Modular Coupling of Transport and Chemistry: Theory and Model Applications

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This report was prepared as an account of work sponsored by Nagra. The viewpoints presented and conclusions reached are those of the author and do not necessarily represent those of Nagra.
Preface

The Waste Management Laboratory at Paul Scherrer Institute is performing work to increase the understanding of multi-species reactive transport in saturated porous media. These investigations are performed in close cooperation with, and with the financial support of the Swiss National Cooperative for the Storage of Radioactive Wastes (NAGRA). The present report is issued simultaneously as a PSI-Bericht and a NAGRA-NTB.
Abstract

For the description of complex processes in the near-field of a radioactive waste repository, the coupling of transport and chemistry is necessary. A reason for the relatively minor use of coupled codes in this area is the high amount of computer time and storage capacity necessary for calculations by conventional codes, and lack of available data. The simple application of the sequentially coupled code MCOTAC, which couples one-dimensional advective, dispersive and diffusive transport with chemical equilibrium complexation and precipitation/dissolution reactions in a porous medium, shows some promising features with respect to applicability to relevant problems. Transport, described by a random walk of multi-species particles, and chemical equilibrium calculations are solved separately, coupled only by an exchange term to ensure mass conservation. The modular-structured code was applied to three problems: a) incongruent dissolution of hydrated silicate gels, b) dissolution of portlandite and c) calcite dissolution and hypothetical dolomite precipitation. This allows for a comparison with other codes and their applications. The incongruent dissolution of cement phases, important for degradation of cementitious materials in a repository, can be included in the model without the problems which occur with a directly coupled code. The handling of a sharp multiple-mineral front system showed a much faster calculation time compared to a directly coupled code application. Altogether, the results are in good agreement with other code calculations. Hence, the chosen modular concept of MCOTAC is more open to an easy extension of the code to include additional processes like sorption, kinetically controlled processes, transport in two or three spatial dimensions, and adaptation to new developments in computing (hardware and software), an important factor for applicability.
Zusammenfassung

Résumé

Le couplage des processus chimiques et de transport est nécessaire lors de la description des phénomènes complexes qui se développent dans le champ proche d'un dépôt final pour déchets radioactifs. Les raisons du peu d'usage fait jusqu'ici de modèles couplés dans ce domaine s'expliquent par les énormes durées de calcul et capacités de stockage des ordinateurs nécessaires pour les programmes conventionnels actuels ainsi que par la pénurie de données. Les premières applications du code MCOTAC couplé de façon séquentiell, qui relie le transport advectif, dispersif et diffusif à une dimension avec un modèle d'équilibre chimique de réactions de complexage et de dissolution/précipitation dans un milieu poreux saturé d'eau, permettent de sérieux espoirs quant à son application pour ce type de problèmes. Le transport, décrit par un "random walk" de particules de multiples species, et les calculs d'équilibres chimiques, sont résolus séparément, reliés seulement par une terme d'échange assurant la conservation de la masse. Le code structuré de façon modulaire a été appliqué à trois problèmes: a) la dissolution incongruente de gels de silicates hydratés, b) la dissolution de portlandite et c) la dissolution de calcite et la précipitation hypothétique de dolomite. Ces essais ont permis une comparaison avec d'autres modèles et leur application. La dissolution incongruente de phases de ciment, importante pour la dégradation de matériaux à base de ciments dans un dépôt final, peut être introduite dans ce modèle sans souffrir des problèmes rencontrés avec un code couplé directment. Le traitement de systèmes de fronts minéraux aigus a nécessité des durées de calcul beaucoup plus courtes par rapport à l'utilisation d'un modèle couplé directment. De façon général on constate une bonne concordance des résultats avec ceux obtenus par d'autres codes de calcul. De plus le concept modulaire choisi pour MCOTAC est plus ouvert à une extension facile du code en ce qui concerne d'autres phénomènes tels que la sorption, des processus contrôlés par la cinétique, des problèmes à plusieurs dimensions ainsi que pour son adaption à nouveaux développements dans le domaine des ordinateurs (hardware et software), ce qui constitue un facteur important pour l'application d'un code.
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## List of symbols

### Parameters and Symbols

- \( a \): Extended Debye-Hückel parameter
- \( A \): Debye-Hückel parameter
- \( A_{ij} \): stoichiometric coefficient matrix used to form all complexes \( i \) by the set basis species \( j \)
- \( A_k \): cross section
- \( B \): Extended Debye-Hückel parameter
- \( B'(j,l') \): Specific Interaction Theory coefficient
- \( B_{jk} \): stoichiometric coefficient matrix used to form all solids \( k \) by the set of basis species \( j \)
- \( c_1, c_2, c_3, c_4 \): thermodynamic constants for temperature dependent formation constants
- \( c(x,t) \): solute concentration depending on location and time
- \( C_i \): concentration of the complex \( i \) [mol/l]
- \( C_i' \): concentration of complex \( i \) at time \( t \)
- \( \dot{C}_i \): concentration of the complex \( i \) [mol]
- \( C_i'' \): concentration of the complex \( i \) within an iteration
- \( \{C_i\} \): activity of the complex \( i \)
- \( dH_0 \): standard enthalpy of the reaction in [kJ/mol]
- \( D \): (constant) dispersion coefficient
- \( D_i \): dispersion coefficient for complex \( i \)
- \( D_j \): dispersion coefficient for species \( j \)
- \( D_{mj} \): molecular diffusion coefficient for species \( j \)
- \( H \): hydraulic head
- \( i \): index of complex species
- \( iteration_i \): index of iteration level
- \( I \): ionic strength
- \( j \): index of basis species
- \( k \): index of solid species
- \( K \): hydraulic conductivity tensor
- \( K_i \): equilibrium constant for complexation reaction \( i \)
- \( K_{ko} \): solubility product for the \( k \)th precipitation/dissolution reaction
- \( m \): index of cell number
- \( m_l \): molality of ion \( l \)
- \( m_{j,i} \): mass vector component for basis species \( j \) (complex \( i \))
- \( n \): index of particle \( n \)
- \( nb(m) \): number of particles in cell \( m \)
\(\bar{n}\)  particle mass vector for particle \(n\)

\(N_c\)  number of complexed species (or complexes)

\(N_j\)  number of basis species

\(N_k\)  number of solid phases

\(N_{\text{max}}\)  maximum number of particles in the model area

\(P_k\)  concentration of the solid phase \(k\) [mol/l]

\(P_k'\)  concentration of solid \(k\) at time \(t\)

\(\hat{P}_k\)  concentration of the solid phase \(k\) [mol]

\(P_k''\)  concentration of the solid phase \(k\) within an iteration

\(P_k^t\)  concentration of the solid phase \(k\) at time \(t\)

\(q_{k,m}\)  activity product forming the solid \(k\) in cell \(m\)

\(q_t\)  activity product forming the solid \(k\)

\(r_i\)  source term for complex \(i\) due to chemical reactions

\(r_j\)  source term for species \(j\) due to chemical reactions (sum of accumulation of basis species \(j\) due to reactions of complexes and solids)

\(r_j^p\)  production rate of basis species \(j\) due to one complexation reaction \(i\)

\(r_j^e\)  production rate of basis species \(j\) due to one precipitation/dissolution reaction \(k\)

\(r_j^{ec}\)  production rate of basis species \(j\) due to all complexation reactions

\(r_j^p\)  production rate of basis species \(j\) due to all precipitation/dissolution reactions

\(R\)  gas constant

\(t\)  time

\(T\)  temperature [K]

\(T_0\)  reference temperature

\(U_j\)  total aqueous concentration of basis species \(j\)

\(v\)  (constant) effective flow velocity

\(v_{\text{Darcy}}\)  Darcy velocity in one dimension

\(\bar{v}_{\text{Darcy}}\)  vector of Darcy velocity

\(v_i\)  effective flow velocity for complex \(i\)

\(v_j\)  effective flow velocity for species \(j\)

\(V\)  cell volume

\(w_{\text{total}}\)  total concentration of basis species \(j\) in cell \(m\)

\(x\)  coordinate in \(x\) direction

\(x_n\)  location of particle \(n\)

\(\bar{x}\)  mean movement of a particle ensemble

\(X_j\)  concentration of the species \(j\) [mol/l]

\(X_j'\)  concentration of basis species \(j\) at time \(t\)

\(\hat{X}_j\)  concentration of the species \(j\) [mol]
$X_j^*$  concentration of the species $j$ within an iteration

$X_j^N$  concentration of the species $j$ at iteration level $N$

$\{X_j\}$  activity of the basis species $j$

$\bar{X}$  vector of the independent variables (basis species and solids)

$Y_j$  residue for the $j$th species

$Y_{N,j+k}$  residue for the solid $k$

$Y_{iteration_i,k+j}$  residue for solid $k$ at iteration level $iteration_i$

$z_j$  signed charge of basis species $j$

$z_i$  signed charge of complex $i$

$Z_n$  normally distributed random number

$Z_{eq}$  equally distributed random number

$Z_\beta$  Jacobian matrix

$\alpha_j$  dispersivity for species $j$

$\beta$  temperature dependent function

$\gamma_j$  activity coefficient of species $j$

$\delta_\beta$  Kronecker symbol

$\Delta P_k$  mass transfer from the solid into the liquid phase with respect to solid $k$

$\Delta t$  time step

$\Delta t_{\text{max}}$  maximum time step

$\Delta x$  cell width

$\Delta m$  tracer mass

$\Delta s_a(n)$  advective movement of a particle $n$

$\Delta s_d(n)$  dispersive movement of a particle $n$

$\Delta x_n$  displacement of particle $n$

$\Delta X_j$  component $j$ of a vector $\bar{X}$

$\varepsilon$  dielectric constant [-]

$\bar{\varepsilon}$  error tolerance for iteration procedure

$\xi_{(j,l,l)}$  Specific Interaction Theory coefficient

$\phi$  porosity
1. Introduction

The performance assessment of a radioactive waste repository requires a detailed knowledge of physical, chemical, hydrological and geological processes for long time spans. In the past, individual models for hydraulics, transport or geochemical processes were developed more or less separately to great sophistication for the individual processes e.g. [Jakob, Hadermann & Roesel, 1989; Konikow & Bredehoeft, 1978; Parkhurst, Thorstenson & Plummer, 1980; Prickett, Naymik & Lonnquist, 1982; Schweingruber, 1980; Tang, Frind & Sudicky, 1981; Westall, Zachary & Morell, 1976]. But most of these models cannot predict coupled processes. Attempts were made to couple at least two models to get a more adequate description of the system [Carnahan, 1985; Carnahan, 1986; Lichtner, 1985; Lichtner, 1992a; Lichtner, 1992b; Mangold & Tsang, 1991; Miller & Benson, 1983; Read, 1991; Rubin & James, 1973]. These models are called coupled codes; they couple predominantly a multi-component transport model with a chemical reaction model, although some couple chemical reactions with a hydraulic model. In general, coupled codes are limited up to now by available computer resources or the lack of data to become a useful tool in modelling coupled systems.

In [Yeh & Tripathi, 1989] coupled codes are divided into three groups with respect to the solution of the coupled transport and chemical equations:

(1) simultaneous mixed differential and algebraic equations

(2) direct substitution of non-linear chemical reactions into the transport equations to reduce the system to a set of non-linear partial differential equations and

(3) considering the system as two sequentially linked sets of partial differential equations and non-linear algebraic equations.

(1) and (2) are also called directly coupled codes because transport and chemistry are directly coupled and solved together in one step. (3) are called sequentially coupled codes because transport and chemistry are treated one after the other and are coupled by an exchange term with or without iteration in between.

In a review [Yeh & Tripathi, 1989], most coupled codes of types (1) and (2) were considered limited to be research tools for one-dimensional descriptions of small systems and only coupled codes of type (3) were recommended for their practicality and flexibility. The advantage of sequentially coupled codes is the possible use of well-known transport and chemical equilibrium codes. The smaller amount of computer storage capacity and CPU-time during development and testing of codes is an important aspect, too. The sequentially coupled codes are not too complex and the application of a model to realistic problems such as incongruent cement dissolution should be possible with reasonable computing time which is a predominant factor concerning applicability. The specification of each submodel is easier and it can be tested separately.

The motivation to create a new modular structured code is the fact that the existing coupled codes are not in a status to be applicable to problems of interest here. The codes are mostly applicable to a special class of problems. They use common computer hard- and software - not being able to use efficiently new trends in computer development, e.g., parallel
computing (parallel architecture computer and parallel programming) to decrease the computing time of coupled code applications. To deal with additional processes or extensions within an existing code is difficult, sometimes in principle, sometimes in the sense of computer resources, and leads to a rewriting of codes (see Appendix C). With a modular coupled code it is possible to add or exchange modules depending on the problem to solve or to port individual modules to an appropriate computer to enhance the applicability of the code.

For initial investigations, a one-dimensional model description is preferable (as for most other coupled codes, too) to minimise the computing time for calculations; even with fast computers, coupled code calculations for complex chemical systems are time consuming. The step to two- or three-dimensional modelling should be possible without rewriting the code. Because generally chemical (equilibrium) calculations for complex chemical systems are more time consuming than transport model calculations, the existing chemical models must be optimised or rewritten due to requirements in a dynamic coupled code calculation. But a link to codes like MINEQL-PSI [Schweingruber, 1980] is necessary to test the dynamic calculations or to include further developments of these codes (e.g. kinetics or incongruent dissolution/precipitation).

Here, the newly developed code MCOTAC (modular coupling of transport and chemistry) is presented with first calculations and a comparison with other codes. It consists of a random-walk transport model for one-dimensional multi-species transport coupled with a chemical equilibrium model. The transport model can easily be extended to more dimensions just by superposition of individual one-dimensional transport steps in x, y, and z direction in space if the flow field is known (can be calculated) at any point in space, although for arbitrary flow fields where the tensorial nature of dispersion has to be taken into account [Kinzelbach, 1987]. Independent particles, each associated with a set of masses of chemical substances, are moved within a flow field in a statistical manner. This is equivalent to the solution of the transport equation for advective-dispersive/diffusive transport [Prickett, Naymik & Lonnquist, 1982]. With the mass vector approach the transport step is done for all solutes in one step, whereas for other transport models (finite difference or finite element methods) the transport equation has to be solved for each solute at each time step. This is more time consuming and an extension to higher dimensions cannot be done by simple superposition. The chemical equilibrium model is taken from the coupled code THCC_DM [Berner, Jacobsen & McKinley, 1987; Carnahan, 1986], there used for static calculations. It includes complexation reactions, dissolution/precipitation reactions as an option to describe multiple mineral fronts, redox reactions (not tested up to now) and the incongruent dissolution of solids, as defined by the Berner model [Berner, 1988] of cement degradation. Because of the special treatment of the solids in the system undergoing incongruent dissolution, this module is preferred inside dynamic calculations. To overcome convergence problems occurring within the chemical equilibrium calculations ([Haworth, Sharland & Tweed, 1989]) an optional user interface is included to allow interactive user action during the dynamic calculations.

The code is open to a modular expansion to two- or three-dimensional applications or to a further coupling to the hydraulics of the system influenced, for example by dissolution/precipitation reactions of solids, if faster computers are available or multi-dimensional calculations are necessary from the viewpoint of the system of interest. Of
course, the extent of knowledge of input parameters in complex multi-dimensional systems is an important factor for predictions. Up to now only small and generally incomplete data sets of one-dimensional column experiments are available and extrapolation to field conditions is difficult. Therefore one-dimensional model calculations can only be tested (more or less) by experimental investigations. But multi-dimensional modelling could lead to a better understanding of real 3D problems. It can give an idea of what and where to measure in nature. To do so, an additional module visualising the high amount of generated data will be necessary for interpretation of complex calculations. This underlines the fact that coupled code modelling incorporates besides transport or chemical reaction modelling also computational considerations such as selection of available hardware and software as well as the form of data presentation.

In Chapter 2, the general equations for reactive multi-species transport in saturated homogeneous porous media are briefly summarised to give the mathematical, physical and chemical background for the concept of modular coupling of transport and equilibrium chemistry described in Chapter 3. There the new approach of multi-species particle random walk is presented. Chapter 4 shows three applications of MCOTAC in comparison to other coupled code applications. Conclusions, recommendations and an outlook to further work and needs are given in Chapter 5. Finally, special details on the chemical solution procedure, the random walk method, computer hard- and software and on different code options are given in Appendices A to E.
2. General coupled equations for reactive multi-species transport

The system which is described by the code MCOTAC consists of a saturated homogeneous porous medium (e.g. a saturated cementitious repository described as an equivalent porous medium) with a specified mineral composition reacting with an aqueous solution (e.g. a groundwater) flowing through the porous medium in one dimension. The system can be divided into a number of REV's (representative elementary volumes) of homogenous composition. This means that each REV can be characterised by a set of parameters which are constant within each volume (in general this is here the width of a cell). These parameters describe the chemical, physical and hydro-geological properties of the REV. A change of the composition of the solid phase or the liquid phase (e.g. of the waste repository) will cause a time-dependent evolution of the system. Transport processes for chemical species in the liquid phase taken into account are advection, dispersion and diffusion. Additional chemical reactions will take place in the liquid phase and with the solid phase which is assumed to be immobile. These chemical processes are assumed to influence the transport within the liquid phase but not the transport parameters like porosity or flow velocity.

2.1 Reactive mass transport equations

The description of the time dependence of all species concentrations separate into two sets of differential equations, one set for the liquid phase and the other for the solid phase. Due to chemical notation the species in the liquid phase are divided into two different groups, the \(N_j\) basis species with concentrations \(X_j\) \((j = 1, ..., N_j)\) and the \(N_c\) complexed species (or complexes) with concentrations \(C_i\) \((i = 1, ..., N_c)\). The basis species are the minimum set of species required to form all other species (basis species, complexed species and solid species) of interest. Complexes are substances in the liquid phase formed by the basis species. The transport equations for basis species concentrations in the liquid phase include advection, dispersion, diffusion and source terms due to chemical (equilibrium) reactions (see e.g. [Yeh & Tripathi, 1989]).

\[
\frac{\partial X_j}{\partial t} + v_j \frac{\partial X_j}{\partial x} - \frac{\partial}{\partial x} \left( D_j \frac{\partial X_j}{\partial x} \right) = r_j
\]

\(j = 1, ..., N_j\)

where:

- \(X_j\) concentration of the species \(j\) \(\text{[mol l}^{-1}\) \]
- \(t\) time \([\text{s}]\)
- \(x\) coordinate in \(x\) direction \([\text{m}]\)
- \(D_j\) (hydrodynamic) dispersion coefficient for species \(j\) with \(D_j = \alpha_j \cdot v_j + D_m, \alpha_j = \text{dispersivity for species } j\) and
\[ D_{m_j} = \text{molecular diffusion coefficient for species } j \left[ \frac{m^2}{s} \right] \]
\[ v_j = \text{effective flow velocity for species } j \left[ \frac{m}{s} \right] \]
\[ r_j = \text{source term for species } j \text{ due to chemical reactions} \left[ \frac{mol}{l \cdot s} \right] \]

This is a set of \( N_j \) differential equations for the basis species. The additional set of differential equations for the complexes is of the same form

\[
\frac{\partial C_i}{\partial t} + v_i \frac{\partial C_i}{\partial x} - \frac{\partial}{\partial x} \left( D_i \frac{\partial C_i}{\partial x} \right) = r_i \quad (2)
\]

\[ i = 1, ..., N_c \]

where

\[ C_i = \text{concentration of the complex } i \left[ \frac{mol}{l} \right] \]
\[ D_i = \text{(hydrodynamic) dispersion coeff. for complex } i \left[ \frac{m^2}{s} \right] \]
\[ v_i = \text{effective flow velocity for complex } i \left[ \frac{m}{s} \right] \]
\[ r_i = \text{source term for complex } i \text{ due to chemical reactions} \left[ \frac{mol}{l \cdot s} \right] \]

Mass balance equations for the \( N_k \) solid phases reduce to rate equations with rates \( r_k \) for precipitation/dissolution of a solid, because the solid phases are assumed to be immobile not taking part in transport processes. Their concentrations \( P_k \) are given in equivalent moles per litre of fluid.

\[
\frac{\partial P_k}{\partial t} = r_k \quad (3)
\]

\[ k = 1, ..., N_k \]

The differential equations (1), (2) and (3) are non-linearly coupled by the source terms describing chemical reactions. \( r_j \) is the sum of accumulation of basis species \( j \) due to reactions of complexes with rates \( r_j^{cc} \) and solids with rates \( r_j^{cp} \) which are themselves sums of reaction rates:

\[
r_j = r_j^{cc} + r_j^{cp} \quad (4)
\]
The formation of complexes $i = 1, \ldots, N_i$ by the set of basis species $j = 1, \ldots, N_j$ (used within the chemical notation) is described by

$$\sum_{j=1}^{N_j} A_{ij} \cdot \dot{X}_j = \dot{C}_i$$

(5)

$$i = 1, \ldots, N_c$$

due to a correct stoichiometric formation of the complexes and the related mass transfer defined by the chemical formula ($\dot{X}_j$ and $\dot{C}_i$ are in units of mol, whereas $X_j$ and $C_i$ are in units of mol/l). $A_{ij}$ is the stoichiometric coefficient matrix used to form all complexes $i$ by a chosen set (or vector) of basis species $j$ and therefore

$$A_{ij} r_i = -\dot{r}_{ji}$$

(6)

is the production rate of basis species $j$ due to one complexation reaction $i$ in solution (production of basis species $j$ due to complexation reaction $i$ corresponds to reduction of complex concentration $i$ with the correct stoichiometry). Then the sum of all complexation reaction rates $r_{j}^{\text{ec}}$ producing the basis species $j$ is given by

$$r_{j}^{\text{ec}} = \sum_{i=1}^{N_i} r_{ji} = -\sum_{i=1}^{N_i} A_{ij} r_i$$

(7)

$$j = 1, \ldots, N_j$$

Equivalently, the formation (dissolution/precipitation) of solids $k = 1, \ldots, N_k$ by the set of basis species $j = 1, \ldots, N_j$ is described by

$$\dot{P}_k = \sum_{j=1}^{N_j} B_{jk} \dot{X}_j$$

(8)

$$k = 1, \ldots, N_k$$

taking into account the correct stoichiometric formation of the solids and the related mass transfer defined by the chemical formula ($\dot{X}_j$ and $\dot{P}_k$ are in units of mol, whereas $X_j$ and $P_k$ are in units of mol/l). $B_{jk}$ is the stoichiometric coefficient matrix used to form all solids $k$ by the chosen set (or vector) of basis species $j$ and therefore

$$B_{jk} r_k = r_{jk}^p$$

(9)

is the production rate of basis species $j$ due to one precipitation/dissolution reaction $k$ (production of basis species $j$ due to precipitation/dissolution reaction $k$ corresponds to reduction of solid concentration $k$ with the correct stoichiometry). Then the sum of all precipitation/dissolution reaction rates $r_{j}^{\text{op}}$ producing the basis species $j$ is given by
Inserting these rate equations into the differential equation for the basis species (Eq. 1), multiplying the differential equation for the complexes (Eq. 2) by $A_j$ and summing over $i = 1 \to N_c$ and adding this to the differential equation for the basis species leads to

$$\frac{\partial}{\partial t} \left( X_j + \sum_{i=1}^{N_c} A_j C_i \right) + v_j \left( \frac{\partial X_j}{\partial x} \right) + v_j \left( \sum_{i=1}^{N_c} A_j \frac{\partial C_i}{\partial x} \right) - \frac{\partial}{\partial x} \left( D_j \frac{\partial X_j}{\partial x} + \sum_{i=1}^{N_c} A_j \left( D_i \frac{\partial C_i}{\partial x} \right) \right) = r_{j}^{eq} + r_{j}^{cp} + \sum_{i=1}^{N_c} A_j r_i$$

$$= - \sum_{k=1}^{N_c} A_k r_k + \sum_{k=1}^{N_c} B_{jk} \frac{\partial P_k}{\partial t} + \sum_{i=1}^{N_c} A_j r_i$$

$$= - \sum_{k=1}^{N_c} B_{jk} \frac{\partial P_k}{\partial t}$$

(11)

$j = 1, \ldots, N_j$

This is the general coupled chemical reaction-transport equation if constant porosity and flow velocity is assumed, and no assumption of chemical equilibrium is made but the rate equations are eliminated. The number of independent variables is $N_j + N_c$ for the transport equations and $N_k$ independent variables for the rate equations. The general equation is a set of $N_j$ equations. The remaining equations to solve the system come from the local equilibrium assumption (the mass action equation): $N_c$ equations for complexation reactions.

---

1 Including porosity changes (porosity not a constant), (Eq. 11) will change to

$$\frac{\partial}{\partial t} \left( X_j + \sum_{i=1}^{N_c} A_j C_i \right) + v_j \left( \frac{\partial X_j}{\partial x} \right) + v_j \left( \sum_{i=1}^{N_c} A_j \frac{\partial C_i}{\partial x} \right) - \frac{\partial}{\partial x} \left( D_j \frac{\partial X_j}{\partial x} + \sum_{i=1}^{N_c} A_j \left( D_i \frac{\partial C_i}{\partial x} \right) \right) = \sum_{k=1}^{N_c} B_{jk} \frac{\partial P_k}{\partial t}$$

[Yeh & Tripathi, 1989], with the Darcy velocity in one dimension $v_Darcy_{j,i}$ given by

$$v_{Darcy_{j,i}} = \nabla \cdot (K \cdot \nabla H) = \nabla \cdot \vec{v}_{Darcy}$$

This implies that an additional coupling to fluid flow is necessary to take into account the porosity changes. $\phi$ becomes a space and time dependent function of the mineralogy (precipitation/dissolution of solids $k$) which influences the flow velocity. Then, the flow equation [Yeh & Tripathi, 1989]

$$\frac{\partial \phi}{\partial t} = \nabla \cdot (K \cdot \nabla H) = \nabla \cdot \vec{v}_{Darcy}$$

has to be solved by an additional module to follow the concept of modular coupling. In this equation $\nabla$ is the nabla operator, $K$ the hydraulic conductivity tensor, $H$ the (hydraulic) head and $\vec{v}_{Darcy}$ the vector of the Darcy velocity. This vector presentation of the flow equation stresses the fact that an one-dimensional calculation of flow would be of very limited applicability and is neglected here, but it will be the objective of future work in respect of coupling two- or three-dimensional transport and chemistry. Although the extension to two or three dimensions with this concept of modular coupling is easy, one has to keep in mind the increase in computer memory and time just for a 'small' two-dimensional example (see App. C)
and $N_N$ equations for precipitation/dissolution reactions; that means $N_N+N_c+N_N$ equations for the same number of unknowns. (This implies that chemical equilibrium is assumed within a REV when chemical processes are much faster than the transport processes.)

Parameters within the transport equations are the flow velocity $v_j$, $v_i$ and the dispersion/diffusion coefficients $D_j$, $D_i$. If $v_j = v_i = v$, a constant; and $D_j = D_i = D$, a constant, then all aqueous species are transported identically. In this case (Eq. 11) reduces to

$$\frac{\partial U_j}{\partial t} + \frac{\partial}{\partial x} \left( vU_j - D \frac{\partial U_j}{\partial x} \right) + \sum_{k=1}^{N_N} B_{jk} \frac{\partial P_k}{\partial t} = 0$$

(11*)

$$j = 1, ..., N_N$$

where

$$U_j = X_j + \sum_{i=1}^{N_N} A_{ij} C_i$$

is the total concentration of the $j$th basis species in the aqueous phase and (Eq. 11*) represents conservation of the basis species.

In addition to these differential equations (Eq. 11) a set of equations must be fulfilled (if chemical equilibrium is assumed) which describe the chemical equilibrium conditions. As mentioned above the set of basis species $X_j$ is used to form all substances of interest in the system (complexes and minerals).

### 2.2 Complexation reaction for chemical equilibrium description

The mathematical statement of chemical equilibrium for each complexation reaction is

$$\{C_i\} = K_i \cdot \prod_{j=1}^{N_N} \{X_j\}^{a_{ji}}$$

(12)

$$i = 1, ..., N_N$$

which are $N_N$ equations for $N_N$ concentrations of the complexes.

$K_i$ is the equilibrium constant which depends on temperature, pressure etc. and must be known for each complexation reaction. $\{C_i\}$ and $\{X_j\}$ are the activities of the complexes and basis species in the solution. The activity is related to the concentration of the complex or basis species by

$$\{X_j\} = \gamma_j \cdot X_j$$

(13)
where $\gamma_j$ is the activity coefficient of species $j$. There exist several approximations for $\gamma_j$ or more conveniently for $\log \gamma_j$ listed in the following table.

**Table 2.1:** Ionic strength corrections and their applicability range [Grenthe & Wanner, 1988; Stumm & Morgan, 1981] where $I$ is the ionic strength [M], $z_j$ is the charge of species $j$ and $A, B, a, \xi, B'$ parameter:

- $A = 1.82 \times 10^6 (\varepsilon T)^{-3/2}$ (\varepsilon: dielectric constant [-], $T$: absolute temperature [K])
- $A = 0.5$ for water at 25 °C
- $B = 50.3 (\varepsilon T)^{-1/2}$; $B = 0.33$ for water at 25 °C
- $a$ adjustable parameter (in [10^{-10} m]) related to ion size
- $\xi (j,l,l)$ interaction coefficient depending on ion pair $j$-l and ionic strength; ($m_i$ molality of ions $l$)
- $B'(j,l')$ ionic strength independent interaction coefficient, $l'$ is a specified summation index and covers all anions if $j$ is a cation and vice versa

<table>
<thead>
<tr>
<th>Approximation</th>
<th>Equation for $\log \gamma_j$</th>
<th>Approximate applicability [ionic strength (M)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye-Hückel</td>
<td>$-A z_j^2 \sqrt{I}$</td>
<td>$&lt; 10^{-2.3}$</td>
</tr>
<tr>
<td>Extended Debye-Hückel</td>
<td>$-A z_j^2 \frac{\sqrt{I}}{1 + Ba \sqrt{I}}$</td>
<td>$&lt; 10^{-1}$</td>
</tr>
<tr>
<td>Güntelberg</td>
<td>$-A z_j^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$</td>
<td>$&lt; 10^{-1}$</td>
</tr>
<tr>
<td>Davies</td>
<td>$-A z_j^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \cdot I \right)$</td>
<td>$&lt; 0.3 - 0.5$</td>
</tr>
<tr>
<td>Specific Interaction Theory</td>
<td>$-A z_j^2 \frac{\sqrt{I}}{1 + Ba \sqrt{I}} + \sum_i \xi(j, l, l) \cdot m_i$</td>
<td>0 - 4</td>
</tr>
<tr>
<td>Pitzer and Brewer</td>
<td>$-z_j^2 \frac{0.5107 \sqrt{I}}{1 + Ba \sqrt{I}} + \sum_{l'} B(j, l') \cdot m_i$</td>
<td>0 - 4</td>
</tr>
</tbody>
</table>
The ionic strength is given by

\[ I = \frac{1}{2} \sum_{j=1}^{N_j} z_j^2 \cdot X_j + \frac{1}{2} \sum_{i=1}^{N_i} z_i^2 \cdot C_i \]  

(14)

where \( z_j \) is the signed charge of basis species \( j \) (complex \( i \)) in solution. With the ionic strength and an extended Debye-Hückel approximation the transfer from ion activities in chemical equilibrium calculations to ion concentrations (or masses per volume) in transport calculation is done.

### 2.3 Precipitation/dissolution reaction for chemical equilibrium description

A pure solid in equilibrium with a solution is assigned by convention an activity of 1. Corresponding to (5), (8) and (12) the mathematical statement of chemical equilibrium for each precipitation/dissolution reaction of the solid phase \( k \) is

\[ K_{so}^k = \prod_{j=1}^{N_j} \{ X_j \}^{B_{jk}} \]  

(15)

\[ j = 1, \ldots, N_k \]

where \( K_{so}^k \) is called the solubility product for the \( k \)th precipitation/dissolution reaction and \( \{ X_j \} \) are the activities of the basis species. With coefficients \( B_{jk} \) (Eq. 9) and known solubility products \( K_{so}^k \) this set of \( N_k \) equations reduces in principle the number of independent unknowns by \( N_k \) (in Eq.'s 1 to 3). But to each occurring solid corresponds a concentration which is not explicitly included in the chemical equilibrium expression (Eq. 15).

The formation constants of aqueous complexes \( K_i \) and the solubility products of solids \( K_{so}^k \) are temperature dependent \((K_i(T)\) and \( K_{so}^k(T)\)). There are several approximations for \( K_i(T) \) or \( K_{so}^k(T)\) [Stumm & Morgan, 1981] that allow chemical equilibrium calculations for systems at different temperatures, if the corresponding data are available.

- \[ \log K_i(T) = c_1 + \frac{c_2}{T} + c_3 \cdot (\log T) + c_4 \cdot T \]  

(16)

where \( c_1, c_2, c_3 \) and \( c_4 \) can be derived from thermodynamic quantities [Pearson & Berner, 1991] or

- \[ \log K_i(T) = \log K(T_0) + \beta(T) \cdot dH_o(T_0) \]  

(17)
where $T$ is the temperature in Kelvin, $T_0$ is the reference temperature, $dH_0$ is the standard enthalpy of the reaction in $[\text{kJ/mol}]$, $R$ is the gas constant, and

$$\beta(T) = \frac{1 - \frac{1}{T}}{R \cdot \ln 10}$$  

(18)

The chemical equilibrium assumption leads to $N_c$ complex reactions (Eq. (12)) and $N_k$ precipitation/dissolution reactions (Eq. (15)). A total mass conservation for $N_f$ basis species within the fluid and the solid phase is necessary because the activity of a solid is set to 1 if it is present (Eq. 15) and there is no explicit solid concentration included in Eq. (15). Including the ionic strength corrections (Table 2.1) and temperature-dependent equilibrium constants (Eq.'s (16) and (17)) it is possible to solve the $N_f$ general equation (11) for the chemical equilibrium case.  

---

2 The number of independent variables (primary species) in the liquid phase is $N_f + N_c - N_e$ (Eq. 12). If $N_k$ additional solids are present the number of independent variables reduces (in principle) to $N_f + N_k$ (Eq. 15) in the liquid phase and grows to $N_k$ in the solid phase. For a coupled calculation it is more suitable to hold the number of primary species constant within the whole system independent of the number of solids present at a certain location. With this an additional mass balance is necessary to include $N_k$ solid concentration if they are present. Doing this the number of primary species remains $N_f$. 

---
3. Concept of modular coupling of transport and chemical equilibrium reactions (solution procedure)

To solve equations (11) for chemical equilibrium conditions additional assumptions were made to couple transport and chemistry sequentially.

(1) The flow field does not change significantly in time scales important to transport and chemical processes so that a constant flow field can be assumed. For simplicity it is assumed that all species in the liquid phase move with the same velocity \( v \) (\( v_j = v_i = v \)) and have the same diffusion/dispersion coefficient \( D \) (\( D_j = D_i = D \)).

(2) Sequential coupling of transport and chemistry (equilibrium chemistry) in the form of sequential coupling the general equation (11) implies that chemical reactions and transport processes can be treated separately. Transport processes are only affected by chemical equilibrium processes at the end of each time step [Frind et al., 1994]. Therefore, it is assumed that there is no interaction between solid and liquid phase during the transport calculation, and the liquid composition remains constant. Formally, in equation (11) the source term \( \sum_{k=1}^{N_s} B_{jk} \frac{\partial R_k}{\partial t} \) is set to zero for the calculation of the individual transport step:

\[
\frac{\partial}{\partial t}\left( X_j + \sum_{i=1}^{N_s} A_i C_i \right) + v \left( \frac{\partial X_j}{\partial x} + \sum_{i=1}^{N_s} A_i \frac{\partial C_i}{\partial x} \right) - \frac{\partial}{\partial x} \left( D \frac{\partial X_j}{\partial x} + \sum_{i=1}^{N_s} A_i \left( D \frac{\partial C_i}{\partial x} \right) \right) = 0 \tag{19}
\]

After each transport step the mass transfer between the solid and the liquid phase (equal to the source term \( \sum_{k=1}^{N_s} B_{jk} \frac{\partial R_k}{\partial t} \) which was neglected in the transport step before) is explicitly calculated by the chemical equilibrium calculation which restores the chemical equilibrium that has been perturbed during the transport step. This leads to equation (11) without transport terms:

\[
\frac{\partial}{\partial t}\left( X_j + \sum_{i=1}^{N_s} A_i C_i + \sum_{k=1}^{N_s} B_{jk} R_k \right) = 0 \tag{20}
\]

or equivalently
and corresponding chemical equilibrium relations (Eq.'s 12, 13, 15). Then the masses in the liquid phase of the re-equilibrated system are taken into account for the next transport step. Both, transport (Eq. 19) and chemical equilibrium calculation (Eq.'s 20 and 21) together represent a calculation of a reactive transport step.

This means that transport occurs for a fixed system of masses (basis species and complexes) in the liquid phase and the general equation (11) separates into two groups of equations:

- A set of \( N \) differential equations for all substances in liquid phase describes the transport step (Eq. 19).

- A set of \( N \) non-linear algebraic equations describes the chemical equilibrium conditions and the mass transfer between the solid and the liquid phase within a defined volume after each time step (Eq. 20 or 21)

In each REV, which serves as a model volume or cell (see Chapt. 3.2), mass conservation is assumed for both groups of equations. This is necessary for sequential coupling of transport and chemistry\(^3\).

The sequential coupling has the advantage of providing two different types of equations which can be solved by standard procedures. Only the exchange term between the two types couples the equations. This can be done in different ways. Here, an explicit coupling is used. For the chemical system (solid and liquid phase) the chemical equilibrium equations are solved to give the source terms for the transport system which is related to the mass transfer between liquid and solid phase. Then the transport is calculated for a defined time step resulting in a new chemical distribution of species in the liquid phase which has to be equilibrated again (and so on, (Fig. 3.1). There is no iteration between transport equations and chemical equilibrium equations at this time which results in a weak coupling controlled by a mass balance step in between the two equation sets to conserve the total mass. One advantage is that there will be no convergence problems for sharp chemical fronts (chemical systems of different compositions). This can be seen in an example later (Chapt. 4.3).

\(^3\) Applicability of this sequential coupling and conditions for the time stepping for transport calculations, especially for the random walk used here, and related heterogeneous chemical equilibrium calculations are discussed in more detail in Chapt. 3.2 and in an example in 4.1.3.
3.1 Chemical equilibrium reaction calculations (the chemical equilibrium step)

Following the solution procedure (Fig. 3.1), the initial chemical equilibrium conditions (at \( t=0 \)) were calculated along a one-dimensional series of \( m \) grid cells (or volumes, see Chapt. 3.2), each defined by a set of initial total concentrations of the basis species in the liquid and the solid phase\(^4\). Therefore, in each cell \( m \) Eq. (21) leads to

---

\(^4\) It is assumed that the chemical system is set up for electroneutrality. Then, in the dynamic calculation no attention must be paid to this point as long as transport parameters are equal for all species in solution. If not, the chemical system can be set up so that at least pairs of complementary charged ions (species) have equal transport parameters to guarantee electroneutrality. Electromigration as addressed in [Haworth et al., 1988] will be investigated within further model development.
where \( w_{j\text{total}} \) is the total concentration of basis species \( j \) in a cell \( m \).

The Newton-Raphson procedure ([Press et al., 1990]) is used to get the solution of the non-linear set of equations (residue equations, see App. A). Values for the ionic strength (Eq. 14), corresponding corrections to the activity coefficient (Table 2.1) and the temperature-dependent log \( K \) values (Eq.'s 16, 17) are included in the iteration.

The total \( N_j + N_k \) residue equations (see App. A) divide into a set of \( N_j \) residue equations for the concentrations of the basis species in the liquid phase and \( N_k \) residue equations for the solid phases. For the liquid phase they are of the form:

\[
Y_j = X_j' + \sum_{i=1}^{N_j} A_{ji} \cdot C_i' + \sum_{k=1}^{N_k} B_{jk} \cdot P_k' - w_{j\text{total}}
\]  

\( j = 1, ..., N_j \)

\( Y_j \) is the difference between the total concentration of basis species \( j \) in solution and in the solid phase and the related approximated concentrations \( X_j', C_i' \) and \( P_k' \) within the iteration procedure. It is the result of mass conservation after a transport step: 'New' concentrations in the liquid phase, 'old' concentrations from the previous time step in the solid phase and the amount of species \( j \) in solution are added up within each grid cell.

The mass conservation equations (22) combine the concentrations in the liquid and solid phase in each grid cell. By definition the activity of a solid is 1 (see above). Therefore a special treatment is necessary for the solid concentrations. If a solid is present an additional mass balance (apart from chemical equilibrium calculations for the liquid phase) occurs in the form of

\[
P_k^{t+\Delta t} = P_k^t + \Delta P_k
\]  

\( k = 1, ..., N_k \)
where $\Delta P_k$ is the mass transfer from the solid into the liquid phase and equal to the change of total concentration in the liquid phase before and after chemical equilibrium calculations. It is the cumulative change of the residues for the solids during the iteration process for chemical equilibrium calculation. The residue equations for the solids are handled as described by [Carnahan, 1986]. In each cell $m$ the activity products $q_{k,m}$ of the basis species which form the solid $k$ are computed

$$q_{k,m} = \prod_{j=1}^{N_j} (\gamma_j \cdot X_j) \bigg|_m$$  \hspace{1cm} (25)

Comparison of the theoretical solubility product $K_{So}$ and the related activity product $q_{k,m}$ gives $N_k$ residues $Y_{N_j+k}$ for the solids:

- **solid present** $q_{k,m} > K_{So}^k$ \hspace{1cm} $Y_{N_j+k} := q_{k,m} - K_{So}^k$
- **solid not present** $q_{k,m} > K_{So}^k$ \hspace{1cm} $Y_{N_j+k} := q_{k,m} - K_{So}^k$ \hspace{1cm} (26)
- **solid not present** $q_{k,m} \leq K_{So}^k$ \hspace{1cm} $Y_{N_j+k} := 0$

$k = 1, \ldots, N_k$

Then the mass transfer $\Delta P_k$ during the chemical equilibrium calculation is given by the cumulative sum of the residues $Y_{N_j+k}$ at iteration $iteration_i$ $\Rightarrow Y_{N_j+k}^{iteration_i}$ for each solid $k$ in each cell $m$ (which updates the actual solid concentration for each iteration step $iteration_i$)

$$\Delta P_k|_m = \sum_{iteration_i = 1}^{end \ of \ iteration} Y_{N_j+k}^{iteration_i} \bigg|_m$$  \hspace{1cm} (27)

$k = 1, \ldots, N_k$

This procedure provides a residue equation for all solids in each cell (see App. A). It is not necessary to change the number of unknowns at nodes (cells) where solids have precipitated or dissolved. This method is more useful in a dynamic chemical equilibrium calculation than methods used in pure equilibrium calculations, e.g. MINEQL, where the change in number
of unknowns causes a change of the system of residue equations in the solution procedure [Schweingruber, 1980].

After the iteration, the final set of basis species concentrations and the complex concentrations are calculated, and the final solid concentrations for each cell are stored for the next chemical equilibrium calculation. This iteration procedure has to be done at each node (grid cell), first, to get the initial concentrations of all species and then, after each transport calculation within the dynamic calculation (Fig. 3.1). The transport calculation normally results in a non-equilibrium between the mobile liquid phase and the immobile solid phase. New re-equilibration calculations are necessary to make sure equilibrium exists within each grid cell, both within the solution and between solids and solution.

3.2 Transport description by random walk of multi-species particles (the transport step)

The method to solve the transport equation (19) for a fixed set of species concentrations in the liquid phase is related to the random-walk method extended to a multi-species transport problem (App. B). Following the procedure sketched in Fig. 3.1 at the beginning of the transport calculation $N_{\text{max}}$ particles are distributed along a one-dimensional domain of interest (Fig. 3.2) similar to the method of characteristics [Konikow & Bredehoeft, 1978]. The particles are used to represent the distribution of masses (concentrations) of all species in the liquid phase. A spatial grid is used to define the location of the immobile solid masses (concentrations). The particle masses are related to the particle location (which fits into a grid cell with defined species concentrations or masses) in form of a particle mass vector at a location $x_n$ at time $t$. The particle location $x_n$ is continuous and not related to a random walk on a regular lattice as described by [Karapiperis & Blankleider, 1992].

![Figure 3.2: Distributed particles are used to represent the concentrations $X_i(m)$ and $C(m)$ within cells $m$, $m+1$, ... in the liquid phase related to their location $x_n$. The immobile solids are represented by concentrations $P_s(m)$ in cell $m$.](image)
Each particle $n$ is related to a particle mass vector $\vec{n}$ to characterise the particle properties. The vector $\vec{n}$ has $N_j + N_c + 2$ components and is defined by

$$\vec{n} := (m_1, m_2, \ldots, m_{N_j}, m_{x_1}, m_{x_2}, \ldots, m_{x_N}, t)$$

(28)

The vector components $m_{j,i}$ ($j = 1, \ldots, N_j$ and $i = 1, \ldots, N_c$) which are species masses per particle (and location and time) are defined by the location $x_n$. The actual particle masses (components $m_{j,i}$) depend on the calculated equilibrium concentrations or total masses in the grid cell (volume $V$) and the actual number of particles $nb(m)$ in the grid cell $m$ which are both a function of time:

$$m_{j,i}\big|_{cell\ m} = \frac{X_{j,m} \cdot V}{nb(m)}_{cell\ m}$$

(29)

$$j = 1, \ldots, N_j$$

$$m_{i}\big|_{cell\ m} = \frac{C_{i,m} \cdot V}{nb(m)}_{cell\ m}$$

(30)

$$i = 1, \ldots, N_c$$

Vice versa, the concentration $X_j(m)$ of a basis species $j$ in cell $m$ is given by the sum over all particles $n$ in cell $m$ and their related vector component $m_j$:

$$X_j(m) = \frac{1}{V} \sum_{particle\ in\ cell\ m} m_j$$

(31)

The grid is used for handling the immobile solid concentrations and the chemical equilibrium calculations where concentrations (activities) are needed. It is set up for the transport so that there are a number of particles in each grid cell to guarantee a statistical description of the transport by a random walk of particles. Further, it depends on the size of the domain of interest, its desired resolution and the maximum number of available particles (related to the number of grid cells).
During the transport time step (discussed later) new particle positions are calculated depending on the transport processes advection, diffusion and dispersion. Each particle \( n \) undergoes a movement during the time step \( \Delta t \), and is a sum of a defined advective step\(^5\)

\[
\Delta s_a(n) = v \cdot \Delta t
\]

\( = \Delta s_a \) (if all species move with the same velocity)

and a random diffusive/dispersive step

\[
\Delta s_d(n) = Z_n \cdot \sqrt{2D \cdot \Delta t}
\]

where \( D = \alpha \cdot v + D_n \) is the (hydrodynamic) dispersion coefficient in one dimension (see Eq. 1) and \( Z_n \) is a normally distributed random number related to the individual random diffusive/dispersive step of particle \( n \).

Then the new particle positions \( x_n \) for particles \( n = 1, ..., N_{\text{max}} \) are given by

\[
x_n = x_{n,\text{old}} + \Delta s_a(n) + \Delta s_d(n)
\]

producing a new particle distribution and related species concentration distribution after each time step (see Fig. 3.3).

\(^5\) In contrast to this defined advective step [Karapiperis & Blankleider, 1992] use for the description of (molecular) advection and dispersion/diffusion a combined (synchronous) random movement on a regular lattice whereas here only dispersion/diffusion is described by a random movement
Figure 3.3: Particle positions before and after a transport step of width $\Delta t$. Particle displacement $\Delta x_n$ of the particle $n$ ($n = 1, ..., N_{\text{max}}$) is the result of a defined advective displacement $\Delta s_n(n)$ equal for all particles and a statistically generated diffusive/dispersive displacement $\Delta s_D(n)$ different for each particle $n$. (The shadowed bar represents the distance $\Delta x_n(t)$ which an individual particle $n$ moves during $\Delta t$)

After the transport step, at time $t' = t + \Delta t$, a new mass balance within each cell has to be done caused by new particle positions. Equation (31) is used for basis species and an equivalent for the complexes. Together with the 'old' concentrations in the immobile solid phase, this gives the total species concentration $w_{j,\text{total}}$ in each cell $m$.

$$
W_j^{t+\Delta t}_{\text{total}} \bigg|_m = \left[ X_j^{t+\Delta t} + \sum_{i=1}^{N_c} A_{ij} \cdot C_{i}^{t+\Delta t} + \sum_{k=1}^{N_k} B_{jk} \cdot P_{jk}^{t+\Delta t} \right]_{\text{cell } m}^{\text{not at equilibrium}}
$$

This causes a chemical non-equilibrium in each cell which is equilibrated (Eq.'s 23-27). The equilibrated chemical system in each cell defines then the equilibrium corrected species concentration $\left[ X_j^{t+\Delta t}, C_i^{t+\Delta t} \text{ and } P_k^{t+\Delta t} \right]_{\text{at equilibrium}}^{\text{cell } m}$ (comp. Eq. 35) in each cell at time $t + \Delta t$ including the mass transfer between liquid and solid phase. The mass (concentration) of each species in the liquid phase in the cell $m$ is then equally distributed to the number of particles $n_{b(m)}$ at their position $x_n$ in each cell (Eq.'s 29 and 30) to calculate the next transport step. The species concentrations in the solid phase are just stored. This closes the dynamic loop in Fig. 3.1.

This concept of sequential coupling transport and chemistry is influenced by the time stepping (for a given grid), discussed in more detail in [Herzer & Kinzelbach, 1989], because it defines the source/sink terms for (total) species concentrations in the cells not at
equilibrium (Eq.'s 31 and 35). This includes additional sources or sinks for heterogeneous chemical systems due to chemical equilibrium between solid and liquid phases. Therefore attention must be paid to the choice of time step width \( \Delta t \) which influences within the random walk approach the individual particle movement. If the time step is larger than the mean time that a particle needs to move through a single cell the particle will not react with the solids of this skipped cell. This introduces an error with respect to chemical equilibrium calculations in subsequent cells in that particles may tunnel cells without an equilibrium calculation in between. This can be avoided if the movement of a particle during the time step \( \Delta t \) (Eq.’s 32 - 34) is lower than the cell width \( \Delta x \):

\[
\Delta x > \Delta s_a(n) + \Delta s_D(n)
\]  

(36)

It can be achieved by choosing for a given cell width \( \Delta x \) a maximum time step \( \Delta t_{max} \) which is related to Eq.’s (32) and (33).

\[
\Delta t_{max} \leq \frac{\Delta x}{v} \quad \text{(for pure advection)}
\]  

(37)

or

\[
\Delta t_{max} \leq \frac{\Delta x^2}{2D_m} \quad \text{(for pure diffusion)}
\]  

(38)

if a mean diffusive movement (over all particles) \( \Delta s_{diff} = \sqrt{2D_m \cdot \Delta t} \) is assumed [Reif, 1976]. For advective and dispersive/diffusive transport a combined condition can be used:

\[
\Delta t_{max} \leq \frac{\Delta x}{v} + \frac{\Delta x^2}{2D}
\]  

(39)

---

6 Further sources or sinks which can be a time variable input at a boundary cell or at other specified cells in the model area need a time dependent input of mass (which must be defined from outside). This is transferred to the actual number of particles within the particular cell.

7 No conditions on the time step width exist for pure random walk transport calculations without chemical reactions or other time dependent source or sink terms. Only in combination with the (heterogeneous) chemical equilibrium calculations (chemical equilibrium step) does a time step limit for the transport step become necessary.
as the sum of advective and dispersive/diffusive displacement and a mean dispersive/diffusive movement of $\Delta s_D = \sqrt{2D \cdot \Delta t}$ is assumed (see Eq. 33).

If condition (37), (38) or (39) holds particles cannot tunnel subsequent cells without a chemical equilibrium calculation and without mass transfer between liquid and solid phase in this cell. On the other hand, if the particle movement during $\Delta t$ is too small (conditions (37) (38) or (39) still hold) an additional numerical dispersion due to concentration averaging within the cells results in an apparent higher dispersion. This mechanism can be explained as follows. Assume a mean movement of a particle of $\Delta x$ within 100 time steps. A particle with a tracer mass vector component $m_1$ just arriving into a cell $(m)$ distributes the whole tracer mass to all particles in that cell (Eq.'s 29-31) after chemical equilibrium calculation. For the next time step the tracer mass reaches already the next cell $(m+1)$ due to particles with a position near the cell boundary to cell $(m+1)$ whereas the tracer front should reach this cell $(m+1)$ only after 100 time steps. This influence of time step size is investigated in more detail within the applications (Chapt. 4).

In addition to the choice of a spatial grid and related time steps, boundary conditions for transport must be defined. The handling of boundary conditions within the multi-species random-walk method in the one-dimensional model is simple and corresponds to those for normal random walk. Only the concentrations of relevant species (here mass vector components) or the behaviour of a particle reaching this boundary cell have to be defined for all times. The mass transfer to particles implies a correct treatment of these boundary conditions. For example, a constant concentration boundary is realised by a constant concentration in the boundary cell where all particles entering or leaving the boundary cell during transport calculation ($\Delta t$) will produce the defined mass per particle (mass vector component of a particle) consistent with the defined concentration.

Compared to the normal random-walk approach, there exist some further important differences in the approach used here. Within normal random walk calculations, particles of identical mass for each species are moved, whereas here particles with mass vector components are moved (Tab. 3.1). An additional time component $t$ indicates the time dependency of the mass vector components (Eq.'s 29 and 30). With this method the transport step is completed by one step for all species in the liquid phase in contrast to finite difference or finite element methods. There, for each species in the liquid phase ($N_j + N_i$), the transport equation has to be solved. If all species behave equally in transport due to equal transport parameters (velocity or dispersion/diffusion coefficient) this means a reduction of calculation time. If species have different transport behaviour (e.g. due to different sorption processes) these species must be represented by different types of particles with corresponding features (particles with another apparent velocity and dispersion/diffusion coefficient). Then the resultant particle distribution is a superposition of movement of all particle sets. In the worst case, if all species behave differently the computation advantage compared to finite difference or finite element methods or the normal random walk approach vanishes.
Table 3.1: Different types and number of particles for normal and multi-species particles random walk

<table>
<thead>
<tr>
<th>'normal' random walk</th>
<th>multi-species particles random walk</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>particle type</strong></td>
<td><strong>particle type</strong></td>
</tr>
<tr>
<td>• N1 particles for species 1 with mass m1</td>
<td>□ Nmax particles with mass vector components, one component for each species mass</td>
</tr>
<tr>
<td>• N2 particles for species 2 with mass m2</td>
<td>□ = □ ( (m_1(m,t), m_2(m,t), \ldots, m_N(m,t)) )</td>
</tr>
<tr>
<td>• N3 particles for species 3 with mass m3</td>
<td>mass vector components depend on the cell m in which the particle fits and time t</td>
</tr>
<tr>
<td>• \ldots</td>
<td></td>
</tr>
<tr>
<td>• NJ particles for species Nj with mass m_Nj</td>
<td></td>
</tr>
<tr>
<td><strong>moving of</strong> ( \sum N_j \cdot N_j ) particles</td>
<td><strong>moving of</strong> Nmax particles</td>
</tr>
<tr>
<td>fixed particle masses</td>
<td>variable particle mass vector components</td>
</tr>
<tr>
<td>variable number of particles</td>
<td>fixed number of particles</td>
</tr>
</tbody>
</table>
4. MCOTAC applications in comparison with other coupled code applications

Three applications of MCOTAC to one-dimensional problems reported in literature were chosen to test the performance of the sequential coupling of transport and chemical equilibrium calculations. They are related to the incongruent or congruent dissolution of cement phases and the occurrence of multiple precipitation/dissolution fronts. The comparison serves as a verification of MCOTAC by comparison with results of other codes and includes calculated species concentration distributions as well as the CPU-time used by the different codes.

4.1 Incongruent dissolution of hydrated calcium silicate (CSH) gels

The incongruent dissolution of cement described by [Berner, 1988] was modelled with the coupled code THCC_DM [Berner, Jacobsen & McKinley, 1987] and MCOTAC. The physical-chemical model was set up in the same way for both codes. After the comparison of the results the behaviour of MCOTAC is investigated concerning the time step width and a reduction of used CPU-time.

4.1.1 The physico-chemical model

The model area consists of a one-dimensional cement block (length equal 20 cm) which is in contact with pure water at x=0. At the other end of the block, at x=20 cm, constant species concentrations are assumed, given by the initial composition of the CSH-water (because the "leaching front" will not reach this area during the calculation time). The model solids which describe an incongruent dissolution of the CSH-gel (as a simplified composition of a cement) are chosen to be "Ca(OH)$_2"$, "CaH$_2$SiO$_4$" and "SiO$_2$" where at least one solid is present. The amount of "cement" is assumed to be 1 kg CSH-gel/litre with a porosity of 0.27 and a calcium to silicate ratio (C/S) of 2.7 in the CSH-gel defined by

$$\frac{Ca \ [mol \ CaH_2SiO_4] + Ca \ [mol \ Ca(OH)_2]}{Si \ [mol \ CaH_2SiO_4] + Si \ [mol \ SiO_2]} = 2.7$$

8 For a more detailed discussion of the results concerning the physico-chemical systems the reader is referred to the list of references.

9 With THCC_DM, some problems occurred for calculations where the C/S ratio (calcium/silicate) in the solid became lower than one. At this limit the cement model changes a solid to describe the incongruent dissolution and the internally generated time step in THCC_DM decreases to zero as a result of convergence problems. These convergence problems do not occur with sequential coupled codes like CHEQMATE [Haworth et al., 1988] used for the same problem.
The precipitation/dissolution reactions are summed up in Table 4.2. Diffusion is assumed to be the only active transport process. The diffusion coefficient is chosen to be \(5 \times 10^{-10} \frac{m^2}{s}\) for all aqueous species (same as in [Haworth, Sharland & Tweed, 1989]). The basic species are \(Ca^{2+}, H_2SiO_3^{2-}, OH^-\) and an inert tracer. Also water dissociation is taken into account. The complex reactions with corresponding \(\log K\) values and the initial composition of the inlet and CSH-gel solution are shown in Tables 4.1a and 4.1b.

**Table 4.1a: Complexation reactions and related equilibrium constants**

<table>
<thead>
<tr>
<th>Chemical reactions</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ca^{2+} + OH^- \leftrightarrow CaOH^+)</td>
<td>1.3</td>
</tr>
<tr>
<td>(H_2SiO_3^{2-} + OH^- + H_2O \leftrightarrow H_3SiO_4^-)</td>
<td>-0.9</td>
</tr>
<tr>
<td>(H_3SiO_4^- + OH^- + H_2O \leftrightarrow H_4SiO_4)</td>
<td>-5.04</td>
</tr>
</tbody>
</table>

**Table 4.1b: Composition of the inlet solution and the initial CSH-gel water (basis species concentrations only)**

<table>
<thead>
<tr>
<th>Basis species</th>
<th>Inlet solution [mol/l]</th>
<th>CSH-gel solution [mol/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tracer (inert)</td>
<td>(1 \times 10^{-3})</td>
<td>0</td>
</tr>
<tr>
<td>(Ca^{2+})</td>
<td>0</td>
<td>(1.6 \times 10^{-2})</td>
</tr>
<tr>
<td>(H_2SiO_3^{2-})</td>
<td>0</td>
<td>(2.09 \times 10^{-6})</td>
</tr>
<tr>
<td>(OH^-)</td>
<td>(1 \times 10^{-7})</td>
<td>(3.79 \times 10^{-2})</td>
</tr>
</tbody>
</table>

A constant spatial grid size \(\Delta x\) was chosen to be 0.01 m which corresponds to a number of cells of 20. The maximum time step size is chosen to be \(\frac{\Delta x^2}{2D} = 1 \times 10^5\) s (Eq. 38) for MCOTAC and THCC_DM calculations.
Table 4.2: Solubility product of model components as a function of C/S ([Berner, 1988] but for a different set of basis species)

<table>
<thead>
<tr>
<th>C/S range</th>
<th>solid components</th>
<th>solubility product log $K_{so}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{C}{S} = 0$</td>
<td>SiO$_2$(s) $\leftrightarrow$ H$_2$SiO$_4$$^2-$ - 2OH$^-$</td>
<td>2.34</td>
</tr>
<tr>
<td>$0 \leq \frac{C}{S} \leq 1$</td>
<td>SiO$_2$(s) $\leftrightarrow$ H$_2$SiO$_4$$^2-$ - 2OH$^-$</td>
<td>3.0 + $\frac{0.792}{\frac{C}{S} - 1.2}$</td>
</tr>
<tr>
<td></td>
<td>Ca$_2$Si$_2$O$_7$(s) $\leftrightarrow$ Ca$^{2+}$ + H$_2$SiO$_4$$^2-$</td>
<td>$-8.16 - \frac{1 - \frac{C}{S}}{\frac{C}{S}}(0.78 + \frac{0.792}{\frac{C}{S} - 1.2})$</td>
</tr>
<tr>
<td>$1 \leq \frac{C}{S} \leq 2.5$</td>
<td>Ca(OH)$_2$(s) $\leftrightarrow$ Ca$^{2+}$ + 2OH$^-$</td>
<td>$-4.945 - \frac{0.338}{\frac{C}{S} - 0.85}$</td>
</tr>
<tr>
<td></td>
<td>Ca$_2$Si$_2$O$_7$(s) $\leftrightarrow$ Ca$^{2+}$ + H$_2$SiO$_4$$^2-$</td>
<td>-8.16</td>
</tr>
<tr>
<td>$\frac{C}{S} &gt; 2.5$</td>
<td>Ca(OH)$_2$(s) $\leftrightarrow$ Ca$^{2+}$ + 2OH$^-$</td>
<td>-5.15</td>
</tr>
<tr>
<td></td>
<td>Ca$_2$Si$_2$O$_7$(s) $\leftrightarrow$ Ca$^{2+}$ + H$_2$SiO$_4$$^2-$</td>
<td>-8.16</td>
</tr>
</tbody>
</table>

4.1.2 Results

a) Pure tracer diffusion

As a test if the transport was handled correctly by MCOTAC an additional tracer diffusion into the model area was calculated (see Tables 4.1a and 4.1b) and compared to an analytical solution [Bear, 1988] for pure tracer diffusion (Fig. 4.1). This test controls the numerical dispersion due to averaging particle concentrations within the cells (Eq.'s 29-31). Fig. 4.1 shows that the tracer transport was calculated correctly for the inert tracer while for the reacting species chemical equilibrium calculations were performed at the same time.
b) Calcium to silicate ratio

The C/S ratio is calculated along the direction of migration for times up to 200 years where the C/S ratio becomes smaller than 1 at the first node and convergence problems occur for THCC_DM preventing a further comparison. The results are shown in Figure 4.2. The calculations are in good agreement. The discrepancies for the C/S profiles near the boundary (distance = 0.01 m) for 0.1, 1 and 10 years occur in the region of high gradient of C/S. The initial boundary conditions produce particles with completely different mass vector components in cells near this sharp front at the boundary. Due to transport calculations the randomly varying number of particles with different mass vector components present in these cells influence the C/S profiles much more at sharp fronts (at early times) than at later times where lower C/S gradients are present.

Further calculations with MCOTAC to regions (cells or nodes >2) where the C/S ratio becomes lower than one need long computing times. For this reason another CSH-gel composition is used to demonstrate MCOTAC calculations in regions where the C/S ratio becomes lower than one for more than one cell. This is done by decreasing the solid concentrations so that the resulting C/S ratio is just above one keeping all other parameters fixed. Now a C/S ratio below one is calculated for subsequent cells which coincides with the precipitation of SiO₂ and complete dissolution of Ca(OH)₂ in these cells (Fig. 4.3). This calculation underlines the handling of incongruent cement dissolution described by the Berner model within MCOTAC.
**Figure 4.2:** C/S ratio calculated by THCC_DM and MCOTAC for different times (time step 1·10^5 s, 1000 particles)

**Figure 4.3:** Temporal development of C/S ratio and solid concentrations Ca(OH)₂ and SiO₂ within the incongruent dissolution model at different locations in the CSH-column (x = 1 cm, 2 cm and 4 cm)
4.1.3 Behaviour of MCOTAC

As mentioned above the sequentially coupled code MCOTAC does not iterate between the transport and chemical equilibrium calculations. Therefore, the choice of the time step width is important (in connection with a fixed grid size), especially for heterogeneous reactions ([Herzer & Kinzelbach, 1989]). The influence of different time steps is shown by the following calculations of the CSH-gel problem. Different time steps are used to calculate C/S profiles at 10 years of migration for a grid size of 0.01 m (Fig. 4.4). In the case of a long time step of $10^5$ s which does not satisfy condition (38) particles transport mass over more than one cell during the time step without taking part in chemical equilibrium calculations. Therefore reactions influencing the solid phase (C/S ratio) take place further within the model area although reaction with the solid phase is still possible near the boundary (because the C/S ratio is still > 1). The pure water with a pH of 7 diffuses far into the cement column before the chemical equilibrium calculation causes reactions with the solids. The result is a flat C/S profile within the cement column, too high near the left boundary and too low further inside the column. For a time step of $1 \cdot 10^5$ s which does satisfy condition (38) a good agreement with a THCC_DM calculation is achieved. If a shorter time step of $10^4$ s is chosen Eq. (38) is still fulfilled but now the additional numerical dispersion (due to averaging of species concentrations within each grid cell after each chemical equilibrium calculation) becomes dominant and the C/S profiles move faster into the column. A further calculation with 40 grid cells (and 2000 particles in the model area to have the same particle density), a grid size of 0.005 m and a time step of $2.5 \cdot 10^4$ s corresponding to Eq. (38) is also in good agreement with the THCC_DM calculation.

The problem of too-small time steps should not occur very often because these short time steps are accompanied by longer calculation times which should be avoided generally for complex coupled code calculations. However the effect of too-short time steps should be kept in mind. The uncertainty in choosing the correct time step width could be controlled by a tracer migration calculation which is also affected by the additional dispersion due to concentration averaging within each cell but which is not affected by chemical reactions. Figure 4.5 shows the tracer diffusion for different time steps as a control tool for the used time step. For very large time steps ($10^6$ s) the particle distribution becomes widely scattered and for the particle number of 1000 some particles move outside the model area. For too-small time steps the additional dispersion results in a longer migration distance into the column than calculated by the analytical solution and the MCOTAC calculation with a maximum time step width of $10^5$ s. Therefore, the tracer movement and conditions (37), (38) or (39) are good tests for choosing the correct time step.
Figure 4.4: C/S ratio at 10 years calculated by THCC_DM and MCOTAC for different time steps and different number of grid cells.
The test case incongruent dissolution then was used as the first performance test for the MCOTAC code. The CPU-times for THCC_DM and MCOTAC calculations were compared for a problem where no convergence difficulties occur for the THCC_DM code. Two maximum time step sizes of $1 \times 10^5$ s and $2 \times 10^5$ s are used for a uniform grid of 20 cells (grid size 0.01 m) and 1000 particles within the MCOTAC transport module. CPU-
times of THCC_DM and MCOTAC calculations for a migration time of 10 years are compared in Table 4.3. It can be seen that there is no CPU-time advantage of MCOTAC.

**Table 4.3:** CPU-times for THCC_DM and MCOTAC calculations for a migration time of 10 years\(^{10}\) and two different maximum time step sizes

<table>
<thead>
<tr>
<th>Model</th>
<th>(\Delta t=1 \cdot 10^5) s</th>
<th>(\Delta t=2 \cdot 10^5) s</th>
</tr>
</thead>
<tbody>
<tr>
<td>THCC_DM</td>
<td>6 min</td>
<td>3 min</td>
</tr>
<tr>
<td>MCOTAC</td>
<td>6 min</td>
<td>3 min</td>
</tr>
</tbody>
</table>

A further reduction of the CPU-time is possible if unnecessary chemical equilibrium calculations can be avoided (e.g. if the species concentration do not change very much in time or in space). But the "unnecessary" should be tested in each application. In the case of the incongruent cement dissolution problem changes of species concentration lower than 10% do not change the results noticeably but reduce the CPU-time nearly by a factor of two. Changes higher than 10% (30%) lead to different results and are not acceptable.

Another possibility of CPU-time reduction is the use of a smaller number of particles in the transport module. But this has its limit in the high fluctuations of species concentrations within the cell for a small number of particles. Then the calculation of chemical equilibrium becomes difficult because the Newton-Raphson procedure gets convergence problems if high concentration fluctuations occur and guesses for species concentrations are far away from the finally calculated concentration (see App. A). The number of particles is not the main factor defining CPU-time. An example calculation with 1000 and 10000 particles (factor of 10) increases the CPU-time by a factor of 4. This underlines the important role of chemical equilibrium calculations in the whole CPU consumption which should be taken into account for future MCOTAC development.

This first application of MCOTAC shows that it is possible to include the Berner model for incongruent dissolution of a CSH-gel without the difficulties in the region of C/S < 1 which is underlined by calculations of subsequent nodes with C/S < 1. The dependency of the time step during calculation was tested with the result that it is important for sequentially coupled codes like MCOTAC and should be controlled by a tracer transport and conditions (37), (38) or (39) if heterogeneous reactions occur. The application also serves as a first performance test of the MCOTAC code and requires CPU-times for THCC_DM and MCOTAC calculations in the same range. A further improvement for the individual chemical equilibrium calculation within MCOTAC seems possible. The presentation of the calculated results is still rudimentary if the amount of calculated data for this simple example is considered; the presentation should be controlled during the calculation. Figure 4.6 shows all species concentrations along the model area for a predefined migration time, and is not

\(^{10}\) For the calculation of 200 years leaching of the CSH-column a CPU time of 180 min is used by MCOTAC for a time step of \(10^3\) s.
very clear on a logarithmic scale. This underlines that additional tools like on-line graphic presentation of results are necessary to manage the high amount of data produced in coupled transport and chemical reaction calculations.

Figure 4.6: Calculated species concentration profiles for different migration times $t$. (Note that the "low resolution" logarithmic scale has been chosen to include all calculated concentration profiles in one figure)
4.2 Portlandite dissolution by several models within the CHEMVAL-project and by MCOTAC

During CHEMVAL stages 3 and 4 [Read, 1991] six computer programs for reactive chemical transport were involved. Three were directly coupled and three sequentially coupled. All models were applied to several test cases and their results were compared as far as possible (bearing in mind the development status of some of the codes). The agreement was satisfactory for the majority of the coupled test cases and there were no systematic differences apparent between the directly and sequentially coupled codes. The discrepancies could be ascribed, in the main, to differences within the chemical data base (data base reduction), and to the variable time/space grids used. Therefore, a CHEMVAL test case was chosen to compare the MCOTAC calculations with several coupled code applications to the same problem described in the CHEMVAL report [Read, 1991]. Test case 1, the dissolution of portlandite Ca(OH)$_2$ and precipitation of calcite CaCO$_3$ along a one-dimensional flow path as cement reacts with a carbonated groundwater, was used here because of its relation to near-field chemistry. The processes considered are aqueous complexation, reversible precipitation/dissolution and one-dimensional advective-dispersive flow. As far as possible the data were extracted out of the CHEMVAL report. But, as stated in the report, each coupled code used its individual system for calculations (time/space grid size, chemical reactions taken into account, equilibrium constants, ionic strength correction used and so on) which was not reported in detail, therefore, a full comparison is not possible. The MCOTAC calculations can be looked at as an additional model calculation for sequentially coupled codes within the other model calculations (see Table 4.4) just to see if there are significant differences in the results.

Table 4.4: Coupled codes used by different institutions within CHEMVAL project

<table>
<thead>
<tr>
<th>coupled code</th>
<th>institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHEMTARD</td>
<td>Atkins Engineering Sciences (AES)</td>
</tr>
<tr>
<td>CHEQMATE</td>
<td>AEA Technology Harwell (AERE)</td>
</tr>
<tr>
<td>STELE</td>
<td>Ecole Nationale Superieure des Mines de Paris (EMP)</td>
</tr>
<tr>
<td>CAT / CEQCSY</td>
<td>Bureau de Recherches Geologique et Minieres (BRGM)</td>
</tr>
<tr>
<td>THCC</td>
<td>Svensk Karnbranslehantering AB (SKB)</td>
</tr>
</tbody>
</table>
The chemical system used here was described by a set of basic species $Ca^{2+}, Na^+, CO_3^{2-}, Cl^-$ and $OH^-$ with following complexation reactions.

**Table 4.5:** Chemical equilibrium reactions for complexes with corresponding log $K$ values (CHEMVAL test case 1 (i), [Read, 1991])

<table>
<thead>
<tr>
<th>complex reactions</th>
<th>log $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ca^{2+} + OH^- \leftrightarrow CaOH^+$</td>
<td>1.3</td>
</tr>
<tr>
<td>$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 (aq)$</td>
<td>3.153</td>
</tr>
<tr>
<td>$Ca^{2+} - OH^- + H_2O + CO_3^{2-} \leftrightarrow CaHCO_3^+$</td>
<td>-2.570</td>
</tr>
<tr>
<td>$Ca^{2+} + Cl^- \leftrightarrow CaCl^+$</td>
<td>0.08</td>
</tr>
<tr>
<td>$-OH^- + H_2O + CO_3^{2-} \leftrightarrow HCO_3^-$</td>
<td>-3.671</td>
</tr>
<tr>
<td>$Na^+ + OH^- \leftrightarrow NaOH(aq)$</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

**Table 4.6:** Chemical equilibrium reactions for solids with corresponding log $K_{so}$ values (CHEMVAL test case 1 (i), [Read, 1991])

<table>
<thead>
<tr>
<th>precipitation/dissolution reactions</th>
<th>log $K_{so}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CaCO_3 (s) \leftrightarrow Ca^{2+} + CO_3^{2-}$</td>
<td>-8.48</td>
</tr>
<tr>
<td>$Ca(OH)_2 (s) \leftrightarrow Ca^{2+} + 2OH^-$</td>
<td>-5.15</td>
</tr>
</tbody>
</table>

For the basis species total concentrations are given for the cement water and a clay groundwater shown in Table 4.7.

It is assumed that calcite is not present in the cement at the start of the simulation and that the cement is just portlandite. For calculations done here, a starting $Ca(OH)_2 (s)$ concentration of 0.7 equivalent mol/l fluid is used\(^\text{11}\).

\(^\text{11}\) No information on the assumed 'cement concentration' (here only portlandite) for test case 1 was found in the CHEMVAL report, only a cementitious solution, slightly supersaturated with respect to portlandite was reported.
Table 4.7: Initial composition, and the related pH, of the equilibrated cement water in the model area and the equilibrated inlet clay water (total concentrations), [Read, 1991]

<table>
<thead>
<tr>
<th>basis species</th>
<th>cement water [mmol/l]</th>
<th>clay water [mmol/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>20</td>
<td>5.5</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>1.0 $\times$ 10$^{-7}$</td>
<td>4.5</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>32</td>
<td>3.2 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>pH</td>
<td>12.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Transport is idealised by one-dimensional advection/dispersion through an isotropic porous medium where no effects of precipitation/dissolution reactions on hydraulic conditions are assumed. The transport parameters are given in Table 4.8.

Table 4.8: Transport parameters within CHEMVAL test case 1 (i), [Read, 1991]

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pore water velocity</td>
<td>$v = 1$ cm/year</td>
</tr>
<tr>
<td>dispersivity</td>
<td>$\alpha = 1$ m</td>
</tr>
<tr>
<td>model length</td>
<td>$L = 10$ m</td>
</tr>
</tbody>
</table>

The boundaries are fixed at constant concentration. For the grid size a 40 to 50 node grid was proposed but two different grids were used in the CHEMVAL calculations, one employing a coarse, the other a fine grid which was found to be more applicable. Nevertheless, here a uniform 50-node grid was used. With this the MCOTAC calculations for the speciation of calcium in initial and boundary solution are shown in Table 4.9 and Figures 4.7 and 4.8.
Table 4.9: MCOTAC calculations for the speciation of calcium in the inlet clay groundwater and the initial cement water in the model area

<table>
<thead>
<tr>
<th></th>
<th>composition of the initial cement water [mmol/l]</th>
<th>composition of the inlet clay groundwater [mmol/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ca^{2+}$</td>
<td>17.5</td>
<td>5.3</td>
</tr>
<tr>
<td>$CaOH^+$</td>
<td>5.5</td>
<td>$1.9 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>$CaCO_3(aq)$</td>
<td>$9.0 \cdot 10^{-8}$</td>
<td>$9.4 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$CaHCO_3^+$</td>
<td>$6.0 \cdot 10^{-12}$</td>
<td>0.065</td>
</tr>
<tr>
<td>$CaCl^+$</td>
<td>0.32</td>
<td>0.036</td>
</tr>
</tbody>
</table>

These values are in the same range as reported in CHEMVAL report on stages 3 and 4 as shown in Figures 4.7 and 4.8. Differences may be explained, as mentioned above, by the individual set up of each model (data base reduction, full data base or smaller number of aqueous species).

Figure 4.7: Calcium speciation in cement water by MCOTAC compared to CHEMVAL test case 1(i) calculations by different coupled codes/institutions (see Tab. 4.9)
Figure 4.8: Calcium speciation in clay water by MCOTAC compared to CHEMVAL test case 1(i) calculations by different coupled codes/institutions (see Tab. 4.9)

For the dynamic calculations a smooth-option (see App. B) is used within MCOTAC to reduce the number of particles during calculation and decrease CPU-time. Without these option the species concentrations in the cells vary too much for the same number of particles to give comparable concentration distributions. Further parameters are a spatial grid size of 0.2 m (50 cells), a maximum time step size of $1 \cdot 10^7$ s and a particle number of 5000. The calculation or computing time for this system up to 200 years of migration was less than two hours on the i860 card within a PC.

The following figures show the concentration of $Na^+$, $Ca^{2+}$, $CaOH^+$ and $CaHCO_3^+$ as a function of distance ($x$) at a migration time of 100 years and the pH profile at 200 years. The calculations from the CHEMVAL project are taken from the report [Read, 1991] by scanning the corresponding figures. The calculations by MCOTAC are then overlaid to the scans. Comparing these calculations one has to keep in mind that the CHEMVAL calculations (Figures 4.9 to 4.13) are results of perhaps two calculations with different spatial grids (which used was not reported). Therefore, differences in the region $x = 0$ m to $x = 2$ m could be caused by a rough grid used by MCOTAC and/or the chosen value for the initial portlandite amount. A sensitivity analysis with MCOTAC with a smaller initial portlandite amount in the column shows lower calcium-related concentration profiles in the region $x = 0$ m to $x = 2$ m.
Figure 4.9: Calculated Na⁺ concentration at 100 years by MCOTAC and coupled codes used within CHEMVAL stage 3 and 4. (The step in the profile near 5m calculated by MCOTAC is due to data output format)

The Na⁺ profile (which should be a test of numerical accuracy within CHEMVAL as the concentration varies very little over the domain) calculated by MCOTAC equals those calculated by other codes up to the values within the portlandite (Fig. 4.9). But these differences could be explained by the incompletely defined chemical system because at $x = 10$ m there should be the initial Na⁺ concentrations. The argument holds also for the Ca²⁺ and CaOH⁺ profile (Figures 4.10 and 4.11). The differences at $x = 1$ m could be caused by the rough grid size used by MCOTAC whereas within CHEMVAL some modellers used two grids, a fine grid between 0 and 2 m, and an additional coarse grid between 0 and 10 m.
Figure 4.10: Calculated $\text{Ca}^{2+}$ concentration at 100 years by MCOTAC and coupled codes used within CHEMVAL stage 3 and 4.

The $\text{CaHCO}_3$ profile (Fig. 4.12) is similar to other calculated curves up to differences at the right boundary representing the differences for the initial chemical equilibrium calculation (Fig. 4.7). The reason could be again the different chemical systems modelled by each code. The pH profile at 200 years (Figure 4.13) also shows discrepancies in the range up to two meters but at the end of the column, where most codes calculated an increasing pH.
MCOTAC calculations give a constant pH as it should be if the pH is buffered by portlandite.

![Graph of CaHCO₃⁺ concentration](image1)

**Figure 4.12**: Calculated CaHCO₃⁺ concentration at 100 years by MCOTAC and coupled codes used within CHEMVAL stage 3 and 4

![Graph of pH](image2)

**Figure 4.13**: Calculated pH at 200 years by MCOTAC and coupled codes used within CHEMVAL stage 3 and 4
Figure 4.14: Calculated equivalent solid concentration for portlandite and calcite at 1 year and 100 years

The calculated solid concentrations shown in Figure 4.14 have no equivalents in the CHEMVAL calculations. The profiles of portlandite and calcite at 1 year and 100 years correspond to an initial solid portlandite amount of 0.7 mol/l. They show a significant portlandite dissolution at the boundary at \( x = 0 \). Calcite precipitation is significant at 100 years migration and is also present at 1 year near the left (inflowing) boundary. The portlandite dissolution front moves continuously to the column end, while the calcite precipitation occurs predominantly near the boundary where the \( CO_3^{2-} \) rich groundwater enters the column. This result shows that local precipitation can occur and effects on porosity (hydraulic effects) which are neglected here may become important in the system.

For the MCOTAC calculations above a smooth-option is used which allows transport calculations with a small number of particles (5000 in these calculations). Without this option the individual concentrations of species in the cells will show statistical variations from cell to cell as demonstrated in Figure 4.15 for the \( Na^+ \) profile. Small differences between the \( Na^+ \) concentration in the inflowing water and initial \( Na^+ \) concentration in the model domain cause a small gradient for the \( Na^+ \) profile. Therefore, at this low concentration level the statistical \( Na^+ \) concentration variations become noticeable compared to the calculations with the smooth-option. The corresponding \( Ca^{2+} \) profiles (Figure 4.16) show the same behaviour but there, the concentration variations look quite small because the total concentration scale of \( Ca^{2+} \) is larger in the model domain than for \( Na^+ \).
**Figure 4.15:** $\text{Na}^+$ profiles calculated by MCOTAC with and without the smooth-option (see App. B) at 100 years (CHEMVAL test case 1 (i)).

**Figure 4.16:** $\text{Ca}^{2+}$ profiles calculated by MCOTAC with and without the smooth-option (see App. B) at 100 years (CHEMVAL test case 1 (i)).

These comparisons of the coupled code calculations done within the CHEMVAL project (and especially test case 1 (i)) with corresponding MCOTAC calculations show reasonably good agreement of results. But they show too, that a complete comparison is not possible because there is no common model system for all codes applied (different codes handle the individual chemical systems differently, e.g., number of complexation reactions taken into
account). For further coupled code testing a common system definition and handling should be the aim to evaluate differences in the codes (models), e.g., between directly coupled and sequentially coupled codes. Another important aspect is the computing time of different codes as a hint of applicability to more complex or realistic problems.

4.3 Calcite dissolution and hypothetical precipitation/dissolution of dolomite by THCC_DM and MST1D compared to MCOTAC

A further one-dimensional use of coupled codes is considered which evaluates the development of a multiple sharp mineral front system with respect to the computing time used. To have comparable results to calculations here, a test case defined by [Engesgaard & Kipp, 1992] is used. The test case was designed to have multiple precipitation-dissolution fronts of calcite and dolomite, recognising that dolomite precipitation is not realistic over the time scale used in the test case. The chemical and physical systems are defined in tables 4.10 to 4.12.

Table 4.10: Chemical reaction system with corresponding logK values [Engesgaard, 1994; Engesgaard & Kipp, 1992]

<table>
<thead>
<tr>
<th>chemical reaction</th>
<th>log K at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃(s) ↔ Ca²⁺ + CO₃²⁻</td>
<td>-8.47</td>
</tr>
<tr>
<td>CaMg(CO₃)₂(s) ↔ Ca²⁺ + Mg²⁺ + 2CO₃²⁻</td>
<td>-17.17</td>
</tr>
<tr>
<td>Ca²⁺ + CO₃²⁻ ↔ CaCO₃</td>
<td>3.225</td>
</tr>
<tr>
<td>Mg²⁺ + CO₃²⁻ ↔ MgCO₃</td>
<td>2.981</td>
</tr>
<tr>
<td>H⁺ + OH⁻ ↔ H₂O</td>
<td>-13.998</td>
</tr>
<tr>
<td>H⁺ + CO₃⁻ ↔ HCO₃⁻</td>
<td>10.329</td>
</tr>
<tr>
<td>H⁺ + HCO₃⁻ ↔ H₂CO₃</td>
<td>16.681</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>inert</td>
</tr>
</tbody>
</table>
Table 4.11: Transport parameters [Engesgaard & Kipp, 1992]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column length</td>
<td>0.5 m</td>
</tr>
<tr>
<td>Pore velocity</td>
<td>$9.37 \cdot 10^{-5} \frac{m}{s}$</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.32</td>
</tr>
<tr>
<td>Bulk density</td>
<td>$1800 \frac{kg}{m^3}$</td>
</tr>
<tr>
<td>Dispersivity</td>
<td>0.0067 m</td>
</tr>
</tbody>
</table>

Table 4.12: Inlet and initial conditions, (*) pH in [-], (**) solid concentration in $\frac{mol}{kg \ soil}$ [Engesgaard & Kipp, 1992]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Inlet concentration $\frac{mol}{kg \ water}$</th>
<th>Initial concentration $\frac{mol}{kg \ water}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.06 (*)</td>
<td>9.91 (*)</td>
</tr>
<tr>
<td>$Ca^{2+}$</td>
<td>0</td>
<td>$1.239 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$CO_3^{2-}$</td>
<td>0</td>
<td>$1.239 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$Mg^{2+}$</td>
<td>$1.10^{-3}$</td>
<td>0</td>
</tr>
<tr>
<td>$Cl^-$</td>
<td>$2.10^{-3}$</td>
<td>0</td>
</tr>
<tr>
<td>$CaCO_3(s)$</td>
<td>-</td>
<td>$2.17 \cdot 10^{-5}$ (***)</td>
</tr>
<tr>
<td>$CaMg(CO_3)_2(s)$</td>
<td>-</td>
<td>0 (***)</td>
</tr>
</tbody>
</table>

For the simulation the model parameters used for MCOTAC calculations are the same as those reported by [Engesgaard, 1994; Engesgaard & Kipp, 1992] (Test case B). These are a limited simulation time of $10^5$ s so that no tracer breakthrough profile would reach the column end during simulation, a cell width of 0.01 m and a starting time step of 200 s. In addition, 5000 particles are used within MCOTAC transport calculations. With this precise system definition the different model applications should be comparable.
The results are shown in Figure 4.17 where the spatial distributions of mineral concentration, pH, concentration of the basis species and the main complex concentrations are calculated for \( t = 21000 \) s. These results include also the comparison of the static chemical equilibrium calculation. The initial chemical conditions which are still valid at the right boundary at \( t=21000 \) s reflect the identical chemical equilibrium calculated by MCOTAC and MST1D (including PHREEQE for chemical equilibrium calculation) used by [Engesgaard & Kipp, 1992]. The sharp dissolution fronts of calcite and dolomite and the precipitation front of dolomite are in good agreement with these calculations as well as the concentration distribution for the basis species and complexes. Calculations for this test case are also done by the directly coupled code THCC_DM with the same parameters used for MCOTAC and MST1D. This allows a comparison with the results calculated by a directly coupled code, and a comparison of the CPU-times used. Figure 4.18 shows the corresponding concentration distributions which show identical concentration profiles for all species for MCOTAC and THCC_DM simulations except small differences in the pH front near the left boundary.

The dissolution of calcite and (hypothetical) precipitation/dissolution of dolomite by a special composition of groundwater calculated by MCOTAC underlines the applicability of the code to multiple mineral front systems. The calculation of this test case by two different codes, the directly coupled code THCC_DM [Carnahan, 1986] and sequentially coupled code MCOTAC allows an additional comparison of computing time (Tab. 4.13) which will become more important for more complex problems.

**Table 4.13:** CPU-time used for the test case simulation by THCC_DM and MCOTAC

<table>
<thead>
<tr>
<th>Model</th>
<th>calculation time (CPU) up to ( T = 21,000 ) s</th>
</tr>
</thead>
<tbody>
<tr>
<td>THCC_DM</td>
<td>55 h</td>
</tr>
<tr>
<td>MCOTAC</td>
<td>(~4) min</td>
</tr>
</tbody>
</table>

The reason for the extremely different CPU-times could be the existence of sharp mineral fronts with different chemical systems at neighbouring nodes. The directly coupled code uses internally generated time step widths starting at some hundreds of seconds then decreasing to less than 1 s to achieve convergence during the calculations whereas the sequentially coupled code uses a time step width of 800 s defined by equations (37), (38) or (39). This advantage can be essential for more complex code applications.
Figure 4.17: Calculated concentration profiles by MCOTAC (dashed lines) compared to results of [Engesgaard & Kipp, 1992], test case B at 21000 s
Figure 4.18: Calculated concentration profiles by MCOTAC (dashed lines) and THCC_DM (solid lines) according to [Engesgaard & Kipp, 1992], test case B at 21000 s
5. Conclusions and recommendations

One-dimensional transport described by the random walk of multi-species particles was coupled within MCOTAC with calculation of chemical equilibria including complexation and precipitation/dissolution reactions. The sequential coupling provides a robust method to describe complex physico-chemical systems. The code's modular composition and the use of a modified random walk method for the transport module simplifies further development of the code. The individual modules of the code have been verified, the transport module against an analytical solution, and the chemical equilibrium module against results of several other speciation calculations. Coupled problems given in the literature helped to test MCOTAC and to judge its range of application.

Three applications of MCOTAC show that the code is applicable to coupled transport/chemical equilibrium reaction problems. The handling of incongruent dissolution is possible as described in section 4.1. Convergence problems reported for THCC_DM calculations in regions where the C/S ratio is below one did not occur for MCOTAC calculations. The CPU-times used for this application are similar to those of THCC_DM. The comparison underlined the importance of the choice of time step for the sequentially coupled code. Because the coupling of transport and chemistry is weak (there is no convergence condition included in the coupling) an additional tracer served as a control parameter for numerical dispersion and a plausible time step condition was derived if heterogeneous chemical reactions occurred.

The second application, the CHEMV AL test case 1(i), showed the importance of well-documented problem definitions. Granted this knowledge, the calculated results of MCOTAC are consistent with the results of the other models/institutions. A comparison of used CPU-time was not possible in this case because there was no information within the CHEMV AL calculations.

With the third application the correct handling of multiple precipitation/dissolution fronts was demonstrated. A comparison of the CPU-time for THCC_DM and MCOTAC shows great differences. The MCOTAC calculation was nearly a factor of 1000 faster than that by THCC_DM. A reason could be the occurrence of multiple precipitation/dissolution fronts implying different chemical systems at neighbouring finite difference nodes. There the internal time step modifier of THCC_DM decreases the time step to values below one second because of the convergence criterion. The reduction in CPU-time achieved by MCOTAC emphasises the potential of sequentially coupled codes for dealing with more complex problems.

The MCOTAC code (written in C and FORTRAN modules) was implemented on two computer platforms, an Intel i860 card as a fast 64-bit inboard within an IBM-compatible PC and on a UNIX workstation. For development, testing and application of the code in this early stage it was necessary to have a fast computer on the table for continuous interaction. A batch type application for coupled code seems to be questionable as the comparison to calculation times on fast batch machines indicates. A further development in the direction of visualisation of calculated data is necessary to handle and control the high amount of data occurring in simple one-dimensional problems. With the modular type of
subroutines a flexible adaptation of the code or parts of it to developments in hard and software is guaranteed.

An extension to more complex systems is planned. This includes an at least two-dimensional transport by superposition of a second transport dimension. This is simply done in the case of a random walk transport description. A $k_D$-type sorption of species could be incorporated in the transport module by the introduction of additional particle sets with the differing transport properties. In contrast to this, sorption is also possible within the chemical equilibrium model. Which type of sorption description is preferred depends on the application at hand. Also a kinetic description of some chemical reactions might be necessary and will cause a revision of the chemical module. A revision of the chemical equilibrium module seems to be unavoidable because this part consumes the most CPU-time during calculations, and it will be desirable to have a faster module. For a more realistic description of physico-chemical systems with precipitation/dissolution reactions, the influence of porosity changes and related changes of the flow field should finally be taken into account by adding a hydraulic module.

Acknowledgements

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References


Appendix A: Newton-Raphson procedure within chemical equilibrium calculations

The Newton-Raphson procedure [Press et al., 1990] is used to solve the non-linear set of equations (22) in the form of the residue equations (23). The $N_j + N_s$ residue equations (23) are solved if the set of basis and solid concentrations exists with $Y_j = 0$. The Newton-Raphson procedure ([Press et al., 1990]) starts from a guess for the concentrations of all basis species in each cell $m^{12}$ (e.g. given by an input file for $t = 0$ or by the concentrations of the previous time step for $t > 0$). The ionic strength (Eq. 14) and related, the ionic strength correction (Tab. 2.1) are calculated for a first approximation for basis (primary) species activities (Eq. 13). Inserting these values into the complexation reaction (Eq. (12) leads to a first calculated approximation of all activities (concentrations) and inserting in (23) gives a first residue vector $Y_j$. These differences $Y_j$ are not equal to zero so that the initial guess for the concentrations of basis species and solids need a correction defined by first order Taylor expansion:

$$Y_j^{N+1} = Y_j^N - \sum_{i=1}^{N_j} \frac{\partial Y_j}{\partial X_i} \cdot \Delta X_i$$  \hspace{1cm} (A.1)

(for basis species) and

$$Y_j^{N+1} = Y_j^N - \sum_{i=1}^{N_j} \frac{\partial q_k}{\partial X_i} \cdot \Delta X_i \quad \text{if} \quad q_k > K_{j\omega}^k \text{ and } P_k > 0$$  \hspace{1cm} (A.2a)

$$Y_j^{N+1} = Y_j^N - \delta_{j\omega} \cdot \Delta X_i \quad \text{if} \quad q_k \leq K_{j\omega}^k \text{ and } P_k \leq 0$$  \hspace{1cm} (A.2b)

$$j = 1, ..., N_j$$

(for solids) where $\Delta X_j$ are components of a vector $\bar{X}$ of the independent variables:

$$\Delta X_j = X_j^N - X_j^{N+1}$$  \hspace{1cm} (A.3)

The application of (A.1) to all basis species and the solids and the assumption of vanishing residues $Y_j^{N+1}$ yields an inhomogeneous linear set of equations

$$\bar{Y}^N = Z \cdot \Delta \bar{X}$$  \hspace{1cm} (A.4)

with the Jacobian matrix$^{13}$

---

$^{12}$ not explicitly indexed within the following formulae

$^{13}$ The elements of the Jacobian matrix are calculated by analytical expressions involving derivatives of the 'integer' expressions for complexes (Eq. 5) and solids (Eq. 8).
The value for \( \bar{X}^{N+1} \) at the \((N+1)\)th iteration is found from the solution of the matrix equation

\[
\begin{bmatrix}
\frac{\partial Y_1}{\partial X_1} & \frac{\partial Y_2}{\partial X_1} & \cdots & \frac{\partial Y_{N_j+N_k}}{\partial X_1} \\
\frac{\partial Y_1}{\partial X_2} & \frac{\partial Y_2}{\partial X_2} & \cdots & \frac{\partial Y_{N_j+N_k}}{\partial X_2} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial Y_1}{\partial X_{N_j+N_k}} & \frac{\partial Y_2}{\partial X_{N_j+N_k}} & \cdots & \frac{\partial Y_{N_j+N_k}}{\partial X_{N_j+N_k}}
\end{bmatrix}
\begin{bmatrix}
Y_1 \\
Y_2 \\
Y_3 \\
\vdots \\
Y_{N_j+N_k}
\end{bmatrix}^{N+1} = \begin{bmatrix}
X_1^N - X_1^{N+1} \\
X_2^N - X_2^{N+1} \\
X_3^N - X_3^{N+1} \\
\vdots \\
X_{N_j+N_k}^N - X_{N_j+N_k}^{N+1}
\end{bmatrix}
\] (A.6)

which is the \((N+1)\)th iteration vector for the values of the concentration of basis species and solids. Then, new values for the concentrations of complexes, new ionic strength corrections and corrections to the log \( K \) values (if necessary) are calculated and so on. The iteration is finished if

\[
\bar{X}^{N+1} = X^N - \Delta \bar{X} = \bar{X}^N - (\bar{X}^N - \bar{X}^{N+1})
\] (A.7)

or if a convergence (cut off) criterion is fulfilled, for example

\[
\bar{e} > \max \left( \frac{Y_j}{X_j}, j = 1, \ldots, N_j; \frac{Y_{N_j+k}}{P_k}, k = 1, \ldots, N_k \right)
\] (A.9)

where \( \bar{e} \) is a small number (error tolerance for the iteration process) defined by the user. The cut off criterion ensures that for the set of non-linear equations a solution vector with basis species and solid species concentration as vector components is found which holds for equations (22) within the given error tolerance.
Appendix B: The Random-Walk-Method

Random walk has its origin in statistical physics for description of diffusion phenomena. The solution of the advection/dispersion differential equation is done by a particle tracking procedure. Tracer particles are moved in a flow field with an additional diffusion/dispersion term [Prickett, Naymik & Lonnquist, 1982]. Each particle is combined with a fixed mass of a substance or fixed masses of different masses of substances with the same behaviour concerning advection, dispersion and diffusion (sorption). The diffusion/dispersion is modelled by a random walk so that in addition to a defined advective step a probabilistic movement is superposed. This random walk with special statistical characteristics is equivalent to the diffusion/dispersion transport processes. The application of the random walk movement to many particles results in a dispersing tracer particle distribution. The total mass of substance(s) is distributed equally to all tracer particles. A bookkeeping for location of tracer particles and the number of tracer particles is necessary. The concentration distribution can be calculated by an overlay of a grid and dividing particle mass(es) within a grid cell by the volume of the grid. Many different boundary and initial conditions can be considered.

The link of a random walk description to transport phenomena can be shown by the following example. For a one-dimensional case and a pulse injection of a tracer mass $\Delta m$ in a clean aquifer at $x=0$ the analytical solution for the concentration as a function of location $x$ and time $t$ (in the case of these specified boundary and initial conditions) is given by [Kinzelbach, 1987]:

$$c(x,t) = \frac{c_0}{\sqrt{4\pi D t}} \cdot e^{-\frac{(x-v t)^2}{4Dt}} \quad (B.1)$$

where $v$ is the flow velocity, $D$ the dispersion coefficient and

$$c_0 = \frac{\Delta m}{A \phi} \quad (B.2)$$

$A$ is the cross section of the one-dimensional aquifer and $\phi$ the porosity. The distribution around a mean $\bar{x} = v \cdot t$ can also be created by stochastic processes by the procedure related to a particle movement given by

$$x = v \cdot t + Z_n \cdot \sqrt{2D t} \quad (B.3)$$

with a normally distributed probability variable $Z_n$ with mean value zero and standard deviation unity (see Eq. 33). The resulting particle distribution $f(x,t)$ combined with a normalising factor is then equal to the concentration distribution (B.1):

---

14 In contrast to this 'hybrid' random walk approach where advection is done by a nonrandom movement it is also possible to describe the whole transport (advection and dispersion/diffusion) by random movement on a lattice as presented by [Karapiperis & Blankleider, 1992] for a cellular automata approach to reaction-transport processes.
\[ c(x,t) = \frac{\Delta m}{A \phi} \cdot f(x,t) \] (B.4)

For a nonuniform or time-dependent flow field \( v(x,t) \) or other time dependent processes (conditions) a discretisation of the time variable in intervals \( \Delta t \) is necessary with a quasi-constant flow velocity (or other quasi-constant conditions concerning time). Then the movement of a particle \( n \) is described as follows\(^\text{15}\)

\[ x_n(t = 0) = x_0 \] (B.5)

\[ x_n(t + \Delta t) = x_n(t) + v(x_n(t), t) \cdot \Delta t + Z_n \cdot \sqrt{2D \cdot (x_n(t), t) \cdot \Delta t} \] (B.6)

This means that particle movement within a single time step is calculated by an advective part defined by a temporally constant flow field (at each location a defined flow velocity)

\(^\text{15}\) For the application of the random walk method one has to keep in mind the following. The space- and time-dependent distribution \( f(x,t) \) of a particle ensemble is only an approximation of a particle ensemble carrying out single steps which is given by the Fokker-Planck Equation [Kinzelbach, 1987]:

\[ \frac{\partial f}{\partial t} + \frac{\partial vf}{\partial x} = \frac{\partial^2}{\partial x^2} (Df) = \frac{\partial}{\partial x} \left( D \frac{\partial f}{\partial x} \right) + \frac{\partial}{\partial x} \left( \frac{\partial D}{\partial x} f \right) \]

which is not equal to the transport equation

\[ \frac{\partial c}{\partial t} + \frac{\partial vc}{\partial x} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \]

because

\[ \frac{\partial f}{\partial t} + \frac{\partial}{\partial x} \left( v \frac{\partial D}{\partial x} f \right) = \frac{\partial}{\partial x} \left( D \frac{\partial f}{\partial x} \right) \]

\[ \frac{\partial f}{\partial t} + \frac{\partial}{\partial x} \left( v f - \frac{\partial D}{\partial x} \cdot f \right) = \frac{\partial}{\partial x} \left( D \frac{\partial f}{\partial x} \right) \]

A substitution of \( \nu' \rightarrow v + \frac{\partial D}{\partial x} \) leads to an equivalent description. For variable dispersion coefficient in space (e.g. by a variable velocity field) it is necessary to apply a 'counter term' in the advective step to get consistency of the transport equation and the form of stochastic single steps. This advective 'counter term' is zero if

\[ \frac{\partial D}{\partial x} = 0 \]

This means that the 'counter term' is negligible if the spatial gradients of \( D \) are small; otherwise this term must be taken into account.
superposed by a random movement following a normal distribution reflecting the dispersive part.

An alternative generation of random numbers was used in [Uffink, 1985]: The dispersive step is of the form:

\[ 2 \cdot (Z_{eq} - 0.5) \cdot \sqrt{6 \cdot D \cdot \Delta t} \]  

(B.7) where \( Z_{eq} \) is an equally distributed random number within interval [0,1]. A comparison of both random number distributions is given in Fig. B1 for a different number of particles. The differences for the random walk transport calculations are negligible in respect to the choice of random number generation ((B.3) for normally distributed random numbers or (B.7) for equally distributed random numbers). Therefore, the choice of an available random number generator on a given hardware platform is only influenced by minimisation of the used CPU-time.

![Diagram](image)

**Figure B1:** Particle distributions generated by equally distributed and normally distributed random numbers for 5000 and 1 million particles within a fictive transport step
Due to statistical variations a larger (smaller) number of particles in the model area is necessary to get a more (less) smooth concentration distribution which directly influences the computing time. Therefore, a fast testing with few particles in the model area is possible, and production simulations take a longer time with many particles. The random-walk method works in each case as a robust tool. An example for the dependency on the number of particles is shown in Fig. B.2 where a pure diffusion of a tracer is calculated for different particle numbers and compared to an analytical solution. An additional smooth option was also tested. It was used if only a small number of particles in the model area were present. The smooth option should only be used for diffusive/dispersive transport where the random movement of particles results in a random varying number of particles in a cell. For pure advective transport there is no random transport step (see Eq.'s 32 -34) and the smooth option makes no sense.

With this smooth option particles transport "concentration" instead of mass as described by equation (29) and (30). Within a cell, each particle gets the same "concentration" (as a concentration vector component) independent of the number of particles in the cell. This is in contrast to equations (29) and (30) where the mass is distributed over the actual number of particles in a cell. There, the distribution of mass can lead to quite different mass vector components (species masses) related to the number of particles in neighboured cells which can cause a statistically growing variation (from cell to cell or from one time step to the next) for a certain species mass as the system develops. These concentration variations can be limited by increasing the number of particles but this increases also computer memory and time used.

For example, let's assume equal and constant concentration $X_1$ in two neighboured cells at time $t_0$, one including two particles the other four due to statistical movement of the particles. Then, without the smooth option, the distribution of mass leads to particles with masses different by a factor of two in the neighboured cells: "heavy" particles with mass $X_1/(2\cdot V)$ and "light" particles with mass $X_1/(4\cdot V)$. After a transport step, one "heavy" and one "light" particle are assumed to have exchanged by a random transport step between the neighboured cells. The result is for cell one, with one "heavy" and one "light" particle, a concentration of $\frac{1}{2}X_1$ and for cell two, with one "heavy" and three "light" particles, a concentration of $\frac{3}{4}X_1$. Redistribution of mass to the particles, and assuming a random movement of all particles for the next time step so that 3 particles have moved from cell two to cell one, and one has moved from cell one to cell two. Then the concentrations in the cells are: $\frac{1}{2}X_1$ in cell one, and $\frac{3}{4}X_1$ in cell two. This demonstrates the statistical variations of the particle number (and concentration) in the cells as time goes on but the mean concentration of both cells will be $X_1$ as it should be. If the smooth option is used for the same example, the concentration is always $X_1$ in both cells because each particle has transported a "mean" concentration $X_1$ due to a rough concentration averaging which will lead to $X_1$ in each cell after each transport step (sum over "concentrations" divided by the number of particles in each cell). Large concentration variations due to the transport calculations will influence the chemical equilibrium calculations where for each time step in each cell guesses for all species concentrations are necessary to solve the set of chemical

16[Ahlstrom et al., 1977] used a similar "smooth filter" that averages concentrations at neighboured nodes in the space domain to decrease CPU-time and producing smooth concentration profiles at the same time.
equilibrium equations by the Newton-Raphson procedure (App. A). If these guesses, which are taken from the previous calculation in each cell, are far away from the solution as it can be for large concentration variations from one time step to the other (or at neighboured cells), the Newton-Raphson procedure takes a longer time to reach the convergence criterion, and the whole calculation time increases. With the smooth option these large concentration variations are omitted by a rough averaging: "transport of concentration" and equal weight for particles reaching or leaving a cell (distribution/collection of "concentration" to/from all particles in a cell, independent on the number of particles). This includes small errors for the mass balance within one time step, that is fulfilled with equations (29) and (30) but in the temporal or spatial mean the small errors cancel out each other, and less varying concentrations in time and space are produced (see Fig.'s B2, 4.15 and 4.16). Again, this influences the guesses for the Newton-Raphson procedure, which are now closer to the solution, and result in a faster convergence, and the whole calculation time decreases in addition to the fact that fewer particles are used which also reduces calculation time. In summary, the smooth option results in a more smooth concentration distribution than without smooth option due to a rough concentration averaging. It allows computations of smooth concentration distributions without increasing the total number of particles in the model area and therefore, without a more time consuming calculation while the calculated mean concentration profile does not change significantly (Fig. B2).

Figure B2: Tracer diffusion calculated by MCOTAC with different numbers of particles within the model area and by an analytical solution for a migration time of 0.1 year (other parameter fixed as in application 1)

The extension of the single species random walk to a multi-species random walk is realised within the MCOTAC transport module in that all particles are linked not with a single mass, but with a vector of masses where each species is related to a mass vector component (see Chapt. 3.2). A calculation is shown in Fig. B3 for a pure transport problem. Two species
diffuse independently from each other into (species B) and out of (species A) a one-dimensional column. The calculation of MCOTAC was done once for the two species where for the analytical solution two calculations are necessary. The agreement of the two calculations is quite good and demonstrates the functionality of a multi-species random walk approach. A further extension of the random-walk method to two or three dimensions is possible if the corresponding flow field is known (or can be calculated) at every point of the model area. The step for one dimension is also done for the other dimensions and the new position in x-, y- and z-direction is the superposition of individual steps in each direction. This shows that the form of the random-walk equations does not change considerably for extensions to more dimensions in contrast to finite difference or finite element methods where the equations and the solution procedure become more complex/complicated.

![Tracer profiles for two species A and B at 0.1 year of migration](image)

**Figure B3:** Tracer profiles for two species A and B at 0.1 year of migration (only diffusion processes are assumed) calculated by MCOTAC (multi-species particle random walk transport module) compared to analytical solution. The diffusion coefficient for both species is $D_m = 1 \times 10^{-10} \text{[m}^2\text{/s]}$, grid size is $\Delta x = 0.01 \text{m}$, the maximum time step is $\Delta t_{\text{max}} = 5 \times 10^5 \text{s}$ and the number of particles is $N_{\text{max}} = 5000$. The initial species concentrations at $t=0$ are: $A = 1 \times 10^{-3} \text{[mol/l]}$ at the left boundary, $A = 0\text{[mol/l]}$ inside the column, $B = 0\text{[mol/l]}$ at the left boundary and $B = 3 \times 10^{-3} \text{[mol/l]}$ inside the column.
Appendix C: Implementation of coupled codes on different hardware systems

Before writing the coupled code MCOTAC the coupled code THCC_DM and some FORTRAN test programs were used to test the available computer resources which are an important factor for coupled code development, testing and application. Several computers were used for a performance test including mainframes, workstations, PC's and a special system: an INTEL PC-inboard i860 (32 MB, 40 MHz) within an IBM compatible 80486 DX (16 MB, 33MHz). A comparison of runtime of a test program and the coupled code THCC_DM is shown in Table C1. The sample program test.for includes some large arrays where some simple calculations are done with the array elements. The other one is the coupled code program THCC_DM.for with a standard example for calculating transport and equilibrium chemistry in one dimension. The two source codes, both written in FORTRAN, were compiled with different sets of compiler option (standard, vectorised, ...).

Table C1: Comparison of computing time for sample programs on different hardware systems (* these times are achieved during single user working on the multi-user systems and are ideal times on these systems. The normal turn-around times should be longer.)

<table>
<thead>
<tr>
<th>Computer</th>
<th>Program and related runtime (turn around time) [sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>test.for</td>
</tr>
<tr>
<td>i860</td>
<td>1.37</td>
</tr>
<tr>
<td>i860 /vector</td>
<td>0.94</td>
</tr>
<tr>
<td>titan / -O3 (parallel)*</td>
<td>0.37</td>
</tr>
<tr>
<td>titan / -O2 (vector)*</td>
<td>210</td>
</tr>
<tr>
<td>titan / -O1 (scalar)*</td>
<td>154</td>
</tr>
<tr>
<td>VAX-Workstation 3100-76</td>
<td>503</td>
</tr>
<tr>
<td>(MICROVAX 3800)</td>
<td>2187</td>
</tr>
<tr>
<td>VAX-Workstation 2000</td>
<td>11580</td>
</tr>
<tr>
<td>VAX9000*</td>
<td>155</td>
</tr>
<tr>
<td>IBM-RISC 6000-520 (UNI Hannover)*</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Table C1 shows that it is possible to have a fast board within a PC that has speed comparable to or better than that of workstations. But this with the known and wide range of other PC software and for a low price (around 12000,-Sfr including one compiler). Compared to workstations or graphics workstation (titan 3020 around 175000,-Sfr) this is a small amount. It is also obvious that most VAX systems cannot be used because the response time of a run is too large which is the same for fast batch machines. Therefore, the development and testing of coupled codes need a number crunccher on the table. Another aspect becomes important if the high amount of produced data during coupled code calculation is considered, which makes it necessary to use graphical data processing units. This excludes also the network solution to run programs on fast multi-user systems because in most cases the network is a bottleneck of the whole system. The same result was obtained in [Tripathi & Yeh, 1993] investigating the performance of different computer systems especially for coupled code applications. That single user systems can have a high performance underlines figure C1 which reflects the temporal development of PC systems compared to mainframes.

**Figure C1:** Development of MIPS power of PC’s compared to mainframes [Bernstein, 1991]

A recent hardware development at the ETH Zürich named MUSIC [Gunzinger et al., 1992a] shows that similar computer systems like the i860 single user system become more important for scientific applications. There a parallel multi processor system was presented which fits on a table but with a performance comparable to a Cray Y-MP or a NEC SX-3 and with a much lower price (see Fig. C2). Further developments in computing technology presages a further applicability of CPU-intensive coupled code applications if the codes are portable to fast systems (e.g. the codes running on the fast MUSIC system must be written in C or ASSEMBLER and no double precision calculation is possible) and if the codes take advantage of the new architectures in hardware and software like parallel processors and programming. A simple calculation shows that applications of MCOTAC which need around two hours CPU-time will need less than 10 minutes on the MUSIC system which then allows more complex applications. But up to now there has been a barrier to run MCOTAC on the MUSIC system. First there are some modules of MCOTAC written in
FORTRAN and second (more important) it is not possible to use double precision on the MUSIC system which is (still) necessary for the iteration calculations. Therefore a further adaptation is necessary either from the hardware or from the software (programming) used.

\textbf{Figure C2: Cost and performance comparison of computer systems and processors [Gunzinger et al., 1992b]}
Appendix D: THCC_DM options and remarks

In THCC_DM [Berner, Jacobsen & McKinley, 1987; Carnahan, 1986] the transport is described by a finite difference formulation which is coupled directly with the chemical equilibrium calculations. It includes the following features for transport and chemical equilibrium calculations:

**Transport:**
- stationary one-dimensional flow field with constant velocity in each finite difference cell
- dispersion and diffusion, constant in location and time for all species the same value
- no sorption or decay
- several boundary conditions (constant flux, constant concentration)

**Chemical equilibrium:**
- number of possible basis species, complexes and solids are 20, 20 and 10
- temperature dependent log $K$
- ionic strength correction
- complexation, precipitation/dissolution and redox reactions
- no reduction of mathematical matrix equation if number of solids change (flags)
- no variable initial conditions for the finite difference cells
- incongruent dissolution, but with convergence problems
- database is not present, therefore data have to extracted from other databases

**Some remarks on THCC_DM**

During the application of THCC_DM convergence problems (for incongruent dissolution problem (Chapt. 4.1) and the multiple front system problem (Chapt. 4.3) lead to very small time steps (up to zero) and therefore to long CPU-times. An explanation could be that different chemical systems with high concentration gradients for some species are directly coupled by the finite difference calculations which cause the convergence problems.

Analysing of THCC_DM with vector compiler options shows a high amount of possible changes in coding to optimise with respect to used CPU-time for calculations.

A large part of the program is used to include heat transport and related options which is not used for modelling incongruent dissolution or other planned applications. This makes the code more complicated for additional changes. Also an elimination of unused parts of the code is very difficult.
Appendix E: MCOTAC code options

MCOTAC transport module describes a multi-species transport in one dimension. Transport processes are advection and dispersion including molecular diffusion within a saturated porous medium. The following transport parameters have to be defined for the transport module:

- grid size and number of grid cells (limited to 50) in one spatial dimension
- maximum time step
- flow velocity (equal for all species)
- dispersivity (equal for all species)
- diffusion coefficient (equal for all species)
- number of particles in the model area (limited to 50000)
- type of random number generator
- type of boundary condition (constant concentration, transmission or reflection boundary)
- smooth option on/off

The chemical equilibrium model has the same options as the chemical equilibrium part of THCC_DM (see App. D) and is able to deal with complexation reactions, precipitation/dissolution reactions including the incongruent dissolution of CSH-phases, and redox reactions (not tested yet). The number of basis species, complexes and solids must be defined which are limited to 20, 20 and 20 respective. For the complexation reactions and the precipitation/dissolution reactions the temperature-dependent equilibrium constants must be given as well as the total concentration of the basis species and guesses for the other concentrations. Parameters for incongruent dissolution must be given if needed. Water dissociation can be taken into account. Several parameters must be defined for the Newton-Raphson iteration procedure like cut off criteria or maximum number of iterations.

In addition to the physical and chemical parameters some output files can be created which are the temporal development of species concentrations at fixed locations or the species profiles along the spatial dimension for given times. A further option of on-line modelling was included: If the program has convergence problems within a calculation for specific chemical systems or system changes new guesses for the Newton-Raphson iteration procedure can be done from outside to overcome the convergence problem and not to lose the perhaps time consuming calculations up to that point.

The code modules or subroutines are partly written in C and FORTRAN which makes it necessary to have compatible C and FORTRAN compilers on the computer. Up to now there is no implementation of on-line graphic output during calculations which would be possible on a multi-processor workstation.