

# **TECHNICAL REPORT 00-10**

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**A Nagra-JNC co-developed  
hyperalkaline water-rock  
interaction code**

**Code description and applications**

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F.B. Neall<sup>1)</sup>, P.A. Smith<sup>2)</sup>, H. Owada<sup>3)</sup>, M. Mihara<sup>4)</sup>

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## ABSTRACT

The initial aim with SANTA-CHEM was to develop a code where the chemical system had to be wholly specified in the input files via a set of species and mineral reactions. The idea was that, by requiring more effort at the stage of describing the chemical system, problems arising from "rubbish in" resulting in "rubbish out" might be avoided. It was further hoped that it would help develop better understanding and chemical judgement amongst users. User-friendliness and simplicity of input were also required so that it would be straightforward to use the code, especially for scoping calculations, which often require repeated running of calculations with only minor modifications to the input.

A further aim was to have a coupled chemical – transport code in which the chemical system was given 'priority' over a simple transport system, so that the chemistry could be explored without hindrance from a complex and time consuming transport model.

The transport model considers one dimensional advective flow with diffusion. It is important to note the following points:

- Flow is assumed to occur in fractures.
- The rock porosity is assumed to be concentrated in the fractures, hence
- Rock matrix porosity is ignored.
- An initial Darcy velocity is specified by the user, along with the hydraulic gradient.
- Darcy velocity may be considered fixed for a calculation (but this can result in unrealistically high particle velocities if the porosity becomes small) or allowed to vary as porosity changes.
- Hydrodynamic dispersion is not included in the current version of SANTA-CHEM.
- For simplicity, in the current version of SANTA-CHEM, the same diffusion coefficient is assumed to apply to all diffusing species.

The chemical model is constructed in terms of **components, (aqueous) species and minerals**, and includes the following:

- Instantaneous equilibrium is assumed between all components and species in solution.
- Mineral dissolution reactions may achieve equilibrium within a single time step or can be controlled by user-defined kinetic rate constants so that equilibrium is approached over several time steps.
- The rate of mineral precipitation reactions is considered to be sufficiently fast that they can be assumed to reach equilibrium within a single time step.
- The rate of mineral dissolution can be dependent or independent of surface area.
- All reactions used in a calculation, both aqueous species and minerals, **must be** explicitly defined by the user along with species stability constants, mineral solubility products and kinetic rate constants, where appropriate.
- It is assumed that all reactions take place at 25° C.
- The extended Davies equation is used for the ionic strength.
- Mineral and solution reactions are written without water being included. This implies that the activity of water is always 1.0, and that water is always present in excess.

This report describes the SANTA-CHEM programme, including governing equations and solution techniques. Appendices include descriptions of the input files needed to run the code, along with definitions of all the input parameters, and examples of the output files with explanation, and test cases for transport and examples of calculations for chemical systems.

## ZUSAMMENFASSUNG

Das eigentliche Ziel von SANTA-CHEM ist die Entwicklung eines geochemischen Codes, bei dem das chemische System in den Eingabefiles mithilfe eines Datensatzes an Spezies und Mineralreaktionen spezifiziert werden muss. Durch diesen grösseren Aufwand bei der Beschreibung des chemischen Systems sollten Schwierigkeiten vermieden werden, die sich aus der Problematik "rubbish in" ergibt "rubbish out" ergeben (d. h. die Qualität eines erhaltenen Modells steht und fällt mit der Qualität der Eingabeparameter). Zudem erhoffte man sich auch, dass damit den Anwendern ein besseres Verständnis bzw. eine bessere Beurteilung des chemischen Systems ermöglicht würde. Benutzerfreundlichkeit und Vereinfachung bei den Eingabedaten waren ebenfalls erforderliche Kriterien im Sinne einer unkomplizierten Anwendung des Codes. Dies gilt insbesondere für Überschlagsrechnungen, für die oft wiederholte Rechenläufe mit nur geringfügiger Modifikation der Eingabefiles erforderlich sind.

Eine weitere Zielsetzung war die Bereitstellung eines gekoppelten chemischen Codes mit einem Transportcode, bei dem das chemische System eindeutig das einfache Transportsystem dominiert, so dass die Chemie ohne Behinderung durch ein komplexes und zeitaufwändiges Transportmodell untersucht werden kann.

Das Transportmodell betrachtet den Fall eines eindimensionalen advektiven Flusses mit Diffusion. Dabei sind folgende Voraussetzungen und Aspekte zu erwähnen:

- Beim Fluss wird angenommen, dass ein solcher in Klüften auftritt.
- Bei der Gesteinsporosität wird davon ausgegangen, dass diese sich auf die Klüfte konzentriert; daraus folgt:
- Die Gesteinsmatrix wird ignoriert.
- Eine anfängliche Darcy-Geschwindigkeit sowie ein hydraulischer Gradient werden durch den Anwender eingegeben.
- Die Darcy-Geschwindigkeit kann für eine Berechnung als fest eingegeben werden (dies kann sich aber in unrealistisch hohen Teilchengeschwindigkeiten äussern, wenn die Porosität gering wird) oder variabel als Funktion der Porosität.
- In der gegenwärtigen Version von SANTA-CHEM ist keine hydrodynamische Dispersion enthalten.
- Zur Vereinfachung werden in der gegenwärtigen Version von SANTA-CHEM für sämtliche diffusive Spezies dieselben Diffusionskoeffizienten angenommen.

Das chemische Modell wird durch **Komponenten, (wässrige) Spezies und Minerale** aufgebaut, dabei gelten folgende Voraussetzungen:

- Es wird ein unmittelbares Gleichgewicht zwischen sämtlichen Komponenten und Spezies in Lösung angenommen.
- Mineralauflösungsreaktionen können ein Gleichgewicht innerhalb eines einzigen Zeitschritts erreichen, oder sie können durch Benutzer-definierte Konstanten für die kinetische Rate kontrolliert werden, so dass ein annäherndes Gleichgewicht über mehrere Zeitschritte erreicht wird.
- Die Rate für Mineralfällungsreaktionen wird als ausreichend schnell erachtet, so dass die Erreichung eines Gleichgewichts innerhalb eines einzigen Zeitschritts angenommen werden kann.
- Die Mineralauflösungsrate kann von der Mineraloberfläche abhängig oder unabhängig sein.

- Alle für eine Berechnung verwendeten Reaktionen, wässrigen Spezies und Minerale **müssen**, soweit möglich, durch den Anwender explizit definiert werden zusammen mit den Stabilitätskonstanten der Spezies, Löslichkeitsprodukten der Minerale und Konstanten der kinetischen Rate.
- Es wird angenommen, dass sämtliche Reaktionen bei einer Temperatur von 25° C ablaufen.
- Für die Ionenstärke wird die erweiterte Davies-Gleichung verwendet.
- Bei den implementierten Mineral- und Lösungsreaktionen ist kein Wasser enthalten; dies hat zur Folge, dass die Aktivität des Wassers immer 1.0 beträgt und Wasser immer im Überschuss vorhanden ist.

Der vorliegende Bericht beschreibt das Programm SANTA-CHEM mit dessen Programmbestimmenden Gleichungen und Lösungsverfahren. Im Anhang ist die Beschreibung der für die Benutzung des Codes notwendigen Eingabefiles zusammen mit der Definition sämtlicher Eingabeparameter enthalten, ausserdem finden sich dort Beispiele für Ausgabefiles mit Erläuterungen und Testfälle für Transportberechnungen sowie Rechenbeispiele für chemische Systeme.



## RESUME

L'objectif principal du code SANTA-CHEM a été le développement d'un code dans lequel le système chimique doit être défini complètement dans les fichiers d'entrée, à l'aide d'un ensemble d'espèces et de réactions minérales. L'idée est qu'en fournissant un effort supplémentaire au stade de la description du système chimique, les problèmes de propagation d'information inadéquate (les "rubbish in" engendrant des "rubbish out") pourraient être évités. On avait aussi l'espoir que cela aiderait les utilisateurs à acquérir une meilleure compréhension et un meilleur jugement sur le plan chimique. On visait de plus à convivialité et à la simplicité des entrées, afin de rendre le code directement utilisable, en particulier pour des calculs de projection qui nécessitent souvent des séquences répétitives de calculs avec seulement des changements mineurs dans les données d'entrée.

Un autre objectif était d'obtenir un code couplant la chimie et le transport dans lequel le système chimique soit prioritaire par rapport à un simple système de transport, afin de permettre l'exploration des aspects chimiques sans subir la lourdeur d'un modèle de transport complexe et gourmand en temps.

Le modèle de transport calcule un écoulement convectif unidimensionnel avec diffusion. Il est important de préciser les points suivants:

- L'écoulement est supposé avoir lieu dans les fissures;
- La porosité de la roche est supposée être confinée aux fissures, donc
- La porosité de matrice de la roche est ignorée;
- Une vitesse de Darcy initiale est spécifiée par l'utilisateur, ainsi que le gradient hydraulique;
- La vitesse de Darcy peut être définie comme fixe pour un calcul (mais ceci peut engendrer des vitesses de particules trop grandes, irréalistes, si la porosité devient petite) ou variable en fonction de la porosité;
- La dispersion hydrodynamique n'est pas incluse dans la version actuelle de SANTA-CHEM;
- Dans la version actuelle de SANTA-CHEM, pour des raisons de simplicité, le même coefficient de diffusion est supposé s'appliquer à toutes les espèces diffusantes.

Le modèle chimique est construit sur la base des **composants**, des **espèces (aqueuses)** et des **minéraux**; il inclut les aspects suivants:

- Un équilibre instantané est supposé entre tous les composants et les espèces en solution;
- Les réactions de dissolution des minéraux peuvent atteindre l'équilibre en un seul pas de temps ou peuvent être contrôlées par des constantes cinétiques faciles à introduire et permettant d'approcher l'équilibre en plusieurs pas de temps;
- La vitesse des réactions de précipitation des minéraux est supposée suffisamment grande pour qu'elles soient considérées avoir atteint l'équilibre en un seul pas de temps;
- La vitesse de dissolution des minéraux peut être ou non dépendante de la surface;
- Toutes les réactions utilisées dans les calculs, qu'il s'agisse d'espèces aqueuses ou de minéraux, doivent être définies explicitement par l'utilisateur, ainsi que les constantes de stabilité des espèces, les produits de solubilité des minéraux et les constantes cinétiques, où cela est approprié;

- Toutes les réactions sont supposées se dérouler à une température de 25° C;
- La force ionique est calculée par l'équation de Davies généralisée;
- Les réactions minérales et de solutions sont écrites sans que l'eau ne soit incluse. Cela implique que l'activité est toujours égale à 1.0 pour l'eau, et que de l'eau est toujours présente en excès.

Le présent rapport décrit le code SANTA-CHEM avec les équations qui le gouvernent et les solutions techniques appliquées. Les annexes comprennent les descriptions des fichiers d'entrée nécessaires au fonctionnement du programme, les définitions de tous les paramètres d'entrée et des exemples de fichiers de résultats avec des explications, ainsi que des cas de test pour le transport et des exemples de calcul pour les systèmes chimiques.

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## 1 INTRODUCTION

"Rubbish in – rubbish out" has long been recognised as a truism of particular relevance to geochemical modelling. Using modern calculational tools, the "rubbish in" in question can be both the chemical model description as well as thermodynamic data. Unfortunately, modern codes that are run in conjunction with large, automatically accessed, databases for solution aqueous speciation and mineral phases can particularly add to the problems of describing an appropriate chemical system, since they do not (usually) include the kind of chemical judgement required for setting up a calculation input file. An example might be the problem of sulphates and sulphides in groundwater – chemical judgement suggests that they are unlikely to be in equilibrium, thus equilibrium redox reactions between the species should not be allowed in this case. Without using such judgements, the calculation is likely to result in nonsense as the code tries to oxidise sulphide or reduce the sulphate to fit an equilibrium model. This in turn will affect other redox sensitive species and, probably, pH. This problem arises if the code searches an 'automatic database' for all reactions involving input species: input of  $\text{SO}_4$  concentration in the groundwater composition will result in its reduction reaction and also sulphide reactions being added to the species equilibria in the chemical system. In other cases, the 'automatic database' results in minerals erroneously added to a chemical system where they appear, on thermodynamic grounds, to be stable but, in fact, the pressure – temperature (P – T) conditions of the system mean that they would not form. For example, groundwater at 25° C may be predicted to be oversaturated with high P – T minerals such as garnet and feldspar or rare zeolites. All such problems are, of course, eminently avoidable if chemical judgement is correctly exercised. The problem is where, due to pressure of time or lack of knowledge, the calculation goes ahead and the inappropriate or incorrect results are used elsewhere.

The initial aim with SANTA-CHEM was to develop a code where the chemical system had to be wholly specified in the input files via a set of species and mineral reactions, without recourse to an extensive 'automatic database'. The idea was that this would help to avoid the types of mistakes described above, and also develop better understanding and chemical judgement amongst users. User-friendliness and simplicity of input were also required so that it would be straightforward to use the code, especially for scoping calculations, which often require repeated running of calculations with only minor modifications to the input.

A further aim was to have a coupled chemical – transport code in which the chemical system was given 'priority' over a simple transport system, so that the chemistry could be explored without hindrance from a complex and time consuming transport model. In this respect, modifying the concept of the box model for transport, used in the original SANTA code (McKIE & MÄDER 2001), was considered a good option.

The SANTA code was developed to model, in a very simple way, the interaction between a tracer and a fractured host rock. The transport path was broken up into a series of identical boxes in which the proportions of rock and water, and their respective properties, could be defined to represent the fracture. The processes of advection, diffusion (including matrix diffusion) and sorption were represented.

The proposed development of SANTA to form SANTA-CHEM would involve a more complex chemical model in which the fluid reacted with the constituent minerals in the boxes. At an early stage, however, it was found that the simple box model could not be extended to reactive transport modelling as originally envisaged, with individual mineral reactions defined explicitly (as the sorption reactions had been in the original model) and a simple transfer of solute between boxes to represent transport. Further, when a more complete description of the chemistry was used, problems were encountered with small inaccuracies in transport resulting in large

oscillations in chemistry, due to the logarithmic description of pH. To overcome this, a more traditional finite difference approach was adopted for the transport model. This allowed more precise solution of the transport equations and a more robust coupling of transport and chemical reactions.

The one dimensional transport path is still split into a series of boxes which are used to define the starting properties of the chemical system: porosity, mineral constituents, initial fluid composition etc.

This report describes the SANTA-CHEM code. Chapter 2 includes a description of the physical and chemical models used, including the underlying assumptions and simplifications, and appropriate applications and limitations of the code. Chapter 3 gives the governing transport and chemical equations while in Chapter 4, the methods used to solve the equations are described. In Chapter 5, an overview of the code is given but without detailed description of all subroutines and their functions. In conclusion, Chapter 6 briefly outlines some possibilities for future developments. Two appendices contain a detailed description of input and output files, definitions of parameters and reasonable parameter values (Appendix A), and a series of test cases and examples (Appendix B) to illustrate inter-code comparisons, setting up of calculational cases and mass balance checks. Appendix C contains a definition of the principal notation used throughout this report.



## 2 DESCRIPTION OF THE SANTA-CHEM MODEL

### 2.1 Transport model

The transport model considers one dimensional advective flow with diffusion. It is important to note the following points:

- Flow is assumed to occur in fractures.
- The rock porosity is assumed to be concentrated in the fractures, hence
- Rock matrix porosity is ignored.
- An initial Darcy velocity is specified by the user, along with the hydraulic gradient.
- Darcy velocity may be considered fixed for a calculation or allowed to vary as porosity changes (according to the cubic law, see section 4.2.1).
- Fixed Darcy velocity can result in unrealistically high particle velocities if the porosity becomes small.
- Hydrodynamic dispersion is not included in the current version of SANTA-CHEM (although it would be a simple extension of the code if required).
- For simplicity, in the current version of SANTA-CHEM, the same diffusion coefficient is assumed to apply to all diffusing species.

### 2.2 Chemical model

The chemical model is constructed in terms of **components**, **(aqueous) species** and **minerals**.

- **Components** are any chemical unit which can be used to write the mineral and species formation reactions and may be single element (e.g. Na or Ca) or multi-element (e.g.  $\text{SO}_4$  or  $\text{HCO}_3$ ). Each element in the chemical system, except oxygen, must be represented by a separate component. Oxygen is represented implicitly by water;  $\text{H}^+$  or  $\text{OH}^-$  must be specified for hydrogen. The components are assumed to have a charge according to their stoichiometry, e.g. Na is assumed to be  $\text{Na}^+$ ,  $\text{CO}_3$  is assumed to be  $\text{CO}_3^{2-}$ , irrespective of their actual speciation in solution. This is to ensure an electronically balanced system.
- **Species** are the chemical units actually occurring in solution (e.g.  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ). Some of these will map one to one with components whereas others will be protonated or deprotonated forms (e.g.  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{H}_2\text{CO}_3$ ), or complexes between components (e.g.  $\text{CaOH}^+$ ). A reaction, written in terms of declared components, is required for each species in the chemical system.
- **Minerals** are solid phases which either pre-exist (and may dissolve) or precipitate in response to oversaturation of the solution. A reaction, written in terms of declared components, is required for each mineral, either present or anticipated, in the chemical system. The choice of secondary minerals (i.e. those which may precipitate but do not occur initially in the system) is important as the results of a calculation may be misleading if the correct minerals are not chosen. There is no simple way to know which are the correct minerals to include in the calculation. A combination of chemical judgement to avoid, for example, high temperature phases, with information from laboratory experiments, natural analogue studies etc. will be required. Trial runs of calculations can then be carried out to investigate the relative stability of potential secondary phases, until an appropriate choice can be made. Going through this process is a valuable part of developing understanding of a chemical system.

- The chemical model assumes instantaneous equilibrium between all components and species in solution which are specified by speciation reactions. Disequilibrium between, e.g.  $\text{SO}_4$  and S, may occur if no reaction linking them is included.
- Mineral dissolution reactions may be considered to achieve equilibrium within a single time step or can be controlled by user-defined kinetic rate constants so that equilibrium is approached over several time steps.
- The rate of mineral precipitation reactions is considered to be sufficiently fast that they can be assumed to reach equilibrium within a single time step. This is reasonable for long time-steps (e.g. 1 year) when modelling over long periods of time, in which case discussion is usually also assumed to proceed to equilibrium in each timestep. For very short time steps, for example, when considering the influence of diffusion in a small scale, the assumption is probably more difficult to justify. If the timestep is of the order of seconds ( $10^{-6}$  year), kinetics are probably necessary for some minerals. At timesteps of intermediate duration, the assumption is justified on the basis that precipitation reactions are usually significantly faster than dissolution reactions, thus the rate determining step is likely to be the dissolution of primary minerals which can be modelled using kinetic rate constants.
- The rate of mineral dissolution can be dependent or independent of surface area. These alternatives represent the cases, respectively, where
  - a) mineral grains are assumed to be dissolving on all sides so that area decreases with volume, or
  - b) mineral grains are assumed to be exposed on only one surface which remains constant in area as volume decreases.
- All reactions used in a calculation, both aqueous species and minerals, **must be** explicitly defined by the user along with species stability constants, mineral solubility products and kinetic rate constants, where appropriate.
- It is assumed that all reactions take place at 25° C. There are no functions included in the code to adjust reaction constants to any other temperature. However, if a full set of reaction constants for another temperature are used and this temperature specified in the input file, a valid calculation can be made.
- The extended Davies equation is used for the ionic strength correction (e.g. STUMM & MORGAN 1996), thus the code is only valid for calculations of solutions of low to moderate ionic strength (maximum 0.1 – 0.5 molar; very significant inaccuracies can arise at > 0.5 M).
- Mineral and solution reactions are written without water being included. This implies that the activity of water is always 1.0, and that water is always present in excess. Care must be taken with calculations in low porosity (low water/rock ratio) systems that hydration reactions do not significantly reduce the mass of water present.

### 3 GOVERNING EQUATIONS

#### 3.1 General equations to be solved

The code SANTA-CHEM is designed to solve the advection-diffusion equation for  $N_c$  migrating and chemically interacting aqueous components in one spatial dimension, in a medium of porosity  $\varepsilon$ , that may be a function of space and time:

$$\frac{\partial c^{(i)}}{\partial t} + \frac{1}{\varepsilon} \left[ \frac{\partial f_a^{(i)}}{\partial x} + \frac{\partial f_d^{(i)}}{\partial x} \right] = S_{disn}^{(i)} + S_{ppt}^{(i)}, \quad i = 1, \dots, N_c, \quad (3.1)$$

where:

$c^{(i)}$	(mol m <sup>-3</sup> )	is the concentration of the $i$ th component,
$f_a^{(i)}$	(mol m <sup>-2</sup> a <sup>-1</sup> )	is the advective flux of the component,
$f_d^{(i)}$	(mol m <sup>-2</sup> a <sup>-1</sup> )	is the dispersive (diffusive) flux of the component,
$S_{disn}^{(i)}$	(mol m <sup>-3</sup> a <sup>-1</sup> )	is a source term that accounts for mineral dissolution,
$S_{ppt}^{(i)}$	(mol m <sup>-3</sup> a <sup>-1</sup> )	is a source term that accounts for mineral precipitation.

If there are  $N_m$  minerals present that can dissolve or precipitate, the source terms must satisfy the mass-balance equation:

$$S_{disn}^{(i)} = \sum_{j=1}^{N_m} (1 - I_j) M_{ij} A^{(j)} d^{(j)}, \quad i = 1, \dots, N_c \quad (3.2)$$

and

$$S_{ppt}^{(i)} = - \sum_{j=1}^{N_m} I_j M_{ij} p^{(j)}, \quad i = 1, \dots, N_c, \quad (3.3)$$

where

$d^{(j)}$	(mol m <sup>-2</sup> a <sup>-1</sup> )	is the rate of dissolution of the $j$ th mineral, per unit area of mineral surfaces,
$p^{(j)}$	(mol m <sup>-3</sup> a <sup>-1</sup> )	is the rate of precipitation of the $j$ th mineral, per unit volume of fluid,
$A^{(j)}$	(m <sup>2</sup> m <sup>-3</sup> )	is the surface area of the mineral, per unit volume of fluid,
$M_{ij}$		is a matrix describing the relationship between mineral dissolution/precipitation and the corresponding changes in aqueous component concentrations, that must be satisfied in order to conserve mass,

and

$$I_j = \begin{cases} 0 & \text{if mineral } j \text{ is dissolving at a given point in space and time,} \\ 1 & \text{if mineral } j \text{ is precipitating at a given point in space and time,} \end{cases}$$

(if a mineral is neither dissolving nor precipitating, then  $d^{(i)} = d^{(j)} = 0$  and the value of  $I_j$  is irrelevant).

An example of Eq. 3.2, for a simple case of  $\text{CaCO}_3$  dissolution in a static system (no advective/dispersive fluxes), is given in Box 3.1.

Box 3.1: Mass balance for  $\text{CaCO}_3$  dissolution in a static system (no advective/dispersive fluxes), expressed in terms of a matrix equation

$$\begin{array}{ccccccc} \left[ \begin{array}{c} \frac{d}{dt} \{ \text{Ca}^{2+} \} \\ \frac{d}{dt} \{ \text{CO}_3^{2-} \} \end{array} \right] & = & 1 & \cdot & \left[ \begin{array}{c} 1 \\ 1 \end{array} \right] & \cdot & \left[ \frac{d}{dt} \text{CaCO}_3(s) \right] \\ \uparrow & & \uparrow & & \uparrow & & \uparrow \\ S_{disn} & & (1-I) & & M & & A \cdot d \end{array}$$

Note: In this report, the brackets { } denote *component* concentrations.  $\text{CaCO}_3(s)$  denotes the amount of solid calcite per unit volume of fluid. *Species* concentrations are denoted elsewhere in the report by square brackets [ ].

### 3.2 Transport processes

The advective flux of the  $i$ th component is related to the component concentration and the Darcy velocity  $q$  ( $\text{m a}^{-1}$ ) through the equation:

$$f_a^{(i)} = qc^{(i)}, \quad (3.4)$$

where, in general, the Darcy velocity is a function of the hydraulic gradient and hydraulic conductivity. Hydraulic conductivity is, in turn a function of the porosity  $\varepsilon$ .

The diffusive flux is given by:

$$f_d^{(i)} = -\varepsilon D \frac{\partial c^{(i)}}{\partial x}, \quad (3.5)$$

where  $D$  ( $\text{m}^2 \text{a}^{-1}$ ) is the pore diffusion coefficient. The product  $\varepsilon D$  is termed the "effective diffusion coefficient", which is the parameter measured in many diffusion experiments.

### 3.3 Mineral dissolution

If a solution is under-saturated with respect to a particular mineral, then that mineral is expected to dissolve (note: supersaturation is dealt with in section 3.4 on precipitation). If a first-order rate law is assumed for this process, the rates of dissolution of the  $N_m$  minerals are given by:

$$d^{(j)} = -\frac{k_j}{K_j} S_j, \quad j = 1, \dots, N_m, \quad (3.6)$$

where  $k_j$  ( $\text{mol m}^{-2} \text{a}^{-1}$ ) is the rate constant for the  $j$ th mineral,  $K_j$  is the solubility product of the mineral and  $S_j$  is the saturation factor for the fluid<sup>1</sup>,

$$S_j = \prod_{i=1}^{N_s} [s^{(i)}]^{F_{ji}} - K_j \quad (3.7)$$

There are  $N_s$  chemical species in solution and  $s^{(i)}$  ( $\text{mol m}^{-3}$ ) is the concentration of the  $i$ th species. An example of Eq. 3.7, again for a simple case of  $\text{CaCO}_3$  dissolution, is given in Box 3.2.

Box 3.2: Derivation of the saturation factor of  $\text{CaCO}_3$ , expressed in terms of a matrix equation

$$[S_{\text{CaCO}_3}] = \log^{-1} \left\{ \begin{array}{c} 1 \\ 1 \\ 0 \\ \vdots \end{array} \right\} \cdot \left[ \log [\text{Ca}^{2+}] \log [\text{CO}_3^{2-}] \dots \text{other species} \dots \right] - K_{\text{CaCO}_3}$$

↑  
 $F$

### 3.4 Chemical speciation and mineral precipitation

In order to solve Eq. 3.1, there remain to be determined the concentrations of the  $N_s$  chemical species (so that Eq. 3.7 can be applied) and the rates of precipitation of  $N_{ppt}$  minerals, i.e. those minerals that, at a particular location in space and time, are precipitating, rather than dissolving:

$$N_{ppt} = \sum_{j=1}^{N_m} I_j \quad (3.8)$$

<sup>1</sup> The saturation factor describes how far the system is from chemical equilibrium, for a particular mineral and at a specific location along the transport path. If  $S_j$  is zero, the system is at equilibrium, if it is positive, the system is over-saturated and, if it is negative, the system is under-saturated. It is related to the Saturation Index which is usually defined as the ratio of the ion activity product to the reaction constant, not the difference as used here. Also, the use in Eq. 3.7 of concentrations, not activities, means that the reaction constants must be corrected for ionic strength. The ionic strength correction is discussed later in this section.

These  $N_{ppt} + N_s$  unknowns are subject to various constraints. These are:

### Mass balance

The aqueous components are distributed among the various species according to the mass-balance equation:

$$c^{(i)} = \sum_{j=1}^{N_s} E_{ij} s_j, \quad j = 1, \dots, N_c \quad (3.9)$$

An example of Eq. 3.9 is given in Box 3.3.

Box 3.3: An example of a mass-balance equation, in matrix form, for aqueous species and components

$$\begin{array}{c} \left[ \begin{array}{c} \{ \text{Ca}^{2+} \} \\ \{ \text{CO}_3^{2-} \} \\ \{ \text{H}^+ \} \end{array} \right] = \begin{array}{c} \left[ \begin{array}{ccccc} 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 \end{array} \right] \cdot \left[ \begin{array}{c} \left[ \begin{array}{c} \text{Ca}^{2+} \\ \text{Ca(OH)}^+ \\ \text{CO}_3^{2-} \\ \text{H}^+ \\ \text{OH}^- \end{array} \right] \\ \uparrow \\ s \end{array} \right] \\ \uparrow \\ c \end{array} \quad \begin{array}{c} \uparrow \\ E \end{array} \end{array}$$

The  $c^{(i)}$ s are also unknowns, but these can be expressed in terms of the rates of mineral precipitation etc. via Eq. 3.1.

### Chemical equilibrium

Aqueous speciation and mineral precipitation are assumed to be rapid processes, with respect to the timescales associated with transport. There are  $N_s - N_c$  equilibrium equations that describe aqueous speciation and  $N_{ppt}$  equilibrium equations that describe mineral precipitation<sup>2</sup>.

In the case of aqueous speciation, the equilibrium equations take the form:

$$\kappa_j = \sum_{i=1}^{N_s} G_{ij} \log_{10} s^{(i)}, \quad j = 1, \dots, N_s - N_c, \quad (3.10)$$

where  $\kappa_j$ ,  $j = 1, \dots, N_s - N_c$  and the matrix  $G_{ij}$  (of reaction coefficients) are parameters that describe each chemical reaction.

<sup>2</sup> The treatment in SANTA-CHEM of the special case in which specific minerals are assumed to be always in equilibrium with aqueous species, irrespective of whether they are dissolving or precipitating, is described in section 4.3.3.

In the case of mineral precipitation (minerals for which  $I_j = 1$  and  $S_j = 0$ ), rearranging Eq. 3.7, the equilibrium equations take the form:

$$I_j \log_{10} K_j = I_j \sum_{i=1}^{N_s} F_{ji} \log_{10} s^{(i)}, \quad j = 1, \dots, N_m \quad (3.11)$$

$N_{ppt}$  of these  $N_m$  equations are non-trivial (for the remainder,  $I_j = 0$ , and thus the left-hand and right-hand sides are zero).

Equations 3.10 and 3.11 can be combined into a single equation by defining a further set of parameters  $\kappa_j, j = N_s - N_c + 1, \dots, N_s - N_c + N_m$  is defined as equal to zero for dissolving minerals, and equal to the log of the solubility product for precipitating minerals:

$$\kappa_{N_s - N_c + j} = I_j \log_{10} K_j, \quad j = 1, \dots, N_m, \quad (3.12)$$

then, from Eq. 3.11:

$$\kappa_{N_s - N_c + j} = I_j \sum_{i=1}^{N_s} F_{ji} \log_{10} s^{(i)}, \quad j = 1, \dots, N_m, \quad (3.13)$$

and:

$$\kappa_j = \sum_{i=1}^{N_s} H_{ji} \log_{10} s^{(i)}, \quad j = 1, \dots, N_s - N_c + N_m, \quad (3.14)$$

where

$$H_{j-(N_s+N_c),i} = \begin{cases} G_{ji} & j = 1, \dots, N_s - N_c \\ I_j F_{j-(N_s+N_c),i} & j = N_s - N_c + 1, \dots, N_s - N_c + N_m \end{cases}, \quad i = 1, \dots, N_s \quad (3.15)$$

In Eq. 3.14, the indices  $j = 1, \dots, N_s - N_c$  correspond to the equations for aqueous speciation and  $j = N_s - N_c + 1, \dots, N_s - N_c + N_m$  correspond to the equations for mineral precipitation.

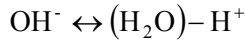
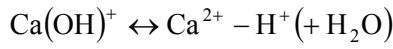
An example of Eq. 3.14 is given in Box 3.4.

Box 3.4: An example chemical equilibria, in matrix form, for aqueous speciation and mineral precipitation

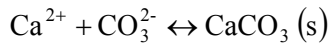
$$\begin{array}{c}
 \left[ \begin{array}{c} \kappa_1 \\ \kappa_2 \\ \kappa_3 \end{array} \right] = \left[ \begin{array}{ccccc} 1 & -1 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 & -1 \\ 1 & 0 & 1 & 0 & 0 \end{array} \right] \cdot \left[ \begin{array}{c} [\text{Ca}^{2+}] \\ [\text{Ca}(\text{OH})^+] \\ [\text{CO}_3^{2-}] \\ [\text{H}^+] \\ [\text{OH}^-] \end{array} \right] \\
 \uparrow \qquad \qquad \qquad \uparrow \qquad \qquad \qquad \uparrow \\
 \kappa \qquad \qquad \qquad H \qquad \qquad \qquad \log_{10} s
 \end{array}$$

It is assumed that all concentrations are diluted, so that the amount of water in the system does not affect the equilibria. Thus, H<sub>2</sub>O does not appear explicitly in these equations.

In this example, there are  $N_s = 5$  aqueous species,  $N_c = 3$  components (Ca<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup> and H<sup>+</sup>) and  $N_{ppt} = 1$  precipitating mineral (CaCO<sub>3</sub> (s)). There are thus  $N_s - N_c = 2$  aqueous speciation reactions



and  $N_{ppt} = 1$  mineral precipitation reaction:



In this latter reaction,  $\kappa_3 = \log_{10} K_{sp}$ , where  $K_{sp}$  is the solubility product.

Although Eq. 3.14 represents  $N_s - N_c + N_m$  equations, only  $N_s - N_c + N_{ppt}$  of these are non-zero. Thus, together with Eq. 3.9, chemical equilibrium and mass balance gives a total of  $N_c + (N - N_c + N_{ppt}) = N_{ppt} + N_s$  non-zero equations for the  $N_{ppt} + N_s$  unknowns associated with Eq. 3.1, and the equation can thus be solved.

#### *Ionic-strength correction*

The solution of Eq. 3.14 is complicated by the fact that the parameters  $\kappa_j, j = 1, \dots, N_s - N_c + N_m$  are not constants, but are functions of the concentrations of the dissolved species, since activities are used to define solubility products and the activity coefficients are ionic-strength dependent (see, for example, STUMM & MORGAN 1996):

$$\kappa_j = \kappa_j^{(0)} - p \sum_{i=1}^{N_s} H_{ji} v_i^2, \quad j = 1, \dots, N_s - N_c + N_m, \quad (3.16)$$



where  $v_i$  is the charge on the  $i$ th species,  $\kappa^{(j)}$ ,  $j = 1, \dots, N_s - N_c + N_m$  are constants, one for each equilibrium reaction, and the second term on the right-hand side is an ionic-strength correction (extended Davies equation) in which:

$$p = -\zeta \left( \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right) \quad (3.17)$$

and the ionic strength

$$\mu = \frac{1}{2} \sum_{i=1}^{N_s} v_i^2 s^{(i)} \quad (3.18)$$

$\zeta$  is the dielectric constant of water, which, in terms of the absolute temperature  $T$  (K), is given by:

$$\zeta = \frac{1.82 \times 10^6}{\sqrt{T(169.1 - 0.301T)^3}} \quad (3.19)$$

Eq. 3.14 cannot be solved for the species concentrations until the  $\kappa$ s parameters are determined. This, however, requires knowledge of the species concentrations, in order to perform an ionic-strength correction via Eq. 3.16 – 3.19. The problem is overcome in SANTA-CHEM using an iterative solution technique. The solution techniques adopted in SANTA-CHEM are described in Chapter 4.

## 4 SOLUTION TECHNIQUES

### 4.1 Discretisation in space and time

#### 4.1.1 Spatial discretisation

In order to model the evolution of the system due to the coupled processes of solute transport and chemical reactions, the one-dimensional transport path, of length  $L$  (m), is modelled as row of  $N$  "boxes", each of length  $\delta L$  (m) =  $L/N$  and cross-sectional area  $A$  (m<sup>2</sup>). A single box is illustrated in Fig. 4.1.

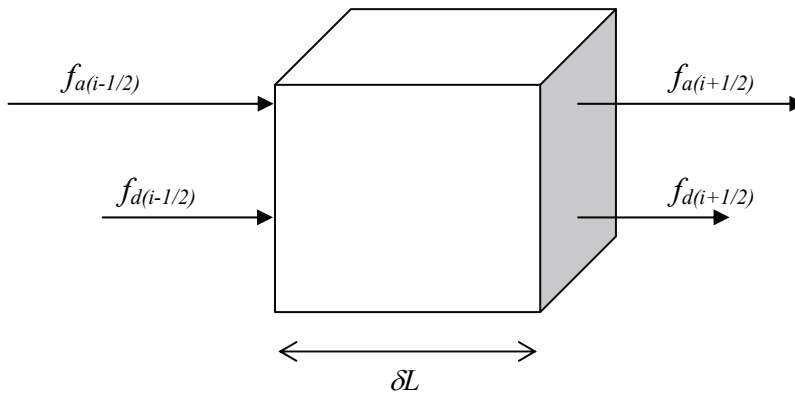


Fig. 4.1: A single box, the  $i$ th in a row of boxes, showing advective and diffusive fluxes across the upstream and downstream boundaries

In order to conserve the mass of a component within the box, its aqueous concentration  $c$  (mol m<sup>-3</sup>) must satisfy the integral form of Eq. 3.1:

$$\int_{\delta L} \frac{\partial c}{\partial t} dx = -\frac{1}{\varepsilon_i} [f_{a(i+1/2)} + f_{d(i+1/2)} - f_{a(i-1/2)} - f_{d(i-1/2)}] + \int_{\delta L} (S_{disn} + S_{ppt}) dx, \quad (4.1)$$

where  $\varepsilon_i$  is the porosity of the box. The component may be generated or removed from solution by the dissolution and precipitation source terms. Aqueous components are transported by the processes of advection and diffusion. The advective and dispersive mass fluxes into and out of the  $i$ th box are defined as:

$f_{a(i-1/2)}$ (mol m <sup>-2</sup> a <sup>-1</sup> ):	the advective flux of the component into the box;
$f_{a(i+1/2)}$ (mol m <sup>-2</sup> a <sup>-1</sup> ):	the advective flux of the component out of the box;
$f_{d(i-1/2)}$ (mol m <sup>-2</sup> a <sup>-1</sup> ):	the diffusive flux of the component into the box;
$f_{d(i+1/2)}$ (mol m <sup>-2</sup> a <sup>-1</sup> ):	the diffusive flux of the component out of the box.

For a sufficiently small box length and time step, the change in concentration in a single time step  $\delta t$  (a) in the  $i$ th box,  $\delta c_i$  (mol m<sup>-3</sup>), is given by the finite-difference approximation to Eq. 4.1:

$$\delta c_i = - \left[ \frac{f_{a(i+1/2)} + f_{d(i+1/2)} - f_{a(i-1/2)} - f_{d(i-1/2)}}{\delta L} \right] \frac{\delta t}{\varepsilon_i} + S_{diss} \delta t + S_{ppt} \delta t \quad (4.2)$$

#### 4.1.2 Time stepping

The following procedure is adopted in order to evaluate  $\delta c_i$  for each box through a succession of time steps.

1. Assign an initial porosity, mineral inventory and inventory of aqueous components to each of the boxes along the transport path.
2. Calculate each term on the right-hand side of Eq. 4.2:
  - evaluate transport; calculate the groundwater flow (Darcy velocity) through the row of boxes, which will be a function of the porosity distribution, and evaluate the fluxes of each aqueous component into, and out of, each box due to the processes of *advection* in flowing groundwater and *diffusion*;
  - evaluate mineral dissolution; allow existing minerals to *dissolve*, to the extent allowed by the kinetics of this process;
  - evaluate mineral precipitation; calculate the aqueous speciation, allowing minerals to precipitate to the extent determined by the speciation, under the assumption of rapid kinetics.

The evaluation of transport, mineral dissolution and mineral precipitation is described in sections 4.2, 4.3 and 4.4, respectively.

3. Evaluate new porosities, mineral inventories and inventories of aqueous components, taking account of the transport and mineral dissolution and precipitation within a time step.
4. Either return to step 2, or, if the required total time has elapsed, exit the time-stepping loop.

The simple time-stepping technique used in SANTA-CHEM is thus explicit<sup>3</sup>, and the user must be aware of the possibility of numerical instability if the time step is too large for a given box size. The technique is also expected to be only first-order accurate. More accurate time-stepping techniques, less susceptible to stability problems, could, if necessary, be implemented at a later development stage.

The time step may be either set to a constant value by the SANTA-CHEM user, or allowed to vary, according to the procedure outlined at the end of this chapter, in section 4.5.

---

<sup>3</sup> An explicit method is one in which the state of the system at a given time can be calculated directly from values that have been calculated for earlier times and stored, so that they are immediately available (see, for example, section 5.3 in WILLIAMS 1973).

## 4.2 Transport

### 4.2.1 Hydraulic properties

The porosity of the rock is expected to be a function of space and time, due to the dissolution and precipitation of minerals. In SANTA-CHEM, flow is assumed to occur in fractures, with dissolution and precipitation occurring at fracture surfaces (Fig. 4.2). This will result in a time-dependent flow, expressed in terms of the Darcy velocity  $q$  ( $\text{m a}^{-1}$ ).

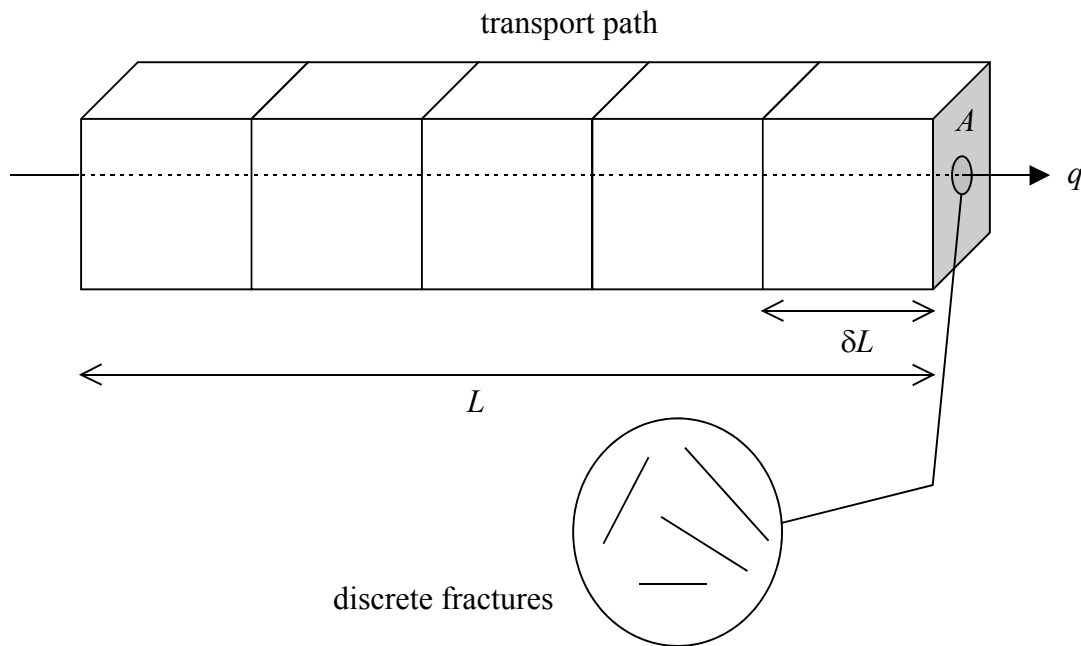


Fig. 4.2: The transport path, which conveys water with a Darcy velocity  $q$ , is discretised into a row of boxes

If the transport path is acted upon by a hydraulic gradient  $i$ , and the  $j$ th box has a hydraulic conductivity  $K_{(j)}$  ( $\text{m a}^{-1}$ ), the Darcy velocity is given by<sup>4</sup>:

$$q = Ni \left( \sum_{j=1}^N K_{(j)}^{-1} \right)^{-1} \quad (4.3)$$

<sup>4</sup> An analogy can be drawn between Ohm's Law relating voltage and current and Darcy's Law, relating hydraulic head difference and Darcy velocity. The resistance in Ohm's Law is analogous to the reciprocal of hydraulic conductivity in Darcy's Law. Just as individual resistances are summed to obtain the total resistance of a series of resistors, the reciprocals of hydraulic conductivities are summed in Eq. 4.3 to obtain an equation for the Darcy velocity through a series of boxes.

The hydraulic conductivity is a function of porosity. According to the Cubic Law, the hydraulic conductivity of a fractured medium<sup>5</sup> is related to the porosity,  $\varepsilon_j$ , via the equation:

$$K_{(j)} = \Omega \varepsilon_j^3, \quad (4.4)$$

where  $\Omega$  ( $\text{m a}^{-1}$ ) is a constant, that can be derived from the geometry of the fractures and the viscosity and density of water. Rather than deriving  $\Omega$  directly, the code requires the user to specify an initial Darcy velocity,  $q_0$  ( $\text{m a}^{-1}$ ), for an initial distribution of porosity,  $\varepsilon_{0,j}$ . Thus, from Eq. 4.3 and Eq. 4.4:

$$q = q_0 \frac{\sum_{j=1}^N (\varepsilon_{0,j})^{-3}}{\sum_{j=1}^N (\varepsilon_j)^{-3}} \quad (4.5)$$

#### 4.2.2 Advection

A 1-D upstream finite-difference scheme is adopted for the evaluation of advective fluxes, that is second- to third-order accurate, depending on the nature of the problem to be solved. In the present document, the numerical algorithm is given without detailed explanation; the reader is referred to KOREN (1993) for further details.

##### *General algorithm*

Denoting the concentration of a component at the mid-point of the  $i$ th box as  $c_i$  (M), the finite-difference analogue of Eq. 3.4 is:

$$f_{a(i+1/2)} = q \left[ c_i + \frac{1}{2} \phi(r_{i+1/2})(c_i - c_{i-1}) \right] \quad \text{for } 2 < i < N-1, \quad (4.6)$$

where:

$$r_{i+1/2} = \frac{c_{i+1} - c_i + \delta}{c_{i+1} - c_{i+2} + \delta}, \quad (4.7)$$

$$\phi(r) = \max \left\{ 0, \min \left[ 2r, \min \left( \frac{1}{3} + \frac{2}{3}r, 2 \right) \right] \right\}, \quad (4.8)$$

---

<sup>5</sup> Different relationships apply for different geometries: e.g. if flow is conceptualised as occurring in tubes. The Cubic Law does not, however, only apply to smooth fractures. A similar relationship, but with an effective aperture that is a function of aperture variability, can be shown to apply to rough fractures (see e.g. ANDO & VOMVORIS 1998).

and  $\delta$  is a very small number, introduced to avoid division by zero in regions of uniform concentration.

*Upstream boundary condition*

Denoting the concentration of a component at the upstream boundary as  $c_{in}$  ( $\text{mol m}^{-3}$ ):

$$f_{a(1/2)} = qc_{in} \quad (4.9)$$

and

$$f_{a(3/2)} = \frac{q}{2}(c_1 + c_2) \quad (4.10)$$

*Downstream boundary condition*

$$f_{a(N+1/2)} = q \left[ c_N + \frac{1}{2}(c_N - c_{N-1}) \right] \quad (4.11)$$

### 4.2.3 Diffusion

The diffusive fluxes are evaluated by a standard, second-order accurate central differences scheme.

*General algorithm*

The finite-difference analogue of Eq. 3.5 is:

$$f_{d(i+1/2)} = \frac{(\varepsilon_i + \varepsilon_{i+1})D}{2\delta L} [(c_{i+1} - c_i)] \quad \text{for } 1 < i < N - 1 \quad (4.12)$$

*Upstream boundary condition*

$$f_{d(1/2)} = \frac{\varepsilon_1 D}{3\delta L} [-8c_{in} + 9c_1 - c_2] \quad (4.13)$$

*Downstream boundary condition*

Assuming a zero-concentration downstream boundary condition:

$$f_{d(N+1/2)} = \frac{\varepsilon_N D}{3\delta L} [9c_N + c_{N-1}] \quad (4.14)$$

#### 4.2.4 Testing

Test cases for the solution techniques for transport are described in Appendix B1. These are limiting cases, where transport is either advection-dominated or diffusion-dominated, for which analytical solutions are available. The test cases show that the solution techniques yield results that converge to the analytical solutions if the box size and the time step are made sufficiently small.

### 4.3 Mineral dissolution

#### 4.3.1 Dissolution options

The source term for component  $i$ , that accounts for mineral dissolution, is evaluated using Eq. 3.2, i.e.:

$$S_{disn}^{(i)} = \sum_{j=1}^{N_m} (1 - I_j) M_{ij} A^{(j)} d^{(j)} \quad (4.15)$$

In SANTA-CHEM, the user has two options for setting the product  $A^{(j)} d^{(j)}$  for any particular mineral  $j$ . In particular, the user may choose to model the kinetics of mineral dissolution explicitly. Alternatively, if the rate of dissolution of a mineral is known to be much faster than the transport processes operating in the system, the user may assume that the mineral/solute system is always in a state of local chemical equilibrium. This avoids the need for very small time steps, that would be required if fast dissolution were to be modelled explicitly.

The relevant equations for these two options are described, below.

#### 4.3.2 Kinetically-controlled dissolution

If this option is selected, the two parameters in the product  $A^{(j)} d^{(j)}$  must be determined separately.

Regarding  $A^{(j)}$ , the surface area of a mineral  $j$  per unit volume of fluid, the SANTA-CHEM user can select from two alternative assumptions:

$$A^{(j)} = \frac{a^{(j)}}{\varepsilon \Psi} \begin{cases} X^{(j)} & \text{(area assumed proportional to total mass of mineral present)} \\ X^{(j)}|_{t=0} & \text{(area assumed independent of total mass of mineral present)} \end{cases}$$

where  $a^{(j)}$  ( $\text{m}^2 \text{mol}^{-1}$ ) is the specific surface area of the mineral,  $X^{(j)}$  (mol) is the time-dependent mineral inventory in a box and  $\Psi$  ( $\text{m}^3$ ) is the box volume.

The latter assumption may be appropriate if, for example, minerals are present as layers, or plates, that become thinner during dissolution, but without significant change in their surface area.

Regarding  $d^{(j)}$ , the rate of dissolution of a mineral  $j$ , Eqs. 3.6, 3.7 and 3.8 are used to evaluate this parameter. In order to apply these equations, the concentrations of the aqueous species must be known. The species concentrations are calculated in the course of evaluating mineral precipi-

tation (section 4.4). At any given time step, following the evaluation of precipitation, the species concentrations in each box are stored and used, in the subsequent time step, to evaluate the mineral dissolution source term.

### 4.3.3 Minerals in equilibrium with aqueous species

If this option is selected, the two parameters in the product  $A^{(i)}d^{(i)}$  need not be determined separately.

In order to implement this option, the procedure is:

- to calculate the (hypothetical) aqueous component concentrations in each box under the hypothetical assumption that the entire inventory of the mineral dissolves during the time step;
- proceed (as always) to evaluate mineral precipitation in the time step (section 4.4).

The dissolution of the entire inventory of a mineral corresponds to a product  $A^{(i)}d^{(i)}$  given by:

$$A^{(j)}d^{(j)} = \frac{1}{\varepsilon\Psi\delta t} X^{(j)} \quad (4.16)$$

Although the (hypothetical) aqueous component concentrations may be very high following the application of this dissolution rate, especially if the mineral inventory is high, super-saturation will result in immediate reprecipitation of solids.

## 4.4 Chemical speciation and mineral precipitation

### 4.4.1 Equations to be solved

At the start of a time step, chemical species in solution satisfy the mass-balance equations (Eq. 3.9) and chemical equilibria (Eq. 3.14). Following the evaluation of transport and mineral dissolution, and their application in Eq. 4.2, the precipitation term in this equation must ensure that these constraints continue to be satisfied.

If  $c_k^{(i)}(t)$  is the concentration of component  $i$  in box  $k$  at time  $t$ , then:

$$c_k^{(i)}(t) = c_k^{(i)}(t - \delta t) + \delta c_k, \quad (4.17)$$

where  $\delta c_k$  is defined in Eq. 4.2.

Consideration of transport and dissolution processes (but without precipitation) results in a hypothetical concentration:

$$\begin{aligned} \tilde{c}^{(i)} &= c_k^{(i)}(t - \delta t) - \left[ \frac{f_{a(k+1/2t)} + f_{d(k+1/2)} - f_{a(k-1/2)} - f_{d(k-1/2)}}{\delta L} \right] \frac{\delta t}{\varepsilon_k} + S_{disn} \delta t \\ &= c_k^{(i)}(t - \delta t) + \delta c_k - S_{ppt}^{(i)} \delta t \end{aligned} \quad (4.18)$$



If  $\delta c_k$  is eliminated from Eq. 4.17 and 4.18:

$$\tilde{c}^{(i)} = c_k^{(i)}(t) - S_{ppt}^{(i)} \delta t \quad (4.19)$$

Substituting Eq. 3.3 and Eq. 3.9 in Eq. 4.19,

$$\tilde{c}^{(i)} = \sum_{j=1}^{N_s} E_{ij} s_j + \delta t \sum_{j=1}^{N_m} I_j M_{ij} p^{(j)} = \sum_{j=1}^{N_s} P_{ij} r_j, \quad i = 1, \dots, N_c, \quad (4.20)$$

where:

$$P_{ij} = \begin{cases} E_{ij} & j = 1, \dots, N_s \\ M_{ij-N_s} & j = N_s + 1, \dots, N_s + N_m \end{cases}, \quad i = 1, \dots, N_c \quad (4.21)$$

and

$$r_j = \begin{cases} s_j & j = 1, \dots, N_s \\ \delta t I_{j-N_s} p^{(j-N_s)} & j = N_s + 1, \dots, N_s + N_m \end{cases} \quad (4.22)$$

In order to evaluate the concentrations of the  $N_s$  aqueous species ( $r_j, j = 1, \dots, N_s$ ) and the amounts of the  $N_{ppt}$  minerals precipitated in a time step (the non-zero elements of  $r_j, j = N_s + 1, \dots, N_s + N_m$ ), Eq. 4.20 provides  $N_c$  equations. The remaining  $N_s - N_c + N_{ppt}$  equations are provided by Eq. 3.14.

Thus, Eq. 4.20 and Eq. 3.14 must be solved for  $r_j, j = 1, \dots, N_s + N_m$ , before Eq. 4.22 can be used to obtain aqueous species concentrations and precipitated amounts. In order to solve Eq. 4.20 and Eq. 3.14, it is necessary to determine which of the minerals are precipitating, and which are dissolving, in a particular box at a particular time step ( $I_j, j = 1, \dots, N_m$ ). This is described in section 4.4.2.

The specific techniques for solving Eq. 4.20 and Eq. 3.14 are presented in section 4.4.3.

#### 4.4.2 Identification of precipitating and dissolving minerals

For each box, and for each time step, the array  $I_j, j = 1, \dots, N_m$  must be evaluated, where:

$$I_j = \begin{cases} 0 & \text{if mineral } j \text{ is dissolving,} \\ 1 & \text{if mineral } j \text{ is precipitating.} \end{cases}$$

The aim is to establish an array that enables the following conditions to be satisfied:

$$\text{If } I_j = \begin{cases} 0 \\ \text{or} \\ 1 \end{cases} \text{ then } \begin{cases} \left\{ \begin{array}{l} p^{(j)} = 0 \\ S_j < 0 \end{array} \right. & \begin{array}{l} \text{(no precipitation occurs)} \\ \text{the solution is undersaturated with respect to mineral } j \end{array} \\ \left\{ \begin{array}{l} p^{(j)} > 0 \\ S_j = 0 \end{array} \right. & \begin{array}{l} \text{precipitation occurs} \\ \text{(the solution is oversaturated with respect to mineral } j) \end{array} \end{cases}$$

where the two conditions in brackets are satisfied automatically by the setting of  $I_j$ . The following iterative procedure adopted in order to ensure that all conditions are satisfied.

1. As a starting point,  $I_j, j = 1, \dots, N_m$  for a particular box at a particular time step is assumed to be equal to that of the same box at the previous time step.
2. This distribution of  $I_j, j = 1, \dots, N_m$  is used in the solution of Eq. 3.14 and Eq. 4.20, and thus obtain the concentrations of the  $N_s$  aqueous species and the amounts of the  $N_{ppt}$  minerals precipitated in a time step.
3. From the aqueous speciation, using Eq. 3.7, the saturation factors  $S_j, j = 1, \dots, N_m$  are calculated for all the minerals.
4. Considering each mineral in turn, identify any mineral for which  $I_j = 0$  and  $S_j > 0$  – i.e. any minerals that are classified as dissolving, but with respect to which the solution is oversaturated.
5. If any such minerals are found, reset  $I_j$  to 1 for the mineral for which  $S_j$  is the greatest and go to step 1. If no such minerals are found, go to step 6.
6. Again considering each mineral in turn, identify any mineral for which  $I_j = 1$  and  $p_j < 0$  – i.e. any minerals that are classified as precipitating, but for which the rate of precipitation is calculated as negative.
7. If any such minerals are found, reset  $I_j$  to 0 for the mineral for which  $p_j$  is the most negative and go to step 1. If no such minerals are found, go to step 8.
8. A consistent array  $I_j, j = 1, \dots, N_m$  has been identified, and SANTA-CHEM proceeds to the next box, or to the next time step.

Occasionally, it has been found that this iterative procedure fails to yield a consistent array. In such cases, an alternative procedure is applied in which, in step 5,  $I_j$  is reset to 1 for *all* minerals for which  $S_j > 0$  and, in step 7,  $I_j$  is reset to 0 for *all* minerals for which  $p_j < 0$ .

In testing SANTA-CHEM, no situations have been found where both iterative procedures fail to yield a consistent array of dissolving and precipitating minerals.

#### 4.4.3 Strategy for solving the equations

Eq. 3.14 and Eq. 4.20, which must be solved in order to obtain the concentrations of aqueous species and the amounts of minerals precipitated in a box in a time step, form a set of  $N_s + N_{ppt}$  coupled, non-linear equations.

In principle, a general non-linear solver, employing, for example, the *Newton Raphson method*, could be applied to solve the entire problem. SANTA-CHEM, however, adopts a more efficient approach. The aim is to treat separately that part of the problem that is, to a large extent, independent of time, depending only on the formulation of the chemical reactions taking place at a

particular location along the transport path. As long as the reactions involved do not change (i.e. no new minerals start precipitating and no previously precipitating minerals start to dissolve), a partial solution can be obtained, stored and used repeatedly at successive time steps. If the reactions change (determined using the procedure outlined in the previous section), then a new partial solution must be obtained and stored.

The method used to obtain a partial solution is *singular-value decomposition*, and is applied to Eq. 3.14. Eq. 3.14 provides  $N_s - N_c + N_{ppt}$  equations for the  $N_s$  aqueous species concentrations. Singular-value decomposition cannot solve for the aqueous species concentrations, since the number of equations is less than the number of unknowns. Rather, it is used to reduce the number of unknowns to the extent allowed by the available equations. In particular, the method allows the species concentrations to be expressed in terms of  $m = N_s - (N_s - N_c + N_{ppt}) = N_c - N_{ppt}$  new unknowns. The relationship between the species concentration and the new unknowns is given in terms of matrices that can be stored and re-used at subsequent time steps. The species concentrations are then eliminated from Eq. 4.20, by substitution. The resulting  $N_c$  non-linear equations contain the  $m = N_c - N_{ppt}$  new unknowns and the  $N_{ppt}$  unknown dissolution rates. The number of unknowns thus matches the number of equations, and the equations are solved using the Newton-Raphson method.

The application of singular-value decomposition and the Newton-Raphson method is described in the following sections. The methods are presented without detailed explanation; the reader is referred to Chapters 2.6 and 9.4 in PRESS et al. (1992) for a full discussion of these methods.

#### 4.4.4 Application of singular-value decomposition

The application of singular-value decomposition in SANTA-CHEM proceeds by the following steps.

1. Express Eq. 3.14 as a matrix equation:

$$\kappa = H s' \quad (4.23)$$

so that the logs of the species concentrations are given by:

$$s' = H^{-1} \kappa \quad (4.24)$$

$s'$  is a column matrix of  $N_s$  elements, containing  $\log_{10} s^{(j)}$ ,  $j = 1, \dots, N_s - N_c + N_m$ .  $\kappa$  is a column matrix of  $N_s$  elements, containing  $\kappa_j$ ,  $j = 1, \dots, N_s - N_c + N_m$ , and augmented by  $N_c - N_m$  zeros to complete the matrix.  $H$  is an  $N_s \times N_s$  matrix, the elements of which are given by Eq. 3.14, but again augmented by  $N_c - N_m$  rows of zeros to complete the square matrix. There are already  $N_m - N_{ppt}$  rows of zeros in  $H$ , corresponding to the dissolving minerals, giving  $(N_c - N_m) + (N_m - N_{ppt}) = N_c - N_{ppt}$  rows of zeros in total.

2. Express matrix  $H$  as the product of an orthogonal matrix  $U$ , a diagonal matrix  $W$  and the transpose of an orthogonal matrix  $V$  ( $V^T = V^{-1}$ ):

$$H = U \cdot \begin{bmatrix} W_1 & & & \\ & W_2 & & \\ & & \dots & \\ & & & W_{N_s} \end{bmatrix} \cdot V^T \quad (4.25)$$

3. Compute the matrices  $V$ ,  $W$  and  $U$ , e.g. by the techniques described in Chapter 2.6 of PRESS et al. (1992). When  $W$  is computed, it contains  $m = N_c - N_{ppt}$  arbitrary diagonal elements, corresponding to the  $m$  rows of zeros in  $H$ . If these arbitrary elements appear in columns  $n_1, n_2, \dots, n_m$ , a *particular solution* to Eq. 3.14,  $s'_{pt}$ , can be written:

$$s'_{pt} = H^{-1} \kappa = V \cdot \begin{bmatrix} z_1 & & & \\ & z_2 & & \\ & & \dots & \\ & & & z_{N_s} \end{bmatrix} \cdot (U^T \cdot \kappa), \quad (4.26)$$

where

$$z_i = \begin{cases} 1/W_i & i \neq n_1, \dots, m \\ 0 & i = n_1, \dots, m \end{cases} \quad (4.27)$$

4. The *general solution* of Eq. 3.14 is obtained by adding to the particular solution a linear combination of columns  $n_1, n_2, \dots, n_m$  of matrix  $V$ :

$$s'_i = s'_{pt} + \sum_{j=1}^m y_j V_{in_j}, \quad (4.28)$$

where  $y_j, j = 1, \dots, m$  are the new unknowns that, together with the  $N_{ppt}$  unknown dissolution rates, must be fixed via the Newton-Raphson solution of Eq. 4.20.

The matrices  $s_{pt}$  and  $V$ , and the parameters  $n_1, n_2, \dots, n_m$  are stored for each cell. They characterise the set of chemical reactions corresponding to Eq. 3.14, and are used repeatedly until the reactions change.

#### 4.4.5 Application of the Newton-Raphson method

The application of the Newton-Raphson method in SANTA-CHEM proceeds by substituting Eq. 4.28 into Eq. 4.22:

$$r_i = \begin{cases} 10^{s'_{pt} + \sum_{j=1}^m y_j V_{in_j}} & i = 1, \dots, N_s \\ \delta t I_{i-N_s} p^{(i-N_s)} & i = N_s + 1, \dots, N_s + N_m \end{cases} \quad (4.29)$$

thus reducing the number of unknowns in Eq. 4.20 to  $N_c$ :

$$\tilde{c}^{(i)} - \sum_{j=1}^{N_s} P_{ij} r_j = f_i(y_1, \dots, y_{m=N_c-N_{ppt}}, I_1 p_1, \dots, I_{N_m} p_{N_m}) = 0, \quad i = 1, \dots, N_c \quad (4.30)$$

(note that  $1 - N_{ppt}$  of terms in the bracket are zero, since they correspond to dissolving minerals, and so are not counted as unknowns).

An initial guess is made for the unknowns in the bracket in Eq. 4.30 (see next section), and then adjusted by the Newton-Raphson method until a set is found that satisfies all  $N_c$  equations in 4.30.

The application of the Newton-Raphson method requires the evaluation of the derivatives of  $f_i$  in Eq. 4.30 with respect to the unknowns:

$$\left. \begin{aligned} \frac{\partial f_i}{\partial y_j} &= \log_e(10) V_{i,n_j} \sum_{k=1}^{N_s} P_{ik} r_k & j = 1, \dots, N_s \\ \frac{\partial f_i}{\partial p^{(j-N_s)}} &= \delta t V_{i,n_j} P_{ij} I_{j-N_s} & j = N_s + 1, \dots, N_s + N_m \end{aligned} \right\} i = 1, \dots, N_c \quad (4.31)$$

Having applied the Newton-Raphson method and determined the unknowns, the concentrations of aqueous species are then found by substituting the  $y_j, j = 1, \dots, m$  into Eq. 4.28. The source term that accounts for mineral precipitation in Eq. 3.1 is obtained by substituting the  $I_j p_j, j = 1, \dots, N_m$  in Eq. 3.3.

#### 4.4.6 Making the initial guess

The most straightforward way to make the initial guess for the unknowns in Eq. 4.30 is to use the values from the solution for the same box, at the previous time step. This guess is not, however, always close enough for the successful application of the Newton-Raphson technique (especially if the reactions change: i.e. a new mineral starts to precipitate or dissolve or a mineral stops precipitating or dissolving), and is, of course, inapplicable at the first time step. In such cases, the technique used is to begin with a known solution of a different problem (i.e. of a problem where the concentrations of the various components are not those of interest), and to gradually "step" towards the problem of interest. If the "steps" are sufficiently small, then the solution for the preceding step should provide an adequate initial guess for the next step.

In the stepping procedure, the unknowns (the  $y$ s and  $p$ s in Eq. 4.30) are initially set to the values from the previous time step or, if this fails, to zero. These  $y$ s and  $p$ s define  $r_{j,0}$  (see Eq. 4.29), which enables a set of component concentrations to be obtained from:

$$\tilde{c}_0^{(i)} = \sum_{j=1}^{N_s} P_{ij} r_{j,0}, \quad i = 1, \dots, N_c \tag{4.32}$$

These component concentrations are not the component concentrations of interest, but provide a first step, from which to approach the required solution. The stepping procedure, for set of  $N$  steps, is outlined in Fig. 4.3.

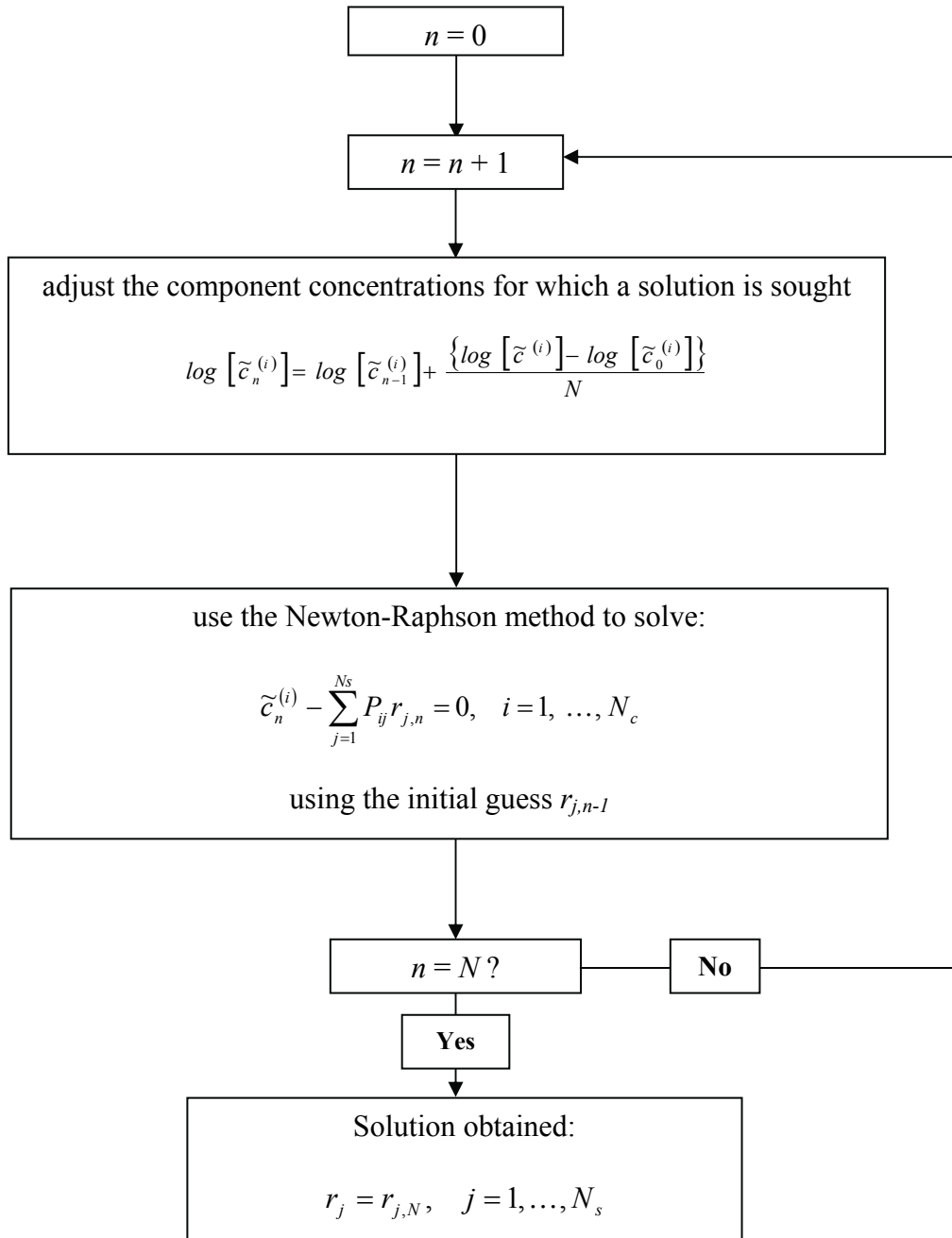


Fig. 4.3: Stepping procedure in which, by the repeated application of the Newton-Raphson method, the required solution is obtained

$N$  may need to be increased repeatedly if this procedure fails. The overall procedure for the application of the Newton-Raphson methods is shown in Fig. 4.4. In SANTA-CHEM, the number of steps ( $N$ ) is increased by factors of 10 until a solution is found. The program exits with an error message if  $N$  exceeds 1000, no solution having been obtained, although this condition has not been found to occur in practice.

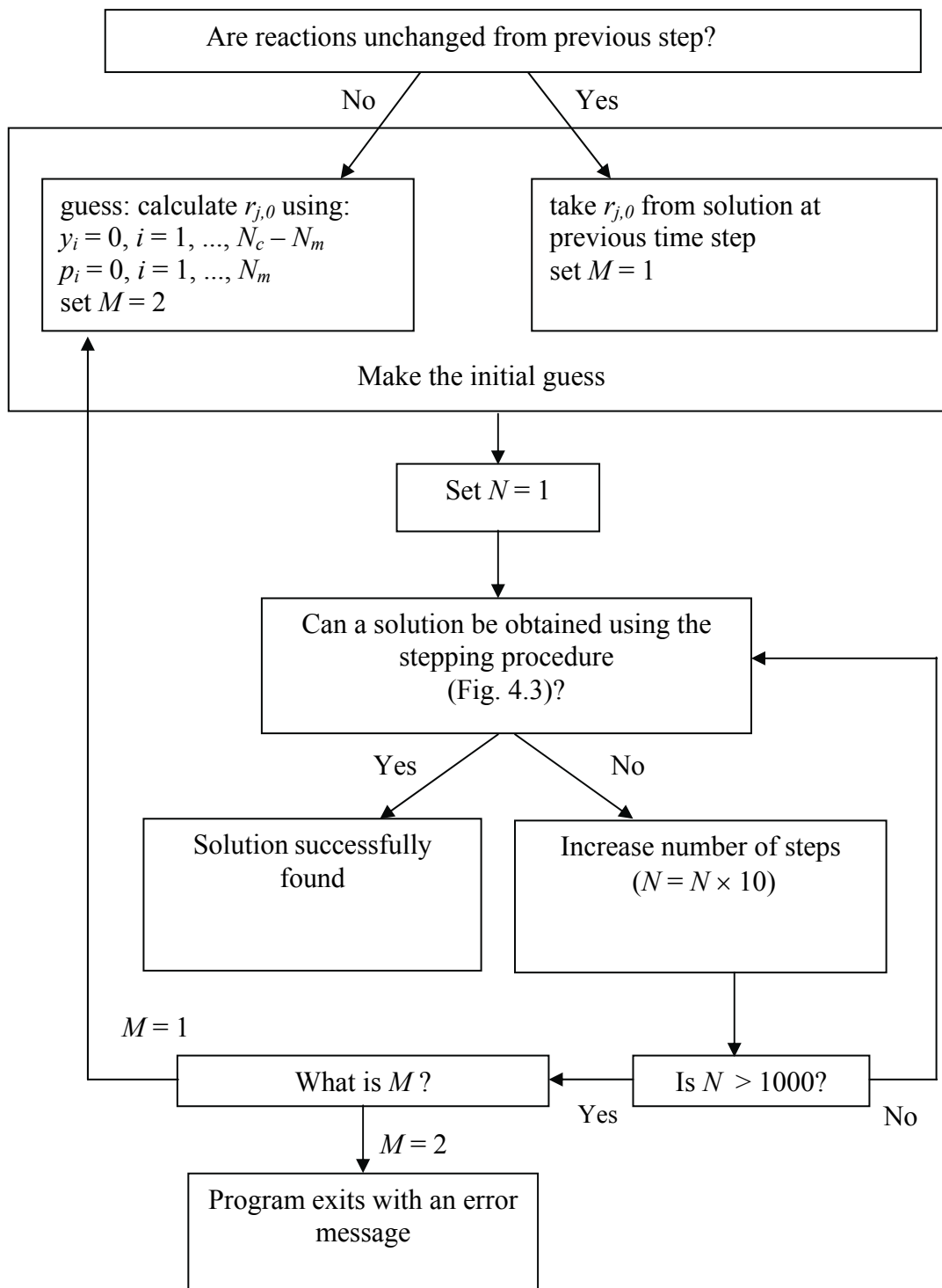


Fig. 4.4: Overall procedure for the application of the Newton-Raphson method

#### 4.4.7 Ionic-strength correction

The preceding sections describe how the concentrations of the aqueous species in a particular box and at a particular time step can be obtained by solving Eq. 3.14 and Eq. 4.20. Solution of Eq. 3.14 presupposes a knowledge of the parameter  $\kappa$ , which, as described in Chapter 3 (Eq. 3.16 – 3.19), must be corrected for the ionic strength.

The ionic-strength correction is made iteratively, as follows:

- (i) Solve Eq. 3.14 and 4.20 without the ionic-strength correction (i.e. setting  $p = 0$  in Eq. 3.16, so that  $\kappa = \kappa^{(0)}$ ).
- (ii) Use the resulting approximate species concentrations to obtain an approximate value of  $p$  via Eqs. 3.17 – 3.19.
- (iii) Use  $p$  to correct  $\kappa$  via Eq. 3.16.
- (iv) Use this corrected  $\kappa$  and re-solve Eq. 3.14 and 4.20 to obtain an improved approximation to the species concentrations.
- (v) If the species concentrations are insensitive to further iteration, then exit the loop. If not, return to step (ii).

Typically, convergence is rapid, and about 3 iterations are sufficient to obtain a good approximation to the concentrations of the aqueous species.

#### 4.5 Varying the time step

The time step  $\delta t$  used by SANTA-CHEM may be either set to a constant value by the user, or allowed to vary, according to the procedure outlined in Fig. 4.5.

In the course of each timestep, SANTA-CHEM uses a provisional timestep to check that:

- the transport of components by advection and diffusion is not so great as to completely evacuate a box in the course of a timestep (which would give rise to the possibility of unphysical, negative concentrations);
- the rate of dissolution of minerals is not so great that chemical equilibrium is "overshot", and the solution becomes over-saturated.

If either of these conditions is not satisfied, then the provisional timestep is reduced (in the case of the second condition, by repeatedly dividing by a factor of 2, until the condition is satisfied).

Once a timestep is found that satisfies both conditions for all components and minerals, and in all boxes, then this timestep is used for the evaluation of transport, dissolution and precipitation.

Following transport, dissolution and precipitation, SANTA-CHEM tests whether or not the convergence towards chemical equilibrium is sufficiently slow to suggest that, at the next timestep, a larger  $\delta t$  can be used. The provisional timestep is increased by a factor of 2 (by setting  $\delta t_c$ ), the programme advances to the next timestep and the criteria are re-assessed.



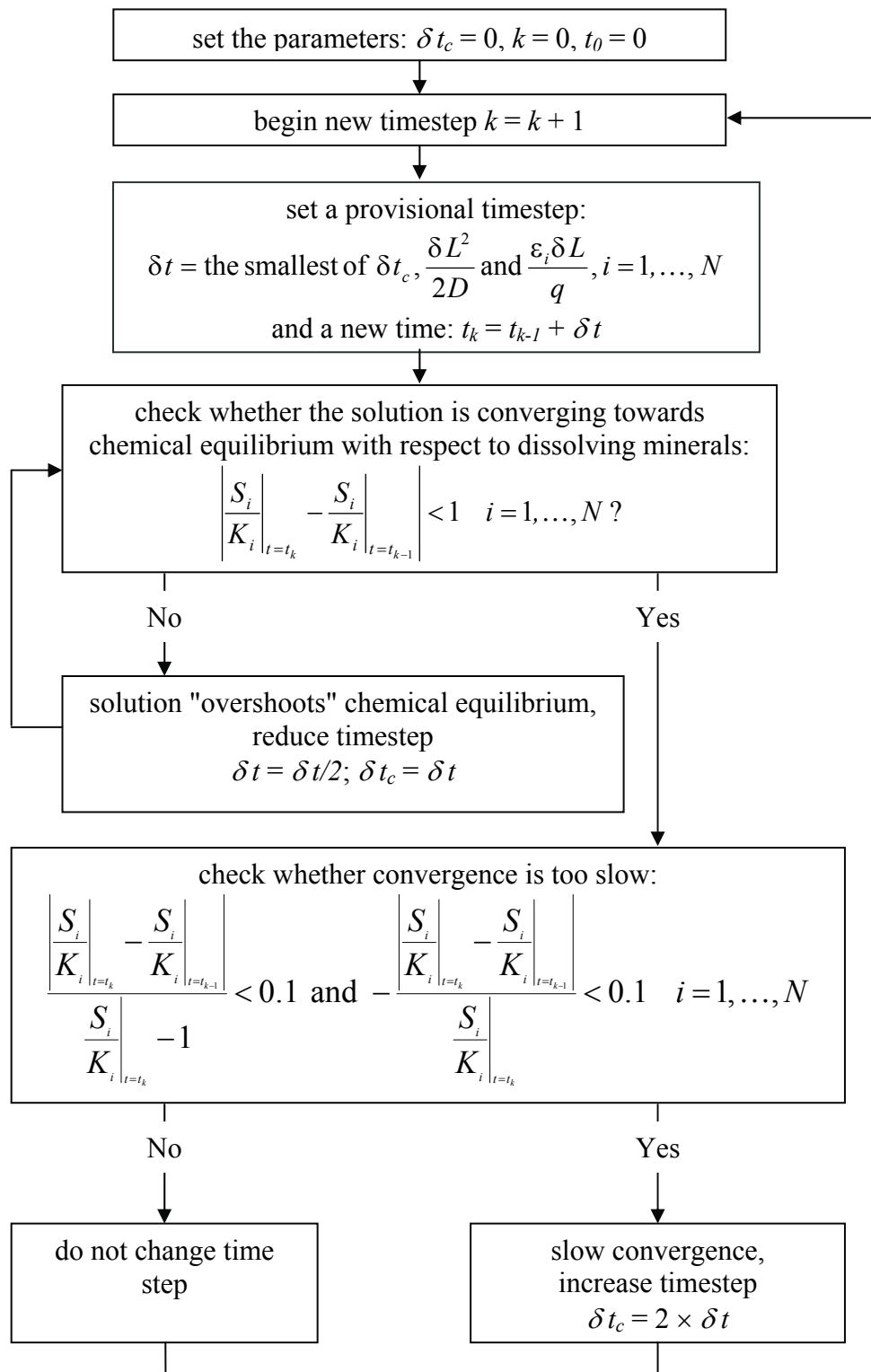


Fig. 4.5: The procedure for automatic varying of the time step in SANTA-CHEM

## 5 OVERVIEW OF THE MAIN SANTA-CHEM PROGRAM

The structure of the main program within SANTA-CHEM, and the subroutines that are called from the main program, are given in Fig. 5.1 and 5.2.

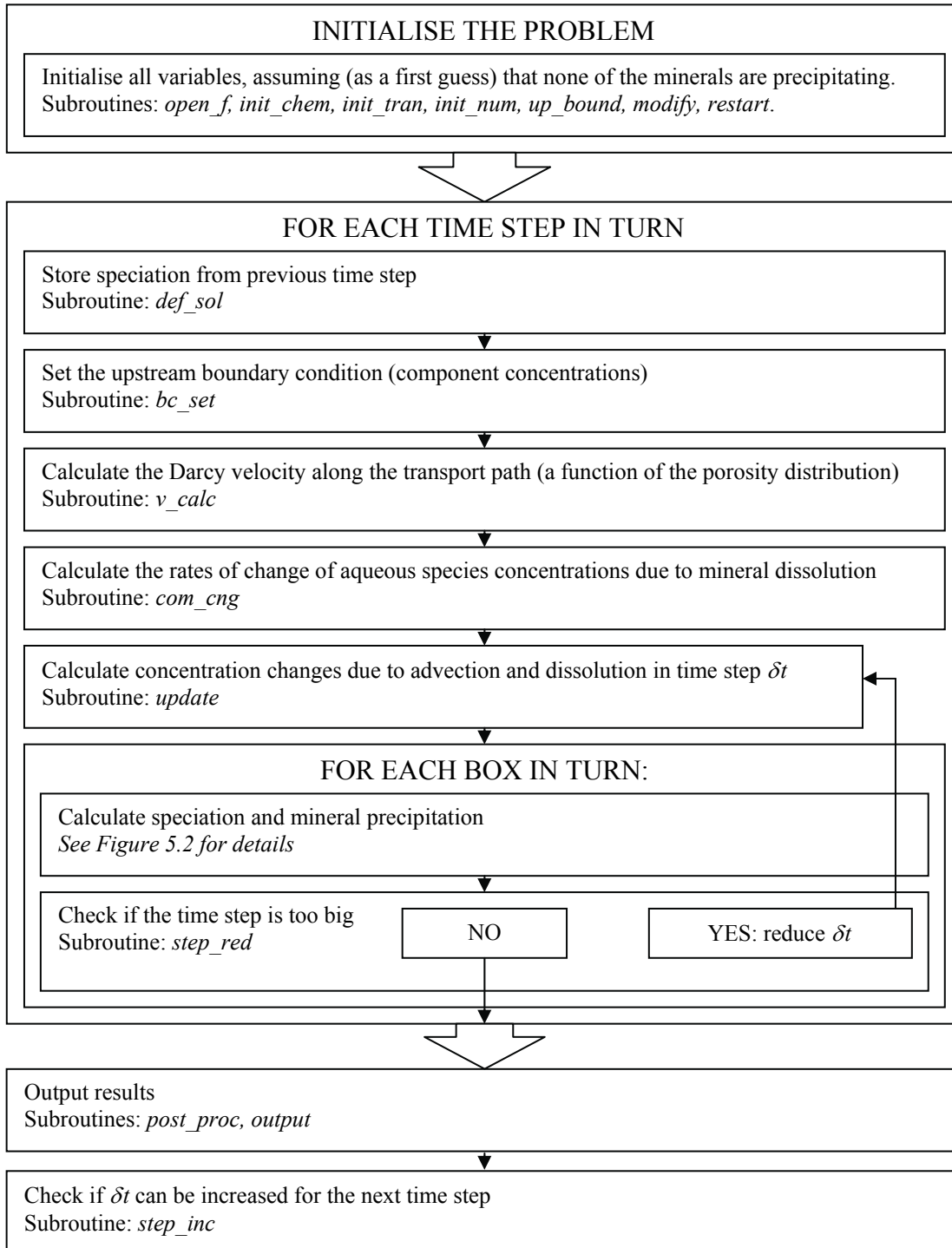


Fig. 5.1: The structure of the SANTA-CHEM main program

Note: The routines for the calculation of speciation and mineral precipitation are shown in Fig. 5.2.

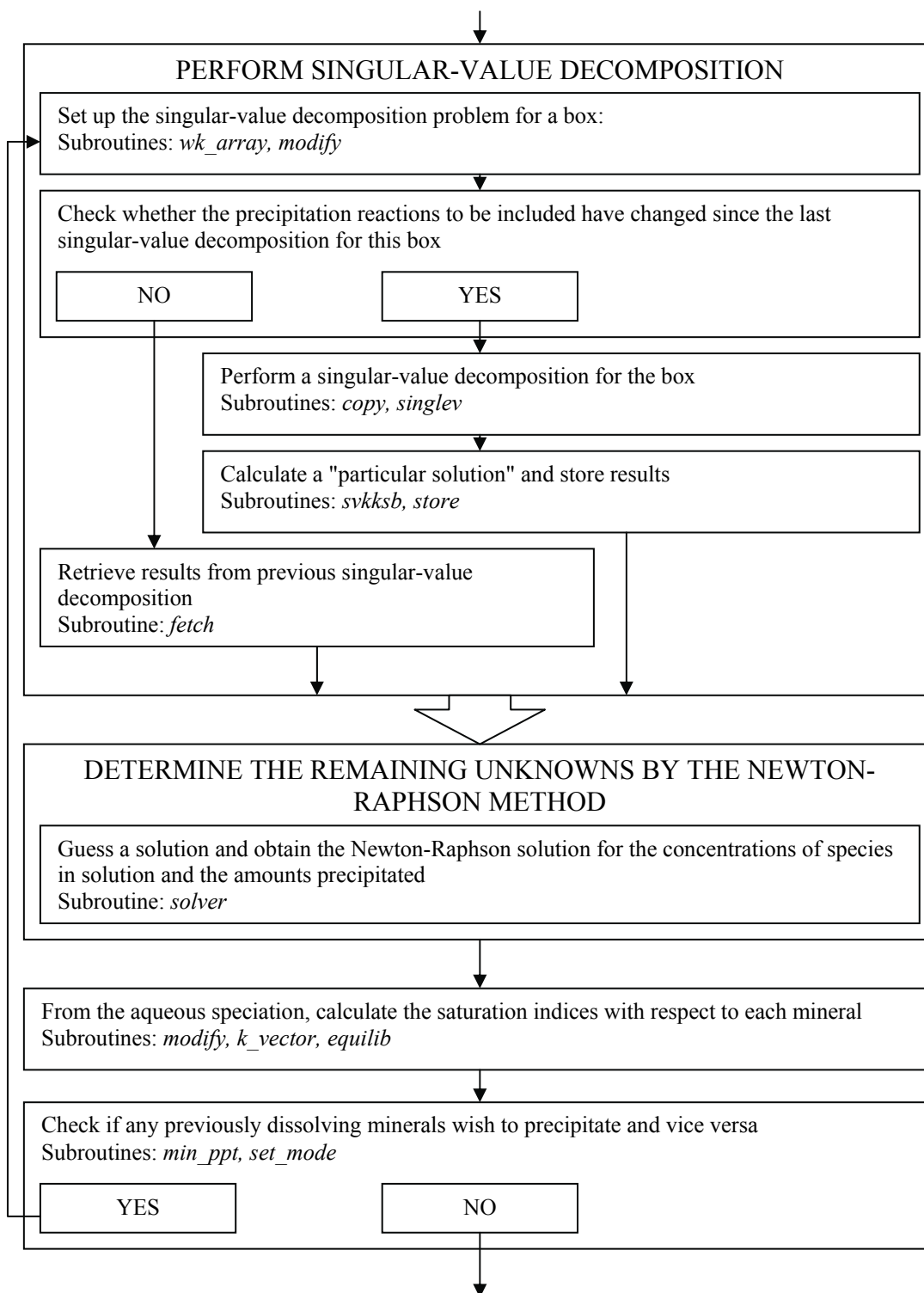


Fig. 5.2: The subroutines used for the calculations of speciation and mineral precipitation

The structure of the input and output files of SANTA-CHEM is described in Appendix A. SANTA-CHEM has 5 input files, namely:

- NUMERICS    in which various parameters related to the accuracy of the numerical techniques are specified;
- RUN\_DATA    in which the number of boxes, their volumes, the initial amounts and dissolution rates of minerals and the initial concentrations of aqueous components are specified (these can vary between boxes);
- TRANSPT    in which parameters related to solute transport are specified, and also the boxes for which output is required;
- DEFAULTS    in which the chemical reactions that can occur in the system are described;
- BOUNDS    in which the concentrations of aqueous components at the upstream boundary are given.

The contents of these files are given in more detail in Appendix A. It should be noted, however, that the initial concentrations of components specified in each box, and also the concentrations of components specified in the upstream boundary condition, must satisfy electroneutrality.

In order to ensure that the electroneutrality condition is satisfied in SANTA-CHEM, the user can select a single component, the  $n$ th, say, that has a charge associated with it. The concentration of this component is not input in either the initial conditions or the upstream boundary condition. Rather, the concentration is calculated so that the electroneutrality condition is met.

The initial concentration of this component in box  $k$  is given by:

$$c_k^{(n)}(0) = - \sum_{i=1}^{N_c} (1 - \delta_{in}) c_k^{(i)}(0) \omega_i / \omega_n, \quad (5.1)$$

where  $\omega_i$  is the charge on the  $i$ th component and  $\delta_{in}$  is the Kronecker delta, defined as:

$$\delta_{in} = \begin{cases} 1 & \text{if } i = n \\ 0 & \text{otherwise} \end{cases} \quad (5.2)$$

A similar expression to Eq. 5.1 is used to calculate the upstream-boundary concentration of the component.

## 6 CONCLUSIONS

SANTA-CHEM was written to model interactions between host rocks and hyperalkaline fluids arising from groundwater degradation of a cementitious repository. A fundamental requirement was that the user must specify the reactions to be considered – both for aqueous species and for minerals – rather than allowing the code to pick all possibilities from an extensive database. When the project was initially defined, redox reactions were excluded from consideration, and a simple method for calculating activity coefficients (extended Davies equation) was the preferred option. As a result SANTA-CHEM is appropriate for scoping calculations and exploration of system behaviour but not for performance assessment calculations. Also, the method of calculating activity coefficients is acceptable to ionic strengths of about 0.5 M but calculations using significantly saline solutions in addition to high pH will exceed this limit. Hence, SANTA-CHEM is limited to calculations using dilute groundwaters at high pH.

Future modifications may wish to address such limitations by:

- including consideration of redox reactions, which may become necessary if redox-sensitive radionuclides are included in calculations;
- introducing water to the reactions so that the activity of water is explicitly considered;
- by having an alternative or additional method of taking account of non-ideal ion activities. For example, REARDON (1990) described a model based on the Pitzer Ion Interaction model for cement-water systems, which could perhaps be modified for use in SANTA-CHEM if such a development was required.

It is expected that the need for further modifications and developments of the code will arise in response to particular applications, such as inclusion of redox-sensitive radionuclides or kinetic data for minerals which cannot be described by the simple first order rate law included in the SANTA-CHEM model.

## 7 ACKNOWLEDGEMENTS

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# **Appendix A1**

## **INPUT FILES**



### A1.1 Chemical system – Defaults.txt

Tab. A1.1 shows an example of a defaults file. All the reactions to be included in the chemical system are defined in terms of the components specified. For each species in solution, ionic charge (*charge*) and stability constant (*K\_value*) are also given. For each mineral, density and molecular weight are given in addition to solubility product value and reaction in terms of the specified components.

Tab. A1.1: Example of a defaults.txt input file

```

Number of species in this problem = 19
Number of components in this problem = 7
-----
components: Ca++ Na+ K+ Al+++ CO3-- H2SiO4-- H+
-----
reactions are of the form:
species(i) <=> n(1).component(1)+n(2).component(2)+....
so that:
log(conc. species(i)) = K + sum_j (n(j)*log(conc. component(j)))
-----
species(i) charge K_value components (right-hand side of eqn.)
-----
Ca++ 2 0.0 1*Ca++
Na+ 1 0.0 1*Na+
K+ 1 0.0 1*K+
Al+++ 3 0.0 1*Al+++
CO3-- -2 0.0 1*CO3--
H2SiO4-- -2 0.0 1*H2SiO4--
Ca(OH)+ 1 -12.598 1*Ca++ -1*H+
KOH 0 -14.46 1*K+ -1*H+
NaOH 0 -14.18 1*Na+ -1*H+
CaCO3 0 3.225 1*Ca++ 1*CO3--
CaHCO3+ 1 11.435 1*Ca++ 1*CO3-- 1*H+
HCO3- -1 10.33 1*CO3-- 1*H+
Al(OH)2+ 1 -10.11 1*Al+++ -2*H+
Al(OH)3 0 -16.94 1*Al+++ -3*H+
Al(OH)4- -1 -22.66 1*Al+++ -4*H+
H4SiO4 0 23.141 1*H2SiO4-- 2*H+
H3SiO4- -1 13.341 1*H2SiO4-- 1*H+
OH- -1 -14.0 -1*H+
H+ 1 0.0 1*H+
-----
Number of minerals in this problem = 3
-----
reactions are of the form:
mineral(i) <=> n(1).component(1)+n(2).component(2)+....
so that:
logK = sum_j (n(j)*log(conc. component(j)))
-----
mineral(i) K_value Density M.Wt components (rt side of eqn.)
-----
albite -65.88 2.70 278.33 1*Na+ 1*Al+++ 3*H2SiO4-- 2*H+
5CSH(1.8) 45.19 2.5 540.45 9*Ca++ 5*H2SiO4-- -8*H+
Ca-phil -103.56 2.23 664.46 1*Ca++ 1*K+ 3*Al+++ 5*H2SiO4-- -2*H+

```

Note: Text in **bold** is essential information which must be given. Normal text forms comment lines which are nonetheless read by the code and must be retained.

**Notes:**

- Up to 10 components, 10 minerals and 30 species can be specified in the problem<sup>6</sup>.
- The reactions must be in terms of the components specified. For example, if the component specified for Si is  $\text{H}_2\text{SiO}_4^{2-}$ , reactions written with  $\text{H}_4\text{SiO}_4$  will cause the program to halt with an error message. The reaction constants must be consistent with the components used.
- The stability constants for *species*, as defined here, have the opposite sign to those given in many other common databases, for example PHREEQE and EQ3/6. Mineral LogKs have the same sign as in PHREEQE and EQ3/6 databases.
- There is no special format with respect to spaces, column width, number of significant figures etc. for input of reactions except that information is read and assigned to parameters in the order given in the comment lines, for example, mineral name is expected to be followed by values for solubility product, density and molecular weight and then by the reaction with a reaction coefficient preceding the component to which it relates.
- The mineral name can be up to 32 characters but, since exactly the same name must be used in the run\_data file, and also in the 'EXTRACT' codes<sup>7</sup>, short names are recommended for simplicity.
- Reaction coefficients may be integers or real numbers.
- Avoid, if possible, components with no reactions. For example, if Cl is included to give a correct ionic charge balance but takes part in no species or mineral reactions, problems may arise. A simple solution is to add one or more species reactions such as NaCl or CaCl.

**A1.2 Initial chemical system – Run\_data.txt**

Tab. A1.2 shows an example of a Run\_data input file. The information in this file sets up the initial chemical conditions for the calculation.

- **Number of boxes** and **box volume** set up the resolution of the problem. Up to 101 boxes can be specified but calculations with large numbers of boxes run slowly, especially if the boxes are small, thus the timestep used may also be very short.
- The initial amounts of minerals can be input in either volume percent (**vol%**) or as moles per box (**mol/box**). The choice of input form is specified in run\_data but does not affect the output. Volume percent can be more useful when mineralogical data is used directly or when changing between box sizes, whereas moles per box allows gives better feedback with respect to amounts of minerals dissolving or precipitating.

---

<sup>6</sup> The sizes of the component, species and mineral arrays are set by three parameters, ip, np and mp. The values of these parameters are set in declare.ini. ip is the maximum number of components, therefore also the maximum number of minerals. np is the maximum number of species. mp is the maximum total number of reactions and is equal to ip + np.

<sup>7</sup> A family of codes which extract data from output files and manipulate them into a form suitable for importing into spreadsheets and graphics packages.

Tab. A1.2: Example of a run\_data.txt input file

Number of boxes					= <b>11</b>
box volume (in dm <sup>3</sup> )					= <b>0.049</b>
initial amounts of minerals (vol% or mol/box)					: <b>vol%</b>
Temperature in Celsius					= <b>25.0</b>
-----					
boxes up to (and including):					<b>5</b>
initial porosity					: <b>0.2</b>
-----					
Concentration of components for this problem (‘e/n’ indicates use electroneutrality condition)					
-----					
<b>Ca++</b>	<b>1.00E-02</b>				
<b>Na+</b>	<b>3.2400E-03</b>				
<b>K+</b>	<b>6.0486E-05</b>				
<b>Al+++</b>	<b>3.48E-7</b>				
<b>CO3--</b>	<b>3.1100E-03</b>				
<b>H2SiO4--</b>	<b>3.47E-04</b>				
<b>H+</b>	<b>e/n</b>				
-----					
Minerals:	initial amount	A (sq.cm/mol)	k (mol/sq.cm/a)	kin/eqm	
-----					
<b>albite</b>	<b>0.0d0</b>	<b>4.659d5</b>	<b>3.154d-6</b>	<b>0</b>	
<b>5CSH(1.8)</b>	<b>1.0d0</b>	<b>1.0d3</b>	<b>1.0d-4</b>	<b>0</b>	
<b>Ca-phil</b>	<b>0.0d0</b>	<b>1.0d0</b>	<b>1.0d-5</b>	<b>0</b>	
-----					
boxes up to (and including):					<b>11</b>
initial porosity					: <b>0.2</b>
-----					
Concentration of components for this problem (‘e/n’ indicates use electroneutrality condition)					
-----					
<b>Ca++</b>	<b>1.070E-04</b>				
<b>Na+</b>	<b>3.2400E-03</b>				
<b>K+</b>	<b>6.0486E-05</b>				
<b>Al+++</b>	<b>3.48E-7</b>				
<b>CO3--</b>	<b>3.1100E-03</b>				
<b>H2SiO4--</b>	<b>3.47E-04</b>				
<b>H+</b>	<b>e/n</b>				
-----					
Minerals:	initial amount	A (sq.cm/mol)	k (mol/sq.cm/a)	kin/eqm	
-----					
<b>albite</b>	<b>0.8d0</b>	<b>4.659d5</b>	<b>3.154d-6</b>	<b>0</b>	
<b>5CSH(1.8)</b>	<b>0.0d0</b>	<b>1.0d3</b>	<b>1.0d-4</b>	<b>0</b>	
<b>Ca-phil</b>	<b>0.0d0</b>	<b>1.0d0</b>	<b>1.0d-5</b>	<b>0</b>	

Note: Text in **bold** is essential information which must be given. Normal text forms comment lines which are nonetheless read by the code and must be retained.

- The temperature in Celsius must be specified but, as mentioned in Chapter 2, there is no facility for altering reaction constants to perform calculations at temperatures other than 25° C. If reaction constants for an alternative temperature are used, then giving this temperature in run\_data ensures that the ionic strength correction is also performed for that temperature.
- The contents of each box – including **initial porosity**, initial pore water composition (**concentrations of components**) and reactive mineral **initial amounts** – can be specified

for each box individually or for groups of boxes. In the example, the first five boxes contain CSH phase (**5CSH1.8**) and a slightly different initial pore water composition to the remaining six boxes, which contain only albite.

- Besides the initial amounts of any minerals, it is necessary to decide whether the dissolution of a mineral will be determined by a rate constant or proceed to equilibrium within one time step. This is denoted by the last column in the minerals input (**kin/eqm**). A zero (**0**) in this column denotes that a mineral will be assumed to come to equilibrium whereas a one (**1**) denotes use of a rate constant which is given in the preceding column (**k** – note: units of moles per cm<sup>2</sup> per year are non-standard). A value for the mineral surface area must also be given if a rate constant is used (**A** in cm<sup>2</sup> per mole).
- The initial pore water composition is given in terms of the specified components in moles per liter. The concentration of the proton (**H<sup>+</sup>**) may be replaced by **e/n**, denoting electroneutrality. In this case the code will assign the proton concentration to form a charge balanced solution. Care must be taken with this option, especially if an incomplete solution composition is used, since small inaccuracies in major ions can result in extreme pH values. If a particular solution pH is required, pre-runs will be necessary to adjust the component concentrations until the H<sup>+</sup> concentration given the required pH value.
- The proportion of a box which is not filled by minerals or pore water (determined by the initial porosity) is considered to contain inert minerals which take no part in the reactions. The volume of inert material will remain constant throughout the calculation.

### A1.3 The upstream boundary condition – bounds.txt

It is possible to specify an upstream boundary condition (or incoming water composition) which varies with time. Tab. A1.3 shows a boundary condition input file where the conditions change after 10 years and again after 100 years.

The solution composition specified as the upstream boundary condition need not be the same as the solution initially present in the boxes (i.e. as in run\_data). The solution composition is specified in the same way as in run\_data in moles per liter of the components. All components must be specified even if the concentration is zero (preferably use a very small value e.g. 1.0d-20. Note: 'd' is required in input files in place of the more normal 'E' for exponent to denote a double precision variable). The concentration of the proton may again be given or the electroneutrality condition used instead.

Tab. A1.3: Example of the upstream boundary condition input file, bounds.txt

```

-----
boundary concentrations
('e/n' indicates use electroneutrality condition)
-----
up to time [a]:  10.0
Ca++          2.171d-2
Na+           3.24d-3
K+            6.07d-5
Al+++         3.48d-5
CO3--         3.11d-3
H2SiO4--      1.308d-6
H+            e/n

up to time [a]:  100.0
Ca++          2.0d-3
Na+           1.5d-4
K+            1.00d-5
Al+++         5.98d-5
CO3--         2.19d-3
H2SiO4--      5.30d-6
H+            e/n

up to time [a]:  9999999.
Ca++          1.000d-4
Na+           3.670d-2
K+            1.65d-5
Al+++         3.00d-5
CO3--         3.11d-3
H2SiO4--      7.63d-6
H+            e/n
..... end

```

Note: Text in **bold** is essential information which must be given. Normal text forms comment lines which are nonetheless read by the code and must be retained.

#### A1.4 Transport parameters – transpt.txt

In the file transpt.txt (Tab. A1.4), a number of important parameters are set which control the transport model and the running of the calculation.

- **Length of box** is straightforward. The box length multiplied by the number of boxes (in run\_data) gives the flow path length for the model. The box volume (in run\_data) divided by the box length gives the area of the box perpendicular to the water flux.
- **Darcy velocity** is the water flux through the model fractures.
- The **initial time step** (years) is an important factor in producing a successful calculation: the code will give an error message if the initial time step chosen is greater than the time taken to replace the water in the first box since this would give calculational difficulties, but too short time steps result in long calculational times for very little useful output. However, where diffusion is important or kinetic rate constants are used, particular care should be taken to ensure that the time step is suitable since non-obvious spurious results can be calculated if the time step is too large. Efforts should be made to optimise the time step for different calculations or use the option of a **variable time step**. In this case the code will choose an appropriate time step after the initial time step (which must thus be specified in all cases).

- A choice of **numerical method** is possible, but for most cases the accurate method is sufficiently fast that it should be used in preference to the simple method.

Tab. A1.4: Example of a transpt.txt input file

<b>0.1</b>	length of box (metres)
<b>1.04d1</b>	Darcy velocity (metres/year)
<b>0.001</b>	Diffusion coefficient (sq. m/year)
<i>3.23d-15</i>	ratio of viscosity to spec. grav. (metres years)
<b>1d2</b>	fracture length per unit area (per metre)
<b>1.0</b>	hydraulic gradient
<b>1.0d-4</b>	initial time step
<b>0</b>	variable time step (1 = yes, 0 = no)
<b>1</b>	numerical method (0 = simple method, 1 = accurate method)
<b>1</b>	dis. rate prop. to S.A. (1 = yes, 0 = no)
<b>0</b>	use cubic law model (1 = yes, 0 = no)
<b>10</b>	number of boxes monitored in output
<b>1 2 3 4 5 6 7 8 9 10</b>	box numbers for output
<b>1</b>	print out every <i>n</i> th time-step

Note: Text in **bold** is essential information which must be given. Normal text forms comment lines which are nonetheless read by the code and must be retained. The value of the ratio of viscosity to specific gravity (*italics*) may be left unchanged under normal circumstances.

- Dissolution rate not proportional to surface area (**dis. rate prop. to S.A.**) corresponds to dissolution of minerals predominantly on one surface so that the surface area remains approximately constant even as the mineral volume decreases. This might be the case for minerals lining a fracture surface reacting with the incoming water.
- Use of **cubic law model** means that changes in porosity due to mineral dissolution and precipitation will cause changes to the incoming water Darcy velocity.
- The final three parameters (**number of boxes monitored in output, box numbers from output, print every *n*th time step**) control the amount of output from the calculation. Results from all boxes or all time steps need not be output to screen or to file. This is particularly useful when more than 10 boxes are used. With 100 boxes, the volume of output means that it is difficult to make use of it. Since a calculation can be restarted, it is often very useful to begin the calculation with output from the first 5 or 10 boxes (where things will happen in the early time steps) in every time step for perhaps the first 10 time steps. This allows the initial calculation to be checked in some detail to make sure the input described the problem correctly etc. The calculation can then be restarted with output from perhaps every 10<sup>th</sup> time step or less depending on the time step used and the length of the calculation.
- In addition, when the code is run, the user is prompted for a decision about the creation of a mass-balance file. This is potentially an enormous file but is again usefully generated at the start of a calculation to check that the calculation is proceeding correctly. It is clearly better to spot an error after 10 time steps than when several hours have been invested in running a major calculation.

Note: **ratio of viscosity to spec. grav.** and **fracture length per unit area** are no longer strictly required due to the use of the simpler relationship between initial Darcy velocity and initial porosity rather than the actual use of the Cubic law.



### A1.5 The numerical parameters – numerics.txt

The running of the code, particularly the Newton-Raphson method and the initial guessing procedure, is controlled by a number of parameters. The values of these are set in the input file numerics.txt (Tab. A1.5).

The values given in the example file in Tab. A1.5 represent optimal settings for most cases which have been determined over the course of the SANTA-CHEM code development. For this reason it is strongly recommended that these values are not changed without very good reason.

- **Tolerance for the Newton-Raphson routine** is the value that controls the precision of the solution found by this routine. A smaller value will require more iterations to produce a solution whereas a larger value may result in inaccuracies in components and species present at low concentrations and may, in particular, influence the pH values. **No. of step increases for Newton-Raphson convergence** controls the process of stepping from an initial guess towards the desired solution. If the code fails initially, the number of steps is increased 10 fold. With a value of 4, the code will exit with an error message after 1000 steps have been tried (see sections 4.4.5 and 4.4.6 for further explanation of the application of the Newton-Raphson method and making the initial guess). Increment for Newton-Raphson convergence is a parameter of this numerical method that should normally be left at the default value of 0.3 (see PRESS et al. 1992 for details of the method).
- A **maximum number of iterations for ionic strength correction** greater than 3 has been found to make no significant difference to the calculated result.
- The **oscillation damping parameter** is an attempt to avoid situations where a mineral is very close to saturation but very small amounts dissolve or precipitate, resulting in an oscillation which prevents the Newton-Raphson procedure from converging on a solution. The magnitude of this parameter must be greater than the tolerance for the Newton-Raphson convergence, or it will be ineffective, but small enough that an accurate solution can still be found.

Tab. A1.5: Example of numerics.txt, the numerical parameters input file

Tolerance for Newton-Raphson routine	= <b>1.d-14</b>
Number of step increases for Newton-Raphson convergence	= <b>4</b>
Increment for Newton-Raphson convergence	= <b>0.3</b>
Maximum number of iterations for ionic strength correction	= <b>3</b>
The oscillation damping parameter (always <= 0.0)	= <b>-1.d-12</b>
Maximum number of stepsize reductions in one pass	= <b>100</b>
Maximum number of attempts to find mineral combination	= <b>10</b>

Note: Under most circumstances, none of the parameter values needs to be changed and these values should be considered as default settings.

- The **maximum number of stepsize reductions in one pass** controls the amount by which a time step can be reduced in one cycle of calculations (i.e. one calculation for each box) when variable stepsize is used.
- For most calculations, if the code has not found a consistent set of stable and dissolving minerals (**Maximum number of attempts to find mineral combination**) in 10 attempts (with a maximum of 10 minerals), there is an error in the problem description. This should be investigated before increasing this value which will result in long calculation times.

## A1.6 Running the code

At run-time, the user is asked a number of questions:

### **RESTART an existing run (Y/N)?**

If data have been stored from a previous run, it can be restarted, otherwise answer N to start a new run.

### **How many timesteps? (default = 10, 0 to EXIT SANTA-CHEM)**

For starting a run, it can be useful to begin with a small number so that output can be checked before launching a long calculation.

### **Generate mass-balance data (Y/N)?**

A file of mass balance data is generated to assist checking the calculations. However, this file rapidly becomes very large so should be generated for only a few, specific time steps.

What data would you like to output to the screen?

- 1: porosity
  - 2: amounts precipitated in a time step (or dissolved)
  - 3: total amounts of minerals
  - 4: species concentrations
  - 5: component concentrations (including pH)
  - 6: cumulative amounts of minerals precipitated (or dissolved)
  - 7: identity of precipitating minerals
- Choose a data type (default = 5)

This controls the type of information scrolling on the screen during a run and does not affect output to files.

After the specified number of time steps have been executed, the program returns to the '**How many time steps**' prompt.

Typing 0 (to EXIT) returns the question:

### **Save data for RESTART later (Y/N)?**

Y will result in a file which can be read in to restart a run at the point at which it was stopped.

In the case of RESTARTING a run:

### **RESTART an existing run (Y/N)?**

Yes – results in further questions:

### **Continue with fixed time step?**

If a fixed time step was specified in the transpt.txt file, it can be changed if desired to a variable time step. A variable time step can also be changed to a fixed time step.

If yes:

### **Input time step (default 1.0e-4)**

If no:

### **Input initial time step (default 1.0e-4)**

In both cases, the default for the time step is taken from the transpt.txt file but can be overridden for the restarted run.

**Output frequency (default = 1)?**

Again the value from the transpt.txt file is taken as the default but can be overridden.

**How many time steps (default = 10)?**

The questions now are a repeat of those for starting a new run, as described above.



# **Appendix A2**

## **OUTPUT FILES**



SANTA-CHEM writes the results of calculations to six output files:

- Compts.txt** – this file lists the component concentrations in moles per liter, including pH (minus log activity) rather than concentration of the proton, for each box specified in bounds.txt and at the time step output frequency also specified in bounds.txt. An example of part of an compts.txt file is shown in Tab. A2.1.
- Species.txt** – this file lists the concentrations, in moles per liter, of all species in the problem for the boxes and time step output frequency specified (Tab. A2.2).
- Porous.txt** – shows the porosity data for specified boxes (Note: porosity is given as proportion, not per cent) (Tab. A2.3).
- Minerals.txt** – lists the total amount of each mineral (in moles per box) in the problem at the end of the output time step (Tab. A2.4).
- Cum\_ppt.txt** – lists the cumulative amount of a mineral precipitated or dissolved, in moles per box, up to and including the output time step. All minerals in a problem are listed (Tab. A2.5).
- Ppt.txt** – lists the rate of each mineral dissolving or precipitating, in moles per year per box, in the output time step (Tab. A2.6).

In addition there are two output files which may be written:

- Mass\_bal.txt** – is written if the question 'Generate mass balance data (Y/N)?' is answered with 'yes'. This contains a description of all the sources of a component in a box and all transfers of that component between boxes. These amounts are totalled to show (if the calculation is running correctly) that masses of each component are correctly accounted for by minerals and solution remaining in a box and solution/component being transported between boxes. This file can become very large since there is output for every component for every box and time step specified in bounds.txt. Thus it is suggested to generate this file only for a few timesteps at the beginning of a calculation to check correct problem definition etc. (Tab. A2.7).
- Rst\_file.txt** – is written if a calculation is halted but the question 'Save data for RESTART later?' is answered with 'yes'. It is used to store all information about the state of the system on exiting so that the calculation can be restarted from the same point, for example, with a different time step, or output frequency.

Tab. A2.1: Example of the output of the first two time steps in Compts.txt (concentrations in moles per liter)

```

=====
step number 0001, step size = 1.000000E-04 a, time = 1.000000E-04 a
Darcy velocity = 1.040000E+01 m/a
-----
component concentrations in boxes
-----
component name box 1 box 2 box 3 box 4 box 5 box 6 box 7 box 8 box 9 box 10
-----
Ca++ 1.170E-03 4.651E-05 4.651E-05 4.651E-05 4.651E-05 4.651E-05 4.651E-05 4.651E-05 4.651E-05 4.651E-05
Na+ 3.430E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03
K+ 9.717E-19 1.929E-15 1.929E-15 1.929E-15 1.929E-15 1.929E-15 1.929E-15 1.929E-15 1.929E-15 1.929E-15
Al+++ 1.064E-05 2.532E-07 2.532E-07 2.532E-07 2.532E-07 2.532E-07 2.532E-07 2.532E-07 2.532E-07 2.532E-07
CO3-- 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03
H2SiO4-- 5.965E-04 5.887E-04 5.887E-04 5.887E-04 5.887E-04 5.887E-04 5.887E-04 5.887E-04 5.887E-04 5.887E-04
pH 10.28886 9.19626 9.19626 9.19626 9.19626 9.19626 9.19626 9.19626 9.19626 9.19626
-----
step number 0002, step size = 1.000000E-04 a, time = 2.000000E-04 a
Darcy velocity = 1.040000E+01 m/a
-----
component concentrations in boxes
-----
component name box 1 box 2 box 3 box 4 box 5 box 6 box 7 box 8 box 9 box 10
-----
Ca++ 2.265E-03 7.575E-05 4.651E-05 4.651E-05 4.651E-05 4.651E-05 4.651E-05 4.651E-05 4.651E-05 4.651E-05
Na+ 3.566E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03 3.421E-03
K+ 1.758E-20 1.070E-15 1.929E-15 1.929E-15 1.929E-15 1.929E-15 1.929E-15 1.929E-15 1.929E-15 1.929E-15
Al+++ 1.479E-04 2.791E-07 2.532E-07 2.532E-07 2.532E-07 2.532E-07 2.532E-07 2.532E-07 2.532E-07 2.532E-07
CO3-- 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03 3.110E-03
H2SiO4-- 9.856E-04 5.881E-04 5.887E-04 5.887E-04 5.887E-04 5.887E-04 5.887E-04 5.887E-04 5.887E-04 5.887E-04
pH 10.96730 9.25654 9.19626 9.19626 9.19626 9.19626 9.19626 9.19626 9.19626 9.19626
-----

```







Tab. A2.4: Example of the output of the first three time steps in Minerals.txt (total amounts in moles/box)

```

=====
step number 0001, step size = 1.00000E-04 a, time = 1.00000E-04 a
Darcy velocity = 1.04000E+01 m/a
-----
mineral          box 1    2    3    4    5
name            3.801E-03 3.801E-03 3.801E-03 3.801E-03 3.801E-03
albite          0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
5CSH(1.8)      5.929E-07 5.928E-07 5.928E-07 5.928E-07 5.928E-07
Ca-phil
-----
mineral          box 1    2    3    4    5
name            3.801E-03 3.801E-03 3.801E-03 3.801E-03 3.801E-03
albite          0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
5CSH(1.8)      5.929E-07 5.928E-07 5.928E-07 5.928E-07 5.928E-07
Ca-phil
-----
step number 0002, step size = 1.00000E-04 a, time = 2.00000E-04 a
Darcy velocity = 1.04000E+01 m/a
-----
mineral          box 1    2    3    4    5
name            3.799E-03 3.801E-03 3.801E-03 3.801E-03 3.801E-03
albite          0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
5CSH(1.8)      6.238E-07 5.928E-07 5.928E-07 5.928E-07 5.928E-07
Ca-phil
-----
mineral          box 1    2    3    4    5
name            3.801E-03 3.801E-03 3.801E-03 3.801E-03 3.801E-03
albite          0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
5CSH(1.8)      5.929E-07 5.928E-07 5.928E-07 5.928E-07 5.928E-07
Ca-phil
-----
step number 0003, step size = 1.00000E-04 a, time = 3.00000E-04 a
Darcy velocity = 1.04000E+01 m/a
-----
mineral          box 1    2    3    4    5
name            3.797E-03 3.801E-03 3.801E-03 3.801E-03 3.801E-03
albite          0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
5CSH(1.8)      6.548E-07 5.928E-07 5.928E-07 5.928E-07 5.928E-07
Ca-phil
-----

```



Tab: A2.6: Example of the first two time steps output in Ppt.txt (rate in moles per year per box)

```

=====
step number 0001, step size = 1.00000E-04 a, time = 1.00000E-04 a
Darcy velocity = 1.04000E+01 m/a
-----
mineral      box 1      box 2      box 3      box 4      box 5      box 6      box 7      box 8      box 9      box 10
name
albite      -1.900E+00 -1.814E+00 -1.814E+00 -1.814E+00 -1.814E+00 -1.814E+00 -1.814E+00 -1.814E+00 -1.814E+00 -1.814E+00
5CSH(1.8)   0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
Ca-phil     6.050E-01 6.049E-01 6.049E-01 6.049E-01 6.049E-01 6.049E-01 6.049E-01 6.049E-01 6.049E-01 6.049E-01
-----
rate precipitated in box
-----

step number 0002, step size = 1.00000E-04 a, time = 2.00000E-04 a
Darcy velocity = 1.04000E+01 m/a
-----
mineral      box 1      box 2      box 3      box 4      box 5      box 6      box 7      box 8      box 9      box 10
name
albite      -1.452E+00 2.440E-03 5.551E-13 5.551E-13 5.551E-13 5.551E-13 5.551E-13 5.551E-13 5.551E-13 5.551E-13
5CSH(1.8)   0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
Ca-phil     3.158E-02 8.093E-12 6.776E-17 6.776E-17 6.776E-17 6.776E-17 6.776E-17 6.776E-17 6.776E-17 6.776E-17
-----

```

Tab. A2.7: Example of output in Mass\_bal.txt for the first three components in the first time step

```

step number      0001, step size = 1.00000E-04 a, time = 1.00000E-04 a
Darcy velocity = 1.04000EH01 m/a
-----
Mass balance for component Ca++
Upstream boundary concentration = 2.1710E-02
box number :      1          2          3          4          5          6          7          8          9          10
initial mass in solution : 1.049E-06  1.049E-06  1.049E-06  1.049E-06  1.049E-06  1.049E-06  1.049E-06  1.049E-06  1.049E-06  1.049E-06
mass transport into box : 1.107E-05  5.453E-08  5.453E-08  5.453E-08  5.453E-08  5.453E-08  5.453E-08  5.453E-08  5.453E-08  5.453E-08
mass transport out of box: 5.453E-08  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00
mass dissolved in box : 5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07
mass precipitated in box: 1.147E-05  4.558E-07  4.558E-07  4.558E-07  4.558E-07  4.558E-07  4.558E-07  4.558E-07  4.558E-07  4.558E-07
final mass in solution:  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20
mass-balance error      :  -1.203E-19  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20  -1.631E-20

Mass balance for component Na+
Upstream boundary concentration = 3.2400E-03
box number :      1          2          3          4          5          6          7          8          9          10
initial mass in solution : 3.175E-05  3.175E-05  3.175E-05  3.175E-05  3.175E-05  3.175E-05  3.175E-05  3.175E-05  3.175E-05  3.175E-05
mass transport into box : 1.651E-06  1.651E-06  1.651E-06  1.651E-06  1.651E-06  1.651E-06  1.651E-06  1.651E-06  1.651E-06  1.651E-06
mass transport out of box: 1.651E-06  3.803E-03  3.803E-03  3.803E-03  3.803E-03  3.803E-03  3.803E-03  3.803E-03  3.803E-03  3.803E-03
mass dissolved in box : 3.801E-03  3.801E-03  3.801E-03  3.801E-03  3.801E-03  3.801E-03  3.801E-03  3.801E-03  3.801E-03  3.801E-03
mass precipitated in box: 3.361E-05  3.353E-05  3.353E-05  3.353E-05  3.353E-05  3.353E-05  3.353E-05  3.353E-05  3.353E-05  3.353E-05
final mass in solution:  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19
mass-balance error      :  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19  -4.337E-19

Mass balance for component K+
Upstream boundary concentration = 6.0700E-05
box number :      1          2          3          4          5          6          7          8          9          10
initial mass in solution : 5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07
mass transport into box : 3.082E-08  3.082E-08  3.082E-08  3.082E-08  3.082E-08  3.082E-08  3.082E-08  3.082E-08  3.082E-08  3.082E-08
mass transport out of box: 3.082E-08  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00  0.000EH+00
mass dissolved in box : 5.929E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07  5.928E-07
mass precipitated in box: 9.522E-21  1.891E-17  1.891E-17  1.891E-17  1.891E-17  1.891E-17  1.891E-17  1.891E-17  1.891E-17  1.891E-17
final mass in solution:  2.118E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22
mass-balance error      :  2.118E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22  -1.059E-22
    
```

The mass-balance error is the difference between the total amount of a component calculated to exist in a box at the end of a time step, compared to the sum of the amount at the beginning of the time step and the amount transported into the box by advection and diffusion. Large errors are indicative of calculational problems

Note: Very small errors in the mass balance are acceptable to reduce calculation times by allowing the Newton-Raphson procedure to get 'close enough'.

# **Appendix B**

## **TEST CASES AND EXAMPLES**





## B1 Transport

In these test cases, in order to allow comparison with approximate or exact analytical solution, a simple system is set up in which:

- no chemical reactions are assumed to take place;
- a single component is considered, the initial concentration of which is zero throughout the rock;
- the concentration is held at  $c_0$  at the upstream boundary.

Neglecting the effects of the downstream boundary, the component concentration is governed by the following solution to the advection-diffusion equation:

$$\frac{c}{c_0} \approx \frac{1}{2} \left\{ \operatorname{erfc} \left[ \frac{x - qt}{2\sqrt{Dt}} \right] + \exp \left[ \frac{qx}{\varepsilon D} \right] \operatorname{erfc} \left[ \frac{x + qt}{2\sqrt{Dt}} \right] \right\} \quad (\text{B1.1})$$

For model testing, however, two limiting types of problems are considered: (i) advection dominated, and (ii) diffusion dominated.

### Advection-dominated problems

Away from the upstream and downstream boundaries, the component concentration for advection-dominated problems ( $t \gg \varepsilon^2 D/q^2$ ) is given by the approximation:

$$\frac{c}{c_0} \approx \frac{1}{2} \operatorname{erfc} \left[ \frac{x - qt}{2\sqrt{Dt}} \right] \quad (\text{B1.2})$$

The problem is solved using SANTA-CHEM, applying the algorithm for advective-diffusive transport described in section 4.2. To demonstrate the advantages of the second- to third-order accurate, 1-D upstream advection scheme given in section 4.2.3, a simple, first-order scheme is also applied, in which Eq. 4.5 is replaced by:

$$f_{a(i+1/2)} = qc_i \quad \text{for } 1 < i < N \quad (\text{B1.3})$$

Such a scheme was used in early versions of SANTA-CHEM, but was superseded, since it is known to give significant "numerical dispersion" (see, for example, Eq. 3.2.8 in SOD 1986), equivalent to an artificial longitudinal dispersion length,  $a_L$ , given by:

$$a_L = \frac{1}{2} \left( \delta L - \frac{q}{\varepsilon} \delta t \right), \quad (\text{B1.4})$$

where  $\delta t$  (a) is the time step. Such artificial dispersion is particularly undesirable when modeling the migration of concentration fronts, which are expected to arise in problems involving coupled chemical reactions and transport.

Fig. B1.1 shows the analytical solution, Eq. B1.2, plotted as a function of  $x$  (i.e. distance along transport path) for the case of:

- a Darcy velocity of  $q = 2.0 \text{ m a}^{-1}$ ;
- a porosity of  $\varepsilon = 0.2$ ;
- a diffusion coefficient of  $D = 0.001 \text{ m}^2 \text{ a}^{-1}$ ,

evaluated a time  $t = 5 \times 10^{-3} \text{ a}$ . Since  $\varepsilon^2 D/q^2$  is  $10^{-5} \text{ a}$ , the problem is expected to be advection-dominated, as defined above, so that Eq. B1.2 is a good approximation to the exact solution B1.1 of the advection-diffusion equation. The plot shows a concentration front that has migrated about 5 cm along the transport path, with some spreading of the front due to diffusion.

The figure also shows the SANTA-CHEM results for this problem, applying the accurate and the simple finite-difference methods, and solving using one hundred, 1 mm boxes, i.e. a transport path length of  $L = 0.1 \text{ m}$  and  $\delta L = 10^{-3} \text{ m}$ , and 1000 fixed time steps of  $\delta t = 5 \times 10^{-6} \text{ a}$ .

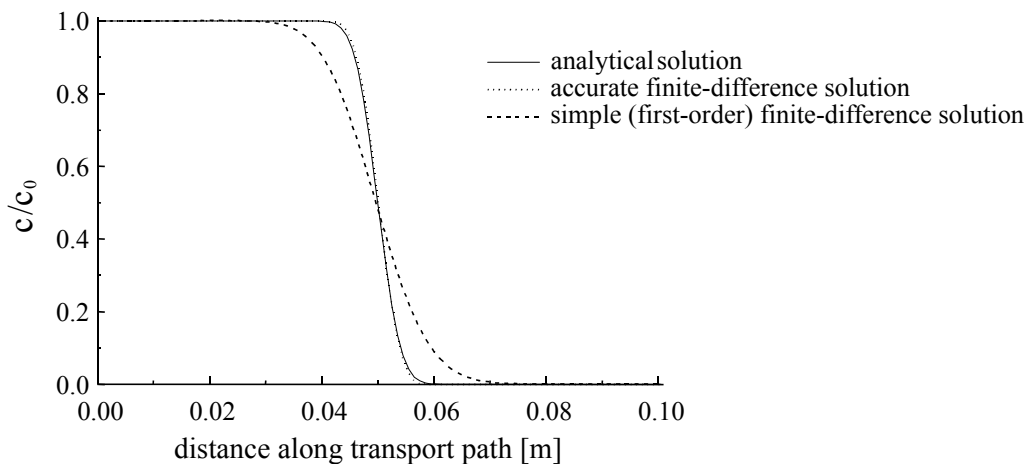


Fig. B1.1: Comparison of the analytical solution for an advection-dominated problem with accurate and simple numerical solutions generated using SANTA-CHEM

The results closely approximate the analytical solution where the algorithm given in section 4.2 is used. As expected, the simple, first-order scheme (Eq. B1.3) gives artificial spreading of the concentration front, and significantly less satisfactory agreement with the analytical solution.

Fig. B1.2 shows the same problem, solved using the accurate finite-difference method of SANTA-CHEM, comparing the results for 1000 fixed time steps of  $\delta t = 5 \times 10^{-6}$  a, 250 fixed time steps of  $\delta t = 10^{-5}$  a and 100 fixed time steps of  $\delta t = 5 \times 10^{-5}$  a. The analytical solution is also shown. The figure shows the convergence of the SANTA-CHEM solutions towards the analytical solution as the time step is reduced.

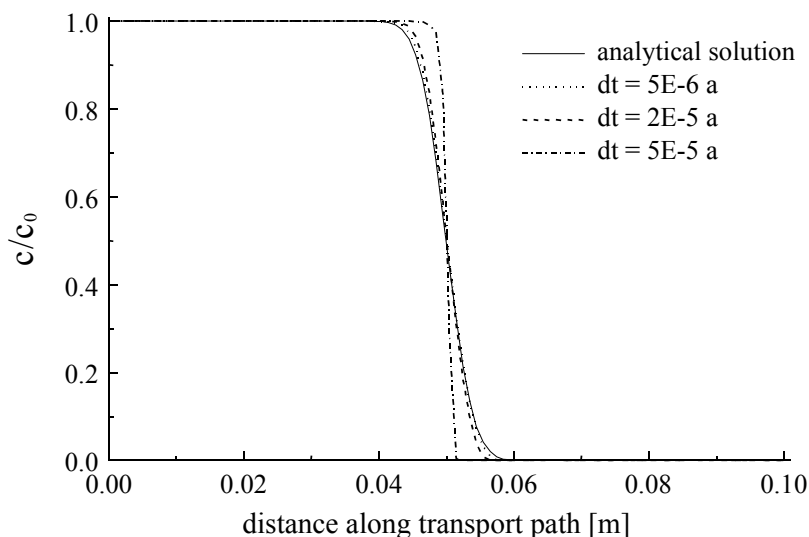


Fig. B1.2: Comparison of the analytical solution for an advection-dominated problem with SANTA-CHEM solutions using different time steps

### Diffusion-dominated problems

If advection is negligible, and before significant concentration reaches the downstream boundary, the component concentration for diffusion-dominated problems is given by the approximation to Eq. B1.1:

$$\frac{c}{c_0} \approx \operatorname{erfc} \left[ \frac{x}{2\sqrt{Dt}} \right] \quad (\text{B1.5})$$

Fig. B1.3 shows the analytical solution, Eq. B1.5, plotted as a function of  $x$  (i.e. distance along transport path) for the case of a diffusion coefficient of  $D = 1.3 \text{ m}^2 \text{ a}^{-1}$ , evaluated time  $t = 5 \times 10^{-5}$  a. The plot shows a distribution of concentration that extends to about 3 cm along the transport path.

The figure also shows the SANTA-CHEM results for this problem, solving using one hundred, 1 mm boxes, i.e. a transport path length of  $L = 0.1 \text{ m}$  and  $\delta L = 10^{-3} \text{ m}$ , and 500 fixed time steps of  $\delta t = 10^{-7}$  a, which closely approximate the analytical solution. Fig. B1.3 also shows the same problem, solved using 5 mm and 10 mm boxes. The results show the convergence of the SANTA-CHEM solutions towards the analytical solution as the box size is reduced.

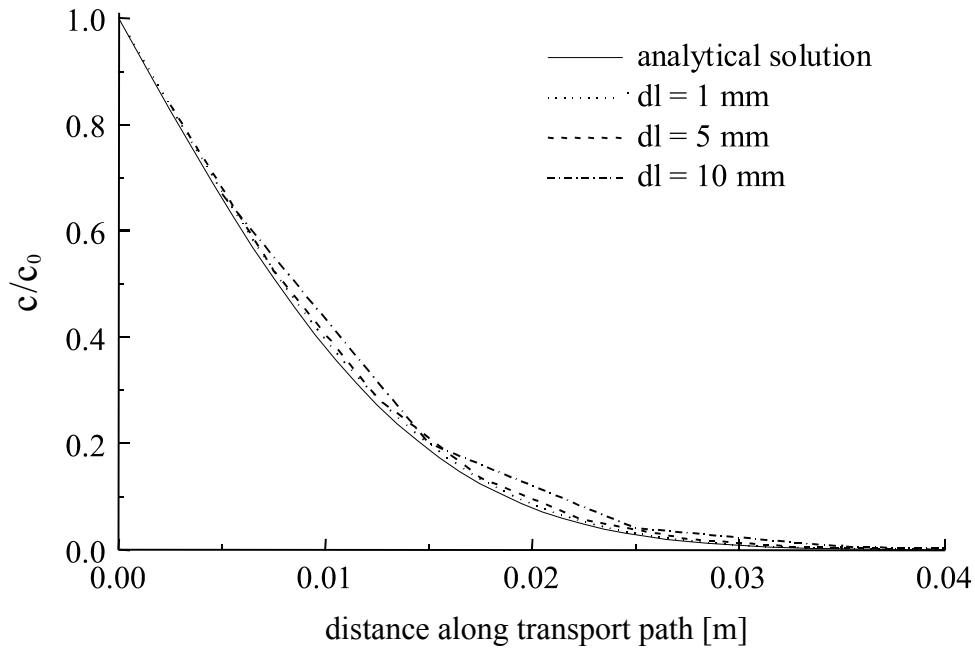


Fig. B1.3: Comparison of the analytical solution for a diffusion-dominated problem with SANTA-CHEM solutions using different box sizes

## B2 Chemistry

Three cases are given to illustrate the use of SANTA-CHEM.

### B2.1 Albite dissolution with and without use of rate constant

The input files (excluding numerics.txt) are shown in Table B2.1. In this example, albite is the sole constituent of the 'rock' which is infiltrated by a high pH solution. The size of the ten boxes is scaled to replicate a column experiment of 1 m length and a diameter of 2.5 cm. A Darcy velocity of  $10.4 \text{ m a}^{-1}$  is used which corresponds to the exchange of one column length of fluid in one week.

Tab. B2.1: Input files for albite dissolution under high pH conditions

Defaults	Run_data	Bound	Transport
<p>Number of species in this problem = 19                      Number of components in this problem = 7                      components: Ca++ Na+ K+ Al+++ CO3-- H2SiO4-- H+                      reactions are of the form:                      species(i) &lt;=&gt; n(1).component(1)+n(2).component(2)+...                      so that:                      log(conc. species(i)) = K + sum_j (n(j)*log(conc. component(j)))                      species(i) charge K_value components (right-hand side of eqn.)</p> <pre> Ca++      2  0.0  1*Ca++ Na+       1  0.0  1*Na+ K+        1  0.0  1*K+ Al+++     3  0.0  1*Al+++ CO3--     -2  0.0  1*CO3-- H2SiO4--  -2  0.0  1*H2SiO4-- Ca(OH)+   -1 -12.598 1*Ca++ -1*H+ KOH       0 -14.46  1*K+   -1*H+ NaOH      0 -14.18  1*Na+  -1*H+ CaHCO3+   0  3.225  1*Ca++  1*CO3-- CaHCO3    1 11.435  1*Ca++  1*CO3--  1*H+ HCO3-     -1 10.33  1*CO3--  1*H+ Al(OH)2+   0 -10.11  1*Al+++ -2*H+ Al(OH)3    0 -16.94  1*Al+++ -3*H+ Al(OH)4-   -1 -22.66  1*Al+++ -4*H+ H4SiO4     0  23.141  1*H2SiO4--  2*H+ H3SiO4-    -1 13.341  1*H2SiO4--  1*H+ OH-        -1 -14.0  -1*H+ H+         1  0.0  1*H+                     </pre> <p>Number of minerals in this problem = 3                      reactions are of the form:                      mineral(i) &lt;=&gt; n(1).component(1)+n(2).component(2)+...                      so that:                      logK = sum_j (n(j)*log(conc. component(j)))                      mineral(i) K_value Density M.Wt. components (rt side of eqn.)</p> <pre> albite    -65.88  2.70  278.33  1*Na+  1*Al+++  3*H2SiO4--  2*H+ 5CSH(1.8) 45.19  2.5  540.45  9*Ca++  5*H2SiO4--  -8*H+ Ca-phill -103.56  2.23  664.46  1*Ca++  1*K+  3*Al+++  5*H2SiO4--  -2*H+                     </pre>	<p>Number of boxes = 10                      box volume (in litres) = 0.049                      initial amounts of minerals : v0% = 25.0                      Temperature in Celsius                      boxes up to (and including): 10                      initial porosity : 0.2                      Concentration of components for this problem ('e/n' indicates use electroneutrality condition)</p> <pre> Ca++      1.070E-04 Na+       3.2400E-03 K+        6.0486E-05 Al+++     3.48E-7 CO3--     3.1100E-03 H2SiO4--  3.47E-04 H+        e/n                     </pre> <p>Minerals: init. amount A (eq.cm/mol) k (mol/sq.cm/a) kin/eqm</p> <pre> albite    0.8d2  4.659d5  5.0d-10  0 5CSH(1.8) 0.0d0  1.0d3  1.0d-4  0 Ca-phill  0.0d0  1.0d0  1.0d-5  0                     </pre>	<p>Boundary concentrations ('e/n' indicates use electroneutrality condition)</p> <pre> up to time [a]: 10.0 Ca++      2.171d-2 Na+       3.25d-3 K+        6.07d-5 Al+++     3.48d-5 CO3--     3.11d-3 H2SiO4--  1.308d-6 H+        e/n                     </pre> <p>..... end</p>	<p>0.1 length of box (metres)                      1.04d1 Darcy velocity (metres/year)                      0.001 Diffusion coefficient (sq. m/year)                      3.23d-15 ato of viscosity to spec. grav. (metres years)                      1d2 fracture length per unit area (per metre)                      1.0 hydraulic gradient                      1.0d-4 initial time step                      0 variable time step (1 = yes, 0 = no)                      1 numerical method (0 = simple, 1 = accurate)                      1 dis. rate prop. to S.A. (1 = yes, 0 = no)                      1 use cubic law model (1 = yes, 0 = no)                      0 number of boxes monitored in output                      1 2 3 4 5 6 7 8 9 10 box numbers for output                      1 print out every nth time-step</p>

Note: The initial pore water composition (run\_data) is not in equilibrium with albite, thus reaction will occur in boxes before the high pH solution reaches them.

The initial calculation assumes that albite dissolution will proceed to equilibrium in a single time step. Additional calculations use a rate constant and surface area. The results of the equilibrium calculation and two kinetic calculations using different values of the rate constant are shown together for comparison in Fig. B2.1 and B2.2. Note that the rate constants are given per year so that an albite rate constant of around  $1.0 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$  becomes  $3.0 \times 10^{-6} \text{ mol cm}^{-2} \text{ a}^{-1}$  in non-standard format. From these calculations, it is clear that when the rate constant is greater than about  $5 \times 10^{-8} \text{ mol cm}^{-2} \text{ a}^{-1}$ , the result, in terms of amount of albite dissolved with time, approaches that of the local equilibrium case for the time step used.

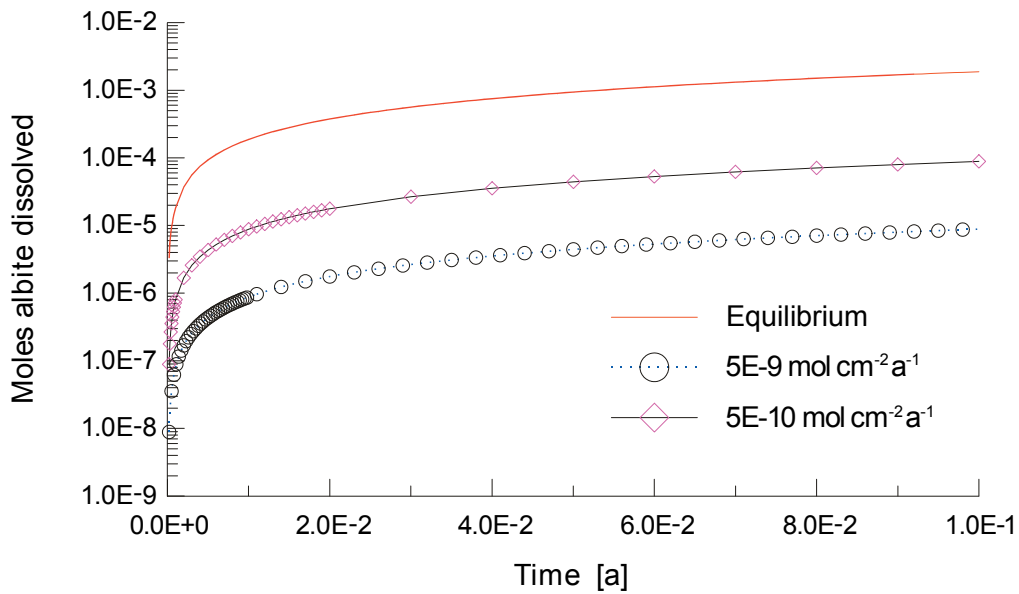


Fig. B2.1: Comparison of equilibrium and kinetic calculations of albite dissolution under high pH conditions

Note: This figure shows the amount of albite dissolved in the first box (10 cm) in the different calculations. A constant time step of  $1 \times 10^{-4} \text{ a}$  was used.

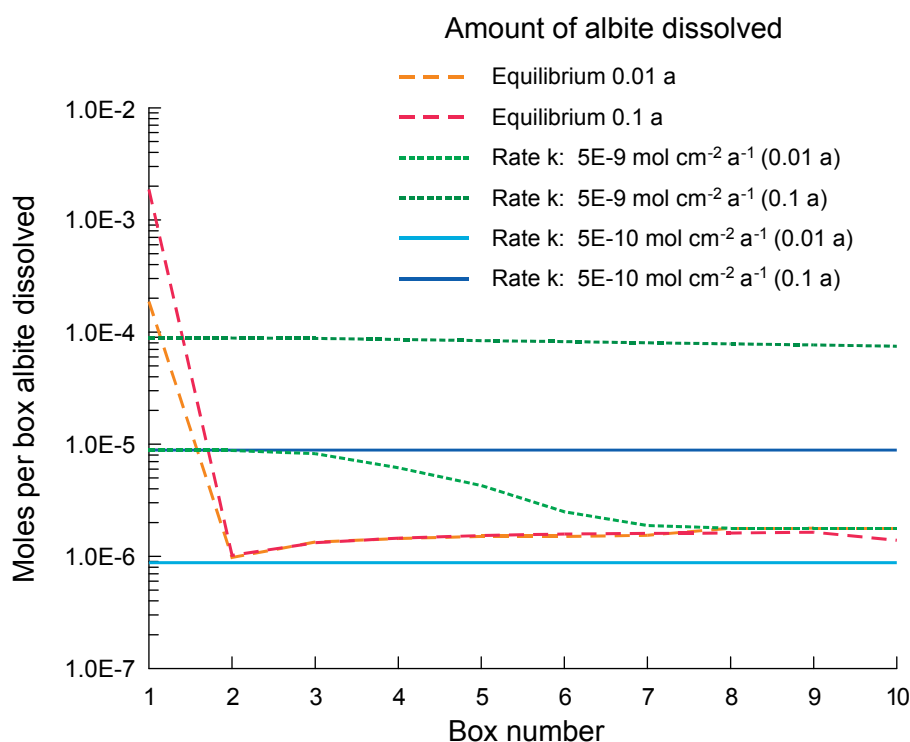


Fig. B2.2: Comparison of equilibrium and kinetic calculations of albite dissolution under high pH conditions

Note: This figure shows the cumulative amount of albite dissolved along the whole column. Note that in the equilibrium case, all albite dissolution takes place in the first box with only minor adjustments to equilibrium solution composition in other boxes. With a low reaction rate constant of  $5 \times 10^{-10}$  mol cm<sup>-2</sup> a<sup>-1</sup>, the rate of albite dissolution is so slow as to be almost independent of the pore water composition since the rate of albite dissolution is almost the same in all boxes despite the high pH front not having reached the final boxes by 0.01. With a rate constant of  $5 \times 10^{-9}$  mol cm<sup>-2</sup> a<sup>-1</sup>, greater albite dissolution in the earlier boxes at 0.01 a, reflecting the higher pH, is clear. By 0.1 a, all boxes have approximately the same pH (about 12.4 in the kinetic calculations and 11.7 in the equilibrium case).

## B2.2 Simplified calculation for the Grimsel Test Site Hyperalkaline Plume in Fractured Rock (HPF) experiment

In this case, a more complex problem with two reactant minerals and three potential secondary phases is used along with a simplified groundwater composition. However, to illustrate the use of different starting conditions in the boxes, box 1 contains portlandite (Ca(OH)<sub>2</sub>) which is allowed to dissolve to equilibrium with the incoming GTS (simplified) groundwater. This portlandite-saturated fluid is then transported into the remaining 9 boxes which contain a mixture of quartz and albite. Albite and quartz dissolution is allowed to proceed to equilibrium so that relatively large timesteps can be used in order to calculate for more than 1 year. However, the timestep is still limited by the box size and Darcy velocity of the groundwater. The input files are shown in Tab. B2.2 and a selection of results is given in Tab. B2.3 and B2.4.

Tab. B2.2: Input files for simple HPF scoping calculation

Defaults	Run_data	Bounds	Transport
<p>Number of species in this problem = 21                      Number of components in this problem = 8                      components: Ca++ Na+ K+ Al+++ CO3-- SO4-- H2SiO4-- H+                      reactions are of the form:                      species(i) &lt;=&gt; n(1).component(1)+n(2).component(2)+...                      so that:                      log(conc. species(i)) = K + sum_j (n(j)*log(conc. component(j)))                      species(i) charge K_value components (right-hand side of eqn.)</p> <pre> Ca++      2  0.0  1*Ca++ Na+       1  0.0  1*Na+ K+        1  0.0  1*K+ Al+++     3  0.0  1*Al+++ CO3--    -2  0.0  1*CO3-- SO4--    -2  0.0  1*SO4-- H2SiO4-- -2  0.0  1*H2SiO4-- Ca(OH)+  1 -12.598 1*Ca++ -1*H+ KOH       0 -14.46  1*K+ -1*H+ NaOH      0 -14.16  1*Na+ -1*H+ CaCO3     0  3.225  1*Ca++ 1*CO3-- CaHCO3+   1 11.435  1*Ca++ 1*CO3-- HCO3-    -1 10.33  1*CO3-- 1*H+ HSO4-    -1 1.988  1*SO4-- 1*H+ Al(OH)2+  1 -10.11  1*Al+++ -2*H+ Al(OH)3   0 -16.94  1*Al+++ -3*H+ Al(OH)4-  -1 -22.66  1*Al+++ -4*H+ H4SiO4    0 23.141  1*H2SiO4-- 2*H+ H3SiO4-  -1 13.341  1*H2SiO4-- 1*H+ OH-       -1 -14.0  -1*H+ H+        1  0.0  1*H+                     </pre> <p>Number of minerals in this problem = 6                      reactions are of the form:                      mineral(i) &lt;=&gt; n(1).component(1)+n(2).component(2)+...                      so that:                      logK = sum_j (n(j)*log(conc. component(j)))                      mineral(i) K_value Density M.Wt components (rt side of eqn.)</p> <pre> portland  22.7  2.25  74.09  1*Ca++ -2*H+ calcite   -8.48  2.65  100.09  1*Ca++ 1*CO3-- albite   -65.88  2.70  278.33  1*Na+ 1*Al+++ 3*H2SiO4-- 2*H+ quartz   -26.98  2.70  60.09  1*H2SiO4-- 2*H+ 5CSH(1.8) 45.19  2.5  540.45  9*Ca++ 5*H2SiO4-- -8*H+ phillip  -104.56  2.25  670.44  2*Na+ 1*K+ 3*Al+++ 5*H2SiO4-- -2*H+                     </pre>	<p>Number of boxes = 10                      box volume (in litres) = 0.001                      initial amounts of minerals (vol% or mol/box) : vol%                      Temperature in Celsius = 25.0                      boxes up to (and including): 1                      initial porosity : 0.1                      Concentration of components for this problem                      ('e/n' indicates use electroneutrality condition)</p> <pre> Ca++      1.9d-2 K+        5.0d-6 Na+       5.3d-4 Al+++     1.0d-20 CO3--    6.6d-6 SO4--    6.1d-5 H2SiO4-- 1.4d-6 H+        e/n                     </pre> <p>Minerals init. amount A(sqcm/mol) k (mol/sqcm/a) kin/eqm</p> <pre> portland  0.0d0  7.307d4  3.154d-4  0 albite    0.0d0  1.0d4  3.154d-3  0 quartz    0.0d0  1.2d5  3.154d-6  0 phillip   0.0  1.676d7  7.0d-5  0 5CSH(1.8) 0.0  6.709d6  1.0d-3  0                     </pre> <p>boxes up to (and including): 10                      initial porosity : 0.1                      Concentration of components for this problem                      ('e/n' indicates use electroneutrality condition)</p> <pre> Ca++      1.4d-4 K+        5.0d-6 Na+       5.3d-4 Al+++     1.0d-20 CO3--    3.327d-4 SO4--    6.1d-5 H2SiO4-- 2.50d-4 H+        e/n                     </pre> <p>Minerals: initial amount A(sqcm/mol) k (mol/sqcm/a)                      kin/eqm</p> <pre> calcite   0.0d0  7.307d4  3.154d-4  0 portland  0.0d0  1.0d4  3.154d-3  0 albite    3.0d1  1.2d5  3.154d-6  0                     </pre>	<p>boundary concentrations                      ('e/n' indicates use electroneutrality condition)                      up to time [a]: 10.0                      Ca++ 1.4d-4                      K+ 5.0d-6                      Na+ 5.3d-4                      Al+++ 1.0d-20                      CO3-- 3.327d-4                      SO4-- 6.1d-5                      H2SiO4-- 2.50d-4                      H+ 4.724d-4                      up to time [a]: 100.0                      Ca++ 1.4d-4                      K+ 5.0d-6                      Na+ 5.3d-4                      Al+++ 1.0d-20                      CO3-- 3.327d-4                      SO4-- 6.1d-5                      H2SiO4-- 2.50d-4                      H+ e/n                      ..... end</p>	<p>length of box (metres)                      Darcy velocity (metres/year)                      Diffusion coefficient (sq. m/year)                      ratio of viscosity to spec. grav. (m years)                      fracture length per unit area (per metre)                      hydraulic gradient                      initial time step                      variable time step (1=yes, 0=no)                      numerical method (0=simple, 1=accurate)                      dis. rate prop. to S.A. (1=yes, 0=no)                      use cubic law model (1=yes, 0=no)                      number of boxes monitored in output                      1 2 3 4 5 6 7 8 9 10 box numbers for output                      1 print out every nth time-step</p>

Note: The first box contains portlandite to generate a hyperalkaline fluid for interaction with the remaining boxes which contain a simplified granite (albite + quartz).



Tab. B2.3: Cumulative amounts of minerals dissolved or precipitated in each box (cum\_ppt) at time steps 1 ( $10^{-3}$  a), 100 ( $10^{-1}$  a) and 1000 (1 a)

step number 0001, step size = 1.00000E-03 a, time = 1.00000E-03 a										
Darcy velocity = 3.00000E-01 m/a										
mineral	cumulative moles pptd/diss in box									
	2	3	4	5	6	7	8	9	10	
portland-8.470E-08	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
calcite 9.748E-10	2.987E-08	6.786E-09	6.786E-09	6.786E-09	6.786E-09	6.786E-09	6.786E-09	6.786E-09	6.786E-09	6.786E-09
albite	0.00E+00	-6.238E-9	-6.120E-9	-6.120E-9	-6.120E-9	-6.120E-9	-6.120E-9	-6.120E-9	-6.120E-9	-6.120E-9
quartz	0.00E+00	-5.632E-08	1.094E-08	1.094E-08	1.094E-08	1.094E-08	1.094E-08	1.094E-08	1.094E-08	1.094E-08
5CSH(1.8)1.502E-10	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
phillip 0.000E+00	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10
step number 0100, step size = 1.00000E-03 a, time = 1.00000E-01 a										
Darcy velocity = 3.00075E-01 m/a										
portland-5.993E-06	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
calcite 9.783E-08	3.124E-08	2.871E-08	2.443E-08	2.107E-08	1.885E-08	1.694E-08	1.296E-08	7.781E-09	6.878E-09	6.878E-09
albite	0.000E+00	-2.696E-08	-6.178E-09	-6.115E-09	-6.127E-09	-6.1104E-09	-6.099E-09	-6.117E-09	-6.120E-09	-6.120E-09
quartz	0.000E+00	-4.446E-06	1.805E-08	1.816E-08	1.741E-08	1.698E-08	1.478E-08	1.186E-08	1.105E-08	1.105E-08
5CSH(1.8)1.492E-08	4.779E-07	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
phillip 0.000E+00	1.985E-09	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10
step number 1000, step size = 1.00000E-03 a, time = 1.00000E+00 a										
Darcy velocity = 3.01136E-01 m/a										
portland-5.979E-05	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
calcite 9.797E-07	3.124E-08	2.871E-08	2.437E-08	2.081E-08	1.898E-08	1.756E-08	1.653E-08	1.574E-08	1.510E-08	1.510E-08
albite	0.000E+00	-2.110E-07	-6.486E-09	-6.180E-09	-6.163E-09	-6.155E-09	-6.147E-09	-6.145E-09	-6.143E-09	-6.143E-09
quartz	0.000E+00	-4.223E-05	1.799E-08	1.800E-08	1.688E-08	1.548E-08	1.506E-08	1.474E-08	1.448E-08	1.448E-08
5CSH(1.8)1.494E-07	5.1134E-06	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
phillip 0.000E+00	1.551E-08	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10	5.000E-10

Note: The amounts of minerals dissolved or precipitated in time step 1, in all boxes except box 1, bring the pore water into equilibrium with albite and quartz. In box 1, portlandite dissolves in incoming groundwater and a small amount of calcite and CSH phase precipitate due to carbonate and silica concentrations in the porewater. The hyperalkaline porewater from box 1 is transported into the other boxes over time resulting in dissolution of quartz and albite in box 2.

Tab. B2.4: Changes in the amounts of minerals in box 1 (hyperalkaline source) and box 2 (host rock)

	Box 1	Box 2				
	Portlandite	Albite	Quartz	CSH	Phillipsite	Porosity
Initial amount (moles/box)	2.733E-2	2.910E-3	8.986E-3	0	0	10 %
Change after 1 a (moles/box)	-5.979E-5	-2.110E-7	-4.233E-5	2.567E-5	1.127E-8	9.987 %
Change after 5 a (moles/box)	-3.008E-4	-1.035E-6	-2.115E-4	1.300E-4	7.608E-8	9.933 %

Note: Even after 5 years, the proportional change in mineral composition in box 2, the first 10 cm adjacent to the hyperalkaline source, is small and suggests that alteration more than a few cm into the rock may be difficult to detect in the GTS HPF experiment unless the water flux is greater than used in the calculation ( $0.3 \text{ m a}^{-1}$ ).

### B2.3 Diffusion of hyperalkaline solution in fracture wall

In the preceding examples, transport by advection has dominated over diffusion but this is unlikely to be the case where hyperalkaline fluid penetrates the walls of a fracture via the connected porosity. To simulate this situation, the third example uses a very low Darcy velocity and a moderate diffusivity so that diffusion dominates over advection. The simplified albite-quartz host rock is used and the input boundary condition, i.e. the fluid in the fracture, has the composition of the (simplified) GTS groundwater equilibrated with portlandite taken from example of section B2.2. Ten boxes are used but each box is only 1 mm deep so that detailed changes within the diffusion zone are not averaged out over deeper boxes. The calculation uses relatively small time steps ( $1 \times 10^{-5} \text{ a} \approx 5 \text{ mins}$ ) so that use of rate constants for albite and quartz dissolution is necessary since equilibrium would not be expected to occur within 5 minutes. The input files are given in Tab. B2.5.

Results of the calculation are given in Fig. B2.3 to B2.5 and Tab. B2.6.

Tab. B2.5: Input files for diffusion of hyperalkaline fluid from a fracture into fracture walls of simplified granite (albite + quartz)

Defaults	Run_data	Bounds	Transport
<p>Number of species in this problem = 21                      Number of components in this problem = 8</p> <p>components: Ca++ Na+ K+ Al+++ CO3-- SO4-- H2SiO4-- H+</p> <p>reactions are of the form:                      species(i) &lt;=&gt; n(1).component(1)+n(2).component(2)+...                      so that                      log(conc. species(i)) = K + sum_j(n(j))*log(conc. component(j))</p> <p>species(i) charge K_value components (right-hand side of eqn.)</p> <pre> Ca++      2  0.0  1*Ca++ Na+       1  0.0  1*Na+ K+        1  0.0  1*K+ Al+++     3  0.0  1*Al+++ CO3--     2  0.0  1*CO3-- SO4--     2  0.0  1*SO4-- H2SiO4--  2  0.0  1*H2SiO4-- Ca(OH)+   1 -12.598 1*Ca++ -1*H+ KOH       0 -14.46  1*K+ -1*H+ NaOH      0 -14.18  1*Na+ -1*H+ CaCO3     0  3.225  1*Ca++ -1*CO3-- CaHCO3+   1 -11.435  1*Ca++  1*CO3-- HCO3-     -1  10.33  1*CO3--  1*H+ H2SO4     -1  1.988  1*SO4--  1*H+ Al(OH)2+  1 -10.11  1*Al+++ -2*H+ Al(OH)3   0 -16.94  1*Al+++ -3*H+ Al(OH)4-  -1 -22.66  1*Al+++ -4*H+ H4SiO4    0  23.141  1*H2SiO4-- 2*H+ H3SiO4-   -1  13.341  1*H2SiO4-- 1*H+ OH-       -1 -14.0  -1*H+ H+        1  0.0  1*H+                     </pre> <p>Number of minerals in this problem = 5</p> <p>reactions are of the form:                      mineral(i) &lt;=&gt; n(1).component(1)+n(2).component(2)+...                      so that                      logK = sum_j(n(j))*log(conc. component(j))</p> <p>mineral(i) K_value Density M.Wt components (rt side of eqn.)</p> <pre> calcite   -8.48  2.85  100.09  1*Ca++ 1*CO3-- albite    -65.88  2.70  278.33  1*Na+ 1*Al+++ 3*H2SiO4-- 2*H+ quartz    -26.98  2.70  60.09  1*H2SiO4-- 2*H+ 5CSH(1.8) 45.19  2.5  540.45  9*Ca++ 5*H2SiO4-- -8*H+ phillip   -104.56  2.25  670.44  2*Na+ 1*K+ 3*Al+++ 5*H2SiO4-- -2*H+                     </pre>	<p>Number of boxes = 10                      box volume (in litres) = 0.0001                      initial amounts of minerals (vol% or mol/box) : vol%                      Temperature in Celsius = 25.0</p> <p>boxes up to (and including): 10                      initial porosity : 0.1</p> <p>Concentration of components for this problem                      (e/n indicates use electroneutrality condition)</p> <pre> Ca++      1.4d-4 K+        5.0d-6 Na+       5.3d-4 Al+++     1.0d-20 CO3--     3.327d-4 SO4--     6.1d-5 H2SiO4--  2.50d-4 H+        e/n                     </pre> <p>Mineral: amount A(sqcm/mol) K(mol/sqcm/a) kin/eqm</p> <pre> calcite   0.0d0  7.307d4  3.154d-4  0 albite    3.0d1  1.2d5  3.154d-6  1 quartz    2.0d1  1.2d5  3.154d-6  1 phillip   0.0  1.676d7  7.0d-5  0 5CSH(1.8) 0.0  6.709d6  1.0d-3  0                     </pre>	<p>Boundary concentrations                      (e/n indicates use electroneutrality condition)</p> <p>up to time [a]: 100.0                      Ca++ 1.926d-2                      K+ 5.0d-6                      Na+ 5.3d-4                      Al+++ 1.0d-20                      CO3-- 6.635d-6                      SO4-- 6.1d-5                      H2SiO4-- 1.350d-6                      H+ e/n ..... end</p>	<p>length of box (metres)                      Darcy velocity (metres/year)                      Diffusion coefficient (sq. m/year)                      ratio of viscosity to spec. grav. (m. v)                      fracture length per unit area (per metre)                      hydraulic gradient                      initial time step                      variable time step (1 = yes, 0 = no)                      numerical method (0 = simple, 1 = accurate)                      dis. rate prop. to S.A. (1 = yes, 0 = no)                      use cubic law model (1 = yes, 0 = no)                      number of boxes monitored in output                      number of boxes for output                      print out every nth time-step</p> <pre> 0.001 1.0d-6 5.0d-4 3.23d-15 1d2 0.1 1.0d-5 0 1 1 1 0 10 1 2 3 4 5 6 7 8 9 10 1 1 1                     </pre>

Note: The short time step necessitates use of a rate constant for albite and quartz dissolution.

Tab. B2.6: Amounts of minerals dissolved or precipitated (moles per box) in a 10 mm deep section of wallrock (albite + quartz) adjacent to a fracture containing portlandite saturated groundwater

step number	0100, step size = 1.00000E-05 a, time = 1.00000E-03 a	cumulative moles pptcd/diss in box									
mineral		1	2	3	4	5	6	7	8	9	10
calcite	3.488E-09	3.644E-09	1.962E-09	7.153E-10	6.791E-10	6.786E-10	6.792E-10	6.786E-10	6.792E-10	5.654E-10	4.928E-26
albite	-7.798E-09	3.719E-10	-5.928E-10	-6.025E-10	-6.120E-10	-6.120E-10	-6.120E-10	-6.120E-10	-6.120E-10	-5.928E-10	-2.050E-09
quartz	-1.642E-07	-7.954E-09	1.801E-09	1.094E-09	1.094E-09	1.094E-09	1.094E-09	1.094E-09	1.094E-09	9.897E-10	2.956E-09
5CSH(1.8)	1.843E-08	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
phillip	1.153E-10	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	4.868E-11
step number	1100, step size = 1.00000E-05 a, time = 1.10000E-02 a										
calcite	3.488E-09	3.924E-09	3.928E-09	3.761E-09	3.386E-09	2.253E-09	7.050E-10	6.792E-10	6.792E-10	5.654E-10	4.928E-26
albite	-5.404E-08	9.442E-09	-5.380E-10	-6.073E-10	-6.067E-10	-5.587E-10	-5.307E-10	-4.252E-10	-4.252E-10	9.228E-11	-2.115E-08
quartz	-1.720E-06	-8.524E-08	1.299E-09	2.478E-09	2.439E-09	1.908E-09	1.094E-09	5.821E-10	5.821E-10	-1.323E-09	4.039E-08
5CSH(1.8)	2.468E-07	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
phillip	7.820E-10	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	4.868E-11
step number	10100, step size = 1.00000E-05 a, time = 1.01000E-01 a										
calcite	3.488E-09	3.644E-09	3.976E-09	3.935E-09	3.750E-09	1.624E-09	6.786E-10	6.786E-10	6.792E-10	5.654E-10	4.928E-26
albite	-4.648E-07	9.009E-08	6.426E-10	-2.218E-10	-6.547E-11	2.312E-10	6.244E-10	6.244E-10	1.178E-09	7.068E-10	-2.077E-07
quartz	-1.541E-05	-7.611E-07	-1.185E-08	5.041E-10	2.318E-11	-1.132E-09	-2.925E-09	-4.975E-09	-4.975E-09	-3.378E-09	4.236E-07
5CSH(1.8)	2.354E-06	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
phillip	6.782E-09	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	5.000E-11	4.868E-11

Note: The small amount of phillipsite ( $5 \times 10^{-11}$  moles per box) precipitated as the pore water in all boxes adjusts to equilibrium with albite and quartz. Calcite is also slightly oversaturated initially but further calcite precipitation occurs as Ca concentrations rise. CSH phase also precipitates due to the rise in Ca, driving dissolution of quartz and, to a lesser extent, albite. There are initially  $2.9 \times 10^{-4}$  moles of albite and  $9 \times 10^{-4}$  moles of quartz per box, so that changes due to dissolution are small. This is reflected in changes to porosity – in box 1 porosity decreases from 10 to 9.88 % after 0.1 a due to the precipitation of CSH phase particularly. Note that the true moles/box of CSH(1.8) is 5 times the value given above since the 5CSH(1.8) has the formula  $\text{Ca}_5(\text{H}_2\text{SiO}_4)_9$ .

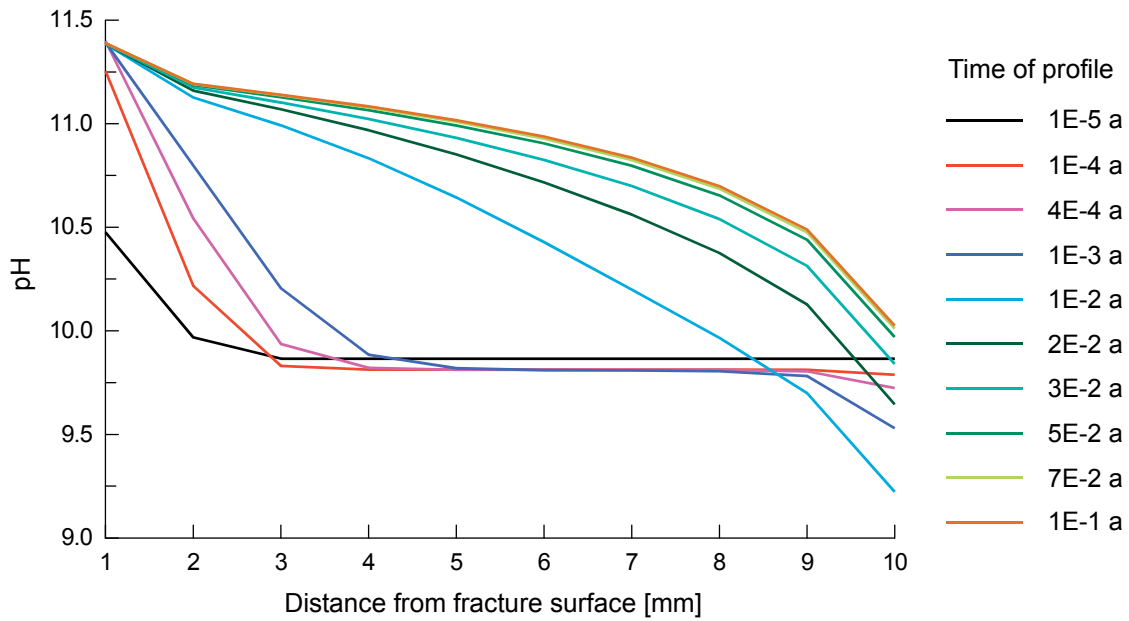


Fig. B2.3: Change in porewater pH with time through a 10 mm (10 box) section of wall rock adjacent to a fracture filled with portlandite-saturated groundwater

Note: After 0.1 a, the profile reaches a steady state. The initial fall in pH from 3 mm outwards reflects the reaction between the pore water and the host rock minerals which are slightly out of equilibrium at the outset. In this calculation, there was no box after the 10<sup>th</sup> so that solute is lost into the 'empty space' after 10 mm – this results in enhanced diffusion and the lowering of pH at the end of the section (box 10). A better result can be obtained by using additional boxes beyond the section of interest to prevent this artefact.

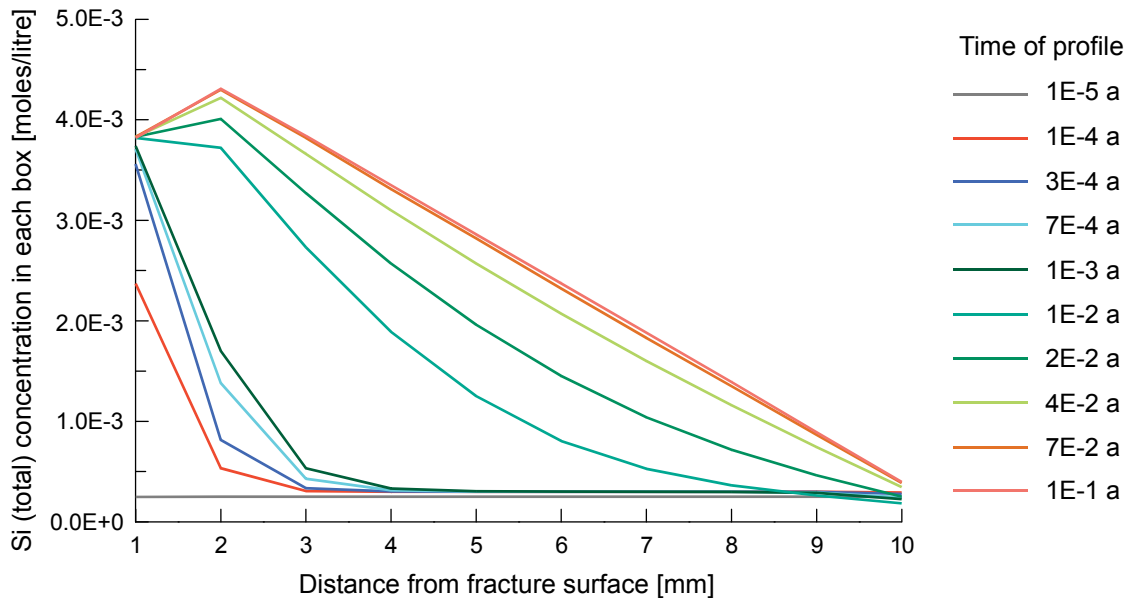


Fig. B2.4: Change in porewater total Si concentration with time through a 10 mm (10 box) section of wall rock adjacent to a fracture filled with portlandite saturated groundwater

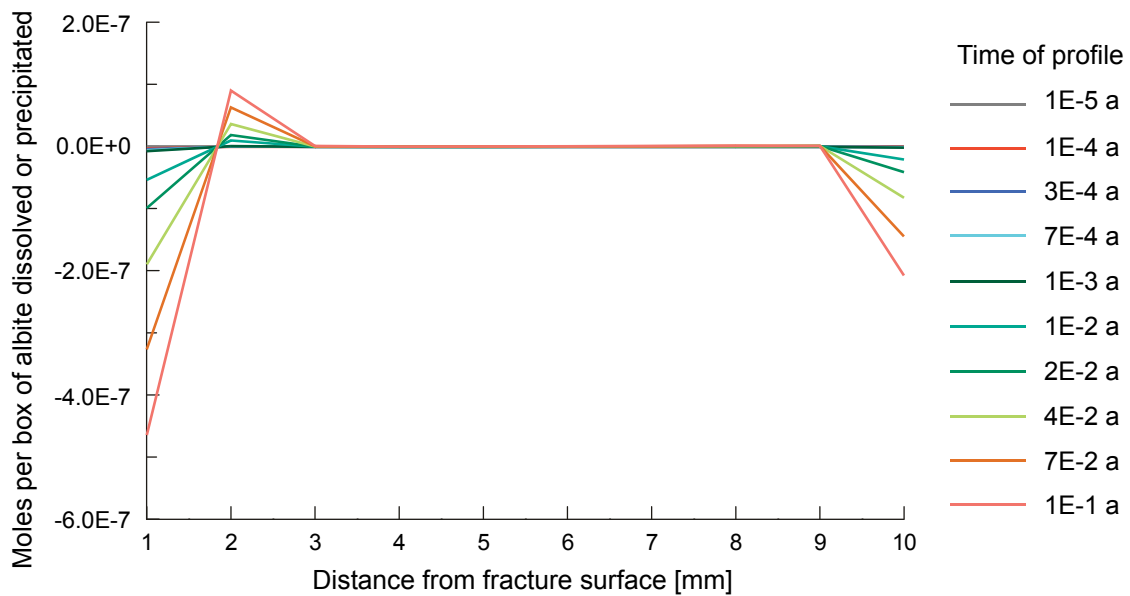


Fig. B2.5: Amount of albite dissolved or precipitated in wall rock adjacent to a fracture filled with portlandite saturated groundwater

Note: Albite dissolution is restricted to the first 1 mm (box 1) after which it precipitates (to equilibrium) due to the lower pH and higher Si (see Figs B2.3 and B2.4, above) concentrations in box 2. The lower Si concentrations in box 1 result from the precipitation of CSH phases in this box caused by diffusion of Ca from the portlandite saturated fluid in the fracture. Approximately 30 times more quartz is dissolved in box 1 than albite, and quartz dissolves slightly in box 2 (see Tab. 2.6).

# **Appendix C**

## **PRINCIPAL NOTATION**





**PRINCIPAL NOTATION**

{}		Denotes component concentrations
[]		Denotes species concentrations
$\Omega$	( $\text{m a}^{-1}$ )	A constant related to fracture geometry and the viscosity and density of water
$\Psi$	( $\text{m}^3$ )	Box volume
$\delta$		A very small number, used in the advection algorithm to avoid division by zero
$\delta L$	(m)	Length of a box
$\delta c_i$	( $\text{mol m}^{-3}$ )	Change of component concentration in the $i$ th box in a time step
$\delta t$	(a)	Time step
$\varepsilon$		Porosity
$\varepsilon_i$		Porosity of the $i$ th box
$\varphi$		Parameter used in the advection algorithm
$\kappa_i$		Parameters that describe equilibrium chemical reactions (solubility products for solids, reaction constants for aqueous species) based on concentrations of species
$\kappa_i^{(0)}$		Parameters that describe equilibrium chemical reactions based on activities of species
$\mu$		Parameter in ionic strength correction
$\nu_i$		Charge on the $i$ th species
$\zeta$		Dielectric constant of water
$A$	( $\text{m}^2$ )	Cross-sectional area of a box
$A^{(i)}$	( $\text{m}^2 \text{m}^{-3}$ )	The surface area of the $i$ th mineral, per unit volume of fluid
$D$	( $\text{m}^2 \text{a}^{-1}$ )	Pore diffusion coefficient
$E$		Integer array (2 dimensional)
$F$		Integer array (2 dimensional) of reaction coefficients for minerals
$G$		Integer array (2 dimensional) of reaction coefficients for species
$H$		Integer array (2 dimensional)
$I$		Integer array (1 dimensional)
$L$	(m)	Length of transport path
$K_{(i)}$	( $\text{m a}^{-1}$ )	Hydraulic conductivity of the $i$ th box
$K_i$		Solubility product of the $i$ th mineral
$K_{sp}$		Solubility product for a particular mineral
$M_{ij}$		A matrix describing the relationship between mineral dissolution/precipitation and the corresponding changes in aqueous component concentrations, that must be satisfied in order to conserve mass

$N$		Number of boxes
$N_c$		Number of aqueous components
$N_m$		Number of minerals
$N_{ppt}$		Number of minerals that, at a particular position and time, are precipitating, rather than dissolving
$N_s$		Number of aqueous species
$P$		Integer array (2 dimensional)
$s^{(i)}$	(mol m <sup>-3</sup> )	Concentration of the $i$ th species in solution
$S_j$		Saturation index with respect to the $j$ th mineral
$S_{disn}^{(i)}$	(mol m <sup>-3</sup> a <sup>-1</sup> )	A source term that accounts for mineral dissolution
$S_{ppt}^{(i)}$	(mol m <sup>-3</sup> a <sup>-1</sup> )	A source term that accounts for mineral precipitation
$T$	(K)	Absolute temperature
$U$		Orthogonal, two-dimensional matrix
$V$		Orthogonal, two-dimensional matrix
$W$		Diagonal matrix
$X^{(i)}$	(mol)	Mineral inventory in the $i$ th box
$a^{(i)}$	(m <sup>2</sup> mol <sup>-1</sup> )	Specific surface area of the $i$ th mineral
$c$	(mol m <sup>-3</sup> )	Component concentration
$c_i$	(mol m <sup>-3</sup> )	Component concentration at the mid-point of the $i$ th box
$c_{in}$	(mol m <sup>-3</sup> )	Component concentration at the upstream boundary
$c^{(i)}$	(mol m <sup>-3</sup> )	The concentration of the $i$ th component
$\tilde{c}^{(i)}$	(mol m <sup>-3</sup> )	Hypothetical concentration of the $i$ th component, considering mineral dissolution in a time step, without corresponding precipitation
$c_j^{(i)}$	(mol m <sup>-3</sup> )	The concentration of component $i$ in box $j$ .
$d^{(i)}$	(mol m <sup>-2</sup> a <sup>-1</sup> )	The rate of dissolution of the $i$ th mineral, per unit area of mineral surfaces
$f_a^{(i)}$	(mol m <sup>-2</sup> a <sup>-1</sup> )	The advective flux of the $i$ th component
$f_{a(i-1/2)}$	(mol m <sup>-2</sup> a <sup>-1</sup> )	The advective flux of a component into the $i$ th box
$f_{a(i+1/2)}$	(mol m <sup>-2</sup> a <sup>-1</sup> )	The advective flux of a component out of the $i$ th box
$f_d^{(i)}$	(mol m <sup>-2</sup> a <sup>-1</sup> )	The dispersive flux of the $i$ th component
$f_{d(i-1/2)}$	(mol m <sup>-2</sup> a <sup>-1</sup> ):	The diffusive flux of a component into the $i$ th box
$f_{d(i+1/2)}$	(mol m <sup>-2</sup> a <sup>-1</sup> ):	The diffusive flux of a component out of the $i$ th box
$k_i$	(mol m <sup>-2</sup> a <sup>-1</sup> )	Rate constant for the dissolution of the $i$ th mineral
$p$		Parameter in ionic-strength correction
$p^{(i)}$	(mol m <sup>-3</sup> a <sup>-1</sup> )	The rate of precipitation of the $i$ th mineral, per unit volume of fluid
$q$	(m a <sup>-1</sup> )	Darcy velocity
$r$	(mol m <sup>-3</sup> )	Real array (one dimensional)
$r_{i+1/2}$		Numerical parameter used in the advection algorithm for the $i$ th box

$s^{(i)}$	(mol m <sup>-3</sup> )	The concentration of the <i>i</i> th species
$s'$		Array containing logs of species concentrations
$s'_{pt}$		Particular solution for $s'$
$t$	(a)	Time
$x$	(m)	Distance in flow direction
$z_i$		Diagonal elements of matrix $W$