

Geochemical Modelling – A Review of Current Capabilities and Future Directions

James Crawford
Department of Chemical Engineering and Technology
Division of Chemical Engineering
Royal Institute of Technology (KTH)
Stockholm

September 1999

SNV Report 262
Naturvårdsverket
Swedish Environmental Protection Agency
106 48 Stockholm, Sweden

ISSN xxxx-xxxx
ISRN SNV-R--262--SE

Stockholm 1999

SUMMARY

In the field of environmental protection, interest is increasingly being focused upon predicting how geochemical systems will evolve over long periods of time. Modelling and computer simulation is a valuable tool that can be used to gain a greater understanding of geochemical processes both to interpret laboratory experiments and field data as well as to make predictions of long term behaviour. In spite of its increasing application, geochemical modelling still remains the preserve of a limited group of specialists.

This review is intended as an introduction to researchers who would like to use geochemical modelling in their work, but have limited knowledge of currently available simulation programs. The review gives an overview of the current capabilities, strengths, weaknesses, and likely future trends in the field of geochemical modelling. It is also intended to be a general guide that explains the concepts and ideas behind these simulation tools without considering detailed technical issues. Although roughly 100 programs have been examined in this review, it does not contain a complete list of all geochemical simulation programs that are available. Many of those excluded have fallen into disuse with the advent of new, more powerful programs that address complex technical issues that were not effectively dealt with earlier. Others are experimental and have not yet reached a wider audience outside of the institutions where they were developed. Instead, attention has been focused upon those programs that have become the mainstay in the area of geochemical modelling and simulation – the programs that are most widely used and technically robust.

Although specific technical details have been avoided as much as possible, it has been necessary to include some discussion about the numerical methods that are frequently used in these programs. Models of coupled transport and geochemical reaction in groundwater are among the most difficult conceptual and mathematical problems known. There are no absolutely dependable means of finding solutions to these problems, and to omit such a discussion can easily lead to misrepresentation of technical capabilities.

CONTENTS

Introduction	1
Goals of Modelling	2
Geochemical Reaction Models	5
Conceptual and Mathematical Formulation	5
Numerical Solution Procedures	6
Uniqueness of Geochemical Model Predictions	7
Processes Simulated	7
Coupled Transport and Reaction Models	9
Conceptual and Mathematical Formulation	9
The Advection-Dispersion-Reaction (ADR) Equation	10
Numerical Solution Procedures	11
Finite Difference and Finite Element Techniques	11
Errors and Numerical Stability	12
Coupling of Transport and Geochemical Reaction Submodels	14
Processes Simulated	15
Reviews of Specific Geochemical Modelling Software	17
Geochemical Reaction Programs (Batch Systems)	18
Coupled Transport and Reaction Programs	20
Support Programs	26
Future Directions in Geochemical Modelling	30
Availability of Reviewed Modelling Software	34
Reviewed Simulation Programs	34
Reviewed Support Programs	37
General Sources of Public Domain Software	37
General Sources of Commercial Software	37
On-line Listings or Descriptions of Software	37
References	38

INTRODUCTION

The past three decades have seen an explosion in the number of simulation programs that are available for the modelling of both natural and man-made geochemical systems. This development has generally gone hand in hand with advances in numerical techniques for solving complex mathematical problems as well as improvements in the speed, calculation capability, and general accessibility of computers.

Although the concepts and ideas that are central to chemical modelling have evolved over a much longer period of time, geochemical modelling in its current form can be traced back to the early 1960's with the pioneering efforts of researchers such as Robert Garrels, Harold Helgesson, and Lars Gunnar Sillén (among others). Simulation programs were originally applied to the understanding of basic issues in aquatic chemistry, the very visible problems of surface water pollution, and the evaluation of diagenetic processes (i.e. involving the natural formation and alteration of rocks).

In recent years, however, these programs have been increasingly applied to the analysis of environmental problems involving groundwater. Growing awareness of potential environmental hazards caused by activities such as mining, geologic disposal of wastes, and chemical spillage have spawned an interest in the ability to anticipate pollution scenarios and design management strategies for the minimisation of environmental impact.

Owing to issues of complexity and the time scales involved, it is often not possible to conduct sufficiently realistic laboratory experiments to observe the long-term behaviour (beyond a few decades) of most geochemical systems. Geochemical models can be used, however, to both interpret and predict processes that may take place over time scales that are not directly achievable in experiments. From a design viewpoint, geochemical modelling can be applied to optimise remediation efforts, identify parameters of importance in groundwater systems, and to help design effective techniques to retard the release of environmentally hazardous substances to groundwater. Although by no means a substitute for experiment, modelling and computer simulation is a valuable predictive tool that can be used to bridge the gap between laboratory experiments, field observations, and the long-term behaviour of geochemical systems.

GOALS OF MODELLING

When attempting to model a geochemical system it is important to begin by clarifying the goals and expectations of the modelling effort. By starting with clearly defined goals, it is possible to focus upon key issues and begin identifying those processes that are likely to be controlling the behaviour of a geochemical system. In addition, the answers to these questions can give indications as to which modelling approach is most appropriate for the task at hand.

The goals of modelling may be roughly divided into four main categories of increasing sophistication:

Modelling Category	Typical questions to be answered
Scenario Analysis	- <i>Will reactive process be constrained by kinetic or transport considerations?</i> - <i>What is the maximum rate at which reactive buffering capacity can be depleted?</i> - <i>What are the bounding cases for the system in question?</i>
Data Interpretation (laboratory/field)	- <i>Are decreased downstream concentrations the result of degradation (mineralisation) or dilution?</i> - <i>What is the overall rate of a reactive process in the system?</i> - <i>Is local thermodynamic equilibrium a reasonable assumption?</i> - <i>Which reactive processes dominate contaminant transport (solubility, complexation, sorption, colloid transport, etc.)?</i>
Procedural Design	- <i>Can pollution problem be managed using passive systems?</i> - <i>What is the optimal well location/pumping rate for contaminant plume capture?</i>
Performance Assessment	- <i>At what rate will a contaminant reach the aquifer?</i>
And Risk Analysis	- <i>Will the site pose a significant pollution threat in the future?</i> - <i>How can we expect contamination levels to change over long periods of time?</i>

Generally speaking, the processes that operate in geochemical systems are very complex. Many of the features that characterise the hydrological and chemical properties of such systems are also subject to a great deal of variation at different

locations and times. Although it is possible to create geochemical models of almost arbitrary complexity, it is frequently counterproductive and unnecessary to do so. The choice of a simpler model incorporating fewer details may be advantageous as it will provide results that are more transparent and thereby more easily understood than a complex model.

Today, it is often the case that the speed of the computer is the limiting factor that is used to determine the appropriate level of complexity for a model rather than the modelling objective itself (Hunt and Zheng, 1999). The danger here lies in that less time is spent understanding the system being modelled as more time is required to manage data input, output, and visualisation. The blame for this is partly cultural in nature (the ingrained idea that “bigger is better” rather than “smaller is smarter”) and also due to the rigorous quality assurance requirements of regulatory authorities (goals that even highly sophisticated models have trouble living up to).

It is important to remember that a geochemical model is only truly useful as a predictive tool if the possibility exists for result validation. In reality, this is a goal that is largely unattainable owing to the complexity of natural systems, the inadequacy of field data, and uncertainty relating to how the system will change over time. A model is, more or less by definition, a simplification of reality and should always be treated as a powerful heuristic tool rather than a source of absolute truth. Notwithstanding this, however, deterministic models can enjoy some degree of predictive success if applied as sub-units within a larger stochastic framework where we can estimate the probability that a forecast may be judged to be true or false (Nordstrom, 1994). This stochastic approach is the heart of risk assessment.

If the level of required detail is uncertain from the outset, the most rational approach is to start with simple calculations and estimates (the so-called “back of the envelope” approach) and gradually add detail to the model as deemed appropriate. This allows the conceptual understanding of the system to mature gradually and this understanding then provides a basis for accepting or rejecting additional parameters and processes that may be of significance.

The skill in geochemical modelling often lies in the ability to identify those processes that are of primary importance and neglect those that are of only minor importance. These may vary considerably depending upon the geological and hydrological setting of the system. A typical, although somewhat trivial example would be the dilemma as to whether effort should be made to simulate a geochemical system in three dimensions (a very difficult undertaking) when a 1-dimensional simulation may be sufficient. In many systems, it can be shown that a 1-dimensional or 2-dimensional calculation is sufficiently accurate by appealing to arguments of symmetry. Moreover, the benefits of simulating a system in two or three dimensions are often outweighed by uncertainties introduced through parameters that cannot be sufficiently well characterised by field or laboratory data.

Some of the processes that may play an important role in the transport of contaminants are illustrated in figure 1 below:

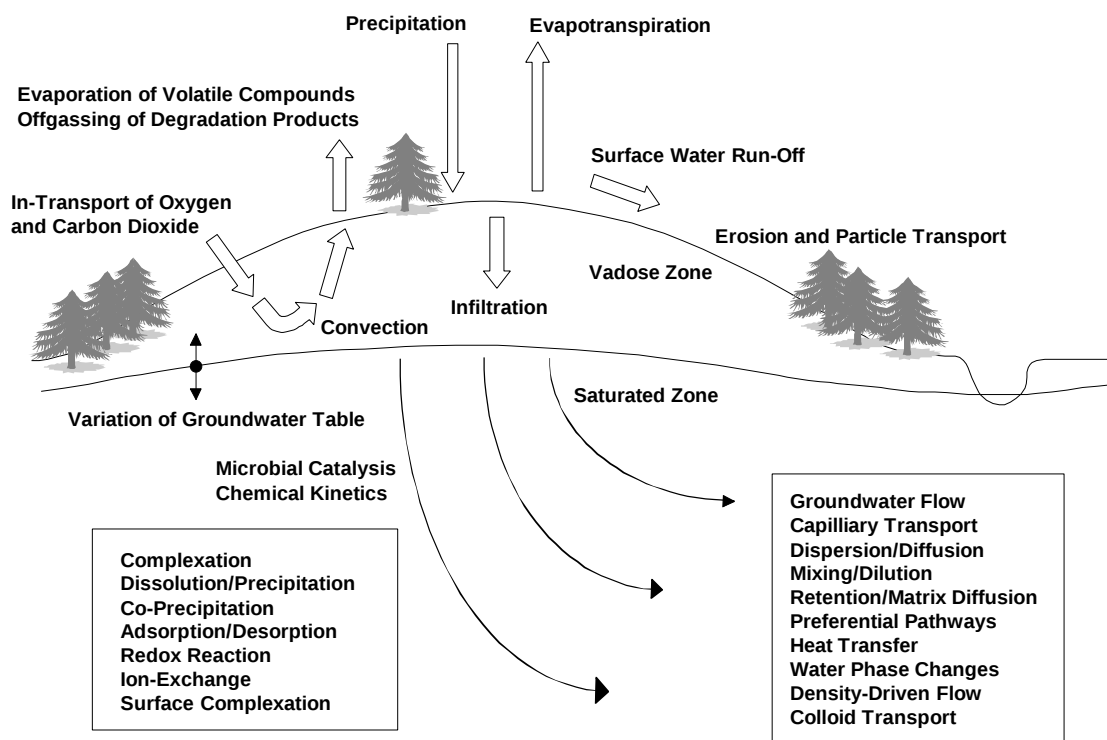


Figure 1 Conceptual diagram, illustrating processes that may be of importance in groundwater contamination problems (adapted from Höglund, 1994)

All geochemical models are based upon principles of mass conservation (mass balance accounting). Mass is neither created nor destroyed in the system, but transferred between solid, aqueous, and gaseous phases. These models can be generally sorted into two distinct categories, however, depending upon the extent to which they incorporate transport processes. Models that do not consider transport processes are referred to as **geochemical reaction models** or simply **batch models**. Models that consider both transport processes and geochemical reactions are referred to as **coupled transport and reaction models**. Both these program categories will be discussed in subsequent chapters.

Conceptual and Mathematical Formulation

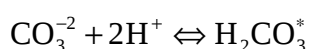
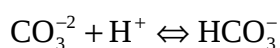
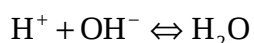
The conceptual formulation of geochemical reaction models is based upon analogy with a stirred tank reactor where the distribution of chemically reactive species is calculated for an aqueous solution. Although mathematically distinct from coupled transport and reaction models, geochemical reaction models are not conceptually decoupled from transport considerations and, indeed, they have been used extensively to evaluate the chemistry of groundwater systems where transport processes do play an important role.

An example of this is the seminal paper of Garrels and Mackenzie (1967) where calculations were performed to show that the composition of water in the ephemeral springs of the Sierra Nevada could be explained by the reaction of rainwater with plagioclase feldspar, biotite, and K-feldspar. This is a case of what is commonly referred to as ***inverse modelling***; attempting to establish reaction mechanisms that explain measured chemical changes that occur as water composition evolves along a flowpath.

The converse of this is ***forward modelling*** in which one attempts to calculate the composition of a water that results from specified reactive processes. Forward modelling is the type of modelling that is usually carried out in design studies and performance assessments. A typical example of forward modelling would be the calculation of the final water composition in an aquifer where infiltrating rainwater is allowed to equilibrate with calcite and dolomite (as might occur in a limestone aquifer).

A third type of conceptual model is also possible. This is referred to as ***reaction path modelling*** or ***mass transfer modelling***. Reaction path modelling is dynamic in the sense that it allows the simulation of how changes in water and mineral phase composition occur over time as defined primary minerals are dissolved in an incremental fashion. At each step in the calculation, the aqueous speciation is calculated and secondary minerals are dissolved or precipitated in order to maintain equilibrium. These models have been widely used to evaluate the chemical weathering processes that occur in natural systems (diagenetic processes). The gradual weathering of igneous rocks to produce clay minerals is a good example of a process where reaction path modelling may be useful. As these models consider the dissolution of primary minerals as a stepwise process, the variable of time is not included implicitly in the calculations. If there is kinetic data available, however, that can be used to relate reaction progress to time, the aqueous composition may be calculated as a function of time in a kinetic geochemical reaction model.

In all geochemical models, the reactions that describe the aqueous composition must be defined in terms of a set of **basis components**. The basis components are the minimum set of fundamental species that are required to describe all the free and derived species (complexes) present in the aqueous solution. If we consider a water containing dissolved carbonate, for example, the relevant aqueous species would be H_2O , H^+ , OH^- , CO_3^{-2} , HCO^- , and H_2CO_3^* . All these species could be described in terms of the set of basis components H_2O , H^+ , and CO_3^{-2} (i.e. all aqueous species can be assembled from combinations of the basis components). This is immediately apparent when we write out the stoichiometry of the individual reactions concerned:



The basis components do not need to be real species that exist in the solution, the only limitations being that they are mutually independent (i.e. they cannot be described in terms of combinations of each other) and that they provide a complete stoichiometric description of the system. The total component concentration is defined to equal to the concentration sum of all free and derived species in the solution for each component. The total carbonate concentration, for example, would then be equal to the concentration sum of CO_3^{-2} , HCO^- , and H_2CO_3^* in the previously described system.

Most geochemical reaction programs are based upon an approach in which the conservation of total component concentrations is combined with a description of chemical equilibrium. Chemical equilibrium may be computed in terms of Gibbs' free energy minimisation or in terms of mass action equations involving equilibrium constants. The method of Gibbs' free energy minimisation is generally regarded as being more mathematically robust than the method using equilibrium constants. Owing to the lack of reliable and internally consistent Gibbs' free energy data, however, geochemists have tended to favour the equilibrium constant method and the overwhelming majority of programs available today are therefore based upon this approach.

Numerical Solution Procedures

The mathematical formulation of the model described above (involving equilibrium constants) results in a system of non-linear algebraic equations that must be solved using a numerical method. Most programs use a modified Newton-Raphson technique to solve the equation system. The numerical solution procedure is fast and reliable in most cases. Being an iterative method, convergence problems may arise in the numerical Newton-Raphson method if the initial values of unknown variables are not sufficiently close to the equilibrium values. Most modern programs, however, incorporate heuristic methods to overcome this.

The other major problem that may arise occurs in systems containing multiple phases (i.e. containing gases or minerals as well as water) where the number of phases exceeds that allowed by the Gibbs' Phase Rule. This leads to a singular matrix in the mathematical formulation of the model and the program will fail to find a solution. Some programs incorporate optimisation routines to avoid some occurrences of singular matrices, but ultimately this and similar problems largely result from poorly composed or ill-conceived program input. Computer programs will generally fail to find a numerical solution for systems that are defined with inconsistent or physically unrealistic parameters.

Uniqueness of Geochemical Model Predictions

One poorly appreciated concern in the field of geochemical modelling that is worth mentioning is the question of uniqueness. It has been formally proven (Warga, 1963) that the numerical solution to the general multicomponent equilibrium problem is unique under conditions of ideality (i.e. dilute concentrations) when the problem is posed in terms of mass balance constraints only. This corresponds to the class of problem where the equilibrium speciation is to be calculated for a solution of known bulk composition. Quite often, however, geochemical modellers combine mass balance constraints (constraints on fluid bulk composition) with mass action constraints. Mass action constraints include fixed pH, pe, and individual species activity, as well as assumptions of gas and mineral equilibrium.

It has been shown that solutions to problems involving mixed mass balance and mass action constraints are not always unique even in thermodynamically ideal systems (Caram and Scriven, 1976; Othmer, 1976). There are occasionally multiple solutions that, although satisfying the problem equally well in a mathematical sense, are not necessarily physically realistic. The mathematical solutions that are not physically realistic are often referred to as ***metastable equilibria***. A computer program will not always converge to the most physically realistic solution and therefore some care needs to be exercised when interpreting simulation results.

Under conditions of non-ideality, the uniqueness proofs are also found to be invalid. In spite of this, for low to moderate ionic strengths activity relations are relatively linear and there have been no reports of metastable equilibria resulting from non-ideality (Bethke, 1992). This, however, does not constitute a proof and the question of uniqueness is somewhat unresolved, most particularly for highly concentrated solutions such as brines.

Processes Simulated

Most programs allow for the precipitation and dissolution of gases and minerals as well as the possibility of fixing the activity of specified components (the hydrogen ion activity, pH, for example). Reaction types that can be handled usually include complexation, ion-exchange, redox reaction, precipitation/dissolution, surface

complexation, and other kinds of adsorption. The major limitation is the quality and availability of thermodynamic data for carrying out reaction calculations. Many programs contain databases of relevant aqueous, gaseous, and mineral phase reactions and the more sophisticated programs can automatically select mineral or gaseous phases that are likely to precipitate and include them in the calculations. Some programs can be used to simulate titrations, evaporative processes, mixing of different solutions, or perform isotope mass balances. Mass balances based upon radiogenic isotopes are used primarily for estimating the age of groundwater (i.e. the time elapsed since it entered a groundwater system). Mass balances that consider stable isotopes are used to understand the source of a water, or processes that may have influenced the chemical properties of the water over time.

Activities of aqueous species are usually calculated using the Davies equation, the Debye-Hückel equation, or the extended Debye-Hückel equation. This approach limits the field of applicability for these models to solution ionic strengths less than or equal to that roughly corresponding to seawater (Parkhurst, 1995). Some programs can be used to simulate high ionic strength aqueous solutions such as brines, using the specific interaction approach proposed by Pitzer (1979). The Pitzer method for activity calculation, however, is weakened at the present time by a lack of reliable literature data, particularly for redox sensitive species.

An increasing number of programs allow the simulation of kinetically mediated processes. These programs generally require user input to define kinetic parameters and sometimes the kinetic reaction equations themselves. Like the Pitzer method for calculating aqueous phase activities, a noted problem is the lack of kinetic data in the literature for many important mineral reaction processes. Programs that simulate kinetically mediated reaction systems use different numerical methods than that described above for equilibrium systems. Such numerical methods are suited to the solution of mixed sets of non-linear algebraic equations and ordinary differential equations.

Conceptual and Mathematical Formulation

Coupled transport and reaction models differ from the geochemical reaction models described previously in that transport processes are included explicitly in the mathematical formulation of the model. These kinds of models have been gaining increasing popularity as attention is focused upon groundwater contamination problems that have resulted from acid rock drainage, waste landfill leachate, repositories for nuclear waste storage, accidental spills, and even agricultural fertilisers or pesticides.

Coupled transport and reaction models can be used to simulate how a geochemical system evolves over time along a fluid flowpath in one, two, or even three dimensions. Similarly to geochemical reaction models, coupled transport and reaction models are based upon the principle of mass conservation. Whereas the mathematical formulation of a geochemical reaction model generally regards a single control volume that is formally decoupled from flow considerations, coupled transport and reaction models discretise the flow medium into a network of interconnected control volumes. In one dimension, this is conceptually analogous to a sequence of mixed tank reactors connected in series as depicted in figure 2, below:

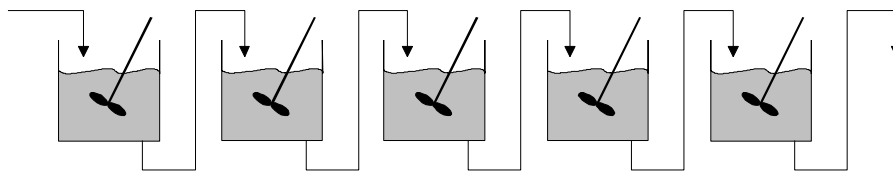


Figure 2 A one-dimensional coupled transport and reaction model shown by analogy as a sequence of interconnected, mixed tank reactors

Critical to the success of a coupled transport and reaction model is a detailed knowledge about the hydrology of the site to be modelled. Frequently it is not possible to obtain the necessary amount or quality of data to satisfactorily characterise the subsurface system for the purpose of a reliable predictive simulation. This problem arises largely from issues of heterogeneity. Heterogeneity in subsurface soils and rock manifests itself in the form of preferential flowpaths, fracture zones, regions of variable hydraulic conductivity and porosity (layered sedimentary rocks and soils), as well as stagnant zones (clay lenses and other flow-isolated porosities in the rock matrix). Hydraulic sources or sinks such as wells, drainage systems, and tree roots also contribute significantly to the heterogeneity of a system. Other artefacts that may impact the reliability of coupled transport and reaction models are the transient nature

of contaminant sources as well as variable boundary conditions relating to water infiltration rates, and hydraulic source or sink terms.

Well tests involving the pumping of water, or the injection and extraction of tracers are often used to obtain input data for models. Input data takes the form of parameters that are estimated directly from experimental measurements as well as parameters that must be estimated by **calibration**. Calibration involves the adjustment of important model parameters until the model is in agreement with measured field data. This is an example of **inverse modelling** in hydrology. A directly estimated parameter differs from a calibrated parameter in that it is obtained without the need to recursively use the simulation model to test its fitness.

There are often theoretical difficulties encountered when interpreting field data from well tests if the geology of the system is poorly characterised. Calibration is not always a guarantee that the model will be a realistic representation of a groundwater system and should therefore be used with care.

The Advection-Dispersion-Reaction (ADR) Equation

The advection-dispersion-reaction (ADR) equation is used most frequently to describe the mathematics of coupled transport and reaction processes. The ADR equation is based upon the assumption of transport within a homogeneous porous medium with a constant flow velocity. One of the conceptual problems associated with the ADR equation is that it assumes (and predicts) scale-independent dispersivity. In real groundwater systems, however, heterogeneities lead to dispersion characteristics that vary depending upon the scale of measurement. In addition to this, the flow field in a real system may vary considerably, depending upon local conditions of porosity and hydraulic conductivity in the medium. Some models, such as the channel network model (Moreno and Neretnieks, 1993), simulate fractured rock systems by assuming that transport occurs within a three-dimensional discrete network of channels rather than a porous medium.

In many cases, coupled transport and reaction models have developed as extensions to existing flow and transport models originally developed to study the hydrology of groundwater systems. Some of these programs have become enormously sophisticated and allow the simulation of very complex aquifer systems. Some also contain graphical user interfaces (GUI's) that allow the user to import geographical and topological data from scanned maps or CAD images to quickly generate complex input files. In the overwhelming majority of cases, however, the hydrological finesse of these programs significantly outweighs their ability to simulate geochemical processes.

Other programs have developed out of geochemical reaction models that have had transport capabilities subsequently incorporated. These programs have sophisticated geochemical simulation capabilities, but are less detailed or robust with regard to the

simulation of transport processes. There have been few programs that incorporate both a sophisticated treatment of hydrological transport processes as well as a rigorous and detailed geochemical reaction model.

Numerical Solution Procedures

Multicomponent, coupled transport and reaction models present enormous computational difficulties both in terms of numerical stability as well as the time required for the simulation of even relatively “simple” problems. The coupling of hydrologic transport and geochemical reaction processes in a mathematical model typically results in a mixed system of partial differential equations and non-linear algebraic equations. The partial differential equations are essentially non-steady state mass balances that relate time changes in the total concentrations of basis components to the hydrologic transport of the components in space. This mass balance includes all dissolved, sorbed, and precipitated species. The non-linear algebraic equations are mass action equations that define the equilibrium chemistry of the system. If kinetic processes are included in the model, some or all of the mass action equations are replaced by partial differential equations that describe the rate-limited transformation of species by chemical reaction.

There are many different ways of solving the coupled hydrologic transport and geochemical reaction equations. Except for some very simple cases, analytical solutions are not available for generalised, coupled transport and reaction problems. For this reason most solution procedures are based upon numerical methods. In order to shed light upon some of the problems and difficulties that simulation programs frequently encounter, it is necessary to consider some of the different approaches that can be used to obtain numerical solutions.

Finite Difference and Finite Element Techniques

The governing equations that must be solved in coupled transport and reaction models describe concentration changes (gradients) in both time and space and therefore contain both time- and space derivatives. The numerical procedures used to solve these equations are based upon techniques of discretisation and are usually finite difference- or finite element methods. In both cases this involves the generation of a **grid** or **mesh** of points (**nodes**) distributed throughout the spatial domain that is to be modelled. The distance between adjacent nodes is referred to as the **cell length**.

In finite difference methods, the fluid is only considered to exist at the nodal points within the grid. Spatial derivatives are then approximated as linear difference equations based upon the concentrations at neighbouring nodes. In finite element methods, on the other hand, the fluid is considered to occupy the regions between grid nodes and the concentrations in the fluid are represented by interpolating polynomials based upon the concentrations at neighbouring nodes. Spatial derivatives are then approximated as the derivatives of these interpolating functions. In both finite

difference and finite element methods, time derivatives are approximated as finite difference equations based upon a discretised time frame. The numerical solution to the unsteady-state problem is obtained by solving the spatially discretised equation system with an appropriate algorithm and then advancing the solution forwards in time using discrete *time steps*.

Finite element methods have become very popular in recent years as the discretisation mesh can be built up from non-rectangular polygons (triangles, for example). This is advantageous as it allows the simulation of unusual geometries in two- and three-dimensional space. The finite difference method, however, requires the discretisation mesh to be made up of rectangular polygons. This tends to limit the flexibility of the method in solving problems that contain non-rectangular geometries.

Errors and Numerical Stability

As both methods are based upon the approximation of real functions with discrete difference equations or interpolating functions, errors may arise in the numerical solution because of the resolution of the grid and the accuracy of the computer being used to perform the calculations. Errors that originate from grid resolution issues are generally referred to as **truncation errors** or **discretisation errors**. The errors that arise due to the accuracy of the computer being used to perform the calculations are called **rounding errors**. What is called the **stability** of the numerical method relates to whether these errors grow in magnitude (an unstable method) or converge to an acceptable limit (a stable method) in the arithmetic operations needed to solve the equations.

A stability constraint that limits the size of time step that can be taken in a coupled transport and reaction simulation is given by a non-dimensional parameter called the Courant number. The Courant number is defined as the product of advective flux and time step size divided by grid cell length. For the numerical solution to be stable, the time step size must be chosen so that the value of the Courant number is always less than 1. Essentially, this means that the fluid medium cannot be transported over a distance exceeding one grid cell in any given time step. This is one of the reasons why coupled transport and reaction programs often need to take very small time steps.

Both the finite difference and finite element methods encounter numerical problems when simulating systems where advection dominates over dispersion and diffusion. In this situation, the numerical solution can exhibit non-physical oscillations in the vicinity of a concentration front (i.e. where the concentration changes rapidly over a short distance). This problem tends to occur when a dimensionless number called the **grid Peclet** number exceeds a value of about 2. The grid Peclet number is defined as the product of grid cell length and advective flux divided by the dispersion/diffusion coefficient. This problem can be to some extent eliminated by increasing the grid resolution and thereby decreasing the cell length.

Increasing the grid resolution everywhere in the spatial domain is very computationally expensive and it is therefore expedient to increase the grid resolution only in those locations where sharp reaction fronts occur. As reaction fronts tend to migrate over time, this often requires special techniques of **front tracking** to be implemented so that the grid can be adapted as necessary to avoid the problem. A related problem that may occur in the vicinity of sharp reaction fronts in advectively dominated systems is that of **numerical dispersion** (sometimes called **numerical diffusion**). Numerical dispersion has the effect of smoothing out concentration profiles in a non-physical manner.

Different implementations of finite difference and finite element methods are susceptible to numerical oscillation and numerical dispersion to varying degrees. Most modern programs incorporate techniques to overcome these problems. Some of the more popular techniques used in current generation software are variations of what is called the **Eulerian-Lagrangian** approach. These and other techniques have been applied with varying degrees of success and are usually lumped together under the description “**high-resolution spatial schemes**”.

In systems where the dissolution and precipitation of minerals is disregarded, time step size restrictions are not a significant problem as only a moderate number of time steps (typically a few hundred to a few thousand) are usually required to simulate how the system will evolve over time. When dissolution and precipitation processes are considered, however, a program may need to take millions or sometimes billions of time steps to simulate even small changes in the spatial distribution of minerals in the flow system. The problem arises because minerals often have very low solubilities and therefore only small amounts can dissolve during the passage of a single pore volume of water through the system. Millions of pore volumes of water may need to be flushed through the system to completely dissolve a mineral and owing to the numerical stability requirements that limit time step size, this demands a large number of time steps. For even relatively simple systems, this results in prohibitively long computational times. This is one of the greatest problems encountered when coupled transport and reaction programs are used to simulate diagenetic processes over long time scales.

An approach called the **quasi-stationary state approximation** is attracting increasing attention due to its ability to side-step some of the restrictions governing time step size. The approximation is based upon the idea that the local accumulation of aqueous species in the water may be sometimes neglected when the quantities of minerals are very large in comparison to the quantities of dissolved species in the water. Neglecting the accumulation of aqueous species allows the evolution of mineral distribution in the system to be simulated as a sequence of punctuated steady states. This allows long time scales to be simulated efficiently with a greatly reduced number of time steps. There are only a few programs available that have the quasi-stationary state approximation directly incorporated in the code. Neretnieks et al. (1997),

however, have shown that it is relatively easy and straightforward to incorporate the quasi-stationary state approximation retrospectively in programs that have not been specifically designed for this.

Coupling of Transport and Geochemical Reaction Submodels

One of the biggest issues in the numerical solution of reactive transport problems is the problem of coupling the reaction and transport terms in the finite difference or finite element formulation of the system. There are a number of different methods by which the coupled transport and reaction problem can be solved. These are:

- Mixed differential-algebraic equation approach (DAE)
- Direct substitution approach (DSA)
- Sequential non-iterative approach (SNIA)
- Sequential iterative approach (SIA)

Although DAE and DSA methods listed above are the most intuitive methods for solving these kinds of problems, they are not widely used for 2- and 3-dimensional systems owing to their excessive RAM memory requirements. The SNIA approach is relatively easy to implement as it separates transport and chemical reaction processes, allowing them to be treated as separate modules in a program. In this technique, a single time step consists of a transport step followed by a separate reaction step using the transported concentrations. Using the physical analogy of series-coupled batch reactors (as depicted in figure 2), this is equivalent to decanting the contents of each reactor into its nearest downstream neighbour during the transport step and then recalculating the distribution of chemical species during the reaction step. By allowing a certain degree of back mixing to occur during the decantation process, both advection and dispersion may be simulated. Owing to its flexibility, this is a very popular method that is often used to extend geochemical reaction programs to enable the simulation of transport processes.

The SIA approach is similar in many respects to the SNIA approach except that iterations are performed between the transport and reaction modules. Both SNIA and SIA approaches are often described as being operator-splitting or time-splitting methods. The SIA approach is generally considered to be more conceptually robust than the SNIA approach although it is prone to convergence problems when simulating certain types of system.

Processes Simulated

Many of the models that are extensions of hydrological models consider purely homogeneous reaction systems. These models simulate only aqueous phase reactions and are often used to predict the spread and degradation of organic contaminant plumes from waste landfills. The degradation of organic contaminants is usually calculated using an instantaneous reaction approach or a Monod-type kinetic formulation that allows for reaction with multiple electron acceptors ($O_{2(aq)}$, NO_3^- , SO_4^{2-} , Fe(III), and Mn(IV), for example). Often, these models can also be used to model sequential decay chains (such as in radioactive decay) and simple adsorption processes. For certain simple chemical processes (e.g. linear adsorption and decay reactions) with specific boundary conditions and spatial geometries, analytical solutions may be available for coupled transport and reaction problems. Programs incorporating these analytical solutions are often useful for making scoping calculations for contaminant migration and they can be used to check the predictions of more complex numerical models.

Some programs have been developed that can simulate heterogeneous reaction systems. These models consider alterations that may occur in the distribution of minerals in the system under the influence of reactive transport processes. The mathematical formulation of models for heterogeneous reaction systems is much more complicated than that for homogeneous reaction systems as zones of dissolution and precipitation form and slowly advance. One of the problems associated with the simulation of heterogeneous reaction systems is the necessity to track the position of these mineral reaction fronts over time. The programs that simulate heterogeneous reaction systems can frequently simulate the entire suite of geochemical reactions that non-transport enabled geochemical reaction programs are capable of.

In general, it is difficult to accurately simulate kinetic processes involving heterogeneous reactions. Kinetic interactions with solid phase materials are usually quite strongly dependent upon the mineral surface area exposed to pore water as well as the residence time of water in the random pores and fractures that characterise most geological media. The exposed mineral surface area and the porosity of the medium changes during diagenesis as a result of the precipitation and dissolution of various minerals. The exposed surface area of some minerals may decrease as a result of the precipitation of other minerals that block their access to the pore water. This is a process referred to as **armouring**. Local changes in the porosity of the medium may give rise to preferential flowpaths. Owing to relationships between mineral surface area and porosity, the creation of preferential flowpaths can be self reinforcing and lead to the formation of **fingered** mineral alteration zones. These are processes that are virtually impossible to predict.

Fortunately, however, it is rarely necessary to know specific details about the formation of fingered zones and it is often sufficient to assume a relatively

homogeneous porous medium. Although one can often neglect small-scale heterogeneities, some information about mineral surface area is still required in order to estimate mineral reaction rates. Mineral dissolution and precipitation rates are frequently modelled using semi-empirical approaches such as the transition state theory (Lasaga, 1981; Aagaard and Helgeson, 1982).

REVIEWS OF SPECIFIC GEOCHEMICAL MODELLING SOFTWARE

There are many programs available both commercially and in the public domain for the simulation of geochemical reaction systems. Some of these programs are specifically designed for batch-type simulations, whilst others incorporate transport capabilities. Owing to the large number of programs that have been targeted for this review, it is not practical to give an individual and detailed description of each and every program. Instead, the programs have been organised into different categories and their capabilities compared in tabular form. Although roughly 100 programs have been reviewed, this is not intended to be a complete and exhaustive list of all geochemical modelling software. In fact, the total number of programs that are available for the simulation of geochemical processes in subsurface systems is likely to be significantly larger than this number.

Many programs have been omitted from the review because they have not been updated for some time and have since become superseded by other, more modern programs. Other programs have been neglected owing to sparsely available information, proprietary reasons, or because they don't appear to be very widely used. A great number of experimental programs have not yet reached a wider audience outside of the institutions where they were developed and therefore have not been reviewed here (with some specific exceptions). Programs that are used for the simulation of flow in groundwater systems, but do not contain geochemical reaction capabilities have also been largely disregarded. Some programs that are actually public domain have been listed as commercial software in the tables. This is because they are only available through commercial vendors who charge a distribution fee.

Information is given about which operating system the distributed software is compiled for. Most of the programs that do not incorporate graphical user interfaces (GUIs) are written in FORTRAN. As the source code is frequently distributed along with the program, it is possible to recompile the programs for other platforms that are not listed. In principle, this is also possible for programs that are written in C/C++. These programs are usually proprietary, however, and the source code is often not distributed along with the software.

Wherever possible the approximate cost of commercially available software is given as well as information about where the software can be obtained and if it can be downloaded directly via Internet. Most of the commercial software cannot be downloaded, although in some cases demo versions are freely available. It was possible to determine the technical capabilities of most public-domain programs by examining the software, user manuals, and test examples that could be downloaded from Internet. This was not always possible for commercial programs and product descriptions available from software vendors were heavily relied upon. In some cases

it was not possible to ascertain exactly if a program was capable of a certain technical feature owing to an incomplete product description, poor documentation, or exaggerated claims made by the vendor. In these cases, the indicated feature in the table has been labelled with a question mark.

Geochemical Reaction Programs (Batch Systems)

Table 1, on the following page gives information concerning programs that are primarily intended for the simulation of geochemical reaction processes in batch systems. The different programs have been compared on the basis of whether a listed feature is incorporated in the program or not. Features that are included in a given program are indicated by a cross symbol (×) in the table. If a program only partially incorporates a given feature, this was indicated with a circle symbol (o). As mentioned previously, if there was uncertainty concerning a program feature this was labelled with a question mark (?). The program features that have been scrutinised are:

Program Information

- *Operating system/computing platform the software is intended for*
- *Program status (public domain or commercial) and cost*
- *Availability over Internet*

Simulation Features

- *Forward modelling*
- *Inverse (geochemical) modelling*
- *Isotope balancing*
- *Reaction path modelling*
- *Mixing processes*
- *Kinetics*

Geochemical Modelling Features

- *Aqueous Complexation*
- *Precipitation/dissolution mass balancing*
- *Gas exchange mass balancing*
- *Redox reaction calculations*
- *Ion-exchange*
- *Simple, linear or non-linear adsorption processes*
- *Surface complexation*
- *Surface complexation with humic or fulvic substances*
- *DNAPL and LNAPL partitioning calculations*
- *Ability to fix species activity (e.g. pH)*

Species Activity Calculation Features

- *Davies model for aqueous species activity*
- *Debye-Hückel or extended Debye-Hückel model for aqueous species activity*
- *Pitzer aqueous species activity model*

General Features

- *Graphical User Interface (If a text-based interface for user input, this is indicated with a T symbol)*
- *Chemical reaction database*
- *Transport capability*

Table 1. Geochemical reaction programs (batch systems)

Program

Platform	Status / Approximate Cost	Internet Availability	Forward Modelling	Inverse Modelling	Isotope Balancing	Reaction Path (incl. titration)	Mixing Processes	Kinetics	Aqueous Complexation	Precipitation/Dissolution Mass Balancing	Gas Exchange Mass Balancing	Redox Reaction	Ion-Exchange	Simple Adsorption (linear / non-linear)	Surface Complexation	Surface Complexation (humic / fulvic)	(D/L)NAPL Partitioning Calculations	Fix Species Activity (e.g. pH)	Davies Activity Model	(Extended) Debye-Hückel Activity Model	Pitzer Activity Model	Graphical Interface	Chemical Reaction Database Included	Transport Capability
AquaChem	Win95/Win98/WinNT	commercial / \$690	no	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	1-A	
CHES	Win95/Win98/WinNT	free	yes	✓		o	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	FB	
ECOSAT	DOS	commercial / \$1200	no	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	?	?	?	?	✓	123-A	
EQ3/6	DOS/Unix	commercial / \$700	no	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	FB	
Geochemist's Workbench	Win95/Win98/WinNT	commercial / \$2800	no	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		
MINEQL+ (v 3.01)	DOS	free	yes	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		
MINEQL+ (v 4.0)	Win95/Win98/WinNT	commercial / \$500	demo	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		
MINTEQA2/PRODEFA2	DOS/Unix/VMS	free	yes	✓		o	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	T		
NETPATH	DOS/Unix	free	yes	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	T		
PHREEQC (v 1.6)	DOS/Unix/Mac	free	yes	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	1-A	
PHREEQC (v 2.0 Beta)	DOS/Linux/Unix	free	yes	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	1-AD	
PHREEQC for Windows	Win95/Win98/WinNT	free	yes	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	1-AD	
PHREEQCI	Win95/Win98/WinNT	free	yes	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	1-A	
PHRQPITZ	DOS/Unix	free	yes	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	T		
SteadyQL	DOS	commercial / \$200	no	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	FB	
WATEQ4F	DOS/Unix	free	yes	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	T		
WEB-PHREEQ	web-based (Java)	free	yes	✓			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		
WHAM	unspecified (Basic)	commercial / \$80	no	✓			✓	✓	✓	o	?	?	✓	✓	✓	✓	✓	?	?	?	?	?		

- ✓ program incorporates indicated capability
- o program partially incorporates indicated capability
- ? unknown capability
- T text-based user interface
- FB flow-through batch reactor simulations
- 1-A 1D advective transport simulations
- 1-AD 1D advective-dispersive transport simulations
- 123-A 1D, and symmetric 2D/3D advective-dispersive transport simulations

Coupled Transport and Reaction Programs

Tables 2a-b (free programs) and Tables 3a-b (commercial programs), on the following pages, give information concerning programs that are intended for the simulation of geochemical reaction processes in flow systems. As previously, the different programs have been compared on the basis of whether a listed feature is incorporated in the program or not. Features that are included in a given program are indicated by a cross symbol (×) in the table. If a program only partially incorporates a given feature, this was indicated with a circle symbol (o). If there was uncertainty concerning a program feature this was labelled with a question mark (?). The program features that have been scrutinised are:

Program Information

- *Operating system/computing platform the software is intended for*
- *Program status (public domain or commercial) and cost*
- *Availability over Internet*

Simulation Features

- *Advective transport*
- *Diffusion/dispersion*
- *1D, 2D, 3D transport simulations*
- *Saturated transport*
- *Unsaturated transport*
- *Gas transport*
- *Colloid transport*
- *DNAPL or LNAPL transport*
- *Heat transport*
- *Simple degradation or decay kinetics*
- *Monod kinetic processes*
- *General homogeneous reaction kinetics*
- *Heterogeneous reaction kinetics*
- *Mobile mineralisation fronts*
- *Unsteady state calculations*
- *Quasi-stationary state calculations*
- *Internal flow field calculation*
- *Dynamic boundary conditions*
- *Spatially variable material properties*

Geochemical Modelling Features

- *Aqueous Complexation*
- *Precipitation/dissolution mass balancing*
- *Gas exchange mass balancing*
- *Redox reaction calculations*
- *Ion-exchange*
- *Simple, linear or non-linear adsorption processes*
- *Surface complexation*
- *Surface complexation with humic or fulvic substances*
- *DNAPL and LNAPL partitioning calculations*

Species Activity Calculation Features

- *Davies model for aqueous species activity*
- *Debye-Hückel or extended Debye-Hückel model for aqueous species activity*
- *Pitzer aqueous species activity model*

General Features

- *Graphical User Interface (If a text-based interface for user input, this is indicated with a T symbol)*
- *Code adapted for multiprocessor computers*
- *Chemical reaction database*

Table 2a. Public-domain coupled transport and geochemical reaction programs

Program

	Platform	Status / Approximate Cost	Internet Availability	Advection	Diffusion / Dispersion	1-D / 2-D / 3-D Transport	Saturated Transport	Unsaturated Transport	Gas Transport	Colloid Transport	(D/L)NAPL Transport	Heat Transport	Simple Degradation / Decay Kinetics	Monod Kinetics	General Homogeneous Reaction Kinetics	Heterogeneous Reaction Kinetics	Mobile Mineralisation Fronts	Unsteady State Calculations	Quasi Stationary State Calculations	Internal Flow Field Calculation	Dynamic Boundary Conditions	Spatially Variable Material Properties	Aqueous Complexation	Precipitation/Dissolution Mass Balancing	Gas Exchange Mass Balancing	Redox Reaction	Ion-Exchange	Simple Adsorption (linear / non-linear)	Surface Complexation	Surface Complexation (humic / fulvic)	(D/L)NAPL Partitioning Calculations	Davies Activity Model	(Extended) Debye-Hückel Activity Model	Pitzer Activity Model	Graphical Interface	Multiprocessor Enabled Code	Chemical Reaction Database Included
2DFATMIC	DOS	free	yes	'	'	12	'	'					'	'							'	'			0		'										
3DFATMIC	DOS	free	yes	'	'	123	'	'					'	'							'	'			0		'										
BIOMOC	DOS	free	yes	'	'	12	'						'	'							'	'			0		'										
BIOPLUME II	DOS	free	yes	'	'	12	'						'	'							'	'	?		0		'										
BIOPLUME III	Win95/Win98/WinNT	free	yes	'	'	12	'						'	'							'	'			0		'										
BIOSCREEN	Win95/Win98/WinNT	free	yes	'	'	12	'						'	'							'	'			0		'										
CHEMFLO	DOS	free	yes	'	'	1	'						'								'	'															
CHEMFRONTS	Uncompiled Fortran Code	contact author	no	'	'	1	'														'	'															
FEHM	DOS/Linux/Unix	free (restricted)	no	'	'	123	'		'		'	'	'		'						'	'			0		'										
FLOTTRAN	Uncompiled Fortran Code	contact author	no	'	'	123	'		'		'	'	'		'						'	'											?	?			
HST3D	DOS/Unix	free	yes	'	'	123	'				'	'	'								'	'															
HydroBioGeoChem123	Win95/Win98/WinNT/Linux/Unix	free	yes	'	'	123	'				'	'	'	'	'	'	'	'	'		'	'		0		'											
MOC	DOS/Unix/Mac	free	yes	'	'	12	'						'								'	'															
MOC3D	DOS/Unix	free	yes	'	'	123	'						'								'	'															
MOFAT	DOS	free	yes	'	'	12	'	'	'		'										'	'															
MPATH	Uncompiled Fortran Code	contact author	no	'	'	1	'														'	'				?	?	?					?	?			?

' program incorporates indicated capability
0 program partially incorporates indicated capability
? unknown capability
T text-based user interface

Table 2b. Public-domain coupled transport and geochemical reaction programs (cont'd)

Program

MT3D
MT3DMS
MULTIFLO
OS3D/GIMRT
PESTAN
PHREEQC (v 1.6)
PHREEQC (v 2.0 Beta)
PHREEQC for Windows
PHREEQCI
RITZ
RT3D
SUTRA
TBC
UNSATCHEM
UNSATCHEM-2D
VLEACH
VS2DT

Platform	Status / Approximate Cost	Internet Availability	Advection	Diffusion / Dispersion	1-D / 2-D / 3-D Transport	Saturated Transport	Unsaturated Transport	Gas Transport	Colloid Transport	(D/L)NAPL Transport	Heat Transport	Simple Degradation / Decay Kinetics	Monod Kinetics	General Homogeneous Reaction Kinetics	Heterogeneous Reaction Kinetics	Mobile Mineralisation Fronts	Unsteady State Calculations	Quasi Stationary State Calculations	Internal Flow Field Calculation	Dynamic Boundary Conditions	Spatially Variable Material Properties	Aqueous Complexation	Precipitation/Dissolution Mass Balancing	Gas Exchange Mass Balancing	Redox Reaction	Ion-Exchange	Simple Adsorption (linear / non-linear)	Surface Complexation	Surface Complexation (humic / fulvic)	(D/L)NAPL Partitioning Calculations	Davies Activity Model	(Extended) Debye-Hückel Activity Model	Pitzer Activity Model	Graphical Interface	Multiprocessor Enabled Code	Chemical Reaction Database Included
DOS/Win95/Win98/WinNT	free	yes	✓	✓	123	✓						✓					✓			✓	✓			0		✓					✓	✓				
DOS/Win95/Win98/WinNT	free	yes	✓	✓	123	✓						✓					✓			✓	✓			0		✓										
Uncompiled Fortran Code	contact author	no	✓	?	?	✓	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?			?
Unix	contact author	no	✓	✓	123	✓											✓			✓	✓					?		✓				✓				
DOS	free	yes	✓	✓	1	✓						✓					✓			?												✓	✓			
DOS/Unix/Mac	free	yes	✓	✓	1	✓											✓															✓	✓			
DOS/Linux/Unix	free	yes	✓	✓	1	✓											✓															✓	✓			
Win95/Win98/WinNT	free	yes	✓	✓	1	✓											✓															✓	✓			
Win95/Win98/WinNT	free	yes	✓	✓	1	✓											✓															✓	✓			
DOS	free	yes	✓	✓	1	✓						✓					✓			?	?															
Win95/Win98/WinNT	free	yes	✓	✓	123	✓						✓					✓			✓	✓				0							✓				
DOS/Unix	free	yes	✓	✓	12	✓						✓					✓			✓	✓											✓	✓			
Uncompiled Fortran Code	free	yes	✓	✓	123	✓						✓					✓			✓	✓			0								✓	✓			
Win95/Win98/WinNT	free	yes	✓	✓	1	✓	✓	✓			✓						✓															✓	✓	✓	✓	
Win95/Win98/WinNT	free	yes	✓	✓	12	✓					✓						✓			✓	✓											✓	✓	✓	✓	
DOS/Unix	free	yes	✓	✓	1	✓	✓	✓									✓			?																
DOS/Unix	free	yes	✓	✓	12	✓	✓	✓				✓					✓			✓	✓															

✓ program incorporates indicated capability
0 program partially incorporates indicated capability
? unknown capability
T text-based user interface

Table 3a. Commercially available coupled transport and geochemical reaction programs

Program

Platform	Status / Approximate Cost	Internet Availability	Advection	Diffusion / Dispersion	1-D / 2-D / 3-D Transport	Saturated Transport	Unsaturated Transport	Gas Transport	Colloid Transport	(D/L)NAPL Transport	Heat Transport	Simple Degradation / Decay Kinetics	Monod Kinetics	General Homogeneous Reaction Kinetics	Heterogeneous Reaction Kinetics	Mobile Mineralisation Fronts	Unsteady State Calculations	Quasi Stationary State Calculations	Internal Flow Field Calculation	Dynamic Boundary Conditions	Spatially Variable Material Properties	Aqueous Complexation	Precipitation/Dissolution Mass Balancing	Gas Exchange Mass Balancing	Redox Reaction	Ion-Exchange	Simple Adsorption (linear / non-linear)	Surface Complexation	Surface Complexation (humic / fulvic)	(D/L)NAPL Partitioning Calculations	Davies Activity Model	(Extended) Debye-Hückel Activity Model	Pitzer Activity Model	Graphical Interface	Multiprocessor Enabled Code	Chemical Reaction Database Included
3DFEMFAT	Uncompiled Fortran Code	commercial / \$1050	no	'	123	'	'																													
ADE 3D	DOS	commercial / \$50	no	'	123	'	'																													
AIRFLOW-SVE	DOS	commercial / \$795	no	'	? 123	'	'																													
AQUA3D	Win95/Win98/WinNT	commercial / \$2000	demo	'	123	'																														
AquaChem	Win95/Win98/WinNT	commercial / \$690	yes	'	1	'																														
AT123D	Win95/Win98/WinNT	commercial / \$520	no	'	123	'																														
BIO1D	DOS	commercial / \$275	no	'	1	'																			0											
BIOF&T 2-D/3-D	Win95/Win98/WinNT	commercial / \$2300	no	'	123	'																			0											
BIOMOD 3-D	Win95/Win98/WinNT	commercial / \$765	no	'	123	'																			0											
ChemPath	Win95/Win98/WinNT	commercial / \$850	no	'	123	'																														
CHEQMATE	Uncompiled Fortran Code	commercial / \$????	no	'	1	'																														
CTAN/W	Win95/Win98/WinNT	commercial / \$2000	no	'	12	'																														
ECOSAT	DOS	commercial / \$1200	no	'	123	'																														
FEFLOW	Win95/Win98/WinNT/Unix	commercial / \$????	no	'	123	'																														
FLONET/TRANS	DOS	commercial / \$615	no	'	12	'																														
FLOWPATH II	Win95/Win98/WinNT/Unix	commercial / \$615	demo	'	12	'																														
FRAC3DVS	DOS	commercial / \$3000	no	'	123	'																														
GCT	Unix (Intel Paragon Supercomputer)	under development	no	'	123	'		?	?		?	?	?					?	?					?			?		?		?	?	?			?
HPS	DOS	commercial / \$50	no	'	123	'																													T	
HST3D-GUI	Win95/Win98/WinNT	commercial / \$1825	no	'	123	'																														
HYDROGEOCHEM	Uncompiled Fortran Code	commercial / \$1575	no	'	123	'																		0												
HYDROGEOCHEM2	Uncompiled Fortran Code	commercial / \$5150	no	'	123	'																		0												

' program incorporates indicated capability
 0 program partially incorporates indicated capability
 ? unknown
 T text-based user interface

Table 3b. Commercially available coupled transport and geochemical reaction programs (cont'd)

Program	Platform	Status / Approximate Cost	Internet Availability	Advection	Diffusion / Dispersion	1-D / 2-D / 3-D Transport	Saturated Transport	Unsaturated Transport	Gas Transport	Colloid Transport	(D/L)NAPL Transport	Heat Transport	Simple Degradation / Decay Kinetics	Monod Kinetics	General Homogeneous Reaction Kinetics	Heterogeneous Reaction Kinetics	Mobile Mineralisation Fronts	Unsteady State Calculations	Quasi Stationary State Calculations	Internal Flow Field Calculation	Dynamic Boundary Conditions	Spatially Variable Material Properties	Aqueous Complexation	Precipitation/Dissolution Mass Balancing	Gas Exchange Mass Balancing	Redox Reaction	Ion-Exchange	Simple Adsorption (linear / non-linear)	Surface Complexation	Surface Complexation (humic / fulvic)	(D/L)NAPL Partitioning Calculations	Davies Activity Model	(Extended) Debye-Hückel Activity Model	Pitzer Activity Model	Graphical Interface	Multiprocessor Enabled Code	Chemical Reaction Database Included	
HYDRUS	Win95/Win98/WinNT	commercial / \$50	no	✓	✓	1	✓	✓				✓	✓			✓	✓	✓	✓	✓	?		?				✓											
HYDRUS 2D	Win95/Win98/WinNT	commercial / \$1200	no	✓	✓	12	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	✓						✓								✓			
KYSPILL	DOS	commercial / \$545	no	✓	✓	123	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	✓							✓							✓			
MARS 2-D/3-D	Win95/Win98/WinNT	commercial / \$2982	no	✓	✓	123	✓	✓			✓	✓	✓		✓	✓	✓	✓	✓	✓	✓							✓				✓			✓			
MIGRATEv9	DOS	commercial / \$1700	demo	✓	✓	12	✓	✓				✓	✓		✓	✓	✓	✓	✓	?	✓						✓								✓			
MOC (MOCINP/MOCGRAF)	DOS	commercial / \$1700	no	✓	✓	12	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	✓					✓	✓								✓			
MODFLOW-SURFACT	Win95/Win98/WinNT	commercial / \$1435	no	✓	✓	123	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	?	✓					✓								✓			
MODFLOWT	DOS	commercial / \$775	demo	✓	✓	123	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	✓						✓								✓			
MOFAT for Windows	Win95/Win98/WinNT	commercial / \$545	no	✓	✓	12	✓	✓	✓		✓	✓	✓		✓	✓	✓	✓	✓	✓	✓						✓								✓			
MS-VMS	Win95/Win98/WinNT	commercial / \$4350	no	✓	✓	123	✓	✓	✓		✓	✓		?		✓	✓	✓	✓	✓	?	✓			0		✓					✓				✓		
MT3D99	DOS	commercial / \$725	no	✓	✓	123	✓					✓	✓		✓	✓	✓	✓	✓	✓	?	✓			0		✓									✓		
MULAT	DOS	commercial / \$500	no	✓	✓	123	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	?	?					✓								T			
PHREEQM-2D	DOS	commercial / \$1200	no	✓	✓	12	✓	✓				✓	✓		0	✓	✓	✓	✓	✓	?	?	✓	✓	✓	?	?	✓			✓	✓		✓			✓	
PLUME	DOS	commercial / \$50	no	✓	✓	123	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	?	?																
POLLUTE	DOS	commercial / \$1570	demo	✓	✓	1	✓	✓				✓		?		✓	✓	?	✓	✓	?	✓			0		✓									✓		
RAND3D	DOS	commercial / \$250	no	✓	✓	123	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	✓	✓					✓											
SESOIL	Win95/Win98/WinNT	commercial / \$900	no	✓	✓	1	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	0	✓			✓								✓			
SOLUTE	DOS	commercial / \$150	no	✓	✓	123	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	?	?					✓									✓		
SOLUTRANS	Win95/Win98/WinNT	commercial / \$385	demo	✓	✓	123						✓	✓		✓	✓	✓	✓	✓	✓	?	?					✓								✓			
SWICHA	DOS	commercial / \$120	no	✓	✓	123	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	?	?					✓											
SWIFT-98	Uncompiled Fortran Code	commercial / \$425	no	✓	✓	123						✓	✓		✓	✓	✓	✓	✓	✓	?	✓					✓									✓		
VAM2D	DOS	commercial / \$1800	no	✓	✓	12	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	?	✓					✓									✓		
WinTran	Win95/Win98/WinNT	commercial / \$580	demo	✓	✓	12	✓	✓				✓	✓		✓	✓	✓	✓	✓	✓	✓	✓					✓									✓		

✓ program incorporates indicated capability
0 program partially incorporates indicated capability
? unknown
T text-based user interface

Support Programs

Many of the programs that have been reviewed in the previous tables do not have a graphical user interface (GUI), or built-in functions for pre- and post-processing of simulation data. It is often very tedious and time-consuming to create input files for groundwater simulation programs. This is particularly true for 3D models that contain unusual geometries, many source and sink terms, or spatially variable material properties. In order to make the task of input file generation and output data visualisation more efficient and user friendly, a number of programs have been developed specifically for this purpose. These programs frequently support a number of different models as sub-components in a complete modelling environment that allows the user to rapidly create input files using graphical tools and to manipulate output data to produce presentation quality graphics.

Many of these programs have functions that allow the user to load a scanned or vectorised image (i.e. CAD-drawing) of a site and automatically generate finite difference or finite element meshes for the simulation. Sources, sinks, and other boundary features can then be easily incorporated in the simulation model using “point and click” mouse techniques. The programs often have functions that allow the user to import borehole data and other information that is required for the model. Post-processing tools typically include a range of 3D visualisation tools sometimes with animation possibilities.

These programs are briefly described in the following section. Note that certain supported programs that are mentioned in the following list (MODFLOW and MODPATH, for example) have not been reviewed in the previous tables, as they do not contain coupled transport and reaction simulation capabilities. Most of these programs are flow models or particle tracking models.

Argus ONE (Open Numerical Environments)

Platform:	Win95/Win98/WinNT
Status/Cost:	commercial / \$500 – \$1600 (depends upon chosen options)
Internet Availability:	demo version can be downloaded
Description:	Argus ONE is a generic environment for numerical modelling of problems in continuum mechanics. “Plug-In Extensions” (PIEs) are available that add functionality to Argus ONE for a given numerical simulation program. PIEs are available for the following programs: MODFLOW, MT3D, MOC3D, SUTRA, HST3D, NAPL, PTC, MODOFC

GMS (Groundwater Modelling System)

Platform:	Win95/Win98/WinNT/Unix
Status/Cost:	commercial / \$3250 – \$6000 (depends upon chosen options)
Internet Availability:	demo version can be downloaded
Description:	Complete modelling environment for groundwater flow and contaminant migration simulations. Originally developed by the Environmental Research Laboratory of Brigham Young University in cooperation with the US department of defence (DoD). The program supports the following programs as sub-modules: MODFLOW, MODPATH, MT3D, FEMWATER, SEEP2D, RT3D

Groundwater Vistas

Platform:	Win95/Win98/WinNT
Status/Cost:	commercial / \$850
Internet Availability:	demo version can be downloaded
Description:	Complete modelling environment for groundwater flow and contaminant migration simulations. The program supports the following programs as sub-modules: MODFLOW, MODPATH, MT3D, PATH3D, MODFLOWT, MODFLOW-SURFACT

ModelCad for Windows

Platform:	Win95/Win98/WinNT
Status/Cost:	commercial / \$500
Internet Availability:	demo version can be downloaded
Description:	Complete modelling environment for groundwater flow and contaminant migration simulations. The program supports the following programs as sub-modules: MODFLOW, MODPATH, PATH3D, MT3D, MT3D96, MODFLOWT

ModIME (Integrated Modelling Environment)

Platform:	DOS
Status/Cost:	commercial / \$385 – \$1045 (depends upon chosen options)
Internet Availability:	no demo version / cannot be downloaded
Description:	Complete modelling environment for groundwater flow and contaminant migration simulations. The program supports the following programs as sub-modules: MODFLOW, PATH3D, MT3D

PMWIN (Processing MODFLOW for Windows)

Platform:	Win95/Win98/WinNT
Status/Cost:	commercial / \$1025
Internet Availability:	demo version can be downloaded
Description:	Complete modelling environment for groundwater flow and contaminant migration simulations. The program supports the following programs as sub-modules: MODFLOW, MODPATH, PMPATH, MT3D, MT3DMS, MT3D96, PEST, UCODE

Visual Groundwater

Platform:	Win95/Win98/WinNT
Status/Cost:	commercial / \$1715
Internet Availability:	no demo version / cannot be downloaded
Description:	3D visualisation program for groundwater data. The program supports importation of visual MODFLOW input and output data files for graphical display.

Visual MODFLOW

Platform:	Win95/Win98/WinNT
Status/Cost:	commercial / \$1015
Internet Availability:	demo version can be downloaded
Description:	Graphical User Interface for the preparation of input files for the MODFLOW, MODPATH, MT3DMS, and RT3D simulation programs

WHI UnSat Suite

Platform:	Win95/Win98/WinNT
Status/Cost:	commercial / \$1115
Internet Availability:	no demo version / cannot be downloaded
Description:	Complete modelling environment for 1D groundwater flow and contaminant migration simulations. The program supports the following programs as sub-modules: VLEACH, PESTAN, VS2DT, HELP

FUTURE DIRECTIONS IN GEOCHEMICAL MODELLING

Today the environmental scientist has a very large array of programs to choose from that can be used for the simulation of groundwater flow and contaminant transport problems. One of the reasons for the great multiplicity of such programs is the fact that it is an almost impossible task to create a generalised model that incorporates all possible physical and geochemical processes. In many cases, programs have been developed with specific applications in mind and thus they incorporate only those features of greatest significance in the system being studied. Another significant problem is the general inadequacy of numerical methods that are needed to solve coupled transport and reaction problems. This manifests itself in the form of numerical instabilities that can cause a program to fail, non-physical artefacts such as oscillation and numerical dispersion, as well as problems relating to time step size and moving reaction fronts.

Coupled transport and reaction programs that incorporate a rigorous treatment of multiphase transport and aqueous chemistry are among the most difficult problems to solve in the realms of modern science. It is by no means a surprise that we are still a long way off from being able to simulate all processes that are likely to occur in a geological system. To illustrate the trends that are likely to have a significant impact on the field of geochemical modelling in the near future, it is instructive to examine some of the experimental codes that are currently under development.

Perhaps the most ambitious project to date is that involving the partnership in computational sciences consortium (PICS) supported by the US Department of Energy (DoE). This consortium includes the Brookhaven National Laboratory (BNL), Oak Ridge national Laboratory (ORNL), University of Texas at Austin, Rice University, State University of New York at Stony Brook, Texas A&M University, University of South Carolina, and Princeton University. The work being carried out is one of nine “Grand Challenge” projects sponsored by the DoE that aim to use high performance computing systems to make fundamental advances in the natural sciences. The intention of the PICS groundwater remediation project is to create a computer code that can be used to explore groundwater problems involving multiphase transport and geochemical reactions.

Owing to the computationally intense character of such problems, the focus is upon the development of new numerical methods as well as codes that take full advantage of the massively parallel architecture of the newer generation of supercomputers (such as the Intel Paragon that contains several thousand Pentium Pro processors). With the aid of an extensive field study programme, considerable effort is also being made to address the ever-present problems of input data uncertainty and interpretation.

Although the GCT code being developed is currently beyond the grasp of most groundwater modellers, many of the ideas and concepts being developed within this and similar multi-disciplinary programmes will filter down to desktop computing applications in due time.

One of the more sophisticated computer programs that has already found a wider audience is the HydroBioGeochem123D (HBGC123D) program developed at the Oak Ridge national Laboratory (ORNL) in co-operation with Pennsylvania University. This program incorporates a rigorous geochemical model in a three dimensional solute transport code. Although this program is one of the more complex programs that are freely available, it is still incapable of simulating multiphase transport of non-aqueous phase liquids (NAPLs) or gas. In addition to this, the flow field must be calculated using an external program such as MODFLOW.

The FLOTRAN program developed at the Los Alamos National Laboratory (LANL) is another example of an experimental code that incorporates rigorous geochemistry in a three-dimensional transport model. This program calculates the flow field internally, considers gas transport, and also includes an equation of state model for water (to predict vaporisation). Another feature that is not available in most other programs is the ability to couple changes in porosity and permeability with alterations in mineral distribution that occur over time.

A program that is notable owing to features that are not present in other codes is the FEHM program. Although this program only contains rudimentary geochemical reaction capabilities, it does contain an equation of state model for water that can handle both vaporisation and ice formation. This program was also developed at Los Alamos National Laboratory (LANL), but may not be distributed outside of the US.

The hydrological features of most programs have reached a reasonably high level of sophistication with regard to their ability to model complex three-dimensional geometries, dynamic boundary conditions, and both saturated and unsaturated transport of water. Many of the programs also have features that enable the simulation of density driven flow such as NAPL transport or saltwater intrusion. At the present time, however, there are only a handful of programs that can simulate systems where heat transfer or gas transport is important. There are no programs amongst those that have been reviewed that have the capability of coupling heat transfer processes with reactive geochemistry and gas convection. Future developments in this direction may be stimulated by the need to anticipate the self-ignition of heaps of coal, forestry material, or mixed organic-pyritic (shale) waste materials. Gas and heat transport in these systems is strongly influenced by reactive processes. In the current generation of software, saturated-unsaturated transport is typically modelled using the Darcy or Richard's equation. If gas or heat transport processes are to be included, more sophisticated approaches are needed that consider water phase changes, temperature

dependent changes in properties such as viscosity, as well as coupling between hydrostatic stress, porosity, and the permeability of the geologic matrix being studied.

Issues of heterogeneity are still largely dealt with in a semi-empirical fashion in most programs and there is great room for improvement in this area. Future developments here will almost certainly involve the incorporation of stochastic methods within deterministic models. This is an idea that is beginning to gain popularity amongst environmental scientists. There are also large conceptual problems relating to how heterogeneity is dealt with in the current generation of models. If models are to consider both the transport and reaction of mobile phases as well as transport and reaction within the geological matrix itself (the diffusion of substances into lumps and aggregates, for example), the system is typically described by a conceptual formulation in more than three spatial dimensions.

There are some programs that accommodate complex geochemical models, although most of these suffer from a lack of hydrological sophistication. Only very few of these programs incorporate the quasi-stationary state approximation that allows the simulation of the long time scales characteristic of diagenetic processes. Many of the difficulties encountered in complex coupled transport and reaction programs relate to imperfect numerical methods and the computing power that is required to perform the simulations. Even with the fast desktop computers that are currently available, it is entirely inappropriate to attempt the simulation of complex three-dimensional systems with detailed geochemical descriptions. These kinds of simulations are, and will remain for the foreseeable future, supercomputing applications.

At present there is a very noticeable lack of basic and internally consistent data for the calculation of aqueous phase activities in concentrated aqueous solutions (such as brines) that are commonly encountered in leaching systems. Similarly, there are still fundamental gaps in our knowledge concerning humic and fulvic complexation, heterogeneous reaction kinetics, and relationships between the changes in porosity and permeability that result from diagenetic processes.

Even when it is possible to have a complete description of geochemical processes in a model, the results obtained are very often influenced strongly by the way in which the modelling “question” is posed and how the system is defined. This modeller’s influence was clearly illustrated in a recent study sponsored by the Swedish Nuclear Fuel Inspectorate (SKI) where a number of researchers were asked independently to provide estimates of plutonium solubility under a given set of conditions (Emrén et al., 1999). The results demonstrated that the use of different modelling approaches (and different modellers) typically resulted in a spread of results covering several orders of magnitude.

Perhaps the most serious gap in our knowledge concerning the modelling of reactive flow systems results from our inability to validate either the conceptual or numerical

models that are proposed. As discussed in previous chapters, advancements in our ability to model complex systems does not necessarily result in predictive results of higher quality. The degree of model complexity should always be weighed up against the modelling objectives and the ability to “validate” the predictions and obtain input data for the model. A complex model, although useful as a testing ground for new ideas, is of little practical value if there is no way of checking the applicability of the results.

AVAILABILITY OF REVIEWED MODELLING SOFTWARE

Reviewed Simulation Programs:

2DFATMIC	http://www.epa.gov/ada/2dfatmic.html
3DFATMIC	http://www.epa.gov/ada/3dfatmic.html
3DFEMFAT	http://www.scisoftware.com/products/3dfemfat_overview/3dfemfat_overview.html
ADE 3D	http://www.mines.edu/research/igwmc/software/igwmcsoft/
AIRFLOW-SVE	http://www.flowpath.com/Software/AIRSVE/airflow.html
AQUA3D	http://www.scisoftware.com/products/aqua3d_overview/aqua3d_overview.html
AquaChem	http://www.rockware.com/catalog/pages/aquachem.html
AT123D	http://www.scisoftware.com/products/at123d_overview/at123d_overview.html
BIO1D	http://www.scisoftware.com/products/bio1d_overview/bio1d_overview.html
BIOF&T 2-D/3-D	http://www.scisoftware.com/products/bioft_overview/bioft_overview.html
BIOMOC	http://water.usgs.gov/software/biomoc.html
BIOMOD 3-D	http://www.scisoftware.com/products/biomod_overview/biomod_overview.html
BIOPLUME II	http://www.epa.gov/ada/bioplume.html
BIOPLUME III	http://www.epa.gov/ada/bioplume3.html
BIOSCREEN	http://www.epa.gov/ada/bioscreen.html
CHEMFLO	http://www.epa.gov/ada/chemflo.html
CHEMFRONTS	Contact: Luis Moreno, Dept. of Chemical Engineering (KAT), Royal Inst. of Technology (KTH), S-100 44 Stockholm, SWEDEN, (lm@ket.kth.se)
ChemPath	http://www.scisoftware.com/products/chempath_overview/chempath_overview.html
CHEQMATE	Contact: Ian Cox, AEA Technology plc, 424.4 Harwell, Didcot, OXON OX11 0RA, UK, (gw.support@aeat.co.uk)
CHESS	http://www.cig.enscm.fr/~vanderlee/chess/
CTRW	http://www.scisoftware.com/products/ctranw_overview/ctranw_overview.html
ECOSAT	http://www.benp.wau.nl/ecosat/ecosat_product_info.htm
EQ3/6	http://www.ep.es.llnl.gov/www-ep/esd/geochem/eq36.html (program description only)
FEFLOW	http://www.scisoftware.com/products/feflow_overview/feflow_overview.html
FEHM	http://www.ees.lanl.gov/EES5/fehm/
FLONET/TRANS	http://www.scisoftware.com/products/flonet_overview/flonet_overview.html
FLOTRAN	Contact: Peter C. Lichtner, LANL EES-5; MS F649, Los Alamos National Laboratory, Los Alamos, NM 87545, USA, (lichtner@lanl.gov)
FLOWPATH II	http://www.scisoftware.com/products/flowpath_overview/flowpath_overview.html
FRAC3DVS	http://www.flowpath.com/Software/Others/frac3d.html
GCT	http://www.isc.tamu.edu/PICS/ (program description only)

Geochemist's Workbench	http://www.rockware.com/catalog/pages/gwb.html	
HPS	http://www.mines.edu/research/igwmc/software/igwmcsoft/	
HST3D	http://water.usgs.gov/software/hst3d.html	
HST3D-GUI	http://www.scisoftware.com/products/hst3d_overview/hst3d_overview.html	
HydroBioGeoChem123	http://hbgc.esd.ornl.gov/main.shtml	
HYDROGEOCHEM	http://www.scisoftware.com/products/hydrogeochem_overview/hydrogeochem_overview.html	
HYDROGEOCHEM2	http://www.scisoftware.com/products/hydrogeochem_2_overview/hydrogeochem_2_overview.html	
HYDRUS	http://www.mines.edu/research/igwmc/software/igwmcsoft/	
HYDRUS 2D	http://www.mines.edu/research/igwmc/software/igwmcsoft/	
KYSPILL	http://www.scisoftware.com/products/kyspill_overview/kyspill_overview.html	
MARS 2-D/3-D	http://www.scisoftware.com/products/mars_overview/mars_overview.html	
MIGRATEv9	http://www.scisoftware.com/products/migratev9_overview/migratev9_overview.html	
MINEQL+ (v 3.01)	http://www.mineql.com/	
MINEQL+ (v 4.0)	http://www.mineql.com/	
MINTEQA2/PRODEFA2	ftp://ftp.epa.gov/epa_ceam/wwwhtml/products.htm	
MOC	http://water.usgs.gov/software/moc.html	
MOC (MOCINP/MOCGRAF)	http://www.scisoftware.com/products/moc_overview/moc_overview.html	
MOC3D	http://water.usgs.gov/software/moc3d.html	
MODFLOW-SURFACT	http://www.scisoftware.com/products/modflow_surfact_overview/modflow_surfact_overview.html	
MODFLOWT	http://www.scisoftware.com/products/modflowt_overview/modflowt_overview.html	
MOFAT	http://www.epa.gov/ada/mofat.html	
MOFAT for Windows	http://www.scisoftware.com/products/mofat_overview/mofat_overview.html	
MPATH	Contact: Peter C. Lichtner, LANL EES-5; MS F649, Los Alamos National Laboratory, Los Alamos, NM 87545, USA, (lichtner@lanl.gov)	
MS-VMS	http://www.scisoftware.com/products/msvms_overview/msvms_overview.html	
MT3D	http://www.epa.gov/ada/mt3d.html	
MT3D99	http://www.scisoftware.com/products/mt3d_overview/mt3d_overview.html	
MT3DMS	http://hydro.geo.ua.edu/mt3d/mt3dms2.htm	
MULAT	http://www.mines.edu/research/igwmc/software/igwmcsoft/	
MULTIFLO	Contact: Peter C. Lichtner, LANL EES-5; MS F649, Los Alamos National Laboratory, Los Alamos, NM 87545, USA, (lichtner@lanl.gov)	
NETPATH	http://water.usgs.gov/software/netpath.html	
OS3D/GIMRT	http://www.earthsci.unibe.ch/tutorial/os3d.htm	(program description only)
	Contact: Carl Steefel, Dept. of Geology, University of South Florida, 4202 E. Fowler Ave., Tampa, FL 33620, USA, (steefel@margaux.cas.usf.edu)	
PESTAN	http://www.epa.gov/ada/pestan.html	

PHREEQC (v 1.6)	http://water.usgs.gov/software/phreeqc.html
PHREEQC (v 2.0 Beta)	http://www.brr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html
PHREEQC for Windows	http://www.geo.vu.nl/users/posv/phreeqc.html
PHREEQCI	http://water.usgs.gov/software/phreeqci.html
PHREEQM-2D	http://www.mines.edu/research/igwmc/software/igwmcsoft/
PHRQPITZ	http://water.usgs.gov/software/phrqpitz.html
PLUME	http://www.mines.edu/research/igwmc/software/igwmcsoft/
POLLUTE	http://www.scisoftware.com/products/pollute_overview/pollute_overview.html
RAND3D	http://www.mines.edu/research/igwmc/software/igwmcsoft/
RITZ	http://www.epa.gov/ada/ritz.html
RT3D	http://bioprocess.pnl.gov/rt3d.htm
SESOIL	http://www.scisoftware.com/products/sesoil_overview/sesoil_overview.html
SOLUTE	http://www.mines.edu/research/igwmc/software/igwmcsoft/
SOLUTRANS	http://www.fittsgeosolutions.com/solutran.htm
SteadyQL	Contact: John C. Westall (Professor), Department of Analytical Chemistry, 231/153A Gilbert Hall, Oregon State University, Corvallis, Oregon 97331-4003, USA, (John.Westall@orst.edu)
SUTRA	http://water.usgs.gov/software/sutra.html
SWICHA	http://www.mines.edu/research/igwmc/software/igwmcsoft/
SWIFT-98	http://www.scisoftware.com/products/swift_overview/swift_overview.html
TBC	http://www.baum.ethz.ch/ihw/soft/tbc.html
UNSATCHEM	http://www.ussl.ars.usda.gov/MODELS/UNSATCHE2.HTM
UNSATCHEM-2D	http://www.ussl.ars.usda.gov/MODELS/UNSATCHE.HTM
VAM2D	http://www.scisoftware.com/products/vam2d_overview/vam2d_overview.html
WATEQ4F	http://water.usgs.gov/software/wateq4f.html
WEB-PHREEQ	http://www.ndsu.nodak.edu/conference/sainieid/geochem/webphreeq/index.shtml
WHAM	http://www.ife.ac.uk/Aquatic_Processes/wham.htm
WinTran	http://www.scisoftware.com/products/wintran_overview/wintran_overview.html
VLEACH	http://www.epa.gov/ada/vleach.html
VS2DT	http://www.epa.gov/ada/vleach.html

Reviewed Support Programs:

Argus ONE	http://www.argusint.com/
GMS	http://www.ems-i.com/gms/index.html
Groundwater Vistas	http://www.groundwatermodels.com/pr01.htm
ModelCad for Windows	http://www.hydrotrak.com//modelcad.htm
ModIME	http://www.scisoftware.com/products/modime_overview/modime_overview.html
PMWIN	http://www.scisoftware.com/products/pmwin_overview/pmwin_overview.html
Visual Groundwater	http://www.flowpath.com/Software/VisualGW/VisualGW.html
Visual MODFLOW	http://www.flowpath.com/Software/VisualMF/VisualMF.html
WHI UnSat Suite	http://www.scisoftware.com/products/whiunsat_overview/whiunsat_overview.html

General Sources of Public Domain Software:

<http://h2o.usgs.gov/software/>
<http://www.epa.gov/ada/models.html>
ftp://ftp.epa.gov/epa_ceam/wwwhtml/products.htm

General Sources of Commercial Software:

<http://www.scisoftware.com/>
<http://www.mines.edu/igwmc/>

On-line Listings or Descriptions of Software:

<http://www.ggsd.com/>
<http://dino.wiz.uni-kassel.de/ecobas.html>
<http://www.mindspring.com/~rbwinston/source.htm>
<http://www.nea.fr/html/dbprog/>
<http://www.thehydrogeologist.com/software.htm>

REFERENCES

- Aagaard P., and Helgeson H.C., (1982) Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions, *Am. J. Sci.*, **282**, pp. 237-285
- Bethke C.M. (1992) The question of uniqueness in geochemical modeling. *Geochim. Cosmochim. Acta.*, **56**, pp. 4315-4320
- Caram H.S. and Scriven L.E. (1976) Non-unique reaction equilibria in non-ideal systems. *Chem. Eng. Sci.* **31**, pp. 163-168
- Emrén A.T., Randy A., Glynn P.D., and McMurry J. (1999, *in preparation*) The modeler's influence on results for calculated solubilities for performance assessments at the Äspö hard-rock laboratory. *SKI Internal Report*, Swedish Nuclear Fuel Inspectorate (SKI), Stockholm, Sweden
- Garrels R.M., and MacKenzie F.T. (1967) Origin of the chemical compositions of some springs and lakes. *Equilibrium Concepts in Natural Water Systems*, Am. Chem. Soc. Adv. Chem. Ser., **67**, pp. 222-242
- Hunt R., and Zheng C. (1999) Debating Complexity in Modelling, EOS, Transactions, American Geophysical Union, Vol **80**, No. 3, pp. 29 (reproduced at <http://hydro.geo.ua.edu/hydro/EosSummary.htm>)
- Höglund L.O. (1994) Models for prediction of metal release – capabilities and needs for development, Paper presented at a workshop on “Retention and mobilization of heavy metals from waste deposits and soils”. Organised by Umeå University Department of Inorganic Chemistry and the Swedish Waste Research Council, at Kronlunds kursgård, October 18-20, 1994
- Lasaga A.C. (1981) Transition state theory. In *Kinetics of Geochemical Processes*, ed. A.C. Lasaga and R.J. Kirkpatrick. Rev. in Mineralogy 8, pp. 135-69, Min. Soc. Am.
- Moreno L., and Neretnieks I. (1993) Fluid flow and solute transport in a network of channels, *J. Contam. Hydrology*, **14**, pp. 163-192
- Neretnieks I., Yu J., and Liu J. (1997) An efficient time scaling technique for coupled geochemical and transport models. *J. Contam. Hydrology*, **26**, pp. 269-277
- Nordstrom D.K. (1994) On the evaluation and application of geochemical models, Appendix 2 in *Proceedings of the 5th CEC Natural Analogue Working Group and Alligator Rivers Analogue Project, an international workshop held in Toledo, Spain, October 5-19, 1992*, EUR 15176 EN, pp. 375-385

Othmer H.G. (1976) Nonuniqueness of equilibria in closed reacting systems. *Chem. Eng. Sci.* **31**, pp. 993-1003

Parkhurst D.L. (1995) Users guide to PHREEQC – A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations, US Geological Survey, Water Resources Inv. Report 95-4227

Pitzer K.S. (1979) Theory – Ion interaction approach: in R.M. Pytkowicz, ed., *Activity Coefficients in Electrolyte Solutions*, vol. 1, CRC Press, Inc., Boca Raton, Florida, pp. 157-208

Warga J. (1963) A convergent procedure for solving the thermochemical equilibrium problem. *J. Soc. Indust. Appl. Math.* **11**, pp. 594-606