thus causing calcite precipitation; and the redox potential is, of course, much higher in the sandstone groundwaters remote from the leachate plume.

Problem 7f: Investigating the likely behaviour of other pollutants in the system modelled.

It is of interest to attempt to predict the likely behaviour in Triassic Sandstone systems of species not present in the Burntstump leachate. The example chosen here is B, with an initial concentration of 100 mg/L with, and without 100mg/L F^-. In this case, unsurprising, B passes through the system unretarded. However, reactive metals could easily be incorporated using the ELEMENTS and SPECIES keywords in PIP.

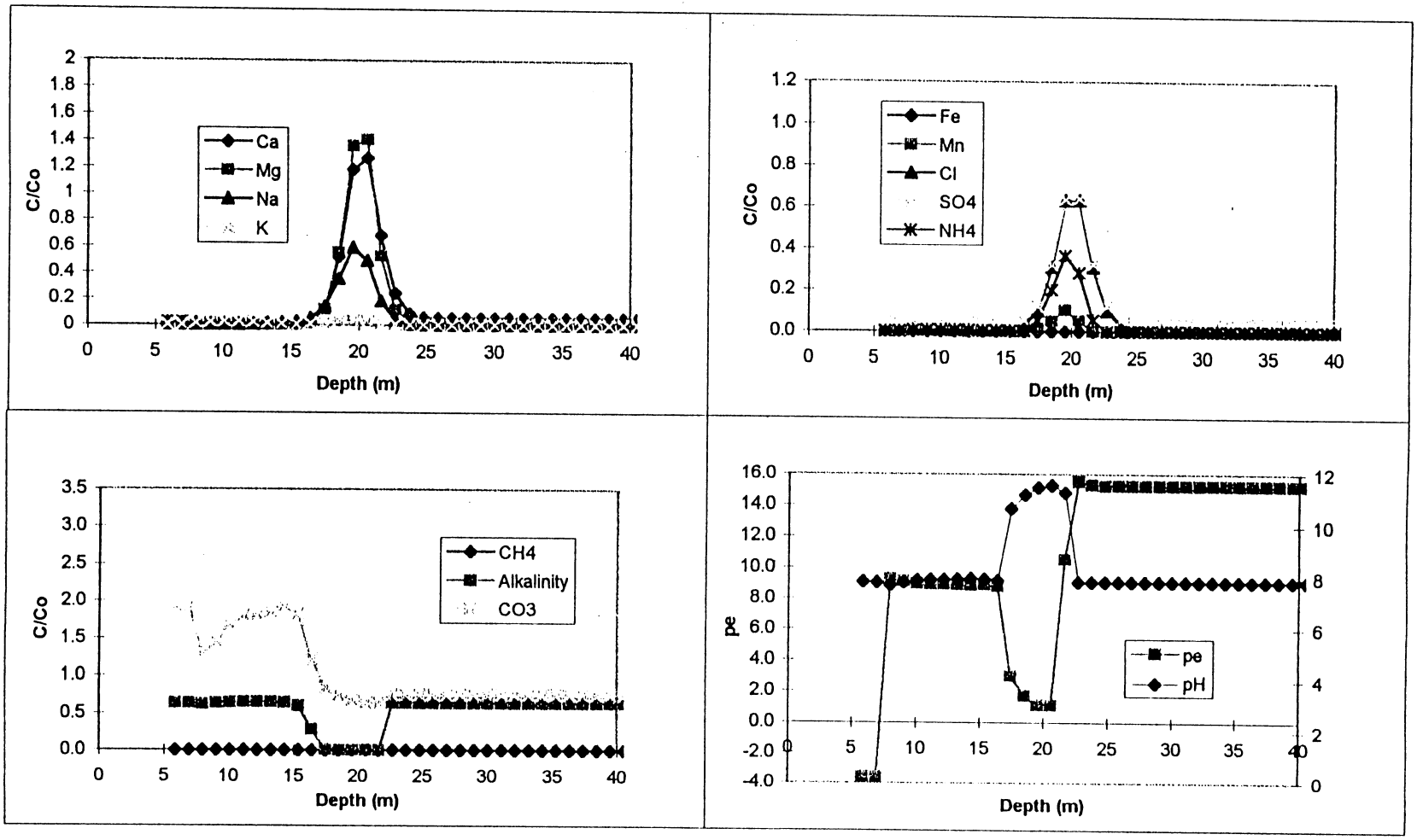


Figure 3.18 Prediction for the Burntstump system when an infinite amount of MnO_2 is made available for dissolution.

4. Representing Landfill Leachate and Triassic Sandstone Using the Package PHREEQM

4.1 Introduction

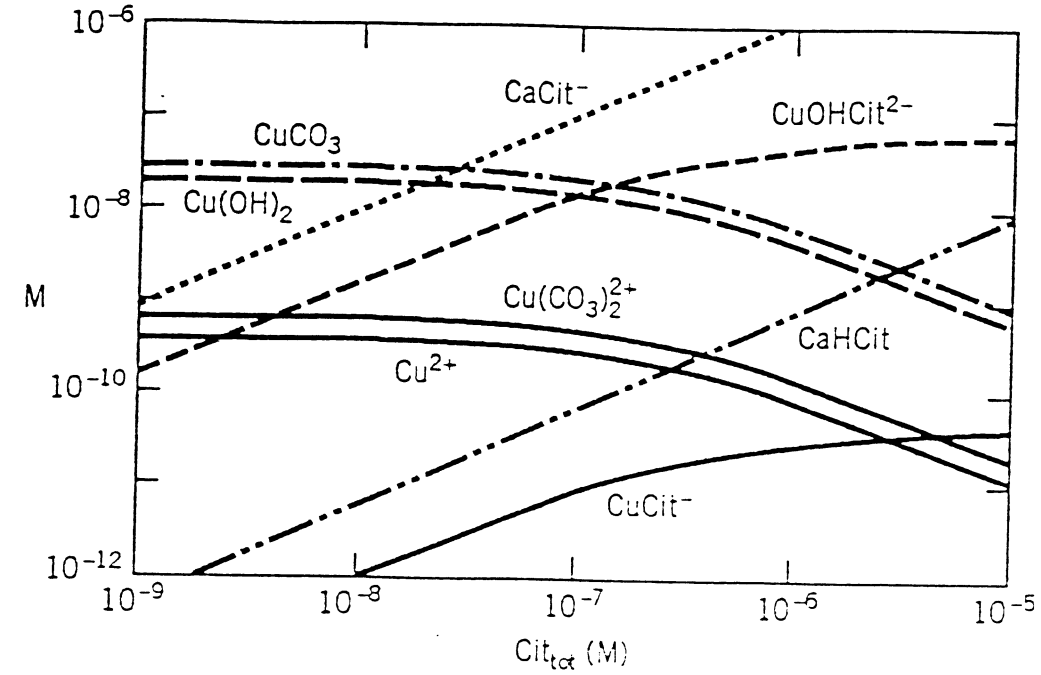
In the following sections the following issues are considered: representing landfill leachate using PHREEQM (Section 4.2); representing solid phase/aqueous phase interactions between Triassic sandstone and landfill leachate using PHREEQM (Section 4.3); the limitations imposed by lack of data availability and by the code (Section 4.4); and conclusions as to the uses of the code (Section 4.5). Each of these sections draws on the results presented in Section 3.

4.2 Representing Landfill Leachate in PHREEQM

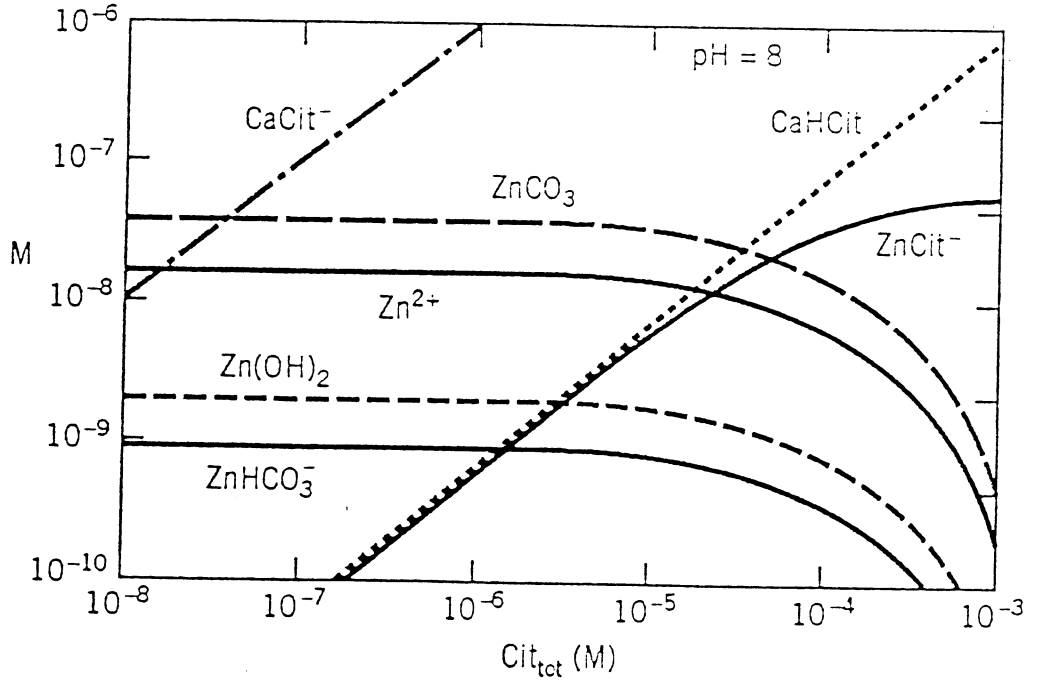
This section deals with the problem of representing landfill leachate of a given composition in PHREEQM: the issues relating to leachate composition heterogeneity in space and time are considered in Section 4.4.

Leachates are complex particulate, colloidal, and "true" solutions. PHREEQM explicitly insiders only "true" solutions, though it would be possible given the code's algorithms to represent explicitly colloid phase movement, albeit crudely. This has not been attempted in the present study. Instead the code has been used to represent chemical mass transfer as indicated by the data collected from conventional chemical analysis of conventionally treated samples: these data mainly indicate dissolved species, but almost certainly also include some colloidal material. For example, experiments have indicated that inductively coupled plasma spectrometry will detect some colloidal SiO_2, but not all. Details on sampling and analytical methods for the data sets examined are given in Thornton et al. (1994), Thornton et al. (1995), and Lewin et al. (1994). All interpretations are based on chemical analyses involving total concentrations (ie free ions plus any other complexed species).

Major and minor cations: It has been assumed in the modelling work that the major cation-forming species (Ca, Mg, Na, K, NH_4) participate to an insignificant extent in organic complexes. In the case of organic acids, complexes only become significant when the organic acid is present at high concentrations. This is often the case for A-phase leachates. Figure 4.1 indicates the amount of complexation with citrates in an example system (total carbonate as C = 2×10^{-3} M; 10^{-3} M Ca^{2+}; pH = 8) (Stumm and Morgan, 1996, page 299). Such calculations could be carried out using PHREEQM, with citrate, for example, being incorporated as a new species: MINTEQA2 (Alison et al., 1990) has acetate complexes in its standard data base, and, as with PHREEQM, other potential organic ligands can be added into the



(a)



(b)

Figure 4.1 Calculated results of titrating a solution containing 5 x 10^{-8} M Cu(II), 5 x 10^{-8} M Zn(II), 10^{-3} M Ca^{2+}, and 2 x 10^{-2} M total carbon at a pH of 8 with citrate (from Stumm and Morgan, 1996, page 299). Only the major species are shown.

model easily using its preprocessor PRODEFA2. Using MINTEQA2, the A and M phase leachates used in the problems 1-5 of Section 3 were found to complex the major cations to the following extents (A phase/M phase):

NH4, K	<1%/<1%;
Na	11%/3%;
Ca	60%/22%;
Mg	64%/25%;
Fe	71%/40%;
Mn	69%/27%.

These calculations assumed that acetate was the only organic complex formed and that total acetate concentrations were equal to TVA concentrations (Thornton et al., 1995).
For humic substances, no general model for complexation is available: however, for heavy metals in particular, though also for other cations, uptake can reduce uncomplexed concentrations by orders of magnitude (Stumm and Morgan, 1996, pages 301-304).
Despite this, the self consistency of, for example, the ion exchange reactions for different leachates and sandstone samples (see below) suggests that, even if occurring extensively, the effect of the organic/cation complexes can be taken into account in the equilibrium constants. The minor cations will potentially also be affected by complexation, though there is no direct evidence from the modelling work in this study.

Trace metals and metalloids: "Trace" metals and metalloids are often more prone to organic complexation than the major ions. However, such interactions are far from fully understood in complex solutions such as landfill leachate, and it seems likely that taking them into account by anything other than a rather crude partitioning model is unlikely ever to be practicable.

Chloride and total dissolved solids: Cl concentrations can be simply incorporated. However, in leachates with very high ionic strengths the method for calculating activity coefficients may need to be chosen with care. The extended Debye-Hückel equation is normally taken to be reasonably valid up to an ionic strength (I) of 0.1M (Stumm and Morgan, 1996, page 103): the WATEQ Debye-Hückel equation (ie the version of the equation used in the aqueous model WATEQ (Plummer et al., 1976)) and the Davies equation (valid to I = 0.5 M) are also available in PHREEQM (see Appelo and Postma, 1993, pages 412-413).

Inorganic Carbon: Representing the inorganic carbon system is particularly difficult, especially if total inorganic carbon (TIC) data are lacking. Determination of the alkalinity of a leachate will often result in very high values because of the buffering role played by organic species: this is particularly the case for acetogenic-phase (A-phase) leachates. Hence alkalinity data should be used very carefully. In the current work, several different approaches have been used:

(i) measured alkalinity has been used in some cases where the amount of volatile fatty acids (VFAs) was known to be limited (problems 3 to 6);
(ii) an estimated alkalinity has been used in some cases where approach (i) was not justifiable; the leachate was assumed to be in equilibrium with aquifer calcite, and the alkalinity calculated using the measured pH and the Ca activity (ideally from preliminary PHREEQE calculations);
(iii) measured total carbon concentrations (TIC + TOC) have been input together with a low pe; the low pe results in conversion of much of the total C to CH_4; the CH_4 is taken here to represent organic species and acts as a facilitator of redox buffering; the choice of pe can only be judged on the basis of the fluid alkalinity, calcite saturation state, or redox pair ratios (eg SO_4/H_2S): in the sense that an arbitrary decision has to be made concerning the carbonate system, option (iii) is very similar to option (ii) (used in the development of the problem 7b simulation, but not in the final model).

Redox parameters: Deciding on the description of the redox state to use in representing a leachate is particularly difficult. Sometimes Pt electrode measurements are available. However, Pt electrodes are only sensitive to certain species, can alter the system they are measuring, and in any case provide only one pe value where in fact many are likely to be appropriate. In addition to deciding on a pe value, it is also sometimes necessary to consider the redox poising of the solution. In some problems, redox reactions may be of limited importance. For example, when dealing with ion exchange systems. However, because of the potential effect of redox reactions on the carbonate system (eg conversion to CH_4), and via this to the cation concentrations, even some apparently simple ion exchange problems can be redox-sensitive. In some problems it may be necessary to investigate different parts of the problem using different pe values: for example, SO_4^{2-}/S^{2-} interactions might be investigated using one pe, and organic carbon oxidation using another (cf the Burntstump field data modelling, problem 7, Section 3). In other cases, such as laboratory experiment interpretations described as problems 1 to 6 in Section 3, there is only one redox-sensitive reaction of interest, and the pe can be chosen relatively easily. A redox buffering capacity will be set up in consequence of almost any redox calculation: for example, setting a low pe might convert input total SO_4 to H_2S, which is then available for back conversion at a later stage; or if S^{2-} is precipitated, the solid phase will act to provide subsequent redox buffering capacity (see problem 7, Section 3).

Organic matter: The main organic content in leachate may offer a substantial buffering capacity. This was not clearly the case in the short term laboratory experiments, but over field time scales organic degradation may be very important. As PHREEQM stands, organic matter is not incorporated. There are several possible ways around the problem:
(i) set up a new organic species in the PHREEQM data base;

(ii) use CH_4 as a surrogate for organic species; and
(iii) input a new species representing organic matter (or representing primary organic matter degradation products).

Option (i), setting up a new organic species, was investigated as part of the Burntstump field data modelling (problem 7). Methanal (CH_2O) was used to represent organic matter: it was introduced using SPECIES (in PIP), and linked to the master species HCO_3. Actual methanal thermodynamic properties were used, yet in principle if CH_2O is to represent a wide range of organic species the thermodynamic properties could be chosen without direct reference to methanal. No account of delay in degradation reactions is possible using this (equilibrium) approach.
Option (ii) is similar to option (i), but involves the use of a species which already exists in the PHREEQM data base - CH_4 - as the surrogate for organic matter. Using this approach, the predicted CH_4 cannot be compared with any measured values for CH_4. Assigning a low pe to the leachate converts TIC to CH_4. Subsequently, as the system becomes oxidised, CH_4 is converted back to inorganic carbon:

$$CH_4 + 3H_2O \rightarrow CO_3^{2-} + 10H^+ + 8e^-$$

thus buffering the redox reaction. The transfers are instant - the model is based on equilibrium reactions - which is somewhat unrealistic. Option (iii) circumvents this problem.
Option (iii) allows organic matter to be injected into the leachate solution as required. This is accomplished by adding CO_3 with THMEAN = 0 (Section 2.5.18) to the solution using the REACTION (PHREEQE) for LAYERSOL (PHREEQM) keywords in PIP. The main limitation with this approach is that in PHREEQM the injection is associated with a specific layer: thus, for example, when modelling the Burntstump field data (problem 7, Section 3) the organic matter content would be injected into both the leachate and any subsequent flushing water. This is not always appropriate. As an alterative to organic matter represented as CO_3 with a low THMEAN, it is possible to inject organic degradation reaction products (CO_2 and CH_4 most conveniently) into the water.
In the simulations of the laboratory experiments (problems 1 -6, Section 3), organic matter was not explicitly modelled as degradation was negligible over the time scale of the experiments. In modelling the Burntstump field data (problem 7), degradation was taken into account by adding CO2 in the cells representing the sandstone: this can be justified as the basis that there is a separate gas phase in the sandstone as the water table is deep at this site. A lower pe (-2.9) was also used in problem 7, and this provides the redox buffering mentioned above under option (ii).

Xenobiotic organic matter (XOM): XOM species can be represented in principle in PHREEQM as new species/elements. By introducing the appropriate thermodynamic data (using SPECIES in PIP) degradation reactions can be modelled. Linear sorption, in principle, can be

incorporated in two ways. Firstly, sorption can be modelled as an additional exchange reaction, provided the sorbed concentration of the XOM is negligible in comparison with the CEC, and its concentration in solution is small in comparison with the other exchanging species:

$$K = \frac{M^+}{(XOM)} \quad \frac{(XOMX)}{(MX)}$$

where M is a cation, XOMX is the sorbed activity of a cationic XOM, and MX is the sorbed activity of the cation;

$$\text{for } (XOM) << (M^+) \text{ and } (XOMX) << (MX)$$

$$K = \text{Constant} \ \frac{(XOMX)}{(XOM)},$$

$$\text{ie,} \quad \frac{K}{\text{Constant}} \ (= K_d) \ = \frac{(XOMX)}{(XOM)}$$

M could be a dummy species rather than any real element. For multi-component ion exchange, the K_d will not be exactly constant. This method relies on the concentrations of the XOM being very much smaller than other exchanging species, both because of the linear isotherm assumption and because the sorption substrates for ion exchange and XOM sorption are usually separate. If several XOMs need modelling, this approach could only be used in separate model runs, unless there is evidence of competition between XOM species. A second more flexible but more involved approach for taking into account XOM sorption is to set up an uncharged sorption substrate species analogous to X^- together with an uncharged dummy species of constant concentration in all solutions which would dominate this substrate. With high K_{XOMX} values (see Section 2.3.3) and the $\gamma_{XOM} = 1$ option (see GFLAG in the SPECIES (SNAME) keyword in PIP, Section 2), the sorption of several XOMs could be modelled.

Although in principle XOM degradation reactions and sorption can be modelled using PHREEQM, there are problems. Degradation reactions are often poorly understood, and thermodynamic data are far from complete. The reactions are often slow, necessitating careful consideration of how they are to be represented in what is basically a equilibrium model. In addition, a lag time before reactions commence is often a feature of organic degradation. Although conceivably modelling using PHREEQM might provide insights into these issues, it is not really the appropriate code to use. In a similar way, there are more appropriate (and simpler) codes which can deal more directly with simple linear retardation. For these reasons, and because of time limitations, the present study has not directly considered the representation of XOMs using PHREEQM, and the suggested approaches given above have not been tested out.

4.3 Representing Solid Phase/Aqueous Phase Interactions Between Triassic Sandstone and Landfill Leachate using PHREEQM

4.3.1 Introduction

The modelling studies reported in Section 3 indicate that the following inorganic rock/water reactions are the most significant during the landfill leachate migration:

ion exchange;
carbonate mineral reactions;
MnO_2/Fe interactions;
metal sulphide precipitation; and
acid neutralising reactions in low carbonate sandstone.

These reaction types are considered individually in the following sections. However, the reactions are not necessarily independent of each other.

4.3.2 Ion Exchange Reactions

4.3.2.1 Introduction

In the modelling work presented in Section 3, it was found necessary to consider ion exchange reactions involving Na, K, Ca, Mg, NH_4, Mn, Fe, and, in one case, Al species. Fe exchange proved to be of limited importance in some cases (see, for example, problem 6, Section 3). Al^{3+} and $Al(OH)^{2+}$ exchange proved a very important mechanism in pH control in the carbonate-free West Midlands sandstone (problem 6, Section 3). Two main questions arise - the form of the equations used for describing the exchange, and the values for the exchange parameters.

4.3.2.2 The Form of the Equations Used to Describe Ion Exchange

The earliest known detailed quantitative work on major species ion exchange reactions in the UK Triassic sandstones, that of Ranasinghe (1988) and Carlyle (1991), assumed an equilibrium constant type expression with sorbed phase concentrations expressed in terms of equivalent fractions (the Gaines-Thomas convention (Gaines and Thomas, 1953)):

$$2M^{+} + NX_2 \rightarrow 2MX + N^{2+}$$

$$K = \frac{(N^{2-})}{(M^{-})^2} \frac{(MX)^2_{EF}}{(NX_2)_{EF}}$$

where (M^{2+}) and (N^{+}) are the cation activities, X is the sorption substrate, and $(MX)_{EF}$ is the sorbed phase activity for M. Assuming sorbed phase activity coefficients are equal to one, in the Gaines-Thomas convention, $(MX)_{EF}$ will be expressed as an equivalent fraction (= concentration of sorbed M in equivalents / total sorbed cations expressed in equivalents (ie CEC)). This assumption appeared to work satisfactorily when interpreting both laboratory and field data for the Merseyside Triassic Sandstones.
However, El-Ghonemy (1997; in press) has shown for samples also from the Merseyside Triassic Sandstones that the selectivity coefficients calculated according to the Gaines-Thomas convention vary with sorption site occupancy: (an example of El-Ghonemy's (1997) results are shown on Figure 4.2). El-Ghonemy (1997) also showed for the same sandstone samples that the values of laboratory-determined cation exchange capacities were dependent on the salt used to displace the sorbed ions. His data indicate that measured cation exchange capacity can vary by up to at least 100% (see below, Section 4.3.2.3). This implies that cation exchange capacity is also a function of exchange site occupancy. He also investigated the Gapon and Vanselow conventions, but considered that the Gaines-Thomas equation was the most appropriate for the Sandstones.
The modelling presented in Section 3 indicates that the Gaines-Thomas convention with constant selectivity coefficients and constant CEC satisfactorily describes the exchange processes occurring, presumably because the site occupancy changes were not extreme. However, if the exchange site population were to change greatly during leachate migration, it is clear from El-Ghonemy's (1997) results that problems with PHREEQM's description might arise when using average selectivity coefficients and an average CEC value. One possible method to avoid this problem has been proposed by El-Ghonemy (1997,b). By estimating the sorbed phase activity coefficients using a procedure justified by a solid solution model, El-Ghonemy (1997, b) suggested that a true equilibrium constant for exchange reactions could be calculated. Although this needs further investigation, it may be possible to implement El-Ghonemy's model using the GFLAG options (SPECIES (SNAME) in PIP), either directly or by adding some simple code.

4.3.2.3 Values for the Exchange Parameters for Triassic Sandstone

Introduction

In the following discussion it should be borne in mind that cation exchange capacity and selectivity coefficients are not constant, but vary with sorbed populations, as shown by El-Ghonemy (1997). In addition, the results discussed for ion exchange parameters come from relatively few sites in relatively few Basins (the Cheshire Basin the case of Ranasinghe (1988), Carlyle (1991), and El-Ghonemy (1997), and the East Midlands and West Midlands Basins in the case of the present study).

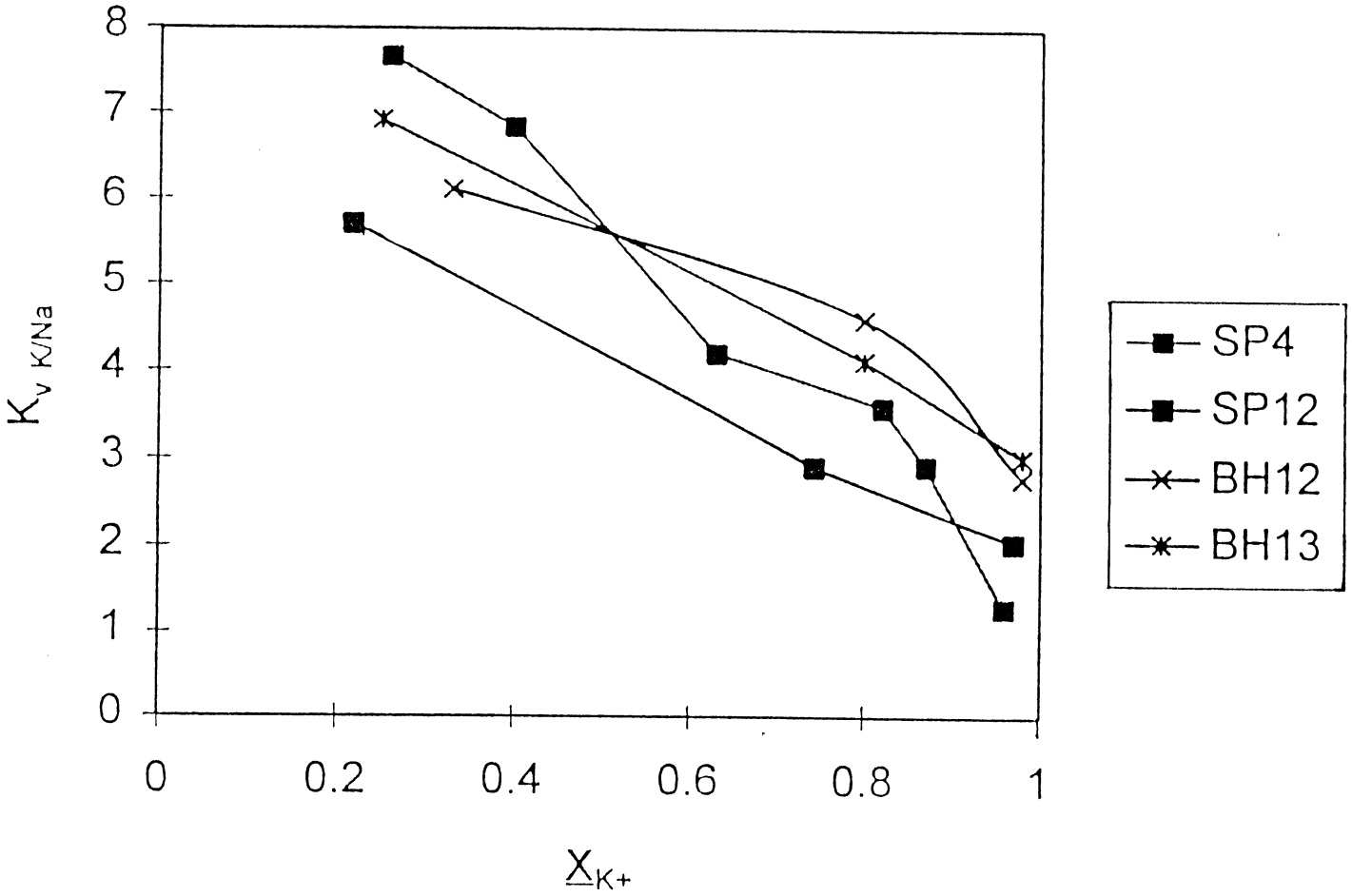


Figure 4.2 A plot of experimentally-determined Gaines-Thomas K/Na convention exchange coefficient against the equivalent fraction of K on the exchanger for four samples of Triassic sandstone. (From El-Ghonemy, in press.)

Selectivity Coefficients

Table 4.1 lists the laboratory data available from the studies of Ranasinghe (1988), Carlyle (1991) and El-Ghonemy (1997) on the determination of Gaines-Thomas exchange parameters. All data are listed in order to illustrate the variability for the results: work continues on the relationship of the variability with geological parameters (Parker, in progress).

Of the data presented in Table 4.1, those of Ranasinghe (1988) are probably the least reliable, being the first known attempt at collecting selectivity data for the Triassic Sandstones. Ranasinghe (1988) followed the method of Reardon et al. (1983) but with intact core plug samples: he saturated the samples with distilled water, allowed time for equilibrium, centrifuged the porewater out and analysed it, resaturated the sample with a high concentration exchange salt solution (LiCl), removed the solution by centrifuging, and finally analysed the solution for major cations. From the concentrations in the distilled water flush and high concentration salt flushes, Ranasinghe (1988) calculated selectivity coefficients: CFC was calculated from the sum of Ca, Mg, Na, and K in the high concentration solution removed from the sample. The traditional use of NH_4 solutions was avoided because of their effect on dissolving of carbonates: this matters little for high CEC samples such as is often the case when working with soils, but can be very important when working with lower CEC materials such as the sandstones.

Table 4.1 also lists the results Carlyle (1991) obtained using a similar method to Ranasinghe (1988). Carlyle (1991) also developed a continuous flush method for determining selectivity coefficients. Intact core samples were flushed until apparent equilibrium had been achieved with a series of solutions. From the chemistry of the waters at equilibrium, and a 1M LiCl measurement of CEC, Carlyle (1991) solved the cubic equation for selectivity coefficients using an optimisation routine. The method has the advantage that the rock can be tested under the concentration ranges expected in the field, and is open to automation: however, it still depends on measuring CEC in a manner which can affect the results, as El-Ghonemy (1997) later showed, and it still forces a Gaines-Thomas type interpretation on the data. The results for this method are also given in Table 4.1. Several interpretations are given in Table 4.2 for each data set: this illustrates the sensitivity of the interpretation to slight errors in input data.

Table 4.1 Summary data for laboratory-determined values for Gaines-Thomas convention selectivity coefficients for Ca, Mg, Na, and K. Brackets indicate values calculated from experiments involving other cations. Outliers have been ignored. N = number of samples.

	Ranasinghe (1988)			Carlyle (1991): Conventional Experiments[1]					
	Mean	Range	n	Mean	Range	n	Mean	Range	n
$K_{K/Na}$	3.43	0.66-7.71	4	2.33	0.13-6.82	16	3.73	1.79-4.70	10
$K_{Ca/Na}$	30.3	8.18-52.4	2	0.38	0.00-0.94	15	0.75	0.31-1.24	9
$K_{Mg/Na}$	(23.0)	(5.11-40.9)	2	(0.28)	(0.0-2.19)	15	(0.63)	(0.40-1.68)	9
$K_{Ca/Mg}$	1.99	1.28-2.73	6	1.36	0.47-5.63	16	1.18	0.38-3.67	13
$K_{a/K}$	14.1	5.15-23.0	5	0.15	0.00-1.71	15	0.26	0.05-1.0	13
$K_{Mg/K}$	(7.09)	(1.9-43.8)	(60)	0.11	0.0-1.52	15	0.22	0.06-1.30	13

	Carlyle (1991) : Flushing Expts[2]			El-Ghonemy (1997)			Appelo & Postma (1993)
	Mean	Range	n	Mean	[Equiv. Fraction][3]	n	Table 5.5, p.160
$K_{K/Na}$	2.77	0.02-5.04	5	6.3-2.6	[0.05-095K^+]	3	5.0(4.0-6.7)
KCa/Na	1.76	0.000-14.5	5	-	-	-	6.3(2.8-11.1)
$K_{Mg/Na}$	(0.56)	(0.000-3.58)	5	-	-	-	4.0(2.8-6.3)
$K_{Ca/Mg}$	2.97	0.48-7.54	5	0.85-2.5	[0.05-0.95 Mg^{2+}]	4	(1.6(0.4-4))[4]
$K_{Ca/K}$	0.18	0.000-0.67	5	0.37-0.60	[0.14-0.93 K^+]	4	(0.25(0.06-0.7))[4]
$K_{Mg/K}$	(0.06)	(0.0-0.48)	5	0.29-0.68	[0.14-0.93 K^+]	4	(0.16(0.06-0.4))[4]

1 *Carlyle (1991) performed two sets of experiments: 10 out of 13 samples from Run 1 were reused in Run 2.*

2 *Several interpretations are possible for each experiment. Mean = mean of (mean values for each interpretation). Range = range for individual interpretations. Samples were a subset of those used in Conventional Experiments.*

3 *Equivalent fraction of given ion in solution at equilibrium with* sandstone.

4 *Calculated from Appelo and Postma's (1993) data assuming ranges for each cation are independent of each other.*

Table 4.2 lists the selectivity coefficients obtained by El-Ghonemy (1997). These data are the most reliable to date. They were obtained using the method of Jensen and Babcock (1973). This method involves flooding several samples each with a solution of fixed cation ratio: once the samples have equilibrated to the solutions, the sorbed populations are desorbed using a high concentration salt solution. From the data, selectivity coefficient variation with exchange site occupancy can be determined.

Table 4.2 Gaines-Thomas convention selectivity coefficients determined by El-Ghonemy (1997) using the Jensen and Babcock (1973) laboratory method. Samples from Speke (SP) and Breeze Hill (BH) observation borehole cores (Cheshire Basin): solutions made up in distilled water.

Equiv.fraction	$K_{K/Na}$				Mean
of K^+ in solution	SP 4	SP 12	BH 12	BH 13	
0.05	-	6.1	6.9	5.8	6.3
0.5	-	4.6	4.1	3.0	3.9
0.95	-	2.8	3.0	2.0	2.6

Equiv. fraction	$K_{Ca/Mg}$				Mean
of Mg^{2+} in solution	SP 4	SP 12	BH 12	BH 13	
0.05	0.66	0.60	1.12	1.0	0.85
0.5	1.49	1.26	1.38	1.02	1.29
0.95	3.23	3.01	1.65	2.15	2.51

Equiv. fraction	$K_{Mg/K}$				Mean
of K^+ in solution	SP 4	SP 12	BH 12	BH 13	
0.143	0.21	0.30	0.39	0.26	0.29
0.500	0.38	0.37	0.39	0.44	0.40
0.931	0.96	0.56	0.61	0.57	0.68

Equiv. fraction	$K_{Ca/K}$				Mean
of K^+ in solution	SP 4	SP 12	BH 12	BH 13	
0.143	0.29	0.40	0.36	0.44	0.37
0.500	0.43	0.52	0.50	0.47	0.48
0.931	0.68	0.52	0.68	0.53	0.60

Comparing the data available (Table 4.1), it is clear that with the exception of some of Ranasinghe's (1988) results, there is general agreement across the studies. The compilation of selectivity coefficient data presented by Appelo and Postma (1993, Table 5.5 page 160), and reproduced here in modified form in Table 4.2, shows

similar ranges to those for the Triassic sandstone, though the $K_{Ca/Na}$ and $K_{Mg/Na}$ values are generally lower for the sandstone.
Data on selectivity coefficients for other species appear not to exist for the Triassic sandstones, although NH4 data are presently being collected (Wehkamp, in progress).
Table 4.3 lists the K values used in the PHREEQM modelling of laboratory data as described in Section 3. Most interpreted values are within or close to the ranges listed for the laboratory results in Table 4.1. However, the Burntstump and West Midlands sandstones appear to sorb K quite strongly, with $K_{K/Na}$ selectivity coefficients being double the usual maximum value. Given the fact that the laboratory ion exchange parameters were determined using solutions made up in distilled water - ie without a background of high ionic strength, high organic species concentrations, and high concentrations of other cations (especially NH4) - the agreement is good.
Also listed in Table 4.3 are the selectivity coefficient values interpreted from the modelling work on the field system at Burntstump. The selectivity for K, NH4, and Fe appears to be much stronger than in the laboratory experiments, but the selectivity for Ca, Mg, and Mn is about the same. The differences may be real: the cation exchange capacity used to interpret the field data is smaller than that measured in the laboratory, and it may be that the system as averaged on a large scale has diffent properties, or that chemical/hydraulic correlations are affecting the results. However, the field system is much less well constrained than the laboratory system, and the differences may well represent errors in, for example, choosing the initial leachate chemical composition (and the fact that only one chemistry was used for the leachate input). Table 4.3 also includes selectivity coefficients crudely corrected for organic complexing as defined in Section 3.2.7. The "corrections" bring some of the values closer to the ranges given by Appelo and Postma (1993, Table 5.5, page 160,; reproduced in modified form in Table 4.1 above). Given the uncertainties, the selectivity coefficient values determined from matching the field data are far less certain than those determined from fitting the laboratory data.
To provide an impression of the validity of obtaining K values by fitting PHREEQM to breakthrough curves, reference can be made to "blind" tests carried out by El-Ghonemy (1997). A set of breakthrough curves resulting from elution of four solutions in sequence through a column were simulated using arbitrarily chosen exchange parameters using PHREEQM. The results were given to El-Ghonemy who then modelled the breakthrough curves without knowing CEC or K values. The results are shown in Table 4.4. It is clear that even with this "perfect" data set, inverse manual solution can result in errors in the tens of percent. Conversely, such errors result in small differences in breakthrough pattern.
There has been no indication in any of the modelling studies outlined in Section 3 that the ion exchange processes are hysteretic.

Table 4.3. Gaines-Thomas convention selectivity coefficients determined from PHREEQM modelling of laboratory and field data on landfill leachate/rock interactions (this study, data from Thornton et al. (1993), Thornton et al. (1995), and Lewin et al. (1994)).

Selectivity Coefficient	Lab Notts A-phase	Lab Notts M-phase	Lab W.Mids M-phase	Field Notts M-phase	
				(i)	(ii)
$K_{K/Na}$	10.47	12.59	12.88	20.0	20.0
$K_{Ca/Na}$	2.51	1.66	2.24	1.6	1.0
$K_{Mg/Na}$	3.98	1.74	2.14	6.3	4.0
$K_{Ca/Mg}$	0.63	0.95	1.05	0.06	0.06
$K_{Ca/K}$	0.15	0.10	0.12	0.08	0.05
$K_{Mg/K}$	0.19	0.10	0.11	0.32	0.20
$K_{Fe/Na}$	3.02	1.70	0.98	10.0	5.6
$K_{Mn/Na}$	2.24	1.78	0.32	1.6	0.9
$K_{NH4/Na}$	3.55	5.37	5.50	31.6	31.6

(i) Values used in PHREEQM. (ii) Values used in PHREEQM "corrected", very crudely, for organic complexing.

Table 4.4 Results of estimating exchange parameters by fitting 1, 2, 3, or 4 sequential breakthrough curves (El-Ghonemy, 1997).

Parameter	Actual values	Interpreted values using 1, 2, 3, or 4 breakthrough curves			
		1	2	3	4
CEC (meq/100g)	1.55	1.25	1.2	1.31	1.55
$K_{Ca/Mg}$	0.5	0.5	0.5	0.6	0.5
$K_{Ca/Na}$	0.7	0.7	0.7	0.6	1.0
$K_{Ca/K}$	0.42	0.42	0.4	0.3	0.4

Cation Exchange Capacities

Measured cation exchange capacity values are listed in Table 4.5. CEC data are more common for the Triassic sandstones than selectivity coefficient data. The magnitude of CEC as estimated using standard high concentration salt solution flushes is dependent on the exchange salt tested and its concentration. El-Ghonemy (1997) found that using NH_4 Cl, LiCl, and CsCl at 0.5 and 1 M concentrations produced variations in measured CEC on the same sample from 1.08 meq/100g (0.5M NH_4Cl) to 2.03 meq/100g (1 M NH_4Cl). CEC determined under conditions of different exchange site occupancy typically resulted in standard derivations of 20% of the mean (eg for K=Na, Ca-Mg, K-Mg, K-Ca experiments each at cation ratios from 5% to 95%, the CEC values for sample SP12 had a mean of 2.09 meq/100g and a standard deviation of 0.398 meq/100g, individual values ranging from 1.04 to 2.11 meq/100g) (El-Ghonemy, 1997). It is concluded that CEC is not a fixed value for the Triassic sandstones, but that its value is typically within the range 0.5-5 meq/100g. El-Ghonemy (1997) has shown that crushing of Triassic sandstone affects measured CEC values to a similar extent as changing exchange salt solution concentrations. An alternative method of estimation is using mineralogical data and the CEC of indivdual minerals (see, for example, Table 5.3 of Appelo and Postma (1993, page 149)).
The CEC values used in the simulations of Section 3 range from 0.96 - 3.24 meq/100g.

In the laboratory experiment modelling work described in Section 3, the CEC values were fixed at the measured values: no trouble was experienced in simulation the breakthrough curves. In the case of the Burntstump field data simulations, the CEC had to be reduced to 0.96 meq/100g, but this is still within the range of the measured values (see Table 4.5). It is probable that there is some correlation between hydraulic properties and chemical properties, and if so, this could bias the value appropriate for the field scale: as clays have higher CECs, it would be expected that the more rapidly moving parts of the plume would have experienced lower than average CEC values, simply because they would be travelling through the higher permeability, less clay rich parts of the rock mass.

Table 4.5 Measured CEC values.

Author	***Method***
Sample	
CEC Value (meq/100g)	
Comments	

Ranasinghe (1988) — *LiCl Flush*

SP 3	SP 11	SP 12	SP 14	SP 15	SP 28
0.74	0.70	1.04	0.83	1.15	0.96

Core from Speke Observation Borehole, Cheshire Basin

Geology: Chester Pebble Beds Formation

Carlyle (1991) — *1M LiCl flush*

Run 1

10a	10b	10cA	10cB	20a	20bA	20bB	35b	50aA	40aB
2.3	1.44	1.83	1.79	1.51	1.15	1.71	1.21	0.85	0.97
40b	55aA	55aB	59a	78a	78b	Mean	St. dev.		
1.00	0.98	0.84	0.95	0.92	0.09	1.22	0.52		

Run 2

10cA	10cB	20	20bB	35b	40aA	40aB	40b	55aA
2.20	1.62	1.17	2.00	0.69	0.71	0.83	1.44	0.60
55aB	59aB	78	78b	Mean	St. dev.			
0.92	0.69	0.81	0.81	1.12	0.51			

Core from ICI Widnes Observation Borehole, Cheshire Basin.
Geology: Chester Pebble Beds Formation

El-Ghonemy (1997) — *0.5M NH_4Cl flush*

	SP4	SP12	BH12	BH13	
Mean	1.69	2.09	4.40*	5.34*	*Ignoring one
St. Dev.	0.39	0.39	0.81*	1.12*	outlier
n	12	12	11	11	

Core from Speke (SP) and Breeze Hill (BH) Observation Boreholes, Cheshire Basin.
Geology: Chester Pebble Beds Formation.

Lewin et al. (1994)
Probably <5 meq/100g
Burntstump Landfill, Nottinghamshire
Geology: Chester Pebble Beds Formation

Thornton et al. (1994)
1.63 meq/100g

Thornton et al. (1994)
3.24 meq/100g
West Midlands Triassic Sand, Sandy Lane Quarry, Bromsgrove

4.3.2.4 Conclusions

(i)The Gaines-Thomas convention exchange equations are appropriate for the Triassic sandstones. The selectivity coefficients vary with exchange site occupancy, but average values appear to produce satisfactory descriptions of breakthrough curves when change in exchange site occupancy is limited. Care is necessary when large changes in site occupancy are likely.
(ii)A more sophisticated representation of ion exchange in Triassic sandstones has been developed by El-Ghonemy (1997, b), and may in future be incorporated into PHREEQM.
(iii)Ranges for selectivity coefficients as determined by laboratory experimentation are given in Table 4.1, and these values give a guide for initial estimates for modelling purposes. There is no knowledge of how selectivity coefficients change with ionic strength.
(iv)Cation exchange capacities vary with method of measurement and exchange site occupancy typically with a standard deviation about the mean of 20%: a factor of 2 is not uncommon between different measurements. Typical measured values are given in Table 4.5: the usual range is 0.5-5 meq/100g, with most values around 1 meq/100g.

4.3.3 Carbonates

4.3.3.1 Introduction

The carbonates most likely to be of relevance in Triassic sandstone/leachate interactions are:

calcite	(dissolution and precipitation);
dolomite	(dissolution but ? not precipitation);
rhodochrosite	(? dissolution and precipitation); and
siderite	(? dissolution and precipitation).

Each is easy to incorporate in a simulation (using PIP via MINERALS for PHREEQE or LAYERSOL (NCELL + MNAME + SIMEX)). Apart from dolomite, the thermodynamic data are accurately known: data for all four minerals are in the PHREEQE database.
The carbonates are of fundamental importance in Triassic sandstone groundwater chemistry, as illustrated by the simulations described in Section 3 (eg cf problems 1 and 6).

4.3.3.2 Calcite

Calcite is a common constituent of Triassic sandstone. However, often at shallow depths it has been removed by dissolution. Where it is present, it will often play a dominant role in pH control, typically buffering it within a range of 7-8. This was seen to be the case in the calcite-containing Nottinghamshire sandstone data used in problems 1 to 5 in Section 3. Calcite dissolution is rapid (eg Lasaga, 1984; Bath

et al., 1987), and dissolution equilibrium can be assumed: precipitation rates are slower, but in terms of field time scales can often be assumed rapid. Samples oversaturated with respect to calcite can arise through incorrect pH measurement (error in pH = error in saturation index), or as a result of mixing of waters during the sampling process. In calcite-free rock, such as in the West Midlands sandstone of problem 6 in Section 3, pH control is effected by exchange reactions and oxyhydroxide interactions, and is much more complex. The details of the process have yet to be determined (Moss and Edmunds, 1992; Buss, in progress). In such cases, pH values are often lower, leading to greater mobility for trace metals (as in Birmingham; see Tellam (1995)), and possibly inhibition of organic degradation.

Even in calcite-free sandstone it is possible for calcite equilibrium to control pH via calcite precipitation. An important mechanism is the release of sorbed Ca leading to oversaturated conditions: precipitation, fall in pH, and rise in CO_2 content follow (problem 1, Section 3). These latter two characteristics can also be the result of organic matter oxidation. Distinguishing between the two possible mechanisms is possible in principle by considering the state of calcite saturation and whether TIC decreases or increases. In practice this may not be easy, given that a saturation index ≥ 0 is a necessary but not sufficient condition, that a satisfactory measurement of TIC is often not available, and that, in the field, samples are often mixed and the system is often very heterogeneous. In Section 3, the laboratory experiment pH values and CO_2 concentrations were in general interpreted to result from inorganic system interactions, whereas in the field system, pH and CO_2 probably result at least in part from organic interactions.

4.3.3.3 Dolomite

Dolomite occurs in some of the UK Triassic sandstones, but often at low volume % (eg Edmunds et al., 1982). Where it is present it is often difficult to distinguish the effects of dolomite dissolution from calcium carbonate dissolution combined with magnesium from other sources, particularly given the frequently strong ion exchange controls on Ca/Mg ratios.

Precipitation of dolomite is very slow, and oversaturated conditions can be maintained for periods long even in the context of landfills. The slow precipitation is the main reason why thermodynamic data for dolomite are poorly constrained. Neither dolomite dissolution or precipitation have been incorporated in the interpretations presented in Section 3.

4.3.3.4 Rhodochrosite and Siderite

Because of the influxes of Mn due to interaction with aquifer Mn oxyhydroxides, rhodochrosite oversaturation is possible. Simulations

of the laboratory experiments (eg problems 1 and 2 in Section 3) indicate that very limited rhodochrosite precipitation took place. This is probably because the residence time within the columns was too short; a contributory reason might also be the complexing of Mn and organic matter, thus allowing more Mn to be retained in solution. Presumably with the much larger time scales of the field systems, rhodochrosite equilibrium will control Mn concentrations, and this was found to be a satisfactory explanation in the case of the simulation of the field data from Burntstump (problem 7). Rhodochrosite is usually not a common mineral at other than trace levels in the Triassic sandstones: Mn oxyhydroxides are much more common.
Siderite may control Fe concentrations in some cases, but in the simulations so far carried out more important solubility controls are oxyhydroxide and sulphide phases.

4.3.4 Mn, Fe, and Their Oxyhydroxides

Triassic sandstones often contain a few % Fe, the Fe being present in a complex mixture of oxyhydroxides. Mn oxyhydroxides are also very common.
The simulations of the laboratory data presented in Section 3 were able to reproduce the Fe and Mn concentrations well using the reaction:

$$2Fe^{2+} + MnO_2 + 4H_2O \rightarrow 2Fe(OH)_3 + Mn^{2+} + 2H^+.$$

The calculated pe agreed reasonably well with the measured Pt electrode Eh values, despite the reaction involving a solid phase. This simple model ignores the effect of organic matter on redox systems, and it is often proposed that MnO_2 reduction is associated with microbial oxidation of DOM (Christensen et al., 1994). In the laboratory experiments it is possible that organic reduction of MnO_2 is not occurring simply because of lack of time to set up the appropriate microbial populations. Even if some organic redox reactions are occurring, the Mn/Fe system appears to be sufficiently decoupled from them that the simulation can ignore the organic reactions: another possibility is that the reaction occurring does involve organic matter, but that coincidentally its stoichiometry is (unusually) the same as the inorganic reaction.
The field data from Burntstump (problem 7, Section 3), appear to show that the high Mn/low Fe concentrations seen in the laboratory experiments also occur in the field, though the relationship is rather more complex. The simulations allow MnO_2 (as birnessite) to be dissolved from the matrix, but Fe is precipitated mainly as pyrite, not as a ferric compound: in the laboratory columns, sulphate reduction did not occur. Although pyrite precipitation appears to be controlling the dissolved Fe concentrations in the simulations for the field data, ferric compounds were allowed to precipitate if conditions were

appropriate: the choice is made by the code. However, no attempt was made to simulate a direct organic /MnO_2 reaction.
Dissolution of Mn and Fe oxyhydroxides may release sorbed/coprecipitated metals. Some of these metals may be quickly taken up by the remaining oxyhydroxides, but some may remain in solution or interact with species in solution and precipitate as sulphides, hydroxides, or carbonates. Modelling would require adding the thermodynamic data for the metals to PHREEQE's data base (using ELEMENTS and SPECIES in PIP). Release of metals could be taken into amount by defining a new mineral with trace amounts of the required metal but with the same thermodynamic properties as the pure mineral (eg $Mn_{0.99}Zn_{0.01}O_2$ in place of MnO_2). Sorption of metals to oxyhydroxides is much more difficult to model using PHREEQM other than rather crudely (see Section 4.3.2): information on sorption on oxyhydroxides is dealt with in detail by Dzombak and Morel (1990), and some information on take up of trace metals on Triassic sandstones is available in Mimides and Lloyd (1987) and Ivanovich et al. (1996).
The Mn oxyhydroxide content of the rock can play a significant role during leachate migration, and the MnO_2 content is an important parameter to measure (problems 1 - 6, 7b, and 7e, Section 3).

4.3.5 Sulphate Reduction/Sulphide Precipitation

In the laboratory experiments outlined in Section 3, sulphate reduction appeared not to be an important process and was not modelled. However, the data from the Burntstump site (problem 7, Section 3) indicates that SO_4 is substantially attenuated in the field system. As a result SO_4 reduction was represented, albeit crudely (see Section 4.2). One result of SO_4 reduction is the potential created for precipitation of metal sulphides. In the case of the Burntstump field data simulations, Fe concentrations are at least partly controlled by pyrite precipitation. To model other sulphides, such as ZnS, it is necessary to include thermodynamic data in PHREEQE's data base (using ELEMENTS, SPECIES and MINERALS in PIP). If trace metal movement is of interest - as might be the case in carbonate-free Triassic sandstone (eg Tellam, 1995) - it is important to record the presence of S^{2-}, even if only by noting olfactory detection of H_2S.

4.3.6 pH Control in Carbonate-Free Triassic Sandstone

If carbonates are present in the sandstone, they are usually the main mineralogical control on the fluid pH. Such controls are relatively easy to simulate using PHREEQM.
If the sandstone is carbonate-free, pH will be influenced by exchange reactions and reactions involving alumino and alumino-silicate minerals (Moss and Edmunds, 1992; Kinniburgh and Edmunds, 1986). These reactions are much more complex, and much remains to be learnt about pH control in carbonate-free Triassic sandstone.

In problem 6 in Section 3, an example model of pH control by an alumino phase is incorporated in the PHREEQM simulation of the carbonate-poor West Midlands Triassic sandstone laboratory experiments. Given the lack of detailed work on the subject, it was not thought appropriate to investigate the very many possible reaction systems which could be involved. The example model involves Al release from exchange sites by displacement by leachate cations. Normally Al would be precipitated at the circum-neutral pHs often found when carbonates are present. However, in the absence of carbonate buffering, the released Al can be hydrolysed, and then precipitated as gibbsite, thus releasing H^+. This lowering of pH decreases alkalinity, thus increasing dissolved CO_2 content, and eventually initiates Al oxyhydroxide dissolution, This, still rather crude model, was able to reproduce the main features of the laboratory breakthrough curves. However, in a field case, CO_2 production from organic degradation might increase the importance of Al oxyhydroxide dissolution relative to the release of sorbed Al. In addition, H^+ exchange will play a role in many cases. Given the present state of knowledge of alumino, and alumino-silicate reactions in the Triassic sandstones, no single model can be proposed: however, PHREEQM is flexible enough to deal with many of the likely appropriate inorganic interactions.
Comparison of the breakthrough curves for the carbonate-containing Nottinghamshire sandstones (problems 1, 2, 3, 4, and 5, Section 3) with those for the carbonate-free West Midlands sandstones (problem 6) indicates the great importance of measuring $CaCO_3$% in the rock if predictions are to be made.
Buss et al. (1997) have proposed a semi-empirical model of the acid neutralising behaviour of carbonate-free Triassic sandstone which involves the use of a Langmuir-form H^+ exchange equation which appears to give satisfactory matches to titration curves. It is hoped to use this model and PHREEQE to investigate the process further.

4.3.7 Comparison of Processes Occurring in the Laboratory and Field

In general, the modelling work has confirmed the previous observations (Thornton et al., 1995) that the processes observed in the laboratory experiments are similar to those occurring the field. However, there are differences. In the laboratory, because of the lack of significant organic degradation and sulphate reduction, MnO_2/Fe reactions dominated the redox system. In the field, significant organic degradation and considerable reduction of sulphate resulted in MnO_2/Fe reactions being less important, but nevertheless still of relevance. Despite these differences, the laboratory results are still of use in indicating which types of reaction are to be considered in interpreting the field data, and in allowing various parameters to be estimated without the problems associated with poorly known boundary conditions so often encountered in field systems.
More laboratory experiments are needed, in particular, to allow study of the interactions of leachate and calcite-free Triassic sandstone.

Beyond this research stage, for routine investigation, if measurements of cation exchange capacity, calcite %, and MnO_2 content are available, there is little need to carry out column type experiments.

4.4 Limitations

4.4.1 Data Issues

There are two main types of issue associated with data availability:

(i) the data required as model inputs have not been measured; and
(ii) the data required for checking model predictions have not been measured.

(i) In this category are included porosity, density, mineralogy, CEC, selectivity coefficient, and other thermodyamic data. Usually porosity and density can be estimated from values in the literature (eg Lovelock, 1977; Campbell, 1982); porosity can also be estimated using Cl breakthrough curves, if any historical data exist (though care needs to be taken using this method as the interpreted value may be affected if the flow does not accord with the assumptions of the dispersive model being used). The minerals likely to be present in any quantity a sandstone sample are relatively few in number: however, for predictive modelling in the absence of historical data it is of particular importance to determine whether calcite is present (its presence or absence is usually clear from the breakthrough curves when historical data are available). The MnO_2 content is also important to measure, yet rarely has been in the past. A measure of CEC is relatively easy to obtain, and is an important parameter: default values can be estimated from Table 4.5 above. Selectivity coefficients are too difficult to measure routinely, and reliance will have to be placed on curve matching or using default values chosen from the data compilation provided in Section 4.3.3.2 (Table 4.1). Other thermodynamic data not included in the PHREEQE database (eg data on species not present in the standard model) need obtaining from the literature: this is not a straightforward task, as self-consistency of the constructed data set needs to be carefully checked. MINTEQA2 (Alison et al., 1990) has a large well tested data base; the code and data base are available from the US EPA.
(ii) Where models are being developed by testing against historical data, problems can arise where critical determinands have not been recorded. Apart from the major ions, pH, and all important contaminant species, it is important to record, if possible, Al content, E_H, TIC, and (even if only by olfactory detection) S^{2-}. Models become very much less well constrained when the latter determinands are not recorded. In all cases where data relating to a specific system are required, there will always be a problem in choosing representative values, given that in reality each property varies in space, and possibly in time also. Such variation may be reflected in data set

inconsistencies (eg in problem 7, Section 3). The greater the heterogeneity, the less certain the simulation. In such cases, sensitivity analysis is extremely important, and it may even become appropriate to set up more than one possible representation of the field system using the data available. A particular problem in heterogeneous systems is the effect of the sampling method: a pumped sample may mix waters of different origins, and the mixed water may be in disequilibrium despite its component waters all being in equilibrium in the aquifer. In addition, there are the usual problems of sampling protocols (eg, purging volumes and rates, sampler materials, sample treatment), variation in each of which will result in changing the chemical characteristics of the water sample: ideally, the sampling method should be modelled.

4.4.2 Model and Code Limitations

In the context of the present study, the main model limitations are:

(i) one dimensional flow only;
(ii) single porosity domain;
(iii) single values for porosity, dispersivity, and average linear velocity in the modelled region;
(iv) no organic species;
(v) few trace metals/metalloids;
(vi) no ability to represent several different redox states simultaneously;
(vii) no oxyhydroxide sorption models;
(viii) no isotopes;
(ix) the difficulty of representing varying input concentrations; and
(x) numerical instability.

Limitations (i) to (iii) mean the flow model is very simple: this is the basic cost for having a powerful geochemical model incorporated in a reactive transport code capable of being run on a standard PC. However, were the model to include dual porosity concepts, for example, it would be necessary to estimate the hydraulic and chemical parameters associated with the two parts of the system. Normally such data would be unavailable, and the final interpretations might be no more certain than they would have been using a single porosity model. Allowing a variable average linear velocity would impose very awkward constraints on the cell size and time step, given the mixing cell concept on which the model is based. Nevertheless, there are often situations where flow mechanisms, and hydraulic\geochemical correlations, will have a very profound effect on leachate migration, and it would be useful to have a tool capable of exploring various possibilities in such systems. This is an active research field (eg Arthur, in progress).
Limitations (iv) and (v) (limited thermodynamic data base) can be circumvented by inputting additional thermodynamic data, which PIP allows to be done easily. The main problem is then in making sure the data are "complete", and self-consistent (see Section 4.4).

Limitation (v) (only one redox state) is an area where much more research is necessary. However, it would be useful to be able to model a solution with more than one redox state.
Limitation (vii) (no oxyhydroxide sorption models) can be circumvented in some cases by manipulation of the exchange or precipitation capability of the model. It would be relatively easy to "hard-wire" in other sorption models.
Limitation (viii) (no isotope models) would rarely be a problem, and is some cases could be circumvented by definition of a new species.
In the case of landfill leachate migration modelling, the source term often changes with time (cf problem 7, Section 3) (limitation (ix)). This is difficult, though not impossible, to model, requiring as it does repeated entry and exits to and from the code, and a great deal of input file manipulation. With some relatively simple addition to file manipulation software, it would be possible to make such tasks much easier.
Limitation (x), numerical instability, is not often a problem. Given the very steep concentration gradients which often occur when changing redox potentials, even the most robust solvers will have some difficulties. Usually change of step size or manipulation of the KNOBS parameters using PIP allow the calculation to be completed.
In addition to these limitations, it would be convenient to have more flexibility in the choice of output. For example, only nine master species can be output to the spreadsheet file at any one time in the current version of PIP: however, this would appear to be a relatively easy problem to resolve.

4.5 Uses of PHREEQM in the Context of Landfill Leachate Migration in Triassic Sandstone and Other Aquifers

There are two general ways in which PHREEQM can be applied:

(i) to simulate historical data and then use the validated model in forecasting; and,
(ii) in absence of historical data, use models based on previous experience to explore possibilities at new sites.

Thus PHREEQM can be used in similar ways to a groundwater flow model. As in the case of groundwater flow modelling, prediction is difficult, and much of the benefit in the application of the model will come from the improved understanding it helps create. For predictions, multiple runs with varying input data, and even concepts, is to be advised, despite the time-consuming nature of the process. For mode (ii) operation, the default values given earlier in Section 4 can be used: it is hoped that as experience is gained from use of PHREEQM and from quantitative laboratory studies, the default values will become better defined, and sensitivity runs on routine modelling work will not need to be so extensive. As discussed in Section 4.3.7, it seems unnecessary, beyond the initial research stage, to undertake column type experiments: measurements of carbonate

%, CEC, and MnO_2 will suffice, at least for carbonate-containing sandstones.
The situations in which PHREEQM might be used to advantage in the context of landfill leachate include:

(i) interpreting the relatively few existing field data sets in order to determine the important processes and provide default values for geochemical properties;
(ii) interpretation of leaching test results and linking of interpreted values to field systems;
(iii) exploring possible impacts of leakage from unlined old sites (in this context it would probably be adequate to set up a series of standard cases);
(iv) exploring possible impacts of leakage through mineral liners into the Triassic sandstones (for information on leachate/mineral liner interaction, see Thornton et al., 1994); and
(v) to investigate whether a particular borehole water is being affected by leachate contamination.

In addition, there is a very wide range of possible uses of PHREEQM for other issues unrelated to landfill leachate, ranging from seawater intrusion through regional water quality variations to borehole corrosion/incrustation studies, sampling, and aquifer storage and recovery. The code is good at dealing with:

(i) ion exchange (eg NH_4);
(ii) specific redox systems (eg MnO_2 stripping from the aquifer);
(iii) the inorganic carbonate system.

It is less good at dealing with:

(i) flow systems more complex than one-dimensional dispersive;
(ii) organic contaminants (though these could be added relatively easily provided justifiable thermodynamic data could be found);
(iii) trace metals (though these could be added relatively easily, the main problem being in adequately taking account of organic-metal complexes, as the chemistry of such interactions are generally poorly understood (eg Stumm and Morgan, 1996, p 298 et seq.);
(iv) systems where multiple redox states are important.

The ability to allow NH_4 behaviour to be modelled using an ion exchange approach rather than the usual potentially very misleading partition coefficient approach is a major advantage. Points (ii) and (iii) are largely limitations in geochemical knowledge rather than model limitations: the code still represents one of the better ways of investigating metal migration problems.
The application to some of the other major UK aquifers will be more limited, given their more marked dual permeability nature.

5. CONCLUSION

PHREEQM is a verified code. The aim of the present study has been to evaluate it for application to landfill leachate migration problems in Triassic sandstone.

Laboratory experiment simulations: PHREEQM was found to be capable of reproducing inorganic species breakthrough curve data patterns from a series of laboratory experiments. A few "core" processes were involved for each of the carbonate-bearing Nottinghamshire sandstone systems studied: equilibration with calcite, ion exchange, and MnO_2 reduction by Fe^{2+}. Cation exchange capacity, calcite content, and MnO_2 content are relatively easy to measure: ion exchange selectivity coefficients are more difficult to measure, but were found to vary over relatively narrow ranges. There is good evidence that the Gaines-Thomas convention is adequate when simulating ion exchange. The carbonate-free sandstone from the West Midlands required a further set of (aluminium species) reactions to be incorporated in the simulation model. More basic research is needed on acid-base reactions in the absence of carbonates, and any shortcomings of the simulation model presented are not due to limitations in the code's aqueous model.
Field data simulations: PHREEQM was found capable of reproducing the inorganic species concentration depth profile patterns available for the Burntstump landfill site, Nottinghamshire. The processes identified in the laboratory experiments were found also to be important in the field. However, probably partly because of the longer time scales in the field system, more organic degradation and sulphate reduction occur, and Mn concentrations are controlled by rhodochrosite precipitation. An implication is that the laboratory experiments are a good but not complete guide to the behaviour in the field system. The field interpretation is less certain than the laboratory interpretations because of the uncertain boundary conditions, the inevitably less good data, and the approximations used when representing the effects of the organic species. The modelling work strongly suggests that it is important to measure aquifer carbonate content, cation exchange capacity, and MnO_2 content, and to measure groundwater total inorganic carbon and sulphide contents (in the absence of analytical data, even recording the olfactory detection of sulphide is of great use).
Performance of PHREEQM: In general, PHREEQM proved to be very flexible in simulating both laboratory and field systems, and enabled self-consistent interpretations to be developed. The main shortcomings in the code as it is presently set up appear to be in the inability to represent systems with multiple redox states, the fact that many species which might be useful in landfill leachate work are missing from the data base, and the simple flow system represented. In environmental systems, little is known of how different redox reactions are or are not coupled, and although a facility to represent redox disequilibrium would be useful, it would add to the code's

flexibility for reproducing observed concentrations without adding any more guiding constraints. Although many (inorganic and organic) species of interest are not currently incorporated in PHREEQM's data base, species can be easily added. Care will need to be taken when choosing which organic species to add, and in obtaining appropriate, self-consistent thermodynamic data especially for organic and inorganic/organic compounds. PHREEQM's flow model is very simple: for example, the effects of transverse dispersion, multiple permeability systems, separate gas phases, and changes in flow rate are difficult or effectively impossible to represent. In the case of the Burntstump site, flow to a first approximation is one dimensional, but lateral, saturated zone flow will sometimes be far from one dimensional. However, in the case of multiple permeability systems, the chemical and hydraulic data necessary to constrain a sophisticated hydraulic and chemical model will usually not be available.

Despite these comments, PHREEQM, even in its present form, is potentially a very useful code for many problems involving Triassic sandstone/groundwater interactions. The success in applying it to the Triassic sandstone suggests that it should also be applicable to the Greensand and Quaternary sand aquifers, but application to the Chalk and Jurassic limestone aquifers would require great care, not because of the chemical reactions involved, which will often be simpler to model than the less carbonate-rich systems of the arenaceous aquifers, but because of the more marked multiple permeability nature of the flow systems in these aquifers.

Application of PHREEQM: The code could be used to great effect in the context of landfill investigations: (a) in interpreting existing field data sets; (b) in interpreting leaching test results and linking them to field systems; (c) in undertaking risk assessments of the impacts of leakage from existing or planned sites; (d) in undertaking risk assessments of the impacts of leakage through mineral liners; (e) in assessing whether an existing borehole water is being affected by leachate. (c), in particular, could be carried out as a general exercise rather than as a site-specific assessment: a library of runs with different leachates and sandstone properties would indicate the range of potential impacts. Trial runs of a model would enable risks associated with metals and ammonium, in particular to be assessed. Predictions of pH would indicate the likelihood of degradation reactions, even if organic species had not been added to the code's data base. Perhaps one of the most important uses would be in predicting ammonium migration, since current approaches using partition coefficients can be highly misleading.

In addition, the PHREEQM package could be used in many other applications, from assessment of well incrustation to assessing chemical effects during aquifer storage and recovery (using its radial flow option).

There is a great potential for application of geochemical codes in risk assessment, and PHREEQM is one of the best yet available.

Further work: The project has suggested that there are some areas of basic chemical knowledge which are require further research if the package is to be used to its full potential: (a) the acid-buffering mechanisms of carbonate-free sandstones; (b) the role of particulates

in leachate chemistry, and the migration of particulates including bacteria; (c) organic degradation reactions, especially in low pH systems; (d) the contribution of organic/inorganic complexes to the mobility of inorganic species (including the effect on ion exchange); (e) the importance of multiple redox states; (f) the chemistry of oxyhydroxide/leachate interactions; and (g) the movement of gases through the unsaturated zone. Most of these objectives are of a fairly long term nature; in the interim, a great deal of useful work could be carried out using PHREEQM, and indeed such work will inevitably contribute to issues (a) to (g).

The study has also indicated that PHREEQM's applicability could be substantially extended by including a number of new chemical species in its data base. This is a relatively straightforward task, in principle, though care needs to be taken when deciding on the reactions and thermodynamic data to be added. A particular need is the incorporation of organics, "trace" metals, and metal/organic complexes. The output files could be modified/customised with advantage. In the longer term, the flow model could be made more sophisticated, though at some stage it becomes inefficient to continue with the basic mixing cell approach.

Finally, although PHREEQM might most frequently be applied to risk analysis on a case-by-case basis, there are some general cases which could be explored with advantage, and subsequently form a library of cases which could be referred to when undertaking first pass risk calculations.

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