

MIN3P-THCm

**A Three-dimensional Numerical Model for
Multicomponent Reactive Transport in Variably
Saturated Porous Media**

User Manual

(Draft)

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ABSTRACT

The MIN3P-THCm code is developed as a multicomponent reactive transport model for variably-saturated porous media in one, two or three spatial dimensions with the extension of heat transport, density-dependent flow, one dimensional hydromechanical coupling, multicomponent diffusion and reactive transport in highly saline solution. Advective-dispersive transport in the aqueous phase, as well as diffusive gas transport can be considered. Darcy velocities are calculated internally using a variably-saturated flow module. The governing equations are discretized using a locally mass conservative finite volume method. The model formulation for reactive transport is based on the global implicit solution approach, which considers reaction and transport processes simultaneously. This formulation enforces a global mass balance between solid, surface, dissolved and gaseous species and thus facilitates the investigation of the interactions of reaction and transport processes. The model can also be used as a batch model for equilibrium speciation problems, kinetic batch problems or for the generation of pC-pH-diagrams.

MIN3P-THCm is characterized by a high degree of flexibility with respect to the definition of the geochemical reaction network to facilitate the application of the model to a wide range of hydrogeological and geochemical problems. Chemical processes included are homogeneous reactions in the aqueous phase, such as complexation and oxidation-reduction reactions, as well as heterogeneous reactions, such as ion exchange, surface complexation, mineral dissolution-precipitation and gas exchange reactions. Reactions within the aqueous phase and dissolution-precipitation reactions can be considered as equilibrium or kinetically-controlled processes.

A new, general framework for kinetically-controlled intra-aqueous and mineral dissolution-precipitation reactions was developed. All kinetically-controlled reactions can be described as reversible or irreversible reaction processes. Different reaction mechanisms for dissolution-precipitation reactions are considered, which can be subdivided into surface- and transport-controlled reactions. This approach allows the consideration of a large number of rate expressions reported in the literature. Related reaction and rate parameters can be incorporated into the model through an accompanying database. The model is primarily designed for problems involving inorganic chemistry, but reactions involving organic chemicals can also be accommodated. Microbially-mediated reactions can be described using a multiplicative Monod approach. The mass dependent fractionation model can be used to determine the isotope fractionation during microbially mediated mass reduction, and precipitation dissolution reactions.

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1 INSTALLING AND RUNNING MIN3P-THCM

The following description is based on the assumption that the program will be installed on a PC with WINDOWS OS. The package can be installed on any drive. This guide assumes that the program will be installed on the d-drive, if this is not the case the drive letter d must be replaced by the actual drive letter:

Extract the program and example files at any location on your computer. The program will extract into a main directory “min3p” that contains a number of subdirectories.

The “bin” directory includes the MIN3P-THCm executable. The “database” directory includes the database files, the “benchmarks_standard” directory includes a set of worked examples, the “simulations” directory is empty and is dedicated for new MIN3P-THCm simulations.

There are several ways to run the program. The simplest way is to copy the executable file under the folder “bin” into the folder containing the input file(s) to be executed. Double click the program will launch a new DOS-window (Figure 1.1). Now provide the name of the input file and return.

```

-----
M   M   I   N   N   333333   P P P P P
MM  MM  I  NN  N    3   P   P
M M M M  I  N  N    3   P   P
M  M  M  I  N  N  N   3333   P P P P P
M   M   I   N   N   N    3   P
M   M   I   N   NN    3   P
M   M   I   N   N   333333   P

      Version 1.0.414.0
      Build Date: 2016/08/29

  A Numerical Model for the Analysis
    of the
  Geochemical Evolution
    of
  Variable-Density
  Mineral-Water-Gas-Systems

      (c) 2000 U. Mayer

      Pitzer equations are included
-----

now provide prefix of problem filename ...
  
```

Figure 1.1: DOS window while launching the MIN3P-THCm program

Alternatively, the program can be started using a batch file (e.g. 1min3p.bat) that is included in each example directory. In this file, the location of the MIN3P-THCm can be specified. To execute the program, double click on file “1min3p.bat”. A DOS window with a welcome screen will appear (Figure 1.1). When prompted, enter the problem specific file name, in the example above: amd_ex, then press enter and the simulation will start. Or you can also put the problem specific file name without extension in a separate file root.dat. In such case, double click on file “1min3p”, MIN3P-THCm will launch the execution automatically.

Due to the potential large number of output files generated by the program, it is highly

recommended to create a directory for each new simulation. You can simply copy an existing example to a new location in the “simulations” directory, and modify the input file using notepad, notepad++, wordpad or a similar ascii text editor (in this case the amd_ex.dat file). Start the simulation as described above:

All of output files generated are ascii text files by default. Most output files have a Tecplot header that can be read by a variety of postprocessing programs (section 2.2). Alternatively, binary output is available when MPI parallel version is used.

IMPORTANT: If you want to run the simulations elsewhere than in the “simulations” directory, you will have to update the path to the database files in the input file (i.e. the prefix.dat file) and the path to the executable in the 1min3p.bat file. This can be avoided by sticking to the simulations directory.

2 FILE STRUCTURE

Required input files can be subdivided into problem specific input files and database files. Additional species or reactions may be specified in the database files. When changing the database files for a specific problem, an original copy of the database should always be maintained (see Section 4 on how to maintain the database and on how to add additional components, species, or reactions to the database).

2.1 INPUT FILES

The input prefix.dat, where prefix is a problem name with up to 72 characters contains the problem-dependent input. This file together with all database files is required to operate the model. Some optional file(s) can be required for specifying material properties, initial condition distributions and/or time dependent boundary conditions. For example, it is optional to specify a depth-dependent temperature field or an initial condition for transient groundwater flow problems. These data may be provided in the files prefix.tem (**tem**perature) and prefix.ivs (**ini**tial condition **vari**ably-saturated flow). All optional input files are listed in Table 2.1. Details about the construction and modification in the prefix.dat will be discussed in the following sections.

Table 2.1: Input file and database files

Type	File name	Description	Requirement
problem specific input files	prefix.dat	General problem specific input	Required
	prefix.tem	Depth dependent temperature field	Optional
	prefix.ivs	Distributed initial condition for flow simulation	Optional
	prefix.hyc	Initial hydraulic conductivity distribution	Optional
	Prefix.bcvs	Transient boundary conditions for flow	Optional
	Prefix.cec	Nodal cation exchange capacity (CEC) and bulk density input (ρ_b)	Optional
	Prefix.spstor	Nodal specific storage (S_s)	Optional
	restart.dat	Restart file	Optional
database files	comp.dbs	Components	Required
	complex.dbs	Aqueous complexation	Required
	redox.dbs	Oxidation-reduction	Required
	gases.dbs	Gas dissolution-exsolution	Required
	sorption.dbs	Ion exchange and surface complexation	Required
	mineral.dbs	Mineral dissolution-precipitation	Required
	Pitzer.xml	Pitzer parameters	Optional

2.2 OUTPUT FILES

A brief summary of all output files can be found in the file prefix_o.flr, which is very helpful for the new users to have an overview of the output files. This file contains the file names, provides a brief description of the content of the files and lists the parameters contained in the files. It is generated on program-execution. The most important output files are summarized in the following

tables (Table 2.2, Table 2.3, Table 2.4, Table 2.5 and Table 2.6). For the remaining output files the user is referred to the file prefix_o.flc, in which the parameters and units of almost all output files are described.

The files prefix_o.gen and prefix.log documents the processes of the execution. If the simulation fails, error messages are normally provided in both files. If the simulation succeeds, “***** normal exit *****” can be found at the end of both file.

Table 2.2: Output files – general model output

File name	Description	TECPLOT Header
prefix_o.gen	General problem specific output, contains feed-back from input file and results of batch simulations including the equilibration of background and source water chemistry Output format: assorted Suffix meaning: gen = general	N
prefix.log	run-specific information on convergence and trouble shooting Output format: assorted Suffix meaning: log = logbook	N
prefix_o.flc	Additional information (parameters and units) about the content of all output files Output format: assorted Suffix meaning: flc = output files	N
Prefix_o.dbg	Debug information (for code developer while debugging) Suffix meaning: dbg = debug	N
prefix_o.psp	Record of all the possible species for a given set of components Output format: assorted Suffix meaning: psp = ‘ possible species ’	N
Prefix_o.dt	Record of time steps and courant number – Transient data Output format: time, delta t, parameter values Suffix meaning: dt = delta time	Y/N
Prefix_o.cnv	Record of concentration input and mineral input for reactive trans	N

Table 2.3: Output files – Output files - flow solution

File name	Description	TECPLOT Header
prefix_x.gsp	hydraulic head, pressure head, water and gas saturations, moisture and gas contents at output time x (0 = initial condition) – contour data Output format: x,(y),(z), parameter values Suffix meaning: gsp = global/spatial/pressure	Y
prefix_x.vel	interfacial velocities at output time x (0 = initial condition) – contour data Output format: x,(y),(z), v_x , (v_y), (v_z) Suffix meaning: vel = velocities	Y
prefix_o.mvs	Mass balance files of liquid – transient data Output format: time, water mass, "water filled volume", "gas filled volume" Suffix meaning: mvs = mass and liquid filled volumes	Y
prefix_o.mvc	Mass balance in total flux – transient data Output format: time, "inflow", "outflow", "change in storage", "root water uptake" Suffix meaning: mvc = mass volume change	Y
prefix_o.mve	Mass balance errors – transient data Output format: time, "absolute mass balance error", "relative mass balance error", "absolute cumulative mass balance error", "relative cumulative mass balance error" Suffix meaning: mve = mass balance (volume) errors	Y

Table 2.4: Output files – reactive transport – contour data.

File name	Description	TECPLOT Header
prefix_x.gst	total aqueous component concentrations at output time x (0 = initial condition) – contour data Output format: x,(y),(z), parameter values Suffix meaning: gst = global/spatial/total aqueous component concentrations	Y
prefix_x.gsc	aqueous species concentrations at output time x (0 = initial condition) – contour data Output format: x,(y),(z), parameter values Suffix meaning: gsc = global/spatial/species concentrations	Y
prefix_x.gsi	reaction rates of intra-aqueous kinetic reactions at output time x – contour data Output format: x,(y),(z), parameter values Suffix meaning: gsi = global/spatial/intra-aqueous kinetic reactions	Y
prefix_x.gsm	master variables (pH, pe, Eh, ionic strength, alkalinity, temperature) at output time x (0 = initial condition) – contour data Output format: x,(y),(z), parameter values Suffix meaning: gsm = global/spatial/master variables	Y

prefix_x.gsg	partial gas pressures at output time level x (0 = initial condition) – contour data Output format: x,(y),(z), parameter values Suffix meaning: gsg = global/spatial/partial gas pressures	Y
prefix_x.gsgr	degassing rates at output time x (0 = initial condition) – contour data Output format: x,(y),(z), parameter values Suffix meaning: gsg r – global/spatial/degassing/rates	Y
prefix_x.gsv	mineral volume fractions at output time x (0 = initial condition) – contour data Output format: x,(y),(z), parameter values Suffix meaning: gsv – global/spatial/volume fractions	Y
prefix_x.gsb	surface species at output time x (0 = initial condition) – contour data Output format: x,(y),(z), parameter values Suffix meaning: gsb – global/spatial/sorbed species	Y
prefix_x.gss	mineral saturation indices at output time x (0 = initial condition) – contour data Output format: x,(y),(z), parameter values Suffix meaning: gss – global/spatial/saturation indices	Y
Prefix_x.cbt	Charge balance output for multicomponent diffusion (MCD) – contour data Output format: x,(y),(z), parameter values, charge balance values Suffix meaning: cbt – charge/balance/time	Y
Prefix_x.gmf	Total flux of each aqueous components for multicomponent diffusion (MCD) - contour data Output format: x,(y),(z), parameter values Suffix meaning: cbt – globe/mass/flux	Y
prefix_x.mac	Mass balance (in moles/d) for the x th aqueous component – transient data Output format: time, parameter values Suffix meaning: mac = total mass of aqueous components	Y

Table 2.5: Output files – reactive transport – transient data

File name	Description	TECPLOT Header
prefix_x.gsd	mineral dissolution-precipitation rates at output time x – contour data Output format: x,(y),(z), parameter values Suffix meaning: gsd = global/spatial/dissolution-precipitation rates	Y
prefix_x.gsx	saturation indices of excluded minerals at output time x – contour data Output format: x,(y),(z), parameter values Suffix meaning: gsd = global/spatial/excluded minerals	Y
prefix_x.gsis	Isotope data at output time x – contour data Output format: x,(y),(z), parameter values Suffix meaning: gsis = global/spatial/isotopes	Y

prefix_x.gbt	total aqueous component concentrations at output location x – transient data Output format: time, parameter values Suffix meaning: gbt = g lobal/ b reakthrough/ t otal aqueous component concentrations	Y
prefix_x.gbc	aqueous species concentrations at output location x – transient data Output format: time, parameter values Suffix meaning: gbc = g lobal/ b reakthrough/ s pecies concentrations	Y
prefix_x.gbi	reaction rates of intra-aqueous kinetic reactions at output location x – transient data Output format: time, parameter values Suffix meaning: gbi = g lobal/ b reakthrough/ i ntra-aqueous kinetic reactions	Y
prefix_x.gbm	master variables (pH, pe, Eh, ionic strength, alkalinity, temperature) at output location x – transient data Output format: time, parameter values Suffix meaning: gbm = g lobal/ b reakthrough/ m aster variables	Y
prefix_x.gbg	partial gas pressures at output location x – transient data Output format: time, parameter values Suffix meaning: gbg = g lobal/ b reakthrough/ p artial gas pressures	Y
prefix_x.gbgr	degassing rates at output location x – transient data Output format: time, parameter values Suffix meaning: gbgr – g lobal/ b reakthrough/ d egassing/ r ates	Y
prefix_x.gbv	mineral volume fractions at output location x – transient data Output format: time, parameter values Suffix meaning: gbv – g lobal/ b reakthrough/ v olume fractions	Y
prefix_x.gbb	surface species at output location x – transient data Output format: time, parameter values Suffix meaning: gbb – g lobal/ b reakthrough/ s orbed species	Y
prefix_x.gbs	mineral saturation indices at output location x – transient data Output format: time, parameter values Suffix meaning: gbs – g lobal/ b reakthrough/ s aturation indices	Y
prefix_x.gbd	mineral dissolution-precipitation rates at output location x – transient data Output format: time, parameter values Suffix meaning: gbd = g lobal/ b reakthrough/ d issolution - precipitation rates	Y
prefix_x.gbx	saturation indices of excluded minerals at output location x – transient data Output format: time, parameter values Suffix meaning: gbx = g lobal/ b reakthrough/ e xcluded minerals	Y
prefix_x.gbhis	Isotope data at output location x – transient data Output format: time, parameter values Suffix meaning: gbhis = g lobal/ b reakthrough/ i sotope fractionation	Y

prefix_o.mas	Total mass (in moles) of all aqueous components – transient data Output format: time, parameter values Suffix meaning: mas = total mass of aqueous components	N
prefix_o.mms	Total mass (in moles) of all mineral components – transient data Output format: time, parameter values Suffix meaning: mms = total mass of mineral components	N
prefix_o.mgs	Total mass (in moles) of all gases– transient data Output format: time, parameter values Suffix meaning: mgs = total mass of gas components	N
prefix_o.mss	Total mass (in moles) of all sorbed species – transient data Output format: time, parameter values Suffix meaning: mss = total mass of sorbed species	N
prefix_o.ebal	System energy balance Output format: time, energy, water filled volume and air filled volume Suffix meaning: ebal = energy balance	Y
prefix_o.ebalc	Energy balance contributions Output format: time, total energy inflow, out flow, and the change in storage Suffix meaning: ebal = energy balance contributions	Y
prefix_o.ebale	Energy balance error Output format: time, total energy inflow, out flow, and the change in storage Suffix meaning: ebal = energy balance contributions	Y
prefix.evap	Climate output Output format: time, parameter values Suffix meaning: evap = evaporation boundary	Y

If the sub-block ‘mass balance’ is specified, the model will perform mass balance calculations including contributions of storage, fluxes across the domain boundary and internal sources and sinks due to the specified geochemical reactions. The total system mass for aqueous phase components, minerals, gases and surface species are reported in the files prefix_o.mas, prefix_o.mms, prefix_o.mgs and prefix_o.mss. Mass balance contributions and cumulative changes are reported for each component, for each mineral phase and for all gaseous species in separate files. The file prefix_o.fls contains additional information on these mass balance files, the corresponding mass balance error files and their content. This file will be created for the specific problem at run-time.

If the sub-block ‘energy balance’ is specified, the model will perform energy balance calculations including contributions of energy fluxes across the domain boundary and internal sources and sinks due to the specified heat transport conditions. The total system energy evolution is reported in the files prefix_o.ebal, prefix_o.ebalc, and prefix_o.ebale. The file prefix_o.ebal includes the solution time [days], total energy [kJ], water filled volume [m³], and air filled volume [m³]. The file prefix_o.ebalc includes the solution time [days], total energy inflow [kJ/day], outflow [kJ/day], and the change in storage [kJ/day].

If the sub-block ‘compute evaporation’ and ‘write transient evaporation info’ are specified, the model will perform evaporation calculations. The evaporation evolution is reported in the files prefix.evap. This file includes the solution time [days], evaporation rate [kg s⁻¹ m⁻²], temperature

[°C], relative humidity [-], wind [m s^{-1}], rainfall rate [$\text{kg s}^{-1} \text{m}^{-2}$], runoff rate [$\text{kg s}^{-1} \text{m}^{-2}$], rain – runoff [$\text{kg s}^{-1} \text{m}^{-2}$], vapour density (r_v) [kg m^{-3}], vapour pressure (P_v) [Pa], solar radiation (R_n) [$\text{J s}^{-1} \text{m}^{-2}$], latent heat of evaporation (L_w) [$\text{J s}^{-1} \text{m}^{-2}$], sensible heat (H_s) [$\text{J s}^{-1} \text{m}^{-2}$], and total energy balance at the atmospheric boundary surface [$\text{J s}^{-1} \text{m}^{-2}$].

Table 2.6: Output files – local geochemistry

File name	Description	TECPLOT Header
prefix_x.lbt	total aqueous component, local geochemistry – transient data, or pC-pH-data Output format: time or pH, parameter values Suffix meaning: lbt = local/breakthrough/total aqueous component concentrations	Y
prefix_x.lbc	aqueous species concentrations, local geochemistry – transient data, or pC-pH-data Output format: time or pH, parameter values Suffix meaning: lbc = local/breakthrough/species concentrations	Y
prefix_x.lbi	reaction rates of intra-aqueous kinetic reactions, local geochemistry – transient data, or pC-pH-data Output format: time or pH, parameter values Suffix meaning: lbi = local/breakthrough/intra-aqueous kinetic reactions	Y
prefix_x.lbm	master variables (pH, pe, Eh, ionic strength, alkalinity, temperature) , local geochemistry – transient data, or pC-pH-data Output format: time or pH, parameter values Suffix meaning: lbm = local/breakthrough/master variables	Y
prefix_x.lbg	partial gas pressures, local geochemistry – transient data, or pC-pH-data Output format: time or pH, parameter values Suffix meaning: lbg = local/breakthrough/partial gas pressures	Y
prefix_x.lbgr	degassing rates, local geochemistry – transient data, or pC-pH-data Output format: time or pH, parameter values Suffix meaning: lbgr – local/breakthrough/degassing /rates	Y
prefix_x.lbv	mineral volume fractions, local geochemistry – transient data, or pC-pH-data Output format: time or pH, parameter values Suffix meaning: lbv – local/breakthrough/volume fractions	Y
prefix_x.lbb	surface species, local geochemistry – transient data, or pC-pH-data Output format: time or pH, parameter values Suffix meaning: lbb – local/breakthrough/sorbed species	Y

prefix_x.lbs	mineral saturation indices, local geochemistry – transient data, or pC-pH-data Output format: time or pH, parameter values Suffix meaning: lbs – local/breakthrough/saturation indices	Y
prefix_x.lbd	mineral dissolution-precipitation rates, local geochemistry – transient data, or pC-pH-data Output format: time or pH, parameter values Suffix meaning: lbd = local/breakthrough/dissolution-precipitation rates	Y
prefix_x.lbx	saturation indices of excluded minerals, local geochemistry – transient data, or pC-pH-data Output format: time or pH, parameter values Suffix meaning: lbx = local/breakthrough/excluded minerals	Y

3 PROBLEM-SPECIFIC INPUT

3.1 OVERVIEW

3.1.1 PREFIX.DAT FILE

The problem-specific input file (prefix.dat) is composed of a series of sections or data blocks (Table 3.1). Each data block contains specific input information and may contain a series of sub-sections or sub-blocks. Each data block is bounded by a keyword at the top and a 'done' statement at the bottom. There are a total of 17 data blocks.

Table 3.1: Data blocks for problem specific input file

Data Block	Keyword
1	'global control parameters'
2	'geochemical system'
3	'spatial discretization'
4	'time step control'
5	'control parameters – local chemistry'
6	'control parameters – variably-saturated flow'
6B	'control parameters – energy balance'
7	'control parameters – reactive transport'
8	'output control'
9	'physical parameters – porous medium'
10	'physical parameters – variably-saturated flow'
10B	'physical parameters – energy balance'
11	'physical parameters – reactive transport'
12	'initial condition – variably-saturated flow'
12B	'initial condition – energy balance'
13	'boundary condition – variably-saturated flow'
13B	'boundary conditions - energy balance'
14	'initial condition – local chemistry'
15	'boundary conditions – reactive transport'
16	'initial condition – reactive transport'
17	'ice sheet loading/unloading'

The sections can appear in any order in the input file, and the order of the subsections within each section can also vary.

3.1.2 TYPES OF SIMULATIONS

MIN3P-THCm can perform six general types of simulations. They are: batch, steady-state flow, transient flow, flow and reactive transport simulations, heat transport and 1D loading/unloading.

Table 3.2: Types of simulations

Simulation Type	Description	Examples
Batch	No-flow modeling of geochemical processes	Speciation calculations, and Kinetic batch experiments
Steady-State Flow	1, 2, or 3-Dimensional flow modelling at steady-state	Flow in column, x-section, or 3-D domain
Transient Flow	As above but with conditions changing with time	As above but with conditions changing with time
Flow and Reactive Transport	As above but with geochemical reactions	Column tests and Groundwater plume evolution
Heat transport	1, 2, or 3-Dimensional heat transport, 'energy balance'	Thermohydraulic coupled processes, e.g. temperature dependent fluid property variation, density dependent flow
Loading/Unloading	1D hydromechanics	Loading/unloading of the subsurface owing to the glaciation formation and retreat

Depending on the type of simulation to be conducted, certain subsections and even entire sections are optional, while others, defining the essential problem-specific parameters, are required. Table 3.3 summarizes the input section requirements for each simulation type (R = Required, O = optional, N = not used):

Table 3.3: Input requirements for simulation types

type	1	2	3	4	5	6/B	7	8	9	10/B	11	12/B	13/B	14	15	16	17
batch	R	R	N	N	O	N	N	N	N	N	N	N	N	R	N	N	N
steady flow	R	N	R	N	N	O	N	O	R	R	N	R	R	N	N	N	N
transient flow	R	N	R	R	N	O	N	O	R	R	N	R	R	N	N	N	N
flow and reactive transport	R	R	R	R	O	O	O	O	R	R	R	R	R	N	R	R	N
heat transport	R	N	N	N	N	R	N	O	N	R	N	R	R	N	N	N	N
loading	R	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	R

3.1.3 COMMENT LINES AND NOTATIONS

Each line starting with an exclamation mark (!) is a comment line and will not be read by the program. The user is encouraged to add comments to the input file whenever deemed necessary. When the program reads the input file, it searches for the required parameter(s). If found, the program will read the required the parameters and then moves to the next line. Therefore, any text found to the right of the required parameter(s) will be ignored and notes can be added without affecting the input file. In the examples, such comments are starting with “;”. The user can use any symbols to distinguish it from the required keywords or parameters.

3.1.4 UNITS

All input is in SI-units, unless otherwise noted.

3.2 GLOBAL CONTROL PARAMETERS (DATA BLOCK 1)

3.2.1 DESCRIPTION OF DATA BLOCK

In this data block the problem title is read and the type of simulation to be conducted is specified. The options are:

- Geochemical batch simulation
- Flow simulation (transient or steady-state and fully- or variably-saturated)
- Flow and reactive transport simulation (transient or steady-state and fully or variably saturated)
- Density dependent flow
- Energy balance
- Loading/unloading because of ice sheet formation/retreat

3.2.2 DESCRIPTION OF INPUT PARAMETERS

3.2.2.1 'global control parameters'

The input is initiated with the header defining the section name ('global control parameters'). In the next line the problem title must be specified (up to 72 characters in quotes). To specify what type of simulation is to be performed, four true/false statements must be specified in the following four input lines:

3.2.2.2 varsat_flow

This statement determines if a flow simulation is to be performed.

3.2.2.3 steady_flow

This statement determines if the flow simulation is to be steady-state or transient.

3.2.2.4 fully_saturated

This statement specifies if the simulation is to be variably-saturated or fully saturated.

3.2.2.5 reactive_transport

This statement specifies if the simulation is to involve reactive transport. The model can also be used to perform geochemical batch simulations. This requires that all true/false statements are set to false.

The table below shows the nine types of simulations possible and indicates the required true/false statements for each scenario.

Table 3.4: Parameter settings for simulation types

Scenarios	True/False Parameters			
	varsat_flow	steady_flow	fully_saturated	reactive_transport
Batch	.false.	.false.	.false.	.false.
Steady-state, Fully-saturated Flow	.true.	.true.	.true.	.false.
Transient, Fully-saturated Flow	.true.	.false.	.true.	.false.
Steady-state, Variably-saturated Flow	.true.	.true.	.false.	.false.
Transient, Variably-saturated Flow	.true.	.false.	.false.	.false.
Steady-state, Fully-saturated Flow, Reactive Transport	.true.	.true.	.true.	.true.
Transient, Fully-saturated Flow, w/ Reactive Transport	.true.	.false.	.true.	.true.
Steady-state, Variably-saturated Flow w/ Reactive Transport	.true.	.true.	.false.	.true.
Transient, Variably-saturated Flow w/ Reactive Transport	.true.	.false.	.false.	.true.

3.2.2.6 Additional keywords

Additional keywords can be added to invoke additional capabilities:

'multicomponent diffusion': The keyword to activate for multicomponent diffusion.
 'hybrid multicomponent diffusion': The keyword to activate for the hybrid multicomponent diffusion. In such cases, the database files (comp.dbs, complex.dbs) needs to be checked to ensure the inclusion of the free aqueous diffusion coefficient (D_0) for each species are provided.

'density dependent flow': This keyword activates the density dependent flow module. The related input parameters must be provided in Data Block 6: 'control parameters - variably-saturated flow' with the keyword 'variable density parameters'.

'compute ice sheet loading/unloading': This keyword activates the function for ice sheet loading/unloading. The parameters for this function must be provided in an additional data block (Data Block 17) with the keywords 'ice sheet loading/unloading' (see section 3.23).

'energy balance': keyword to activate energy balance calculations. Additional parameters must be provided through the following data blocks: Data Block 6B: 'control parameters - energy balance', Data Block 10B: 'physical parameters - energy balance', Data block 12B: 'initial condition - energy balance', Data Block 13B: 'boundary conditions - energy balance'.

'backup frequency' followed by the number of time steps (N_t) used to control the frequency of backing up intermediate calculation results. These data can be used for restarting a simulation. Default value is 10. Generally, there are two files to save the previous results – restart.tmp1 and restart.tmp2. The file restart.tmp1 saves at the given number of time steps (N_t), while the later file documents the results at doubled number of specified time steps ($2*N_t$). The documented results include all the spatial data needed for the restart of the simulation. In the first line, the parameters are: current solution time (I/O units), estimated time step for reactive transport, estimated time step

for variably saturated flow, next read time for flow boundary condition(s), pointer to next output time for contour data. From the second line on the documented parameters depend on the processes in the simulation. For example, for the reactive transport simulation, the ionic strength, total free species of the new and old time levels, mineral concentration at the new and old time levels etc. (see example 2 below).

'restart': keyword to activate the restart function using the last saved results. This function is especially useful for time consuming calculations if the simulation is accidentally terminated and needs to be continued. When this function is activated, an additional file restart.dat file (usually rename of the restart.tmp1 or restart.tmp2, whichever is the latest generated) is needed.

3.2.3 EXAMPLE DATA FILE INPUT

Example 1: General global control parameter

```
! -----
'global control parameters'
'Flow Simulation - Nickel Rim - Reactive Wall - Base Case'
.true.                ;varsat_flow
.true.                ;steady_flow
.true.                ;fully_saturated
.false.               ;reactive_transport

'done'
```

Example 2: Density dependent flow and backup frequency

```
! -----
'global control parameters'
'Sedimentary basin'
.true.                ;varsat_flow
.false.               ;steady_flow
.true.                ;fully_saturated
.true.                ;reactive_transport

'density dependent flow'
'backup frequency'
20
'done'
```

Example 3: Restart function

```
! Data Block 1: global control parameters
! -----
!
'global control parameters'
'Title: EBS-TF:B3.1.2b_MCD WyNa(Ca)02 ion exchange Na-mont'
.true.                ;varsat_flow
.true.                ;steady_flow
.true.                ;fully_saturated
.true.                ;reactive_transport

'restart'

'multicomponent diffusion'

'done'
```

3.2.4 DESCRIPTION OF EXAMPLE INPUT

Example 1: The example input defines a steady state flow simulation under fully-saturated conditions; reactive transport is excluded. The title is used to identify run-specific information.

Example 2: The example input defines a transient saturated density dependent flow with reactive transport. The 'backup frequency' is set to 20, which indicates that the restart.tmp1 will be generated in every 20 time steps, and the restart.tmp2 in every 40 time steps.

Example 3: The example input defines a simulation with restart function for a saturated steady state flow with reactive transport including multicomponent diffusion.

3.2.5 ADDITIONAL NOTES

It is highly recommended that a modeling problem is approached in a step by step manner. For example, the user can start by simulating flow only until satisfied with the results, then perform initial geochemical simulations using the batch module. In the final step the reactive transport simulation can be added. This stepwise approach limits the number of new parameters for each simulation and will make troubleshooting much easier.

3.3 GEOCHEMICAL SYSTEM (DATA BLOCK 2)

3.3.1 DESCRIPTION OF DATA BLOCK

All problem-specific geochemical species, the redox master variable, minerals, sorbed species and reactions are defined in this data block. In addition, the input unit of the aqueous components' concentration, the temperature and the database to be used for the simulation, can be specified.

3.3.2 DESCRIPTION OF INPUT PARAMETERS

3.3.2.1 'geochemical system'

The data block 'geochemical system' is composed of a series of sub-blocks. The sub-block 'components' is required for all simulations. The all possible sub-blocks are tabulated in Table 3.5.

Table 3.5: Summary of input parameters for data block 'geochemical system'

Name*	Description	Database File	Required?
'components'	Components to be considered	'comp.dbs'	Y
'secondary aqueous species'	Equilibrium complexation reactions	'complex.dbs'	N
'redox couples'	Equilibrium oxidation-reduction reactions	'redox.dbs'	N
'gases'	Gas dissolution- exsolution reactions	'gases.dbs'	N
'sorbed species'	Ion exchange or surface complexation reactions	'sorption.dbs'	N
'sorbed species of surface-complex'	Surface complexation reactions	'sorption.dbs'	N
'sorbed species of ion-exchange'	Ion exchange reactions	'sorption.dbs'	N
'linear sorption'	Linear sorption model (K_d)	-	N

	concept)		
'minerals'	Kinetically-controlled mineral dissolution precipitation reactions	'mineral.dbs'	N
'excluded minerals'	Excluded mineral phases, do not participate in reactions, but saturation index is calculated	'mineral.dbs'	N
'biomass components'	Biomass component for simulating biomass growth and biogeochemical reactions		N
'intra-aqueous kinetic reactions'	Kinetically-controlled complexation and oxidation reduction reactions	'redox.dbs'	N
'compute alkalinity'	Used to calculate and output alkalinity	none	N
'define input units'	Define input units	none	N
'define temperature'	Define temperature	none	N
'define temperature field'	Define temperature field	prefix.tem	N
'combine mineralogical parameters'	Combine same mineral having different reactions	none	N
'use pitzer model'	Use the Pitzer model	pitzer.xml	N
'use macinnes convention'	Use the Macinnes convention for the Pitzer model	none	N
*All keyword headings must appear on a single line in the input file.			

Each of these entries is considered a sub-block and is followed by the number of the species/reactions and by the names of these species (see example input). The names of the reactions or species can be found in the database files. All specified reactions and species must be composed of components specified for that simulation.

3.3.2.2 'components'

This sub-block requires the specification of the number and names of components. Possible choices for components are defined in the database comp.dbs. The components are the basis species for the geochemical system considered. All other species or reactions consist of or involve one or more components.

Simulations including isotopes require that related components or species and minerals etc. for each isotopes to be considered are included in this data block as well as in the database (see section 4). For example, The geochemical components including light (^{32}S) and heavy (^{34}S) sulfur isotopes can be defined as the following:

```
'components'
8           ;number of components
'ca+2'
'fe+2'
'so4-2'
'34so4-2'
'h+1'
```

```
'co3-2'
'hs-1'
'34hs-1'
```

The geochemical system considers 8 components including 4 isotope components of sulfur: 'so4-2', '34so4-2', and 'hs-1', '34hs-1'. The 'so4-2' and 'hs-1' represent the components containing light (³²S) isotopes and '34so4-2' and '34hs-1' including the heavy (³⁴S) isotopes.

3.3.2.3 'non-aqueous components'

This sub-block requires the specification of the number, names and type of the non-aqueous components. An example of the usage is:

```
'non-aqueous components'
1                               ;number of non-aqueous components
'=feoh(s)' 'surface'          ;names of non-aqueous components
```

The example defines one non-aqueous component `=feoh(s)` as the surface for surface complexation reactions.

3.3.2.4 'biomass components'

This sub-block requires the specification of the number and names of biomass components. Possible choices for biomass components are defined in the database comp.dbs. Normally, the active biomass is defined as 'c5h7o2n', and the inactive or dead biomass is defined as 'c5h7o2n(d)'. Biomass exists in the pore network, but it is treated as immobile. The related biogeochemical reactions should be specified using the keyword 'intra-aqueous kinetic reactions' followed by the number of reactions and 'name' representing the reactions that are defined in the database redox.dbs. Their rate constants in [s⁻¹] of each reaction should be specified following the keywords 'scaling for intra-aqueous kinetic reactions' for all reactions. One example of the biogeochemical reactions is given as the following (Molins et al. 2014, benchmark level column 2):

```
'intra-aqueous kinetic reactions'
7
'no3-no2-tot'
'no2-n2-tot'
'no3-cr6'
'no2-cr6'
'no3-no2-assim'
'no2-n2-assim'
'c5h7o2n-dec'

'scaling for intra-aqueous kinetic reactions'
4.0d-5      ;'no3-no2-tot'
2.0d-5      ;'no2-n2-tot'
4.7565d-8   ;'no3-cr6'
1.5855d-8   ;'no2-cr6'
4.0d-6      ;'no3-n2-assim'
2.0d-6      ;'no2-n2-assim'
1.250d-7    ;'c5h7o2n-dec'
```

There are seven biogeochemical reactions considered in the calculation. The first six reactions are the microbially mediated reactions (for detailed description the user is referred to Table 1.62 in Section 1.5.21 in the Verification Report). The last reaction represents the biomass decay. The rate constants of the reactions mentioned above are specified in the data block under the keyword 'scaling for intra-aqueous kinetic reactions' (see the description of the benchmark 'Microbially mediated chromium reduction' in Subsection 1.5.21.3 of the Verification Report).

3.3.2.5 'secondary aqueous species'

This sub-block requires the specification of the number and names of secondary aqueous components. Possible choices for secondary aqueous components are defined in the database complex.dbs. The easiest way to find the possible secondary aqueous components is to run a batch simulation with the specified primary components, all possible secondary aqueous components will be listed in file *_o.psp file.

Simulation of isotopes as secondary aqueous species requires that each isotope of a particular secondary species is included in the database and as a secondary aqueous component in the input file. For example, an input file for the simulation of sulfur isotope fractionation may look like this:

```
'secondary aqueous species'
28 ;number of secondary aqueous species
'caoh+'
'cahco3+'
'caco3aq'
'caso4aq'
'ca34so4aq'
'cahso4+'
'cah34so4+'
'feoh+'
'feoh3-1'
'feso4aq'
'fe34so4aq'
'fehso4+'
'feh34so4+'
'fehco3+'
'feco3aq'
'feoh2aq'
'fe (hs) 2aq'
'fe (h34s) 2aq'
'fe (hs) 3-'
'fe (h34s) 3-'
'hco3-'
'h2co3aq'
'hso4-'
'h34so4-'
'h2saq'
'h234saq'
's-2'
'34s-2'
```

The example input block defines a geochemical system with 28 secondary aqueous species including pairs of isotope species of sulfur such as 'caso4aq', 'ca34so4aq', and 'h2saq', 'h234saq'. The species 'caso4aq' and 'h2saq' represent the light ³²S isotopes and 'ca34so4aq' and 'h234saq' represent the heavier ³⁴S isotopes.

3.3.2.6 'minerals'

This sub-block requires the specification of the number and names of minerals. Possible choices for minerals are defined in the database mineral.dbs.

Simulations including isotope bearing minerals require the specification of minerals for each isotope of concern is included in the input file as well as in the database mineral.dbs. For example, The following data block specifies 9 minerals, in which 6 minerals contain sulfur isotopes:

```
'minerals'
9 ;number of minerals (nm)
'ch2o-h2s-m'
'ch2o-34h2s-m'
'calcite'
'siderite(d)'
```

```
'gypsum_iso'
'34gypsum_iso'
'mackinaw_iso'
'34mackinaw_iso'
'dolomite'
```

3.3.2.7 'linear sorption'

This sub-block requires the specification of the number and names of the sorbed species according to the linear sorption model (constant K_d):

$$q = K_d c \quad \text{Equation 3-1}$$

$$R = 1 + \frac{\rho_b}{\theta} K_d = 1 + K_s \quad \text{Equation 3-2}$$

where q is the amount sorbed per weight of solid, c is amount in solution per unit volume of solution; R is the retardation factor, θ is porosity [-], ρ_b is bulk density in [kg L^{-1}]. K_d is usually expressed in [L kg^{-1}] and measured in batch tests or column experiments. K_s is a dimensionless linear sorption coefficient, which is specified in Data Block 14: 'initial condition - reactive transport'.

An example input for two sorbed species ($^{85}\text{Sr}^{2+}$ and $^{60}\text{Co}^{2+}$) obeying linear sorption model:

```
'linear sorption'
2                ; number of sorbed species
'sr_85+2'       ; Names of sorbed species, one in each line
'co_60+2'
```

3.3.2.8 'sorbed species'

This sub-block requires the specification of the number and names of the sorbed species of ion exchange or surface complexation reactions. The related parameters should be provided in Data Block 14: initial condition - reactive transport using the keyword 'sorption parameter input' (see Section 3.20.2.4). If the ion exchange reactions are specified, the CEC (Cation Exchange Capacity) and the dry bulk density of the porous media should be provided. If the surface complexation reactions are specified, the related parameters are: the surface site, its mass, surface area and the site density. An example:

```
'sorbed species'
6
'mg-x (na) '
'na-x (na) '
'k-x (na) '
'zn-x (na) '
'pb-x (na) '
'ca-x (na) '
```

In the example, six ion exchange species are defined, which implies six ion exchange reactions defined in the database file sorption.dbs.

In the following example, five surface complexation species are defined, which implies five surface complexation reactions defined in the database file sorption.dbs. The name and type of the surface are specified under the keyword 'non-aqueous components'.

```
'sorbed species'
5                               ;number of sorbed species
'=feoh2+(s) '                  ;names of sorbed species
'=feo-(s) '
'=feozn+(s) '
'=feopb+(s) '
'=feohca+2(s) '
```

It is important to point out that the keywords 'sorbed species' can be used for surface complexation or ion exchange reactions if only one of them needs to be considered. However, this keywords 'sorbed species' cannot be used for the case when both surface complexation and ion exchange reactions have to be considered simultaneously. To overcome this problem, both keywords 'sorbed species of surface-complex' and 'sorbed species of ion-exchange' have to be defined as described in the following sections.

3.3.2.9 'sorbed species of surface-complex'

This sub-block requires the specification of the number and names of the sorbed species of surface-complexation reactions. It can be separately applied and has the same functionality as the sub-block 'sorbed species' for surface complexation reactions. An example:

```
'sorbed species of surface-complex'
5                               ;number of sorbed species
'=feoh2+(s) '                  ;names of sorbed species
'=feo-(s) '
'=feozn+(s) '
'=feopb+(s) '
'=feohca+2(s) '
```

In the example, five surface complexation species are defined, which implies corresponding five surface complexation reactions are defined in the database file sorption.dbs. The name and type of the surface are specified under the keyword 'non-aqueous components'. The advantage of this sub-block lies in that it can be combined with the sub-block 'sorbed species of ion-exchange' to include both ion exchange and surface complexation reactions simultaneously.

3.3.2.10 'sorbed species of ion-exchange'

This sub-block requires the specification of the number and names of the sorbed species of ion exchange reactions. It can be separately applied and has the same functionality as the sub-block 'sorbed species' for the specification of ion exchange reactions. An example:

```
'sorbed species of ion-exchange'
6
'mg-x (na) '
'na-x (na) '
'k-x (na) '
'zn-x (na) '
'pb-x (na) '
'ca-x (na) '
```

In the example, six ion exchange species are included, which implies the corresponding six ion exchange reactions are defined in the database file sorption.dbs. The advantage of this sub-block over the keywords 'sorbed species' lies in that it can be combined with the sub-block 'sorbed species of surface complex' to include both ion exchange and surface complexation reactions in the simulation.

3.3.2.11 'surface sites of ion-exchange'

This sub-block specifies the number and names of the surface sites of ion exchange reactions when the multisite ion exchange model is applied (Xie et al. 2014b). An example for the usage of the keyword 'surface sites of ion-exchange' is:

```
'surface sites of ion-exchange'
3                ; total number of ion exchange sites
'-FES'          ; names of sites
'-II'
'-PS'
```

In the example, three ion exchange sites are defined: -FES, -II and -PS (Bradbury and Baeyens, 2000). The fraction of each sites should be specified through the keyword 'CEC fraction of multisite ion exchange' (in Data Block 14: initial condition - reactive transport).

3.3.2.12 'database directory'

The geochemical database to be used for the simulation must be specified following the text string 'database directory'. The full or relative path of the database must be entered, e.g.:

```
'database directory'
'd:\min3p\database\default'
```

Important is to make sure that the required database files (such as comp.dbs, complex.dbs, mineral.dbs, sorption.dbs, redox.dbs and gases.dbs) are placed under the provided directory (see Section 4). The 'default' database is based on the databases from MINTEQA2 (Allison et al., 1991) and WATEQ4F (Ball and Nordstrom, 1991).

If the multicomponent diffusion model (MCD) or the hybrid multicomponent diffusion model (hMCD) is used, the diffusion coefficients in free water (D_0) for each primary and secondary species must be provided through the databases (i.e. in the file comp.dbs for primary species, in the file complex.dbs for secondary species).

Below is an example for the modified database entries (D_0 value highlighted in bold) in comp.dbs. Free phase diffusion coefficients must be included at the end of each entry in units of $[m^2 s^{-1}]$:

```
ca+2      2.0      6.00 .17      40.08000      .00 0.792d-9
cd+2      2.0      .00 .00      112.39940      .00 0.719d-9
cl-1      -1.0     3.00 .01      35.45300      .00 2.032d-9
```

This means that the D_0 of the primary species Ca^{2+} is $0.792 \times 10^{-9} m^2 s^{-1}$, D_0 of Cd^{2+} is $0.719 \times 10^{-9} m^2 s^{-1}$ and D_0 of Cl^- is $2.032 \times 10^{-9} m^2 s^{-1}$.

In addition, an example for entering the D_0 value (highlighted in bold) for secondary species in the database is shown below. The diffusion coefficients are included in complex.dbs at the end of the first line of each Data Block:

```
oh-  13.3620  -13.9980  -1.00 3.50 .00 17.0074  1.00 5.273d-9
      2   h2o           1.000 h+1           -1.000
```

This means that the D_0 of the secondary species OH^- is $5.273 \times 10^{-9} m^2 s^{-1}$.

If Pitzer model is required due to the high salinity in the solution, the file Pitzer.xml file is needed.

3.3.2.13 'compute alkalinity'

If desired, the program calculates alkalinity, carbonate and non-carbonate alkalinity and writes the results to the files prefix_x.gsm and prefix_x.gbm. Alkalinity calculations are activated with the command:

```
'compute alkalinity'
```

3.3.2.14 'define input units'

By default, the program assumes that all aqueous component concentrations will be provided in mol L⁻¹ H₂O. Other possible input units are mg L⁻¹, mmol L⁻¹ and g L⁻¹. For example:

```
'define input units'  
'mg/l'
```

This information specifies the unit of aqueous concentrations in mg L⁻¹.

3.3.2.15 'define temperature'

By default, the standard temperature (25°C) is assumed for all geochemical calculations. This implies that if temperature is not explicitly provided. If the environmental temperature is different, it can be specified using 'define temperature' followed by the temperature in °C. For example, the following information specifies 10°C as the environmental temperature:

```
'define temperature'  
10.0
```

3.3.2.16 'define temperature field'

It is also possible to define a depth and time dependent temperature field. This option is activated using the command:

```
'define temperature field'
```

If activated, the program expects that a file with the name prefix.tem exists. This file must follow the format:

N	z ₁	z ₂	...	z _N
	T _{1,1}	T _{1,2}	...	T _{1,N}
	T _{2,1}	T _{2,2}	...	T _{2,N}

	T _{M,1}	T _{M,2}	...	T _{M,N}

where N is the time increments for reading the next temperature, z₁ to z_N, are the depth coordinates of the temperature points, and T_{1,1} to T_{M,N} are the observed temperatures. The program interpolates these temperature values over the spatial solution domain and updates the temperature while advancing in time. Once the last specified input time is reached, the program reverts to the first input time. This allows the simulation of temperature effects on geochemical reactions due to seasonal changes by specifying only one yearly temperature cycle.

3.3.2.17 'define sorption type'

This sub-block defines the sorption type, which is followed by a sub-keyword. Currently, surface

complexation or ion exchange can be considered. By default, ion exchange type 'gaines-thomas' is specified. This indicates if the sorption type is not specified, sorption type will be treated as the type of ion exchange based on the 'gaines-thomas' model. If the sorption type is 'surface-complexation', it can be specified using 'define sorption type' followed by 'surface-complex':

```
'define sorption type'
'surface-complex'
```

Related keywords are: 'non-aqueous components' for specifying the surface name and the 'sorbed species' for the specification of absorbed species.

```
!surface complexation
'non-aqueous components'
1                      ;number of non-aqueous components
'=soh'  'surface'      ;names of non-aqueous components

'sorbed species'
3                      ;number of sorbed species
'=soh2+'               ;names of sorbed species
'=so-'
'=sa'
```

Example for the specification of the geochemical system considering sorption by ion exchange is:

```
! Data Block 2: geochemical system (example ionx)
! -----
!
'geochemical system'

'use new database format'

'database directory'
'..\benchmarks\database\default'

'define input units'
'mg/l'

'components'
6                      ;number of components (nc-1)
'na+1'                 ;component names
'k+1'
'mg+2'
'ca+2'
'cl-1'
'h+1'

'redox couples'
0

'secondary aqueous species'
1                      ;number of secondary aqueous species
'oh-'                 ;names of secondary aqueous species

'sorbed species'
3                      ;number of sorbed species
'na-x(na)'            ;names of sorbed species
'ca-x(na)v'
'mg-x(na)v'

'minerals'
0                      ;number of minerals (nm)

'excluded minerals'
```

0

'done'

Example for the specification of the geochemical system considering sorption by surface complexation is:

```
! Data Block 2: geochemical system
! -----
!
'geochemical system'

'use new database format'

'database directory'
'..\benchmarks\database\surftest'

'define sorption type'
'surface-complex'

'components'
3                               ;number of components (nc-1)
'h+1'                           ;component names
'ha'
'na+1'

'non-aqueous components'
1                               ;number of non-aqueous components
'=soh' 'surface'                ;names of non-aqueous components

'secondary aqueous species'
2                               ;number of secondary aqueous species
'oh-'                           ;names of secondary aqueous species
'a-'

'sorbed species'
3                               ;number of sorbed species
'=soh2+'                         ;names of sorbed species
'=so-'
'=sa'

'done'
```

This example defines a geochemical system including three components (i.e. 'h+1', 'ha', 'na+1'), two secondary species (i.e. 'oh-' and 'a-'), in which 'a-' stands for anions. In addition, it defines also surface complexation with the surface name '=soh' under the keywords 'non-aqueous components'. Three potential surface species (i.e. '=soh2+', '=so-', '=sa') are also included.

3.3.2.18 'combine mineralogical parameters'

If a solid mineral can react with different reactants (e.g. $\text{Fe}^0(\text{s})$ by several oxidants) in the system, this function can combine all related reactions to calculate the total volume fractions of the mineral after joining various reactions. To activate this function, the keyword 'combine mineralogical parameters' should put after the 'minerals' block and be followed by mineral names in the same number and order as those in block 'minerals'. The names of the minerals to be combined should be different in the block 'minerals' for representing different reactions, but should be replaced with the same name in the block 'combine mineralogical parameters' to stand for the common reacting mineral (e.g. $\text{Fe}^0(\text{s})$). The volume fractions (VFs) of all minerals are provided in the initial condition section in the same order as provided in block 'minerals'. The VFs of those minerals to be combined should be assigned with the total VF of the common reacting mineral, i.e. the same amount (see section 3.21.14 example 2). The reaction stoichiometry and reaction constants of all

minerals have to be provided in the database file mineral.dbs.

A sample for minerals input involving 'combine mineralogical parameters' is provided below:

```
'minerals'
12                               ;number of minerals (nm)
'fe_0_h2o_3'
'fe_0_cr'
'fe_0_tce'
'fe_0_cdce'
'fe_0_vc'
'fe_0_so4_2'
'calcite'
'siderite(d)'
'fe(oh)2(s)'
'cr(oh)3(a)'
'mackinawite'
'ferrihydrite'

'combine mineralogical parameters'
'fe_0_h2o_3'
'fe_0_h2o_3'
'fe_0_h2o_3'
'fe_0_h2o_3'
'fe_0_h2o_3'
'fe_0_h2o_3'
'calcite'
'siderite(d)'
'fe(oh)2(s)'
'cr(oh)3(a)'
'mackinawite'
'ferrihydrite'
```

In this example, the first 6 'minerals' defined in the first parts representing six different chemical reactions that the zero valent iron (Fe^0) participates. The first mineral (i.e. 'fe-0_h2o_3') defines the reaction of Fe^0 with water. The other five minerals representing other reactions defined in the mineral.dbs. The first six minerals in the second part are replaced with the same mineral 'fe-0_h2o_3'. Consequently, the total VFs of Fe^0 will be calculated based on the amount at the initial or previous time step plus the total change owing to the first six reactions during the current time step.

3.3.2.19 'use pitzer model'

This sub-keyword defines the activity correction of the aqueous species according to the HMW Pitzer model (Harvie et al., 1984; Bea et al., 2010). In such case, the corresponding database pitzer.xml should be provided.

3.3.2.20 'use macinnes convention'

This sub-keyword should be only used if the Pitzer model is activated. Through this sub-keyword, all individual-ion activity coefficients are scaled according to the MacInnes (1919) convention.

A sample for minerals input involving 'use pitzer model' and 'use macinnes convention' is provided below:

```
! Data Block 2: geochemical system
! -----
!
'geochemical system'

'use pitzer model'
```

```
'use macinnes convention'

'use new database format'

'database directory'
'database\default'
... ..
```

3.3.3 EXAMPLE DATA FILE INPUT

The specification of the geochemical system is provided in the data block 2. Typical input format is shown in the following examples:

Example 1: Geochemical system including 9 aqueous components, redox reactions and intra-aqueous kinetic reaction and mineral dissolution and precipitations:

```
! -----
'geochemical system'

'components'
9                               ;number of components (nc-1)
'ca+2'                          ;component names
'co3-2'
'h+1'
'fe+2'
'fe+3'
'so4-2'
'hs-1'
'o2(aq)'
'ch2o'

'redox couples'
1                               ;number of redox couples
'fe+2' 'fe+3'                  ;names of redox couples

'secondary aqueous species'
26                              ;number of secondary aqueous species
'oh-'                          ;names of secondary aqueous species
'caoh+'
'cahco3+'
'caco3aq'
'caso4aq'
'cahso4+'
'feoh+'
'feoh3-1'
'feso4aq'
'fehso4+'
'fehco3+'
'feco3aq'
'feoh2aq'
'fe (hs) 2aq'
'fe (hs) 3-'
'feoh+2'
'feso4+'
'fehso42+'
'feoh2+'
'feoh3aq'
'feoh4-'
'fe (so4) 2-'
'hco3-'
'h2co3aq'
'hso4-'
'h2saq'

'gases'
2                               ;number of gases
```

```

'o2(g) '           ;names of gases
'co2(g) '

'minerals'
5                 ;number of minerals
'pyrite'         ;mineral names
'calcite'
'ferrihydrite'
'siderite'
'gypsum'

'excluded minerals'
2
'goethite'
'aragonite'

'intra-aqueous kinetic reactions'
1                 ;number of intra-aqueous reactions
'so4-reduction' ;names of intra-aqueous reactions

'database directory'
'd:\min3p\database\wall2'

'define temperature'
10.0

'done'

```

Example 2: To include reactions with microbial growth and decay, 'biomass components' must be added to data block 2.

```

'components'
12                ;number of components
'h+1'            ;component names
'na+1'
'ca+2'
'cl-1'
'co3-2'
'ch3coo-'
'no3-1'
'no2-1'
'n2(aq)'
'nh4+1'
'cro4-2'
'cr(oh)2+'

'biomass components'
2                 ;number of biomass components
'c5h7o2n'        ;biomass component names
'c5h7o2n(d)'

```

3.3.4 DESCRIPTION OF EXAMPLE INPUT

The first example input includes 9 components. The Fe(II)/Fe(III) redox couple is assumed to be at equilibrium. The problem also includes 26 secondary aqueous species, 2 gases, and 5 minerals. The saturation indices of 2 additional minerals will be calculated. Sulfate reduction is specified to be a kinetically controlled reaction. The location of the database to be used, wall2, has been specified. The temperature has been specified as 10 degrees Celsius.

The second example input includes 12 components. In addition, two biomass components are defined: the active biomass 'c5h7o2n' and the inactive (dead) biomass 'c5h7o2n(d)'.

3.3.5 ADDITIONAL COMMENTS

3.3.5.1 Choosing aqueous species

It is possible to determine all the possible species for a given set of components by conducting a preliminary simulation with only the components specified. The program will generate a file (prefix_o.psp, where 'psp' stands for 'possible species') containing the names of species and reactions, which can be specified. The desired species and reactions can be copied from this file into the problem-specific input file.

3.3.5.2 Redox notes

If redox couples are specified, it is necessary to include 'o2(aq)' as a component, since this species is used as the redox master variable.

3.3.5.3 Adding additional species

If necessary, additional geochemical reactions can be specified in the database files (see Section 4). This is particularly useful for kinetically-controlled reactions. **HOWEVER, THE DEFAULT DATABASE SHOULD NEVER BE MODIFIED.** Additions or changes should be done in a copy of the default database. See Section 4 (Modifying Database, Specifying Kinetically Controlled Reactions)

3.4 SPATIAL DISCRETIZATION (DATA BLOCK 3)

3.4.1 DESCRIPTION OF DATA BLOCK

In this data block the dimensions of the simulation are specified (1D, 2D or 3D) and the geometry of the domain in Cartesian and cylindrical coordinates is defined. The spatial discretization of the model is based on a control volume (block centered finite difference) method, and the domain must be regular (column, rectangle, or 3D block). However, the grid spacing can be varied in all three directions. The model uses half-cells on the boundaries, which means that the grid coordinates will correspond to the actual size of the solution domain.

3.4.2 DESCRIPTION OF INPUT PARAMETERS

3.4.2.1 'spatial discretization'

The data block for spatial discretization can be divided into sub-blocks; the first section specifies the parameters for the x-direction, while the second and third sub-blocks specify the parameters for the y- and z-directions, respectively. Within each sub-block, the first line is used to specify the number of discretization intervals or zones in that direction. If the spacing is to be uniform this value will be "1". For example, setting this value to "3" will yield three discretization zones. Within each of these zones, the grid spacing will be uniform; however the spacing may differ between zones. The discretization within each zone is specified by a series of data file entries indicating the number of cells (control volumes) within the interval followed by the spatial coordinates indicating the start and end locations for that interval (in meters).

It is necessary to specify values for all three dimensions, even for 1D- and 2D-simulations. The default values to specify are a "1" for number of zones and number of cells (control volumes) and 0.0 and 1.0 for min and max values, respectively. Orientation of your particular problem within the

x-y-z coordinate system is flexible. However, when modeling variably-saturated flow, the vertical direction must be oriented in the z direction.

3.4.2.2 'radial coordinates'

MIN3P-THCm is valid for Cartesian (default) as well as radial/cylindrical coordinate. It is very easy to specify the spatial discretization in radial coordinates – simply adding the keyword 'radial coordinates' (highlighted in bold in the second example below) in Data Block 3: spatial discretization, which is described in the previous subsection. Using this keyword, the first coordinate (i.e. the x-coordinate of the Cartesian system) is considered to be the radial coordinate r. The second coordinate is not discretized if the radial coordinate option is activated. If the z-coordinate is discretized, a cylindrical coordinate system is specified.

3.4.3 EXAMPLE DATA FILE INPUT

An example for a two-dimensional Cartesian coordinate discretization (x-z-plane) is:

```
! -----
'spatial discretization'
3                ;number of discretization intervals in x

20              ;number of control volumes in x
0. 4.0         ;xmin,xmax

40              ;number of control volumes in x
4.0 10.0       ;xmin,xmax

40              ;number of control volumes in x
10.0 20.0     ;xmin,xmax

! -----
1                ;number of discretization intervals in y

1                ;number of control volumes in y
0. 1.0         ;ymin,ymax

! -----
1                ;number of discretization intervals in z

20              ;number of control volumes in z
0. 4.          ;zmin,zmax

'done'
```

An example for a one-dimensional radial coordinate discretization is:

```
! Data Block 3: spatial discretization
! -----
!
'spatial discretization'
1                ;number of discretization intervals in r
1000            ;number of control volumes in interval r
0.0000E+00  0.1000E+04 ;rmin, rmax
1                ;number of discretization intervals in y
1                ;number of control volumes in interval
0. 1.0         ;ymin,ymax
1                ;number of discretization intervals in z
1                ;number of control volumes in interval
0. 1.0         ;zmin,zmax

'radial coordinates'
```

'done'

3.4.4 DESCRIPTION OF EXAMPLE INPUT

The first example input file is for a 2D-simulation in the x-z plane in Cartesian coordinate and default values have been specified for the y-axis. The total distance in the x-direction is 20 m and the total distance in the z direction is 4 m. The domain in x direction is divided into three intervals. The first interval extends from 0 to 4 m and contains 20 cells (each 0.2 m in length). The second interval extends from 4 to 10 m and contains 40 cells (each 0.15 m in length) and the third interval extends from 10 to 20 m and contains 40 cells (each 0.25 m in length). The discretization in z-direction is uniform from 0 to 4 m and contains 20 cells (each 0.2 m in length).

The second example input file is for a 1D-simulation in radial direction. In comparison to the first example, the specification of the spatial data is the same except the additional inclusion of the keyword 'radial coordinates', which enable the code to treat the first coordinate as radial coordinate.

3.4.5 ADDITIONAL NOTES

The decision of how many zones and what degree of discretization is required will be governed by the following factors:

Required Resolution: The spatial resolution should be capable of resolving the spatial scale of the governing physical and chemical processes.

Site specific considerations: The coordinates specified in this section are consistent with the location of the boundaries defining the zones. If, for example, a rock with a different composition is to be specified, it is of advantage to specify this zone already when defining the spatial discretization. This allows defining exactly the areal extent of the various mineral assemblages.

Computation Limitations: The degree of discretization will be limited by the amount of memory the computer has available.

Half cells at the boundaries: By default, the control volumes (cells) at the boundaries are in half size in comparison to the internal cells. In such case, the centroid points of the cells at the boundaries locate exact on the boundaries, which make it easy for the boundary condition assignment and plotting of the simulated results especially on the boundaries. Alternatively, use the keyword 'full cells' in this Data Block, no half cells will be used.

3.5 TIME STEP CONTROL (DATA BLOCK 4)

3.5.1 DESCRIPTION OF DATA BLOCK

This data block controls the time steps and the final solution time. This data block is required for transient flow simulations and all reactive transport simulations. The units for the output can be specified in years, days, hours, or seconds.

The code includes an adaptive time stepping scheme, which only requires the specification of a minimum time step and a maximum time step. The minimum time step is used initially and the time step will increase to maximize efficiency. If difficulties are encountered during a simulation, the time step may decrease and, therefore, a very small minimum time step should be chosen to avoid failure of program execution. The maximum time step may affect the accuracy of the model

results. Very large time steps may lead to extensive numerical dispersion. However, many reactive transport problems, where mineral dissolution precipitation reactions control the geochemical evolution of the system allow very large time steps. Since the model is based on a fully-implicit method, there is practically no limit for the maximum time step size.

3.5.2 DESCRIPTION OF INPUT PARAMETERS

3.5.2.1 'time step control - global system'

Five parameters must be specified in this data block. They are tabulated below.

Table 3.6: Summary of input parameters for data block 'time step control – global system'

Parameter	Description
time unit	Possible units: 'years', 'days', 'hours', or 'seconds'
start time	generally set to '0.0'
final solution time	generally the length of time of the simulation
maximum time step	Specifies the maximum # of time steps
minimum time step	Specifies the minimum # of time steps

The maximum and minimum time step parameters constrain the range of time steps that will be used by the code to solve the transient flow or reactive transport solution. The values selected for the minimum time step must be sufficiently small to insure that sufficient convergence occurs. This is particularly important at the beginning of the simulation. The value selected for the maximum time step may control the length of time required for a solution to be reached; increasing this value may result in a shorter run time.

3.5.3 EXAMPLE DATA FILE INPUT

Example: time step specification

```
! -----
'time step control - global system'

'days'                ;time unit
0.0                   ;time at start of solution
1095.0                ;final solution time
10.0                  ;maximum time step
1.0d-8                ;minimum time step

'done'
```

3.5.3.1 Description of Example Input

The example input defines a simulation time of 1095 days with a maximum time increment of 10 days and a starting time step of 10^{-8} days.

3.5.3.2 Additional Comments

Note that all physical and chemical input parameters such as hydraulic conductivities, diffusion coefficients, boundary fluxes, etc. are to be specified in time units of seconds independent of the

time unit specified for the time step control. The chosen time unit will only affect the output times to be specified in section 4.8. This was done to allow the user to specify the simulation time and the output times on a meaningful time scale.

3.6 CONTROL PARAMETERS–LOCAL CHEMISTRY (DATA BLOCK 5)

3.6.1 DESCRIPTION OF DATA BLOCK

In this section, numerical and chemical parameters affecting the batch chemistry calculations are defined. The entire section is optional, default values are specified for all parameters in the code. Modify this section only if you are interested in enhancing the model performance, or if convergence problems occur.

3.6.2 DESCRIPTION OF INPUT PARAMETERS

3.6.2.1 'control parameters - local geochemistry'

This data block is composed of 4 sub-blocks described below.

3.6.2.2 'newton iteration settings'

In this sub-block an increment for numerical differentiation and the convergence tolerance can be specified. The increment for numerical differentiation is used to calculate numerical derivatives according to the formula

$$\frac{\partial F(C_j^c)}{\partial C_j^c} = \frac{F(C_j^c + \zeta_j) - F(C_j^c)}{\zeta_j} \quad \text{Equation 3-3}$$

where ζ_j is the increment for numerical differentiation for component A_j^c , which is defined relative to the species concentration:

$$\zeta_j = \xi C_j^c \quad \text{Equation 3-4}$$

The value specified in the input file corresponds to ξ . The convergence tolerance defines the accuracy of the concentrations calculated during local geochemical calculations (batch, boundary or initial conditions). A solution is considered converged if the logarithm of all concentration updates in the solution domain is smaller than the convergence tolerance ε :

$$\Delta \ln C_{j,act}^c = \varepsilon \quad \text{Equation 3-5}$$

3.6.2.3 'output time unit'

This sub-block can be used to specify the time unit for the output of transient evolution of the system if local geochemical calculations involve kinetic reactions.

3.6.2.4 'maximum ionic strength'

This sub-block specifies the maximum ionic strength of the solution. During convergence, it is possible that unrealistic values for ionic strength will be calculated. To avoid potential convergence problems an upper limit for the maximum ionic strength can be defined.

3.6.2.5 'minimum activity for h2o'

This sub-block is used to specify a minimum activity for water. This approach has been adopted from the geochemical equilibrium model MINTEQA2 (Allison et al., 1991).

3.6.2.6 'redox reactions'

This sub-block is used to specify redox reaction type. It is currently specified for equilibrium redox reactions only.

3.6.2.7 'finite minerals'

This sub-block is used to specify finite mineral. If it is true, the amount of minerals is limited. Otherwise, the amount of minerals is unlimited.

3.6.2.8 'activity update settings'

This sub-block is used to define update technique for activity coefficients for local chemistry. Currently, two options are available: 'no_update' – unity activity coefficient; 'double_update' – update activity coefficients during Newton iterations for the local chemical reaction calculations.

3.6.2.9 'define minimum reaction rate'

This sub-block is used to define minimum reaction rate of minerals for local chemical reaction calculations. The parameter cannot be zero. Default value in the code is 1e-300.

3.6.2.10 'sparse block matrices' and 'dense block matrices'

This keywords are used to define the type of matrices as sparse block matrices, which is also the default value for most geochemical processes except for multicomponent diffusion. Otherwise, the keyword 'dense block matrices' should be specified.

Default values, possible settings and recommended ranges for these parameters are defined in Table 3.7:

Table 3.7: Summary of input parameters for data block 'control parameters – local chemistry'

Sub-block	Parameter	Default value	Possible parameter settings	Recommended range
'newton iteration settings'	increment for numerical differentiation	10 ⁻⁴	-	10 ⁻⁸ -10 ⁻⁴
	convergence tolerance	10 ⁻⁶	-	10 ⁻⁸ -10 ⁻⁴
'output time unit'	time unit	'days'	'seconds' 'hours' 'days' 'years'	-

'maximum ionic strength'	value for ionic strength	2.0	-	>1
'minimum activity for h2o'	value for activity of H ₂ O	0.5	-	<0.75
'redox reactions'	logic	.true.	'true.'	-
'finite minerals'	logic	.true.	'true.' or '.false.'	-
'activity update settings'	Type of activity updating	-	'no_update', 'double_update'	-
'define minimum reaction rate'	Minimum reaction rate	1.0e-300	-	<1e-10, >0.0
'sparse block matrices'	-			
'dense block matrices'	-			

3.6.3 EXAMPLE DATA FILE INPUT

An example of the control parameters for local geochemistry:

```
! -----
'control parameters - local geochemistry'

'newton iteration settings'
1.d-4                ;factor for numerical differentiation
1.d-6                ;convergence tolerance

'output time unit'
'days'              ;time unit (local chemistry)

'maximum ionic strength'
1.0d0               ;max. ionic strength

'minimum activity for h2o'
0.5d0               ;min. activity for h2o

'done'
```

3.6.3.1 Additional Comments

Setting the numerical parameters in the sub-block 'newton iteration settings' to values outside the recommended ranges may lead to erroneous results or convergence failure. For calculations involving solutions with high ionic strength, the user should make sure that the settings for maximum ionic strength and minimum activity for H₂O do not affect the activity calculations.

3.7 CONTROL PARAMETERS – VARIABLY-SATURATED FLOW (DATA BLOCK 6)

3.7.1 DESCRIPTION OF DATA BLOCK

In this data block, numerical and control parameters affecting the flow calculations are defined.

This entire section is optional, default values are specified for all parameters in the code. This section can be invoked to enhance the model performance, or if convergence problems occur.

3.7.2 DESCRIPTION OF INPUT PARAMETERS

3.7.2.1 'control parameters - variably-saturated flow'

The sub-blocks for this data block are described below, and are also summarized in Table 3.8 together with the corresponding default settings, possible parameter settings and the recommended range for the parameters.

3.7.2.2 'mass balance'

If the text string 'mass balance' is included, the model will perform mass balance calculations including contributions of storage and fluxes across the domain boundary. Total system mass, mass balance contributions as change per time unit and as cumulative changes are reported in the files prefix_o.mvs and prefix_o.mvc. Mass balance errors are documented in the file and prefix_o.mve. Additional information about the content of these files can be found in the file prefix_o.flr, which is created at run-time.

3.7.2.3 'variable density parameters'

If the text string 'density dependent flow' is included in the input file under 'global control parameters', the model will perform density-driven flow. The related parameters are provided under the keywords 'variable density parameters'. An example is provided below:

```
'variable density parameters'
1.0d3           ;ref_dens, reference density, [kg m-3]
0.0            ;dro/dc, Coefficient of density variation, [-]
4              ;maxit_sia, maximum number of Picard iterations, [-]
2              ;iter_target, target number of Picard iterations, [-]
0.1           ;tol_sia, Picard iteration convergence tolerance, [-]
0.1           ;courant, target courant number, [-]
```

The example input file specifies the density dependent flow and Picard iteration parameters. These parameters include the reference solution density in kg m⁻³, the coefficient of the solution density dependence on the total dissolved solids in [-], the maximum and target number of Picard iterations, Picard iteration convergence tolerance, and the target courant number.

3.7.2.4 'input units for boundary and initial conditions'

This sub-block controls the input units for the flow problem. The default unit is 'hydraulic head' in [m], as an alternative 'pressure head' (input unit also in [m] but will be internally converted into [Pa] for the calculation) can be specified using the keyword 'input units for boundary and initial conditions'. The program expects that initial and first type boundary conditions in Section 12 ('initial condition – variably-saturated flow') and Section 13 ('boundary conditions – variably-saturated flow') are specified in consistent units. For example, if 'pressure head' is specified, the media hydraulic conductivity uses the unit for permeability [m²] as described in the following subsection. An example:

```
! Data Block 6: control parameters - variably saturated flow
! -----
!
!control parameters - variably saturated flow'
```

```

'mass balance'

'density model'
'pitzer'

'update porosity'
1.0d-6          ! Factor for minimum porosity

'iterative solver'

'variable density parameters'
1000.0d0        ;freshwater density g/L
0.688d0         ;linear density coefficient d(rho)/d(TDS)
8               ;max # Picard flow-RT iterations
5               ;Picard iteration target (# iterations)
0.1d0          ;maximum density update: Picard convergence g/L
1.0d50         ;Courant criteria target

'newton iteration settings'
1.0d-4         ;increment for numerical differentiation
100            ;max. number of newton iterations
1.0d-6         ;convergence tolerance
1.0d0         ;sw_star

'input units for boundary and initial conditions'
'hydraulic head'      ;input unit

'input units for media permeability'
'hydraulic conductivity'

'solver settings'
3               ;level_vs, incomplete factorization level
100            ;msolvit_vs, max. number of solver iterations
0              ;idetail_vs, solver information level
1.0d-10        ;restol_vs, solver residual tolerance
1.0d-10        ;deltol_vs, solver update tolerance

'done'

```

The example input specifies the units to be [m] for pressure head and [m²] for hydraulic conductivity.

3.7.2.5 ‘input units for media permeability’

This sub-block controls the input units for the media permeability. The default unit is [m s⁻¹] for ‘hydraulic conductivity’, as an alternative the unit [m²] for ‘permeability’ can be specified (see the example in the previous subsection).

3.7.2.6 ‘centered weighting’

For variably-saturated flow problems, upstream weighting of the relative permeability term leads to a more efficient solution with little loss of accuracy [Forsyth et al., 1995]. Therefore, upstream weighting is used for the relative permeability term of the unsaturated flow equation by default. If the text string ‘centered weighting’ is specified, centered spatial weighting will be used instead. This setting will have an effect only if partially-saturated conditions exist in the solution domain. In the case of upstream weighting, the relative permeability ($k_{ra,kl}$) between the centroids of the control volumes k and l are assigned according to:

$$k_{ra,kl} = k_{ra,k} \quad \text{if } h_k \geq h_l \quad \text{Equation 3-6}$$

$$k_{ra,kl} = k_{ra,l} \quad \text{if } h_k < h_l \quad \text{Equation 3-7}$$

In which, $k_{ra,k}$ and $k_{ra,l}$ refer to the relative permeabilities of the k^{th} and l^{th} control volumes, respectively. The h_k and h_l are the hydraulic heads in the k^{th} and l^{th} control volumes, respectively. For centered weighting, the relative permeability are calculated according to:

$$k_{ra,kl} = \frac{k_{ra,k} + k_{ra,l}}{2} \quad \text{Equation 3-8}$$

3.7.2.7 ‘compute underrelaxation factor’

This sub-block invokes an automatic computation of under-relaxation factors for the solution of the variably-saturated flow problem [modified from Cooley, 1983 and Therrien and Sudicky, 1996]. The value below this subsection heading defines the maximum tolerable update for hydraulic head in [m]. If the computed update after application of the under-relaxation factor is larger than the maximum specified update, the update is locally set to the specified maximum update. This approach ensures that intermediate computed hydraulic head values remain in a physically reasonable range, which enhances convergence.

3.7.2.8 ‘newton iteration settings’

This sub-block allows the specification of a number of parameters affecting the Newton-Raphson iteration loop. The first parameter identifies the increment used for the construction of the numerical derivatives:

$$\frac{\partial F(h)}{\partial h} = \frac{F(h + \xi) - F(h)}{\xi} \quad \text{Equation 3-9}$$

where h is hydraulic head and ξ is the increment for numerical differentiation. The following parameter identifies the maximum number of Newton iterations to be performed, before a solution is considered non-convergent. For transient flow simulations, the time step is repeated with a reduced time increment, if the number of iterations exceeds the maximum number of iterations. In the steady state case, the simulation is terminated and reported non-convergent. The next parameter specifies the convergence tolerance. A solution is considered converged if all updates for hydraulic head in the solution domain are smaller than the convergence tolerance ε :

$$h\Delta_{max} < \varepsilon \quad \text{Equation 3-10}$$

The model also includes an adaptive time stepping scheme modified after Forsyth and Sammon [1986] and Therrien and Sudicky [1996], which uses the changes in aqueous phase saturation to determine the anticipated time increment. The anticipated saturation change per time step is the last parameter specified in this subsection.

3.7.2.9 ‘solver settings’

This sub-block allows the user to specify parameters affecting the efficiency of the sparse iterative matrix solver WATSOLV (VanderKwaak et al., 1997). The incomplete factorization level defines the quality of the preconditioner matrix. The level of preconditioning is set to 0 by default. For

difficult problems a higher level of preconditioning may be required to ensure convergence, this will also require more computer memory and increase the computational effort per solver iteration. The next parameter defines the maximum number of solver iterations. If the maximum number of solver iterations is exceeded, the solver (inner) iteration is considered non-convergent. If a transient simulation is conducted, the time step will be repeated with a decreased time increment. For a steady-state solution, the simulation will be terminated and reported non-convergent. In this case, it will be necessary to either increase the maximum number of iterations or the factorization level (improve quality of solution procedure), or to decrease the maximum allowed update (decrease difficulty of problem). The solver information level specifies how much information will be written to the file prefix.log and to the screen. Three different levels are available:

- 0 no information
- 1 information on outer iteration (Newton iteration)
- 2 information on outer and inner iteration (Newton and solver iteration)

By default, the information level is set to 1. The next two parameters define the solver residual tolerance and the solver update tolerance. These parameters must be set to values smaller than the convergence tolerance of the Newton iteration (commonly one order of magnitude smaller).

The solver package WATSOLV (VanderKwaak et al., 1997) includes different types of ordering schemes for the matrix equations in compressed format (RCM=Reverse Cuthill McKee-ordering and natural ordering). By default, RCM-ordering is used. If the text string 'natural ordering' is included, natural ordering is used instead.

Table 3.8: Summary of input parameters for section 'control parameters – variably-saturated flow'

Sub-block	Parameter	Default value	Possible parameter settings	Recommended range
'mass balance'	-	-	-	-
'input units for initial and boundary conditions'	input unit	'hydraulic head'	'hydraulic head' 'pressure head'	-
'centered weighting' ¹⁾	-	-	-	-
'compute underrelaxation factor' ¹⁾	maximum update [m]	10.0	-	0.1-100.0
'newton iteration settings'	increment for numerical differentiation [m]	10 ⁻⁴	-	10 ⁻⁶ -10 ⁻⁴
	maximum number of newton iterations	15	-	10-30
	convergence tolerance	10 ⁻⁶	-	10 ⁻⁷ -10 ⁻⁴
	anticipated saturation change per time step [#]	0.1	-	0.1-0.3
'solver settings'	incomplete factorization level	0	-	0-2
	maximum number of solver iterations	100	-	100-1000

	solver information level	1	0,1,2	-
	solver residual tolerance [m]	10^{-7}	-	10^{-8} - 10^{-5}
	solver update tolerance [m]	10^{-7}	-	10^{-8} - 10^{-5}
'natural ordering'	-	-	-	-

- only applicable under variably-saturated conditions

3.7.3 EXAMPLE DATA FILE INPUT

An example is:

```
! -----
'control parameters - variably-saturated flow'

'mass balance'                ;compute mass balance

'input units for boundary and initial conditions'
'hydraulic head'              ;input unit

'centered weighting'          ;use centered weighting

'compute underrelaxation factor'
100.0                          ;max. allowed update

'newton iteration settings'
1.0d-6                          ;increment for numerical differentiation
80                              ;max. number of newton iterations
1.0d-4                          ;convergence tolerance
0.3                             ;sw_star

'solver settings'
0                               ;incomplete factorization level
100                             ;max. number of solver iterations
0                               ;solver information level
1.0d-7                          ;solver residual tolerance
1.0d-7                          ;solver update tolerance

'natural ordering'            ;use natural ordering in solver

'done'
```

3.7.4 DESCRIPTION OF EXAMPLE INPUT

In the example input section, mass balance calculations are performed, hydraulic head is used as input unit for initial and boundary conditions; centered weighting is used for the relative permeability. Automatic underrelaxation factor computation for variably-saturated flow is enabled with a maximum tolerable update of 100 m. The increment for numerical differentiation is set to 10^{-6} m, the maximum number of Newton iterations is set to 80, the convergence tolerance is set to 10^{-4} m, and the anticipated change of saturation per time step is 0.3. The incomplete factorization level is set to the default value 0; the number of solver iterations is restricted to 100. The solver information level is set to 0. Values for solver residual tolerance and solver update tolerance are set to 10^{-7} . The solver uses a natural ordering scheme for the preconditioner matrix.

3.8 CONTROL PARAMETER – ENERGY BALANCE

3.8.1 DESCRIPTION OF DATA BLOCK

In this section, numerical and control parameters affecting the energy balance (heat transport calculations) are defined using the header 'control parameters - energy balance'.

3.8.2 DESCRIPTION OF INPUT PARAMETERS

3.8.2.1 'energy balance'

The sub-keyword 'energy balance' should be given if energy balance must be calculated.

3.8.2.2 'update viscosity'

If the sub-block 'update viscosity' is specified, the viscosity of the aqueous phase (μ_a) depending on the temperature will be considered. Two empirical viscosity models are available: Diersch model and sutra model. The Diersch model is computed as (e.g. see Lever and Jackson, 1985; Diersch and Kolditz, 2002):

$$\mu_a = \mu_f f_T^\mu f_C^\mu \quad \text{Equation 3-11}$$

$$f_T^\mu = \frac{1 + 0.7063\sigma_f - 0.04832\sigma_f^3}{1 + 0.7063\sigma - 0.04832\sigma^3} \quad \text{Equation 3-12}$$

Where μ_f represents the reference viscosity, and $\sigma = (T - 150)/100$, with temperature T provided in units of °C. Alternatively, the viscosity-temperature dependence (f_T^μ) can be computed based on the expression presented by Voss and Provost (2008):

$$f_T^\mu = \frac{10^{\left(\frac{24837}{T+13315}\right)}}{10^{\left(\frac{24837}{T_f+13315}\right)}} \quad \text{Equation 3-13}$$

where T_f is the reference temperature. This model is used in the code SUTRA and thus called here the sutra model.

To specify the model, the sub-keyword 'viscosity model' should be provided followed by the name of the model: 'sutra' or 'diersch'.

3.8.2.3 'spatial weighting'

Three different spatial weighting schemes can be used to describe heat transport, which is the same as those used for reactive transport (see Section 3.10.2.2).

3.8.2.4 'compute evaporation'

The sub-keyword 'compute evaporation' activates the evaporation calculation. This function is only applicable in unsaturated condition and energy balance calculation (see Bea et al. 2012). It is to note that additional parameters should be provided in a separate data block under the header 'control parameters - evaporation' (see section 3.9).

3.8.2.5 'reference tds'

The sub-keyword 'reference tds' specifies the reference **total dry substance** in the solution. This parameter is used to calculate the reference solute mass fraction during the viscosity updating (Equation 3-11) owing to the solute concentration according to (e.g. see Lever and Jackson, 1985; Diersch and Kolditz, 2002):

$$f_c^\mu = \frac{1 + 1.85\omega - 4.1\omega^2 + 44.5\omega^3}{1 + 1.85\omega_f - 4.1\omega_f^2 + 44.5\omega_f^3} \quad \text{Equation 3-14}$$

where ω and ω_f are the solute mass fractions in the fluid for the actual and reference viscosities, respectively. ω_f is calculated as the ratio of the reference total dry substance and the reference density of the solution. The unit of the reference TDS is [kg m⁻³ solution].

3.8.2.6 'reference temperature for density'

The sub-keyword 'reference temperature for density' specifies the reference temperature for the density and viscosity calculations.

3.8.2.7 'energy balance parameters'

The sub-keyword 'energy balance parameters' specifies the linear density – temperature dependence coefficient ($d\rho/dT$). The dependence of density on temperature, $\Delta\rho_T$ can be computed using linear relationship as:

$$\Delta\rho_T \approx \frac{\partial\rho}{\partial T} \Delta T \quad \text{Equation 3-15}$$

3.8.2.8 'non-linear density'

The sub-keyword 'non-linear density' specifies the non-linear density – temperature dependence coefficient ($d\rho/dT$) calculated according to Equation 3-5 and the empirical relationship provided by Yusa and Oishi (1989):

$$\frac{\partial\rho}{\partial T} = -4.8434 + 2.1814 \times 10^{-2} T - 2.9540 \times 10^{-5} T^2 \quad \text{Equation 3-16}$$

In which, T is temperature in Kelvin. The relation is valid for 373.15K < T < 593.15K.

3.8.2.9 'thermal conductivity model'

The sub-keyword 'thermal conductivity model' specifies the thermal conductivity models. Currently, there are five models implemented in MIN3P-THCm. 'model 1' is for saturated porous media and calculated:

$$\lambda = \phi\lambda_a + (1 - \phi)\lambda_s \quad \text{Equation 3-17}$$

In which ϕ is the porosity, λ_a is the thermal conductivity of the aqueous phase, and λ_s is the thermal conductivity of the solid phase.

'model 2' is based on an empirical equation as a function of water saturation (S_a) (Bea et al., 2012; Chung and Horton, 1987; Sakai et al., 2009):

$$\lambda = b_1 + b_2\phi S_a + b_3\sqrt{\phi S_a} \quad \text{Equation 3-18}$$

In which, values of 0.228, -2.406, and 4.909 W m⁻¹ °C⁻¹ are currently implemented for the variables b_1 , b_2 , and b_3 , respectively (Bea et al., 2012).

'model 3' is for unsaturated porous media and calculated as:

$$\lambda = \lambda_s^{1-\phi} \lambda_a^\phi \sqrt{S_a} + \lambda_s^{1-\phi} \lambda_g^\phi \sqrt{1 - S_a} \quad \text{Equation 3-19}$$

where λ_g is the thermal conductivity of the gas.

'model 4' is calculated as:

$$\lambda = \left(\lambda_s^{1-\phi} \lambda_a^\phi\right)^{S_a} + \left(\lambda_s^{1-\phi} \lambda_g^\phi\right)^{1-S_a} \quad \text{Equation 3-20}$$

'model 5' is calculated as:

$$\lambda = [\lambda_s(1 - \phi)^n + \lambda_a\phi^n]^{S_a} [\lambda_s(1 - \phi)^n + \lambda_g\phi^n]^{1-S_a} \quad \text{Equation 3-21}$$

where n is a coefficient that should be provided in the MIN3P-THCm input file following 'model 5'.

3.8.2.10 'newton iteration settings'

This sub-block defines the parameters affecting the Newton iteration. Similar to the definitions for the reactive transport, the parameters are used to specify the settings of the Newton iteration for heat transport (see section 3.9.2.9).

3.8.2.11 'solver settings'

The solver package WATSOLV (VanderKwaak et al., 1997) is also used for the solution of the heat transport problem. The settings defined in the sub-block 'solver settings' are therefore equivalent to the one for the variably-saturated flow problem as described in the section 3.7.2.9.

All other parameters are listed in Table 3.9 with the corresponding default settings, possible parameter settings and the recommended range for the parameters.

3.8.3 DATA FILE INPUT

Two examples were provided to demonstrate the functions. The first example is:

```

! -----
'control parameters - energy balance'

'update viscosity'

'viscosity model'
'sutra'

'reference tds'
0.0d0

'spatial weighting'
'centered'

'gravity constant'
9.81d0

'non-storage term in flow equation'

'reference temperature for density'
20.0d0

'energy balance parameters'
-0.375d0          ;linear density coefficient d(rho)/d(T)

'newton iteration settings'
1.0d-4            ;increment for numerical differentiation
30               ;max. number of newton iterations
1.0d-7           ;convergence tolerance
5.0d0            ;maximum log cycles update

'solver settings'
1                ;level_vs, incomplete factorization level
100             ;msolvit_vs, max. number of solver iterations
0               ;idetail_vs, solver information level
1.0d-10         ;restol_vs, solver residual tolerance
1.0d-10         ;deltol_vs, solver update tolerance

'done'

```

The second example provides the input option of evaporation:

```

! Data Block 6B: control parameters - energy balance
! -----
!
'control parameters - energy balance'

'energy balance'

'upstream factor for heat equation'
1.0d0

'thermal conductivity model'
'model 2'
1.0d0

'compute evaporation'

'reference temperature for density'
25.0d0

'energy balance parameters'
0.0          ;linear density coefficient d(rho)/d(T)

'newton iteration settings'
1.0d-3       ;increment for numerical differentiation
100         ;max. number of newton iterations
1.0d-6      ;convergence tolerance

```

```

15.0d0                ;maximum log cycles update

'solver settings'
0                    ;level_vs, incomplete factorization level
100                 ;msolvit_vs, max. number of solver iterations
0                  ;idetail_vs, solver information level
1.0d-10            ;restol_vs, solver residual tolerance
1.0d-10            ;deltol_vs, solver update tolerance

'done'
! -----

```

3.8.4 DESCRIPTION OF EXAMPLE INPUT

In the first example, energy balance calculation is performed. The code uses centered weighting for heat transport in the aqueous phase. The Sutra viscosity – temperature dependence model is applied to update the dynamic viscosity of the aqueous phase. The reference total dry substance was set to 0.0, means that the viscosity change due to solute in the solution is neglected. No storage term is considered in the flow calculation. The reference temperature for density is 20.0°C. The aqueous phase density is linearly dependent on the temperature in the coefficient $-0.375 \text{ kg m}^{-3} \text{ }^{\circ}\text{C}^{-1}$. An increment of 10^{-4} (relative to the actual temperature) is specified. The maximum number of iterations in the Newton loop is 30. The maximum update is locally restricted to 5 log cycles. The solution is deemed sufficiently accurate, if the magnitude of the logarithm of the temperature update is less than 10^{-7} . The sparse iterative matrix solver will operate with a level 1-preconditioning, use natural ordering of the Jacobian matrix and will perform 100 solver iterations before the solution is considered non-convergent. The information level is set to 0, providing no information on the Newton-loop. The solver residual tolerance and solver update tolerance have been specified three orders of magnitude more stringent than the convergence tolerance.

In the second example, ‘model 2’ is selected for calculation of the thermal conductivity (λ) as a function of aqueous saturation.

The key words ‘energy balance’ and ‘compute evaporation’ activate the energy balance equations and computation of evaporation rates. The linear density coefficient to determine the dependence of density on temperature ($\frac{\partial \rho}{\partial T}$) is also specified in this input and in this case is equal to zero.

Table 3.9: Summary of input parameters for section ‘control parameters - energy balance’

Subsection	Parameter	Default value	Possible parameter settings	Recommended range/parameter
‘energy balance’	-	-	-	-
‘compute evaporation’	-	-	-	-
‘update viscosity’	‘viscosity model’	-	‘sutra’ ‘diersch’	‘diersch’
‘spatial weighting’	type of weighting scheme	‘upstream’	‘upstream’ ‘centered’ ‘van leer’	‘upstream’
‘reference tds’	Reference total dry	10^{-20}	-	-

	substance			
'reference temperature for density'	Reference temperature for density in [°C]	20.0	-	-
'gravity constant'	gravitational acceleration [m s ⁻²]	9.80665	-	-
'energy balance parameters'	Linear density – temperature dependence coefficient (dp/dT) in [M L ⁻³ °C ⁻¹]	-0.34	-	-
'non-linear density'	Non-linear dependence of density with temperature	-	-	-
'logarithm in unknowns'	Derivatives with respect to log Pa and log T are considered, if true	.false.	.false. .true.	-
'non-advection'	Non-advection in energy balance	-	-	-
'non-dispersion'	Non-dispersion in energy balance	-	-	-
'non-conduction'	on-conduction in energy balance	-	-	-
'non-storage term in flow equation'	Non-storage term is computed in flow equation	-	-	-
'non-storage term in heat equation'	Non-storage term is computed in heat equation	-	-	-
'newton iteration settings'	increment for numerical differentiation [m]	10 ⁻⁴	-	10 ⁻⁶ -10 ⁻⁴
	maximum number of Newton iterations	30	-	20-60
	convergence tolerance in log cycles	10 ⁻⁶	-	10 ⁻⁷ -10 ⁻⁴
	maximum temperature update in log cycles	1.0	-	1.0-5.0
'solver settings'	incomplete factorization level	0	-	0-2
	maximum number of solver iterations	100	-	100-1000
	solver information level	1	0,1,2	-
	solver residual tolerance [m]	10 ⁻⁷	-	10 ⁻⁸ -10 ⁻⁵
	solver update tolerance [m]	10 ⁻⁷	-	10 ⁻⁸ -10 ⁻⁵

3.9 CONTROL PARAMETERS – EVAPORATION

This Data Block specifies the parameters to calculate the evaporation rate. It includes the specification of a tortuosity model for vapour flow (τ_v), a reference vapour diffusivity, and a model to determine the porous medium surface resistance to flow (r_s). The model for calculation of the saturated vapour density (ρ_{sv}) is also defined in this Data Block. The enhanced factor in thermal vapour fluxes is also specified in this Data Block.

Importantly, this Data Block also allows you to specify the desired weather conditions for your simulation. Correspondence parameters such as relative humidity, temperature, solar radiation, rainfall, and evaporation rate are specified. Parameters for each of these aspects can be specified directly in the prefix.dat file, or else may be specified in the separate ‘atmospheric’ file (.atm) (see subsection 3.9.5). A sinusoidal function with both daily and annual cycles may be specified in Data Block 6B for both temperature and relative humidity. If the sinusoidal function is used, a maximum, minimum, and amplitude must be specified for each parameter in the input file. An example of the output if temperature and relative humidity values are applied in as sinusoidal functions is depicted in Figure 3.1.

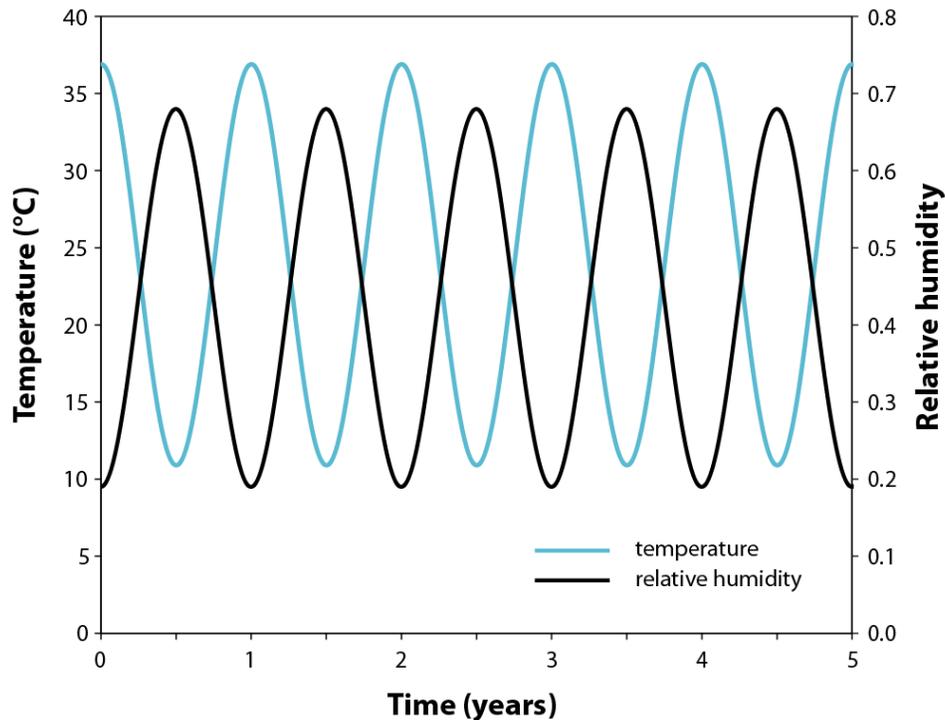


Figure 3.1: MIN3P-THCm output example when a sinusoidal function for climate variables is employed.

3.9.1 DESCRIPTION OF DATA BLOCK

In this section, control parameters affecting the evaporation model are defined using the header 'control parameters - evaporation'. It is to note that the keywords 'compute evaporation' is required under the header 'control parameters – energy balance' to activate the evaporation model (see section 3.8.2.4).

3.9.2 DESCRIPTION OF INPUT PARAMETERS

3.9.2.1 'write transient evaporation info'

The sub-keyword 'write transient evaporation info' controls the output of transient evaporation information (e.g. time, evaporation rate, temperature, wind speed, rainfall, run off etc.) in the file prefix.evap.

3.9.2.2 'vapour density model'

If the sub-block 'vapour density model' is specified, the vapor density (ρ_v) is considered to be dependent on the relative humidity (H_r), salinity represented by the activity of water and the temperature-dependent saturated vapor density (ρ_{sv}) (Bea et al. 2012; Saaltink et al., 2005):

$$\rho_v = H_r a_w \rho_{sv} \quad \text{Equation 3-22}$$

Two empirical saturated vapor density models are available: the default model and the Saito et al. (2006) model.

The default model is the vapor density is calculated:

$$\rho_{sv} = \frac{M_w P_v}{RT} \quad \text{Equation 3-23}$$

The Saito et al. (2006) model is computed (e.g. Saito et al., 2006):

$$\rho_{sv} = 10^{-3} \frac{\exp(31.3716 - \frac{6014.79}{T} - 7.92495 \cdot 10^{-3}T)}{T} \quad \text{Equation 3-24}$$

3.9.2.3 'update vapor density derivatives'

If the keyword 'update vapor density derivatives' is specified, the vapor density derivatives will be updated in each time increment.

3.9.2.4 'temperature gain factor for soil'

The parameter 'temperature gain factor for soil' specifies the gain factor (G_{at}), which corrects the temperature dependence of the surface tension (equals to 7 in the study by Nimmo and Miller (1986).

3.9.2.5 'reference vapor diffusivity'

The parameter 'reference vapor diffusivity' specifies the reference vapor diffusion coefficient in [$\text{m}^2 \text{s}^{-1}$].

3.9.2.6 'enhanced factor in isothermal vapor fluxes'

The parameter 'enhanced factor in isothermal vapor fluxes' specifies the enhanced factor (η) in isothermal vapor fluxes [-].

3.9.2.7 'compute enhanced factor in thermal vapor fluxes'

If the keyword 'compute enhanced factor in thermal vapor fluxes' is specified, the enhanced factor (η) in isothermal vapor fluxes will be calculated according to (Sakai et al. 2009):

$$\eta = a + 3S_a - (a - 1)e^{-\left[\left(1 + \frac{2.6}{\sqrt{f_c}}\right)S_a\right]^4} \quad \text{Equation 3-25}$$

The parameters f_c (clay fraction in [%]) and a (empirical coefficient [-]) should be provided.

If the keyword is not provided, the enhanced factor is equal to 1.0.

3.9.2.8 'soil surface resistance to vapor flow'

The keyword 'soil surface resistance to vapor flow' followed by model name specifies the model to account the effect of soil surface resistance (r_s) on vapor diffusion. Four models are implemented in MIN3P-THCm. Model 1 is defined (Bittelli et al., 2008):

$$r_s = 3.5 \left(\frac{1}{S_a}\right)^{2.3} + 33.5 \quad \text{Equation 3-26}$$

The formulation of the model 2 is defined:

$$r_s = -805.0 + 4140.0\phi(1 - S_a) \quad \text{Equation 3-27}$$

The formulation of the model 3 is defined:

$$r_s = 10^{0.3563(0.15 - \phi S_a)} \quad \text{Equation 3-28}$$

The formulation of the model 4 is defined (Simunek et al., 2009):

$$r_s = \begin{cases} r_0 e^{35.63(S_r - \phi S_a)}, & \text{if } S_r \geq \phi S_a \\ r_0, & \text{if } S_r < \phi S_a \end{cases} \quad \text{Equation 3-29}$$

In which r_0 is the surface resistance [s m⁻¹], which should theoretically be equal to the resistance to molecular diffusion across to the water surface (=10) (van de Griend and Owe, 1994). If no model is specified, the default value of r_s is 0.0.

3.9.2.9 'split divergence of vapor density'

The keyword 'split divergence of vapor density' enables the calculation of the vapour flux according to:

$$\nabla \cdot q_v = \nabla \cdot \phi S_v \tau_v D_w \left(\eta \frac{\partial \rho_v}{\partial T} \nabla T + \frac{\partial \rho_v}{\partial P_l} \nabla P_l \right) \quad \text{Equation 3-30}$$

In which, the effect of temperature and liquid pressure on the vapour density is separately accounted. Otherwise,

$$\nabla \cdot q_v = \nabla \cdot \phi S_v \tau_v D_w \nabla \rho_v \quad \text{Equation 3-31}$$

3.9.2.10 'tortuosity model to vapor flow'

The keyword 'tortuosity model to vapor flow' followed by the model name specifies the tortuosity model for the calculation of diffusive vapour flow transport. The default model is:

$$\tau_v = \phi S_g \quad \text{Equation 3-32}$$

Alternatively, Millington model ('millington') and no tortuosity model ('not consider') can be specified. The Millington model is defined:

$$\tau_v = \phi S_g \frac{(\phi S_g)^{7/3}}{\phi^2} \quad \text{Equation 3-33}$$

If the tortuosity effect can be neglected ($\tau_v = 1$), the model 'not consider' can be specified.

3.9.2.11 'relative humidity parameters'

The keyword 'relative humidity parameters' leads to the input of parameters for the relative humidity calculation. The following logical parameter specifies the way of parameters' input. If it is .false., a sinusoidal function with both daily and annual cycles may be specified in Data Block 6B for relative humidity.

$$H_r = \overline{H_r} + \Delta H_{ry} \cos \left[\frac{2\pi(t - t_{ymax})}{365} \right] + \Delta H_{rd} \cos[2\pi(t - t_{dmax})] \quad \text{Equation 3-34}$$

If the sinusoidal function is used, a maximum, minimum, and amplitude must be specified for each parameter in the input file. In such case, the required parameters are provided in the following order:

- Averaged relative humidity of the atmosphere $\overline{H_r}$ [-]
- Annually amplitude in the relative humidity ΔH_{ry} [-]
- Diurnal amplitude in the relative humidity ΔH_{rd} [-]
- Time during the year when relative humidity is maximum t_{ymax} [time units depends on units of the problem]
- Time during the day when relative humidity is maximum t_{dmax} [time units depends on units of the problem]

Alternatively, the parameters may be read from a separate file (prefix.atm) in the same folder of the input file prefix.dat if the logic parameter is set to '.true.' (see section 3.9.5).

3.9.2.12 'temperature parameters'

The keyword 'temperature parameters' leads to the input of parameters for the temperature of the atmosphere. The data structure is the same as the previous section relative humidity parameters'. A sinusoidal function with both daily and annual cycles may be specified in Data Block 6B for atmosphere temperature, if the following parameters are provided in the Data Block:

- Averaged temperature of the atmosphere $\overline{T_a}$ [°C]
- Annual temperature increment ΔT_{ay} [°C]
- Daily temperature increment ΔT_{ad} [-]
- Time during the year when atmospheric temperature is maximum t_{ymax} [time units depends on units of the problem]
- Time during the day when atmospheric temperature is maximum t_{dmax} [time units depends on units of the problem]

The related equation is:

$$T_a = \overline{T_a} + \Delta T_{ay} \cos \left[\frac{2\pi(t - t_{ymax})}{365} \right] + \Delta T_{ad} \cos[2\pi(t - t_{dmax})] \quad \text{Equation 3-35}$$

Alternatively, the parameters for the temperature of the atmosphere can be read from the separate file `prefix.atm` as described before.

3.9.2.13 'solar radiation parameters'

The keyword `'solar radiation parameters'` leads to the specification of parameters for the solar radiation. The next two logical parameters (for radiation and the cloud index parameters) specify whether the parameters should be read from the file `prefix.atm` (see section 3.9.5). If both logical parameters are `.true.`, or the second one is `.true.`, the corresponding parameters should be read from the `prefix.atm` file. If only the first logical parameter is `.true.`, the radiation parameters should be given in the `prefix.atm` file. In such case, the cloud index in the `prefix.atm` will be neglected. Otherwise, the following parameters are specified:

- Factors to multiply radiation term [-]
- Latitude of the place [rad]. Positive value when it locates in the northern part of the earth, otherwise, negative value.
- Time when January is starting. For example, if the experiment starts on July 1, the value is 182.5 days.
- Time corresponding to noon during the daylight period
- Time when autumn is starting (e.g., September 21 in the northern hemisphere, March 21 in the southern hemisphere)
- Cloud index (0=completely clouded sky, 1=clear sky)
- Albedo of dry soil
- Albedo of wet soil

3.9.2.14 'rain parameters'

The keyword `'rain parameters'` leads to the specification of the leakage coefficient (γ_l) for runoff term (J_{sr}). The surface runoff is considered in the water balance equations as a part of the 'source/sink' term ' f_w '.

$$J_{sr} = \gamma_l(P_l - P_{atm}); \quad P_l > P_{atm} \quad \text{Equation 3-36}$$

To read rainfall events from the `prefix.atm` file, the logical parameter followed by the keyword `'rain parameters'` is set to `.true.` If it is set to `.false.`, the leakage coefficient for rain runoff term should be provided in the next line.

3.9.2.15 'evaporation parameters'

The keyword 'evaporation parameters' leads to the specification of the parameters needed for the evaporation flux calculation. In the next two lines, two logical parameters specify the options for the parameter input. If the first one is set to '.false.', the evaporation rate [$\text{kg m}^{-2} \text{s}^{-1}$] is to be read from the file prefix.atm (see section 3.9.5). If the first one is set to '.true.', the evaporation rate is to be calculated and the related six parameters and/or the wind parameters should be provided in this block. The six parameters are:

- Imposed evaporation rate [$\text{kg m}^{-2} \text{s}^{-1}$];
- Factor to multiply evaporation term [-];
- Roughness length [m]
- Screen height where parameters were measured [m]
- Stability factor [-]
- Density of air in the atmosphere [kg m^{-3}];

The next terms deal with the input of wind related parameters starting with a logical parameter, which defines option for the wind parameter input. If it is set to '.true.', the wind speed(s) in [m s^{-1}] will be read from the file prefix.atm (see section 3.9.5). Otherwise, a sinusoidal function may be applied for wind speed, although this may not be very representative of natural wind speed variations.

$$v_a = \bar{v}_a + \Delta v_{ay} \cos \left[\frac{2\pi(t - t_{ymax})}{365} \right] + \Delta v_{ad} \cos[2\pi(t - t_{dmax})] \quad \text{Equation 3-37}$$

In such case, five parameters have to be provided in the following five lines including:

- Averaged wind speed \bar{v}_a in [m s^{-1}];
- Wind speed amplitude during year Δv_{ay} in [m s^{-1}];
- Wind speed amplitude during day Δv_{ad} [m s^{-1}];
- The time at maximum wind speed during year t_{ymax} [units of the problem];
- The time at maximum wind speed during day t_{dmax} [units of the problem].

3.9.3 DATA FILE INPUT

The following example demonstrates the usage of the evaporation model.

```
! Data Block 6B: control parameters - evaporation
! -----
!
'control parameters - evaporation'

'write transient evaporation info'

'temperature gain factor for soil'
7.0d0

'update vapor density derivatives'

'reference vapor diffusivity'
2.12d-5

!'enhanced factor in isothermal vapor fluxes'
8.0d0

'soil surface resistance to vapor flow'
```

```

'model 3'

!'split divergence of vapor density'

'tortuosity model to vapor flow'
'millington'

'compute enhanced factor in thermal vapor fluxes'
2.0          ! clay fraction content
8.0          ! nabla cte

'relative humidity parameters'
.false.      ! Read Hr from file
0.85d0      ! Relative humidity of the atmosphere (average)
0.245d0     ! relative humidity (amplitude during the year)
0.00d0      ! relative humidity (amplitude during the day)
182.5d0     ! Time for maximum relative humidity during year [units of the problem]
0.5d0      ! Maximum during day [units of the problem]

'temperature parameters'
.false.      ! Read temp from file
23.9d0     ! Temperature of the atmosphere
13.0d0     ! Temperature (amplitude during the year)
0.0        ! Temperature (amplitude during the day)
0.5        ! maximum time during year [units of the problem]
0.5d0     ! maximum time during day [units of the problem]

'solar radiation parameters'
.false.      ! Read radiation from file
.false.      ! Read cloud index from file
0.0d0      ! Factor to multiply radiation term
-29.0d0     ! Latitude of the place
182.5d0     ! Time when January is starting
0.5d0      ! Time corresponding to moon
273.5d0     ! Time when autumn is starting
0.5d0      ! Cloud index (0=completely clouded sky, 1=clear sky)
0.2d0      ! Albedo dry soil
0.1d0      ! Albedo wet soil

'rain parameters'
.false.      ! Read rain events from file
-100.0d0    ! Leakage coefficient for runoff term

'evaporation parameters'
.false.      ! Compute evaporation rate based on aerodynamic relationship
.true.      ! Read evaporation rate from file (only if compute evaporation rate is false)
1.9675E-06  ! Imposed evaporation rate [kg/m2/s]
1.0         ! Factor to multiply evaporation term
0.001d0     ! Roughness length [m]
0.001d0     ! Screen height where parameters were measured [m]
1.0         ! Stability factor
1.112d0     ! Density of air in the atmosphere
.false.      ! Read wind
1.          ! Wind speed [m s-1]
0.0         ! Wind speed amplitude during year [m s-1]
0.0         ! Wind speed amplitude during day [m s-1]
0.0         ! Maximum wind speed during year [units of the problem]
0.0         ! Maximum wind speed during day [units of the problem]

'done'

```

3.9.4 DESCRIPTION OF EXAMPLE INPUT

In the above input, model 3 is used to calculate the porous medium resistance to flow (r_s), and the default model (Millington, 1959) for tortuosity (τ_v) is used.

The enhanced thermal vapour flux is calculated using a clay content (f_c) of 2.0%, and an empirical

constant (a) of 15.

Because nothing is specified for calculation of the saturated vapour density (r_{sv}), it is calculated internally according to the default model. The alternative model after Saito et al. (2006) could instead be activated through the following input inserted after the keyword ‘write transient evaporation info’:

```
'vapour density model'  
'saito et al. (2006)'  
.true.
```

The relative humidity (H_r) parameters are specified as a sinusoidal function with an average of 0.85 and annual amplitude of 0.245. No daily amplitude is specified, thus no diurnal fluctuations are specified and the relative humidity is constant for the entire day (24 hours). The maximum value for relative humidity occurs at day 182 of every year.

Similarly, the temperature (T) is defined by a sinusoidal function, with an average temperature of 23.9 °C and amplitude of 13.0 °C (i.e., temperature varies between 10.9-36.9 °C throughout the year). No diurnal fluctuations in temperature are specified therefore the temperature is constant for the entire day (24 hours). The annual temperature maximum occurs at 0.5 days (i.e., at noon on the first day of the simulation). Thus, the temperature and relative humidity functions are antiphase.

The solar radiation is calculated internally (see in the theory manual section 2.1.6.2 Atmospheric boundary condition) rather than specified in the prefix.atm file. Similarly, the cloud index is specified in the prefix.dat file at a value of 0.5 (partly cloudy). The latitude is -29° or 29°S, therefore the location is in the Southern hemisphere. January is specified to start at day 182.5 of every year, which implies that the summer occurs midway through each year in the simulation as it is in the Southern hemisphere. This value should therefore correspond to the time of the temperature maximum and relative humidity minimum that are specified in the previous input. Noon is set to equal 0.5 days, such that 0.0 days is midnight. If daily amplitude is specified for the temperature and relative humidity, care should be taken that the maximum values for these parameters properly correspond to the ‘noon’ value (i.e., peak temperature should occur at noon). The time when autumn is starting is day 273.5 of each year, or April 1).

The rain events are read in from the prefix.atm file, with a leakage coefficient for the runoff equation (γ_l) of -100.

The evaporation rate is calculated using the aerodynamic relationship (Equations 2-100 to 2-103 in the theory manual section Atmospheric boundary condition). A roughness length (z_0) of 0.001 m is specified. The screen height (z_a) is 0.001 m. The stability factor (θ ; Equation 2-115) is 1.0. The density of air in the atmosphere (r_g^{atm} ; Equation 2-114) is 1.112 kg m⁻³. The wind speed is specified in the prefix.dat file and is a constant (i.e. 1.0 m s⁻¹) throughout each day and year.

3.9.5 ATMOSPHERIC (.ATM) FILE INPUT

Some parameters for the atmospheric boundary condition can be specified through a separate file prefix.atm if at least one of the logic parameters in the example in section 3.9.3 is ‘true’. In this file, the following parameters should be included.

3.9.5.1 Time

The simulation time is the first column in the prefix.atm file. Its unit should be the same as given in the data block ‘time step control - global system’. Recommended unit is days.

3.9.5.2 Temperature

The temperature (temp) in the prefix.atm file is the second column and is specified in °C. If the temperature is specified in the prefix.dat file rather than the prefix.atm file, values of zero are specified in the temperature column in the prefix.atm file.

3.9.5.3 Relative humidity

The relative humidity (Hr) in the prefix.atm file is the third column and is specified as a fraction ranging from 0 to 1. If the relative humidity is specified in the prefix.dat file rather than the prefix.atm file, values of zero are specified in the hr column in the prefix.atm file.

3.9.5.4 Wind

The wind (wind) in the prefix.atm file is the fourth column and is specified in m s^{-1} . If the wind is specified in the prefix.dat file rather than the prefix.atm file, values of zero are specified in the wind column in the prefix.atm file.

3.9.5.5 Radiation

The radiation (R_n) in the prefix.atm file is the fifth column and is specified in $\text{J m}^{-2} \text{s}^{-1}$. If the radiation is calculated internally using values defined in the prefix.dat file, values of zero are specified in the radiation column in the prefix.atm file. To read radiation values from the prefix.atm file, 'read radiation from file' in Data Block 6B(2) is set to 'true.'

3.9.5.6 Rainfall

The rainfall rate is calculated from values provided by the user in the prefix.atm file. The rainfall (rain) column is the sixth column in the prefix.atm file. Example input for the prefix.atm file is shown in Table 3.10.

Table 3.10: Example rainfall input in atmosphere file

Time [days]	Rain [m]
0	0.00
10	2.3×10^{-3}
10.21	0.00
15	5.0×10^{-3}
15.42	0.00

The rainfall rate is calculated from this input as Rain divided by Time. In the example input file, no rainfall occurs for the first ten days. This is followed by a 5 hour interval over which a total of 2.3×10^{-3} m of rain is applied. Thus, the rainfall rate over this period is 1.28×10^{-4} mm/s. Following this event, there is no rain until day 15, at which point a rainfall event of 1.28×10^{-4} mm/s occurs for 10 hours. From a functional standpoint, care must be taken to ensure sufficient significant digits are specified in the prefix.atm file to properly apply the desired rainfall interval. For example, if a rainfall event is to occur on day 9240 for two hours, the entries in the time column must contain at least 6 significant digits (i.e., 9240.08 days). Certain editing programs will truncate significant digits, therefore it is important as the user to check over prefix.atm files to ensure the proper values are maintained. The double precision format is highly recommended.

3.9.5.7 Cloud index

The cloud index (I_n) in the prefix.atm file is the seventh column and is specified as a fraction between 0 and 1, with 0 being complete cloud cover, and 1 being clear skies. If the cloud index is defined in the prefix.dat file, values of zero are specified in the cloud index column in the prefix.atm file.

3.9.5.8 Evaporation

The evaporation rate can be specified in the prefix.dat file [$\text{kg m}^{-2} \text{s}^{-1}$]. If the evaporation rate is specified in the prefix.dat file or is calculated internally using values defined in the prefix.dat file, values of zero are specified in the evap rate column in the prefix.atm file.

An example of the prefix.atm file is:

```
-----
Time Tatm[°C]  Hr [-]  WindSpeed [m/s]  Radiation [KJ day-1 m-2]  Rain [m]  Cloud index [-]
Evap rate [kg/m2/s]
-----
0.00E+00 0.0000000E+00  0.0000000E+00  0.0000000E+00  000.0d0  0.0  0.00000E+00  1.5d-6
5.00E+00 0.0000000E+00  0.0000000E+00  0.0000000E+00  000.0d0  0.0  0.00000E+00  2.2d-6
10.00E+00 0.000000E+00  0.0000000E+00  0.0000000E+00  000.0d0  0.0  0.00000E+00  2.3d-6
16.0 0.0000000E+00  0.0000000E+00  0.0000000E+00  0.00000d0  0.0  0.000000E+00  2.8d-6
-1.0
-----
```

The first three lines are used for the header, which are only for the description of the parameters to be provided and are skipped by the program. From the fourth line on, the required parameters must be provided in the order: Time, temperature of the atmosphere, relative humidity, net solar radiation, rainfall, cloud index, and the evaporation rate. The number format is flexible as long as there is space(s) between two parameters. The last negative value -1.0 terminates the read function.

3.10 CONTROL PARAMETERS – REACTIVE TRANSPORT (DATA BLOCK 7)

3.10.1 DESCRIPTION OF DATA BLOCK

In this section, numerical and control parameters affecting the reactive transport calculations are defined. The entire section is optional, default values are specified for all parameters in the code. This section may be modified to enhance the model performance, or potentially correct convergence problems.

3.10.2 DESCRIPTION OF INPUT PARAMETERS

The content of this section is similar to Section 3.6. The input parameters are described below, and are also summarized in Table 3.11 together with the corresponding default settings, possible parameter settings and the recommended range for the parameters.

3.10.2.1 ‘mass balance’

If the sub-block ‘mass balance’ is specified, the model will perform mass balance calculations including contributions of storage, fluxes across the domain boundary and internal sources and sinks due to the specified geochemical reactions. The total system mass for aqueous phase components, minerals, gases and surface species are reported in the files prefix_o.mas, prefix_o.mms, prefix_o.mgs and prefix_o.mss. Mass balance contributions and cumulative changes are reported for each component, for each mineral phase and for all gaseous species in separate files. The file prefix_o.flr contains additional information on these mass balance files, the corresponding mass balance error files and their content. This file will be created for the specific problem at run-time.

3.10.2.2 ‘spatial weighting’

Three different spatial weighting schemes can be used to describe advective transport. These options are controlled under the sub-block ‘spatial weighting’ and are identified by their names. The three options are ‘upstream’, ‘van leer’ and ‘centered’. By default, upstream weighting will be used. In this case the concentrations for the advective mass transport term are assigned based on:

$$\begin{aligned} T_{j,kl}^a &= T_{j,k}^a && \text{if } v_{a,kl} \geq 0 \\ T_{j,kl}^a &= T_{j,l}^a && \text{if } v_{a,kl} < 0 \end{aligned} \quad \text{Equation 3-38}$$

where $T_{j,kl}^a$ is the concentration at the interface of two adjacent control volumes, $T_{j,k}^a$ and $T_{j,l}^a$ are the concentration in the control volumes k and l , while $v_{a,kl}$ defines the Darcy flux from control volume k to l . For centered weighting, the interfacial concentrations are defined based on:

$$T_{j,kl}^a = \frac{T_{j,k}^a + T_{j,l}^a}{2} \quad \text{Equation 3-39}$$

If centered weighting is used, it is necessary to obey the Peclet criterion to ensure convergence. The following requirements have to be obeyed:

$$Pe = \frac{v_{a,kl} \Delta x}{D_{a,kl}} < 2 \quad \text{Equation 3-40}$$

where Δx defines the distance between the center of the two adjacent control volumes and $D_{a,kl}$ is the effective dispersion coefficient. If the Van Leer–flux limiter is specified, the interfacial concentrations are calculated based on:

$$T_{j,kl}^a = T_{j,k}^a + \sigma(r_{kl}) \frac{T_{j,k}^a + T_{j,l}^a}{2} \quad \text{Equation 3-41}$$

where $\sigma(r_{kl})$ is the Van Leer flux limiter and r_{kl} is a smoothness sensor. $\sigma(r_{kl})$ ranges from 0 to 2 and is calculated internally (van Leer, 1994, Unger et al., 1996). The present implementation of the Van Leer flux limiter requires the Courant criteria to be obeyed:

$$Cr = \frac{v_{a,kl} \Delta t}{\Delta x} < 1 \quad \text{Equation 3-42}$$

where Δt defines the time increment. Neither the Courant, nor the Peclet restrictions apply for

upstream weighting, however, upstream weighting may lead to excessive numerical dispersion.

3.10.2.3 'activity update settings'

The model allows several options to update activity coefficients for aqueous species. It is possible to exclude activity updates altogether by specifying 'no update' or 'no_update' under the sub-block 'activity update settings'. By default the activity coefficients are updated after completion of each time step ('time lagged' or 'time_lagged') (Lichtner, personal communication, 1997). Alternatively, the option 'double update' or 'double_update' can be used. In this case, the activity coefficients for all aqueous species are updated twice per Newton-iteration to maximize accuracy on the cost of performance. Comparisons have shown that differences between the option 'time lagged' and 'double update' are minimal. 'time lagged' is therefore the recommended option for calculations including activity corrections.

The input format is:

```
'activity update settings'
'time_lagged'           ;type of activity update
```

3.10.2.4 'tortuosity correction'

The sub-block 'tortuosity correction' defines the options for tortuosity corrections. There are four options: 'millington', 'archie', 'assigned tau' and 'no correction'. If the text string below the sub-block 'tortuosity correction' is set to 'millington', the tortuosity in the aqueous and gas phase is calculated based on the relationship defined by Millington (1959):

$$\tau = S_p^{7/3} \phi^{1/3} \quad \text{Equation 3-43}$$

where S_p is the phase saturation and ϕ is porosity. In such case, the tortuosity will be calculated according to the porosity. An example of the input format:

```
! Data Block 7: control parameters - reactive transport
! -----
!
'control parameters - reactive transport'

'spatial weighting'
'upstream'           ;spatial weighting

'tortuosity correction'
'millington'
```

The example input specifies the tortuosity is updated according to Millington equation. No tortuosity parameter is needed in Data block 9 (see Section 3.12). Note: The keyword 'millington' is also used to specify the tortuosity correction model for vapor (see section 3.9.2.10).

Similarly, if the text string below the sub-block 'tortuosity correction' is set to 'archie', the tortuosity in the aqueous and gas phase is calculated based on the relationship defined as:

$$\tau = S_p \phi^\alpha \quad \text{Equation 3-44}$$

In which α is the coefficient of the Archie's law. To use this function, add 'update tortuosity' to

block 7 and alpha value to block 9. The initial tortuosity and α can be specified in Data block 9 to each material zone. An example input:

in block 7: control parameters - reactive transport

```
'tortuosity correction'
'archie'

'update tortuosity'
```

in block 9: physical parameters - porous medium

```
'number and name of zone'
1
'concrete'
0.1      ;porosity
0.0383   ;tortuosity
2.0      ;alpha, tortuosity update factor
```

The example input defines that the tortuosity is updated according to the Archie's law with a tortuosity update factor $\alpha = 2.0$. The initial tortuosity τ_0 is 0.0383. Note: In this model, the tortuosity is calculated according to Equation 3-44. τ_0 is not used but it is needed in the input file so that the coefficient α can be correctly read.

Another option for the update of tortuosity is the assigned tortuosity using 'assigned tau'. In such case, the assigned tortuosity will be used for the effective diffusion coefficient calculation. This can be specified in the input file (i.e. for each material zone) or through external file with extension prefix.tor (i.e. for each control volume, see section 3.12.5).

in block 7: control parameters - reactive transport

```
'tortuosity correction'
'assigned tau'

'update tortuosity'
```

in block 9: physical parameters - porous medium

```
'number and name of zone'
1
'concrete'
0.1      ;porosity
0.0383   ;tortuosity
```

If 'no correction' is specified, tortuosity corrections are neglected and tortuosity is set to unity.

3.10.2.5 'spatial averaging - diffusion'

The effective diffusion coefficient (D_e) is a physical parameter of each control volume. In order to calculate the diffusive flux between two connected control volumes, a representative D_e has to be calculated using the parameters of both control volumes. For example, if the control volumes have different size, spatially weighted averaged D_e might be more reasonable. Considering the D_e is calculated based on the D_0 , porosity and tortuosity, there are different ways to calculate the representative depending on the averaging method (e.g. arithmetic or harmonic) and the order of averaging (e.g. averaging the effective porosity and tortuosity first and then calculate the representative D_e , or calculate the D_e in each control volume and then spatially weighted averaging

to obtain the representative D_e). In MIN3P-THCm, three different spatial averaging methods for the effective diffusion coefficient (D_e) were implemented: the arithmetic averaging method, the arithmetic D_e averaging method and the harmonic averaging method.

The arithmetic averaging method (using key word 'arithmetic'): first calculate the representative effective porosity and tortuosity through arithmetic method (i.e. sum of the parameters of connected pair of control volumes divided by two), then calculated the representative D_e . An example input:

```
'spatial averaging - diffusion'      ; Keyword
  'arithmetic'
```

The arithmetic D_e averaging method (using key word 'arithmetic D_e '): first calculate the D_e of each control volume using the corresponding effective porosity and tortuosity; then calculated the representative D_e using the arithmetic method and the D_e of the connected pair of control volumes. An example input:

```
' spatial averaging - diffusion'      ; Keyword
  'arithmetic De'
```

The harmonic averaging method (using key word 'harmonic'): first calculate the D_e of each control volume using the corresponding effective porosity and tortuosity; then calculated the representative D_e using the arithmetic method and the D_e of the connected pair of control volumes. An example input:

```
' spatial averaging - diffusion'      ; Keyword
  'harmonic'
```

3.10.2.6 'gas advection'

The sub-block 'gas advection' enables gas advection simulation.

3.10.2.7 'cumulative mole fractions'

The sub-block 'cumulative mole fractions' enables to provide cumulative gas pressure value in the output file prefix_x.gsg.

3.10.2.8 'enable gravity for gas phase'

The sub-block 'enable gravity for gas phase' enables the code to take the gravity into consideration for gas advection simulation.

3.10.2.9 'degassing'

The sub-block 'degassing' enables degassing of dissolved gases from the saturated zone, if the sum of the partial gas pressures exceeds the confining pressure. The value specified below the subkeywords defines the degassing rate in $\text{mol L}^{-1} \text{H}_2\text{O s}^{-1}$. An example of the input format is:

```
'degassing'                          ;allow degassing
1.0d-8                                ;rate constant [mol L-1 h2o s-1]
```

3.10.2.10 'update porosity'

The sub-block 'update porosity' enables to keep track of porosity changes due to dissolution-precipitation reactions. If this statement is enabled, porosity is calculated based on:

$$\phi^{t+\Delta t} = \phi^t - \sum_{i=1}^{N_m} \phi_i^{t+\Delta t} - \phi_i^t \quad \text{Equation 3-45}$$

The porosity update will also affect the calculation of the effective diffusion coefficients. If this option is enabled, the time step should be kept sufficiently small to provide an accurate solution. This is necessary, because the update of the porosities is done explicitly after completion of a time step. Usually porosity changes are relatively slow and this simplification does not lead to significant inaccuracies.

3.10.2.11 'update permeability'

When the sub-block 'update permeability' is specified, the initial hydraulic conductivities are modified based on a normalized version of the Carman-Kozeny relationship. The update is of the form as described in Equation 3-24 in the MIN3P-THCm Theory Manual section 3.5.

If this option is enabled, the option 'update porosity' will be enabled automatically. As for the porosity-update, the time step needs to be kept sufficiently small, because flow and transport are treated as decoupled processes.

3.10.2.12 'newton iteration settings'

This sub-block defines the parameters affecting the Newton iteration. Similar to the definitions for the geochemical batch module, the increment for numerical differentiation is used to calculate numerical derivatives according to the formula (Equation 3-3).

The following parameter specifies the anticipated number of Newton iterations, which is used internally to calculate an estimate for the time increment for the next time step. The next parameter identifies the maximum number of Newton iterations to be performed, before a solution is considered non-convergent. The time step is repeated with a reduced time increment, if the actual number of Newton iterations exceeds the maximum number of Newton iterations. The maximum number of Newton iterations must be larger than the anticipated number of Newton iterations (commonly 3 times).

In the following the anticipated update for the primary unknowns (concentrations of components as free species) in log concentration [mol L⁻¹] cycles is specified. Below this parameter, the maximum tolerable update (in log concentration [mol L⁻¹] cycles) is specified. The computed update is set to the maximum tolerable update, if the computed value is larger than the maximum allowed value. This is done to ensure that the computed concentrations remain sufficiently close to the actual solution. Similar to the requirements for the maximum number of Newton iterations, the maximum tolerable update must be larger than the desired update (usually 2-3 times larger).

The convergence tolerance defines the accuracy of the concentrations calculated during the reactive transport simulation. A solution is considered converged if the logarithm of all concentration updates at each spatial discretization point in the solution domain is smaller than the convergence tolerance ϵ (Equation 3-5).

3.10.2.13 'solver settings'

The solver package WATSOLV (VanderKwaak et al., 1997) is also used for the solution of the reactive transport problem. The settings defined in the sub-block 'solver settings' are therefore equivalent to the one for the variably-saturated flow problem and are described in the section on 'control parameters – variably-saturated flow'.

3.10.3 DATA FILE INPUT

An example is:

```
! -----
'control parameters - reactive transport'

'mass balance'

'spatial weighting'
'upstream'                ;spatial weighting

'activity update settings'
'time lagged'             ;type of activity update

'update porosity'        ;porosity changes

'update permeability'    ;permeability = f(porosity)

'tortuosity correction'
'millington'            ;Millington-Quirk tortuosity correction

'newton iteration settings'
1.d-4                   ;increment for numerical differentiation
20                      ;anticipated number of Newton iterations
60                      ;max. number of Newton iterations
1.0d0                   ;anticipated update in log cycles
2.0d0                   ;maximum update in log cycles
1.d-6                   ;convergence tolerance (global system)

'solver settings'
0                       ;incomplete factorization level
100                     ;max. number of solver iterations
1                       ;information level
1.d-7                   ;solver residual tolerance
1.d-7                   ;solver update tolerance

'natural ordering'      ;natural ordering

'degassing'
1.0×10-8                ;degassing rate [mol L-1 s-1]

'done'
```

3.10.4 DESCRIPTION OF EXAMPLE INPUT

In the example input file, mass balance calculations are performed. The code uses upstream weighting for advective transport in the aqueous phase. Activity coefficients are updated after completion of each time step. The tortuosity is corrected based on the relationship by Millington [1959]. An increment of 10^{-4} (relative to the actual concentration of each primary unknown) is specified. The anticipated and maximum number of iterations in the Newton loop are 20 and 60, respectively. The anticipated update is 1 log concentration cycle, while the maximum update is locally restricted to 2 log cycles. The solution is deemed sufficiently accurate, if the magnitude of the logarithm of the concentration update is less than 10^{-6} . The sparse iterative matrix solver will operate with a level 0-preconditioning, use natural ordering of the Jacobian matrix and will perform 100 solver iterations before the solution is considered non-convergent. The information level is set to 1, providing information on the Newton-loop, but not on the inner iteration. The solver residual tolerance and solver update tolerance have been specified one order of magnitude more stringent than the convergence tolerance. Degassing has been specified at a rate of 1.0×10^{-8} mol L⁻¹ s⁻¹.

Table 3.11: Summary of input parameters for section ‘control parameters – reactive transport’

Subsection	Parameter	Default value	Possible parameter settings	Recommended range/parameter
‘mass balance’	-	-	-	-
‘spatial weighting’	type of weighting scheme	‘upstream’	‘upstream’ ‘centered’ ‘van leer’	‘upstream’
‘activity update settings’	type of activity update	‘time lagged’	‘no update’ ‘time lagged’ ‘double update’	‘time lagged’
‘tortuosity correction’	type of tortuosity correction	‘millington’	‘millington’ ‘no correction’	‘millington’
‘degassing’	degassing rate	0.0	-	system-dependent
‘update porosity’	-	-	-	-
‘update permeability’	-	-	-	-
‘user-specified underrelaxation factor’	underrelaxation factor	1.0	-	1.0
‘newton iteration settings’	increment for numerical differentiation [m]	10^{-4}	-	10^{-6} - 10^{-4}
	anticipated number of Newton iterations	12	-	10-20
	maximum number of Newton iterations	15	-	20-60
	anticipated concentration update in log cycles	0.5	-	0.5-1.5
	maximum concentration update in log cycles	1.0	-	1.0-3.0
	convergence tolerance in log cycles	10^{-6}	-	10^{-7} - 10^{-4}
‘solver settings’	incomplete factorization level	0	-	0-2
	maximum number of solver iterations	100	-	100-1000
	solver information level	1	0,1,2	-
	solver residual tolerance [m]	10^{-7}	-	10^{-8} - 10^{-5}

	solver update tolerance [m]	10 ⁻⁷	-	10 ⁻⁸ -10 ⁻⁵
'natural ordering'	-	-	-	-

3.11 OUTPUT CONTROL (DATA BLOCK 8)

3.11.1 DESCRIPTION OF DATA BLOCK

In this data block, the output from the simulation is specified. Data can be output as a 'snapshot' at a specified time (spatial data) or as data through time at a specified location (transient data). Spatial data in 1D typically would consist of a linear plot of concentration with distance for a specified time; for a 2D simulation, the concentration data can be visualized as a 2D contour plot. Transient data typically consists of a plot of concentration with time (breakthrough curve). This section is entirely optional for all flow and reactive transport simulations and will not be considered for any batch chemistry simulations. If this section is not specified, the output will only be written at the end of the simulation.

3.11.2 DESCRIPTION OF INPUT PARAMETERS

3.11.2.1 'output control'

This data block contains up to three sub-blocks, which are described below. If isotope geochemistry is considered, an additional keyword 'isotope output' is required (see below).

3.11.2.2 'output of spatial data'

The first parameter for specifying spatial data output is the number of desired output times. This value follows the sub-block header 'output of spatial data'. The second line contains the times at which the output is desired. Only 4 output times can be specified per line, if the number of output times exceeds 4, the values for the output times have to be specified in the next line. The time units used are the same as those specified in the Section 4 ('time step control'). Spatial data is written to the files prefix_*.gs*, as described in Section and can be post-processed with TECPLOT (Amtec, 2003). For example, the file prefix_1.gst will contain spatial data at the first (1) specified output time for total aqueous component concentrations (t). Other output files are described in section 2.2.

3.11.2.3 'output of transient data'

The first parameter for specifying transient data output is the number of desired output locations. This line follows the sub-block header 'output of transient data.' The following parameter defines how often transient data is written to the output file (i.e.: setting this parameter to 3 means that output data will be written to the output files every third time step). This is used to reduce the size of transient output files (e.g. *.gbt) when the time step is too small. The third line specifies the control volume numbers of the output locations.

Only 4 output locations can be specified per line, if the number of output locations exceeds 4, the values for the output locations have to be specified in the next line. Transient data is written to the files prefix_*.gb*, as described in Section 2. For example, the file prefix_1.gbt will contain transient data for the first (1) specified output location for total aqueous component concentrations

(t).

The control volume numbers can be calculated from the spatial discretization parameters defined in Section 'spatial discretization' (section 3.4). Numbering of the grid is performed in x-direction first, then in y-direction and finally in z-direction (Figure 3.2).

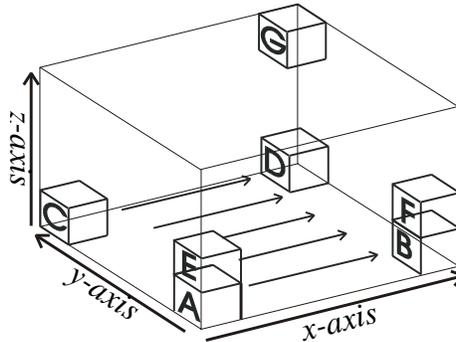


Figure 3.2: Spatial discretization and numbering principle

Example:

```
'output of transient data'
5                               ;number of output locations (transient data)
1                               ;time steps between output (transient data)
1 15 85 95                     ;control volume number for transient data
101
```

This example specified the output of the transient data for five selected control volumes (i.e. 1, 15, 85, 95 and 101). The number of time steps for the output is 1, which means the output at every time step.

3.11.2.4 'output in terms of depth'

The spatial discretization is based on a Cartesian coordinate system, and by default the output in vertical direction is reported in terms of elevation. Optionally, the output can also be reported in terms of depth by adding the line 'output in terms of depth' to the input file. In this case the z-coordinates will be transformed prior to output based on:

$$z_i = z_{\max} - z_i$$

where z_{\max} is the maximum elevation in the solution domain (calculated internally) and z_i correspond to the elevations prior coordinate transformation and to depth values after transformation is completed.

3.11.2.5 'isotope output'

The first parameter for specifying isotope related parameters output is the number of isotope component sets. This line follows the sub-block header 'isotope output'. The second line specifies the number of components in each set followed by the master isotope and other isotopes. The ratios of standard for delta value calculations (R_{std}) should be provided in the third line. If the number of isotope component sets is greater than one, the parameters for each isotope component set should be provided following the second and third lines mentioned before. The format is as follows:

```
'isotope output'
2                               ;number of isotope component sets for output
2 'so4-2' '34so4-2'           ;number of components in set, master isotope, other isotopes,
4.5005d-2                       ;and ratios of standard for delta value calculations
2 'hs-1' '34hs-1'
4.5005d-2
```

The example input block specifies two sets of isotope components for output. One set is sulfate (i.e. 'so4-2' as the master isotope component, followed by the isotope component '34so4-2'), and the other one is sulfide (i.e. 'hs-1' and '34hs-1'). The master isotope is the isotope that is used in the numerator of the delta value calculations, ^{32}S in the case of sulfur. The R_{std} values for both sets are $4.5005\text{E-}2$ as the accepted sulfur isotope ratio of the standard Canyon Diablo troilite (CDT) reference material (Gibson et al. 2011).

3.11.3 EXAMPLE DATA FILE INPUT

An example is as the following:

```
! -----
'output control'

'output of spatial data'
6                               ;number of output times (spatial data)
1.0  2.0  5.0  10.0           ;specified output times (spatial data)
20.0 50.0

'output of transient data'
4                               ;number of output locations (transient data)
2                               ;time steps between output (transient data)
50  650  1250  1850          ;control volume number for transient data

'output in terms of depth'

'done'
```

3.11.4 DESCRIPTION OF EXAMPLE INPUT

In the sample input file spatial output will be written at the specified 6 output time: 1.0, 2.0, 5.0, 10.0, 20.0 and 50.0 time units. In total, six spatial output files will be generated. Breakthrough curves will be generated for the specified 4 locations (i.e. control volumes 50, 650, 1250, and 1850). The output of the transient data will be written every second time step and will be reported in terms of depth.

3.12 PHYSICAL PARAMETERS: POROUS MEDIUM (DATA BLOCK 9)

3.12.1 DESCRIPTION OF DATA BLOCK

This data block is used to specify the zones that are used to discretize a variety of physical properties across the model domain. In this section, the porosity is also specified for each zone. The zone names specified in this section are reused in other input sections to allocate physical parameters specific to variably-saturated flow or reactive transport.

3.12.2 DESCRIPTION OF INPUT PARAMETERS

3.12.2.1 'physical parameters - porous medium'

The first parameter that must be specified in this data block is the number of material property zones. This value is specified in the second line of this input section immediately below the heading 'physical parameters - porous medium'.

3.12.2.2 'number and name of zone'

Each zone is defined by its own sub-block, which is bounded at the top by the statement 'number and name of zone' and at the bottom by the statement 'end of zone'. Each of these input blocks requires the same input sequence.

The first parameter within each block is the zone number. This value is placed immediately after the subkeywords 'number and name of zone'. Property zones are numbered sequentially starting with 1 and the number of the final zone should be the same as the total number of property zones specified in the beginning of this section. The zones can be specified in any order.

The second input parameter is the name of the zone. This parameter consists of a word or a short sentence (up to 72 characters) describing the specific material property zone. The zone name must be placed in single quotes below the zone number. This name identifies each zone and will be used in additional input sections to allocate other material properties, specific to flow or transport simulations. It is therefore important that the name is unique to that zone and that it be reproduced exactly in future input sections.

The third parameter is the porosity for the zone; this value is specified directly below the property zone name.

The fourth parameter is the tortuosity for the zone. This parameter is specified following the porosity in a separate line.

The last parameter defines the 'extent of zone'. Under this parameter the dimensions of the zone are defined. MIN3P-THCm allows the simulation of flow and reactive transport in three spatial dimensions. The following input defines the location of minimum and maximum coordinates in the x, y and z-directions (in meters) for the material properties to be allocated. If a 1D or 2D-simulation is conducted, the minimum and maximum coordinates for the excluded dimensions should be specified as 0.0 and 1.0, respectively.

Material properties must be specified for every control volume in the domain. If this is not done, the program will stop when executed and report an error to the file prefix.log. On the other hand, it is possible to overwrite existing material properties with new material properties. If this is done, a warning will be issued to the file prefix.log in case material properties have been overwritten accidentally. In some applications, it may be most efficient to assign background values to the entire domain first (see zone 'aquifer' in example input). Any subsequent property zone will simply overlay and replace previous data within the dimensions of that zone. Material properties are assigned to the center of the control volumes. If the center of a control volume falls into a property zone, the entire control volume is assigned the property of that zone. It is unnecessary for the dimensions of each zone to correspond exactly to the edges of the control volumes as defined in the section 'spatial discretization' (Figure 3.3)

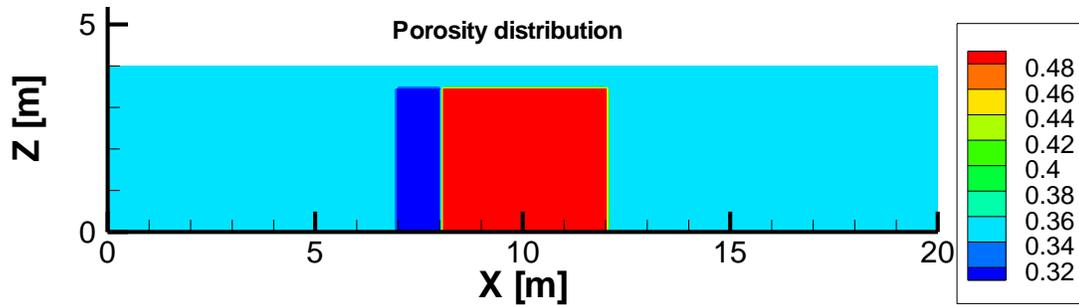


Figure 3.3: Allocation of material properties to discretized solution domain.

3.12.3 EXAMPLE DATA FILE INPUT

An example input file:

```

! -----
'physical parameters - porous medium'
3                               ;number of property zones

! -----
'number and name of zone'
1
'aquifer'
0.35                           ;porosity
0.05                           ;tortuosity

'extent of zone'
0.0 20.0 0.0 1.0 0.0 4.0

'end of zone'
! -----
'number and name of zone'
2
'reactive barrier'
0.50                           ;porosity
0.15                           ;tortuosity

'extent of zone'
8.0 12.0 0.0 1.0 0.0 3.5

'end of zone'
! -----
'number and name of zone'
3
'sand, up-gradient'
0.30                           ;porosity
0.04                           ;tortuosity

'extent of zone'
7.0 8.0 0.0 1.0 0.0 3.5

'end of zone'

'done'

```

3.12.4 DESCRIPTION OF EXAMPLE INPUT

In the example file, the number of material property zones is 3. The names for the three zones in the example file are 'aquifer', 'reactive barrier' and 'sand, up-gradient'. The porosity of the different zones varies from 0.3 to 0.5. The tortuosity of the different zones is in the range of 0.04 to 0.15. Aquifer properties are initially assigned to the entire domain and subsequently overlain by locally defined property zones. For example, the dimensions of the 2nd property zone entitled 'reactive barrier' extend from 8 to 12 m in the x-direction, 0.0-1.0m in the y-direction (default values since scenario is 2D) and 0.0 to 3.5 m in the z-direction. This zone overlay the original property zone 'aquifer'. The zone 'sand, up-gradient' allocates property zones to a sand layer located up-gradient of the reactive barrier (see Figure 3.3).

3.12.5 DISTRIBUTED PARAMETERS INPUT

Many distributed porous medium properties, initial concentrations of components and minerals, and transient flow boundary conditions can be specified through external files in MIN3P-THCm. Generally, the specification of spatial distribution parameters or conditions requires corresponding geometry data. MIN3P-THCm uses the x, y, and z-coordinates even for 1D problems. It is important to note that MIN3P-THCm doesn't read and use the x,y,z-coordinate in the external files to specify the parameters. Instead, the code assumes that the external files have the same order of control volumes as the code discretized the domain. Therefore, it is important to keep the same order of the control volumes created by the code when providing distributed files by external files. Additionally, the first three lines (headers) are skipped while reading the file(s). The easiest way to do that is to run the example without external files and use the spatial output files such as prefix_0.gst, prefix_0.gsp etc. as a template, and modify the porosity values at all control volumes only.

MIN3P-THCm specifies initially distributed porosity and tortuosity by reading from an external data file. To activate the function for distributed porosity, the keywords 'read porosity field from file' has to be in the Data Block 9: 'physical parameters - porous medium'. An example for the activation using the keywords is:

```
! Data Block 9: physical parameters - porous medium
! -----!
'physical parameters - porous medium'
1                ;number of property zones
! -----
'read porosity field from file'
! -----
'number and name of zone'
1
'basin'
0.01                ;porosity

'extent of zone'
0.0 440000.0 0.0 1.0 0.0 4000.0
'end of zone'
'done'
```

In such case, a file in the same name as the input file but with extension prefix.por should be provided in the same directory as the input file. The first three lines are the header, which are ignored by the code (This is valid for all external files with spatial data as mentioned below). After that the x,y,z-coordinates plus the corresponding porosity for each control volume should be provided, one line for each control volume. An example of the prefix.por file format is:

```

title = "dataset basin"
variables = "x", "y", "z","porosity"
zone t = "field initial",i = 1000, j = 150, k = 1, f=point
0.0000000E+00 0.0000000E+00 0.0000000E+00 0.1733083E-02
0.4404404E+03 0.0000000E+00 0.0000000E+00 0.2735083E-02
0.8808806E+03 0.0000000E+00 0.0000000E+00 0.8310352E-02
0.1321321E+04 0.0000000E+00 0.0000000E+00 0.7133083E-02
0.1761762E+04 0.0000000E+00 0.0000000E+00 0.1733083E-02
0.2202202E+04 0.0000000E+00 0.0000000E+00 0.1733083E-02
... ..

```

In the same way, the distributed tortuosity values can be read from a file prefix.tor, if the keywords 'read tortuosity field from file' can be found in the Data Block 9: 'physical parameters - porous medium'. An example of the prefix.tor file is:

```

title = "dataset basin"
variables = "x", "y", "z","tortuosity"
zone t = "field initial",i = 1000, j = 150, k = 1, f=point
0.0000000E+00 0.0000000E+00 0.0000000E+00 0.1733083E-02
0.4404404E+03 0.0000000E+00 0.0000000E+00 0.2733083E-02
0.8808806E+03 0.0000000E+00 0.0000000E+00 0.7731073E-02
0.1321321E+04 0.0000000E+00 0.0000000E+00 0.6512083E-02
0.1761762E+04 0.0000000E+00 0.0000000E+00 0.1733083E-02
0.2202202E+04 0.0000000E+00 0.0000000E+00 0.1733083E-02
... ..

```

3.13 PHYSICAL PARAMETERS-VARIABLELY-SATURATED FLOW (DATA BLOCK 10)

3.13.1 DESCRIPTION OF DATA BLOCK

This data block specifies physical parameters affecting the flow solution only. Parameters must be specified for each of the zones defined in Data block 9 ('physical parameters – porous medium') and are identified by the names of the zones. In the case of fully-saturated conditions, the hydraulic conductivity for each spatial dimension in use needs to be specified. In the case of variably-saturated conditions, soil hydraulic function parameters (van Genuchten parameters, Woesten and van Genuchten, 1988) must be additionally specified. These empirical soil function parameters describe the vertical distribution of water in the unsaturated zone and provide a relationship between that water distribution and the effective hydraulic conductivity. Transient simulations require the definition of a specific storage coefficient.

3.13.2 DESCRIPTION OF INPUT PARAMETERS

3.13.2.1 'physical parameters – variably saturated flow'

A sub-block is required for each material property zone defined in the previous section ('physical parameters – variably saturated flow'). Each material property zone is identified by the name of the zone as specified in the previous section 'physical parameters - porous medium'. The input for each material property zone is ended with the statement 'end of zone'. Within each sub-block the following parameters are defined.

3.13.2.2 'hydraulic conductivity in ?-direction'

The hydraulic conductivity must be provided for any flow problem. Only the hydraulic conductivities for the active dimensions need to be specified. For example, a 1D-simulation in x-direction only requires the specification of 'hydraulic conductivity in x-direction' and the corresponding hydraulic conductivity value. The unit of hydraulic conductivity is in [m day⁻¹].

3.13.2.3 'specific storage coefficient'

For transient simulations it is necessary to define a specific storage coefficient, introduced by the identifier 'specific storage coefficient'.

3.13.2.4 'soil hydraulic function parameters'

If the simulation involves unsaturated flow, it is also necessary to define a number of soil hydraulic function parameters, including the residual saturation of the medium, the van Genuchten parameters α , n , and l , and the air entry pressure ($p \times 10$). These parameters need to be specified below the subkeywords 'soil hydraulic function parameters'.

3.13.2.5 'residual gas saturation'

If the simulation involves unsaturated flow and density dependent flow, it is also possible to define the residual gas saturation S_g^r . In such case, the gas saturation is calculated as:

$$S_g = 1 - S_w + S_g^r \quad \text{Equation 3-46}$$

Table 3.12: Summary of input parameters for section 'physical parameters – variably-saturated flow'

Keywords			Required/ Optional	
'physical parameters – variably-saturated flow'			required	
Subsection*	Parameter	Description	Required/ Optional	
N ^{dim} -zones	'hydraulic conductivity in x-direction'	K_{xx} [m d ⁻¹]	hydraulic conductivity in x-direction	only required if number of control volumes in x-direction > 1
	'hydraulic conductivity in y-direction'	K_{yy} [m d ⁻¹]	hydraulic conductivity in y-direction	only required if number of control volumes in y-direction > 1
	'hydraulic conductivity in z-direction'	K_{zz} [m d ⁻¹]	hydraulic conductivity in z-direction	only required if number of control volumes in z-direction > 1
	'specific storage coefficient'	S_s [m ⁻¹]	specific storage coefficient	only required for transient flow conditions
	'soil hydraulic function parameters'	S_w^r [-]	residual saturation	only required if not fully saturated
		α [m ⁻¹]	van Genuchten α	
n [-]		van Genuchten n		

		l [-]	van Genuchten l	
		$p \times 10$ [m]	air entry pressure	
	Gas residual saturation	S_g^r [-]	Gas residual saturation	only required if not fully saturated and density dependent flow
Section Closing				Required/Optional
'done'				required

3.13.3 EXAMPLE DATA FILE INPUT

a. Fully Saturated Example

```
! Section 10: physical parameters - variably-saturated flow
! -----
!
'physical parameters - variably-saturated flow'

! -----
'aquifer'                ;name of zone

'hydraulic conductivity in x-direction'
1.80d-5                  ;K_xx

'hydraulic conductivity in z-direction'
1.80d-6                  ;K_zz

'end of zone'

! -----
'tailings'              ;name of zone

'hydraulic conductivity in x-direction'
5.00d-6                  ;K_xx

'hydraulic conductivity in z-direction'
1.00d-6                  ;K_zz

'end of zone'

'done'
```

b. Variably-saturated Example

```
! Section 10: physical parameters - variably-saturated flow
! -----
!
'physical parameters - variably-saturated flow'

! -----
'silty sand'

'hydraulic conductivity in z-direction'
6.0d-6                  ;K_zz

'specific storage coefficient'
1.0d-5

'soil hydraulic function parameters'
```

```

0.25          ;residual saturation
1.50          ;van genuchten - alpha
2.80          ;van genuchten - n
0.5           ;expn
0.0           ;air entry pressure

'end of zone'

'done'

```

3.13.4 DESCRIPTION OF EXAMPLE INPUT

Two examples are provided for this data block. The first example is applicable for a steady state flow problem under fully-saturated conditions, while the second example includes all necessary input parameters for a transient simulation under variably-saturated conditions. The first example contains two material property zones identified by the names 'aquifer' and 'tailings'. The example is for a 2D-vertical cross-section located in the x-z-plane. Therefore the hydraulic conductivities in these two directions are specified. The hydraulic conductivity in the vertical direction for both material property zones is lower than in the horizontal direction.

The second example contains only one material property zone ('silty sand') and provides the parameters needed for a 1D-unsaturated flow problem in z-direction. In addition to the first example input section, the specific storage coefficient and the soil hydraulic function parameters are specified.

3.13.5 DISTRIBUTED PARAMETERS INPUT

The specific storage coefficient can be specified through a separate file with the extension prefix.spstor through the keywords 'read specific storage coefficient from file' in the Data Block 10: 'physical parameters - variably-saturated flow'. An example for the activation using keywords is:

```

! Data Block 10: physical parameters - variably saturated flow
! -----
'physical parameters - variably saturated flow'
! -----
'read specific storage coefficient from file'
'read hydraulic conductivity field from file'
'read skempton coefficient from file'
! -----
'basin'          ;name of zone

'hydraulic conductivity in x-direction'
0.1
'hydraulic conductivity in y-direction'
0.1
'hydraulic conductivity in z-direction'
0.1
'specific storage coefficient'
1.0d-5
'end of zone'
'done!...'

```

The data needed in file prefix.spstor is three header lines followed by the x,y,z-coordinates and the specific storage coefficient of each control volume as the following:

```

title = "dataset basin"
variables = "x", "y", "z","specific storage"

```

```

zone t = "field",i = 450, j = 100, k = 1, f=point
0.0000000E+00 0.0000000E+00 0.0000000E+00 0.1589782E-06
0.9931983E+03 0.0000000E+00 0.0000000E+00 0.1589782E-06
0.1986396E+04 0.0000000E+00 0.0000000E+00 0.1589782E-06
0.2979594E+04 0.0000000E+00 0.0000000E+00 0.1589782E-06
... ..

```

Similarly, the hydraulic conductivities in three coordinates (k_{xx} , k_{yy} , k_{zz}) can be specified in the same way using the keywords: 'read hydraulic conductivity field from file'. For 1D problems, the corresponding $k_{??}$ must be provided, the other two $k_{??}$ values can be any number (e.g. the same value as before). The file should be named with the extension prefix.hyc in the following format:

```

title = "dataset basin"
variables = "x", "y", "z", "kxx", "kyy", "kzz"
zone t = "field",i = 450, j = 100, k = 1, f=point
0.0000000E+00 0.0000000E+00 0.0000000E+00 0.4095668E-13 0.4095668E-13 0.4095668E-14
0.9931983E+03 0.0000000E+00 0.0000000E+00 0.4095668E-13 0.4095668E-13 0.4095668E-14
0.1986396E+04 0.0000000E+00 0.0000000E+00 0.4095668E-13 0.4095668E-13 0.4095668E-14
0.2979594E+04 0.0000000E+00 0.0000000E+00 0.4095668E-13 0.4095668E-13 0.4095668E-14
0.3972792E+04 0.0000000E+00 0.0000000E+00 0.4095668E-13 0.4095668E-13 0.4095668E-14
... ..

```

If permeability is used instead of hydraulic conductivity, the distributed permeabilities can be specified in the same way as distributed hydraulic conductivities using the keywords: 'read permeability field from file'. The file should be with the same extension prefix.hyc and provides permeability at each control volume.

When ice sheet loading/unloading is considered, the nodal Skempton coefficients can be specified in the same way. Skempton coefficients (see section 3.23.5) at all control volumes are specified through a separate file prefix.skempton in the following format.

```

title = "dataset basin"
variables = "x", "y", "z", "skempton"
zone t = "field",i = 450, j = 100, k = 1, f=point
0.0000000E+00 0.0000000E+00 0.0000000E+00 0.9518758E+00
0.9799555E+03 0.0000000E+00 0.0000000E+00 0.9518758E+00
0.1959911E+04 0.0000000E+00 0.0000000E+00 0.9518758E+00
0.2939866E+04 0.0000000E+00 0.0000000E+00 0.9518758E+00
... ..

```

To facilitate this input, the keywords 'read skempton coefficient from file' should be included in the data block 10: 'physical parameters - variably saturated flow'. This parameter is applied to calculate the pore water pressure induced by the ice sheet covered on the top.

3.14 PHYSICAL PARAMETERS - ENERGY BALANCE (DATA BLOCK 10B)

3.14.1 DESCRIPTION OF DATA BLOCK

This data block specifies physical parameters affecting the heat transport solution only. Parameters must be specified for each of the zones defined in Data block 9 ('physical parameters – porous medium') and are identified by the names of the zones. Parameters to be specified include specific heat of water, thermal conductivities of water and solid, dispersivities and solid bulk densities.

3.14.2 DESCRIPTION OF INPUT PARAMETERS

3.14.2.1 'physical parameters - energy balance'

A sub-block is required for each material property zone defined in the previous section ('physical parameters - energy balance'). Each material property zone is suggested to be identified by the name of the zone as specified in the section 3.12 (Data Block 9) to avoid confusion. However, the zone names can also be different if the thermal property zones are different to other physical property zones. In such case, the thermal property zone names should be kept for the data block for initial conditions – energy balance. The input for each material property zone is ended with the statement 'end of zone'. An exception to this format is the 'specific heat of water' and 'gas thermal conductivity', which are specified only once. All related parameters including the keywords, description, units and requirements are listed in Table 3.13.

3.14.2.2 'specific heat of water'

The specification of specific heat of water is only necessary once in this section, because the specific heat of water is specified for water/solution, which is independent of porous medium properties.

3.14.2.3 'specific heat of air'

Similar to the specific heat of water, the specification of specific heat of air is only necessary once in this section.

3.14.2.4 'gas thermal conductivity'

The specification of 'gas thermal conductivity' is only necessary if not fully saturated. It is also independent of porous medium properties.

3.14.2.5 'specific heat of solid'

The sub-keyword 'specific heat of solid' specifies the specific heat capacity of solids (the porous medium). It is dependent of the porous medium properties, and should be defined for each thermal property zones.

3.14.2.6 'water thermal conductivity in ?-direction'

Water thermal conductivity specifies the thermal conductivity of the aqueous phases and must be provided for any heat transport problem. Only the water thermal conductivities for the active dimensions need to be specified. For example, a 1D-simulation in x-direction only requires the specification of 'water thermal conductivity in x-direction' and the corresponding thermal conductivity value.

3.14.2.7 'solid thermal conductivity in ?-direction'

Similarly, solid thermal conductivity specifies the thermal conductivity of the solid phases must be provided for any heat transport problem.

3.14.2.8 Thermal dispersivities

Thermal dispersivities are porous medium parameters, and need to be defined for each thermal property zones. Thermal dispersivities may be specified in longitudinal direction, and in transverse horizontal and transverse vertical directions. Thermal dispersivities are initiated by the headers 'longitudinal dispersivity', 'transverse horizontal dispersivity' and 'transverse vertical dispersivity', followed by the appropriate dispersivity values. Only the relevant dispersivities need to be specified.

Which dispersivities are required is a function of the active dimensions (in x, y and z-direction) in the solution domain (see Table 3.13 for the required dispersivities). The input for each zone is ended with the statement 'end of zone'.

3.14.2.9 'read energy balance parameters from file'

The physical parameters for energy balance can be specified through a separate file with the extension prefix.energybal if the keywords 'read energy balance parameters from file' can be found in the Data Block 10B: 'physical parameters - energy balance'. An example of the activation using keywords is:

```
! Data Block 10B: physical parameters - energy balance
! -----
'physical parameters - energy balance'
1
'read energy balance parameters from file'

'specific heat of water'
4182.0d0

'number and name of zone'
1
'pepe rompe'

'specific heat of solid'
840.0d0

'water thermal conductivity in x-direction'
0.6d0

'water thermal conductivity in y-direction'
0.6d0

'water thermal conductivity in z-direction'
0.6d0

'solid thermal conductivity in x-direction'
3.5d0

'solid thermal conductivity in y-direction'
3.5d0

'solid thermal conductivity in z-direction'
3.5d0

'longitudinal dispersivity'
4.0

'transverse vertical dispersivity'
1.0

'transverse horizontal dispersivity'
1.0

'solid bulk density'
2650.0d0

'extent of zone'
0.0 440000.0d0 0.0 1.0 0.0 4000.0
'end of zone'
'done'
```

The data required in the file prefix.energybal should include the x,y,z-coordinates, the thermal capacity in $[J\ kg^{-1}\ K^{-1}]$, thermal conductivity for water in x,y,z-coordinates in $[J\ s^{-1}\ m^{-1}\ K^{-1}]$, thermal conductivity for solid in x,y,z-coordinates in $[J\ s^{-1}\ m^{-1}\ K^{-1}]$, longitudinal dispersion coefficient for

heat equation, transverse horizontal dispersion coefficient for heat equation, transverse vertical dispersion coefficient for heat equation (unit [m]), and solid bulk dry density in [kg m⁻³] of each control volume. An example of the prefix.energybal is:

```

title = "dataset basin"
variables = "x", "y", "z", "heatcapsol", "heatcondwx", "heatcondwy", "heatcondwz",
"heatcondsx", "heatcondsy", "heatcondsz", "disheatx", "disheaty", "disheatz", "denssol"
zone t = "field",i = 300, j = 85, k = 1, f=point
0.0000000E+00 0.0000000E+00 0.0000000E+00 0.6820000E+03 0.6000000E+00 0.6000000E+00
0.6000000E+00 0.2600000E+01 0.2600000E+01 0.2600000E+01 0.3000000E+02 0.3000000E+02
0.3000000E+02 0.2750000E+04
0.1491458E+04 0.0000000E+00 0.0000000E+00 0.6820000E+03 0.6000000E+00 0.6000000E+00
0.6000000E+00 0.2600000E+01 0.2600000E+01 0.2600000E+01 0.3000000E+02 0.3000000E+02
0.3000000E+02 0.2750000E+04
0.2982916E+04 0.0000000E+00 0.0000000E+00 0.6820000E+03 0.6000000E+00 0.6000000E+00
0.6000000E+00 0.2600000E+01 0.2600000E+01 0.2600000E+01 0.3000000E+02 0.3000000E+02
0.3000000E+02 0.2750000E+04
0.4474374E+04 0.0000000E+00 0.0000000E+00 0.6820000E+03 0.6000000E+00 0.6000000E+00
0.6000000E+00 0.2600000E+01 0.2600000E+01 0.2600000E+01 0.3000000E+02 0.3000000E+02
0.3000000E+02 0.2750000E+04
0.5965829E+04 0.0000000E+00 0.0000000E+00 0.6820000E+03 0.6000000E+00 0.6000000E+00
0.6000000E+00 0.2600000E+01 0.2600000E+01 0.2600000E+01 0.3000000E+02 0.3000000E+02
0.3000000E+02 0.2750000E+04
0.7457292E+04 0.0000000E+00 0.0000000E+00 0.6820000E+03 0.6000000E+00 0.6000000E+00
0.6000000E+00 0.2600000E+01 0.2600000E+01 0.2600000E+01 0.3000000E+02 0.3000000E+02
0.3000000E+02 0.2750000E+04
0.8948750E+04 0.0000000E+00 0.0000000E+00 0.6820000E+03 0.6000000E+00 0.6000000E+00
0.6000000E+00 0.2600000E+01 0.2600000E+01 0.2600000E+01 0.3000000E+02 0.3000000E+02
0.3000000E+02 0.2750000E+04
0.1044021E+05 0.0000000E+00 0.0000000E+00 0.6820000E+03 0.6000000E+00 0.6000000E+00
0.6000000E+00 0.2600000E+01 0.2600000E+01 0.2600000E+01 0.3000000E+02 0.3000000E+02
0.3000000E+02 0.2750000E+04
... ..

```

Table 3.13: Summary of input parameters for section ‘physical parameters – energy balance’

Keywords			Required/Optional	
'physical parameters - energy balance'			required for any energy balance simulation	
Subsection*	Parameter	Description	Required/Optional	
'specific heat of water'	c_w^0 [J kg ⁻¹ °C ⁻¹]	Specific heat of the aqueous phase	Required for any heat transport simulation	
'specific heat of air'	C_g^0 [J kg ⁻¹ °C ⁻¹]	Specific heat of the gas phase	Required for unsaturated heat transport simulation	
'gas thermal conductivity'	λ^g [W m ⁻¹ °C ⁻¹]	Thermal conductivity for gas	Only required if not fully saturated	
N ^{nmz} -zones	'specific heat of solid'	c_s^0 [J kg ⁻¹ °C ⁻¹]	Specific heat of the solid phase	Required for any heat transport simulation
	'water thermal conductivity in x-direction'	λ_{xx}^w [W m ⁻¹ °C ⁻¹]	water thermal conductivity in x-direction	only required if number of control volumes in x-direction > 1
	'water thermal conductivity in y-direction'	λ_{yy}^w [W m ⁻¹ °C ⁻¹]	water thermal conductivity in y-direction	only required if number of control volumes in y-direction > 1

'water thermal conductivity in z-direction'	λ_{zz}^w [W m ⁻¹ °C ⁻¹]	water thermal conductivity in z-direction	only required if number of control volumes in z-direction > 1
'solid thermal conductivity in x-direction'	λ_{xx}^s [W m ⁻¹ °C ⁻¹]	solid thermal conductivity in x-direction	only required if number of control volumes in x-direction > 1
'solid thermal conductivity in y-direction'	λ_{yy}^s [W m ⁻¹ °C ⁻¹]	solid thermal conductivity in y-direction	only required if number of control volumes in y-direction > 1
'solid thermal conductivity in z-direction'	λ_{zz}^s [W m ⁻¹ °C ⁻¹]	solid thermal conductivity in z-direction	only required if number of control volumes in z-direction > 1
'longitudinal dispersivity'	α_l [m]	longitudinal thermal dispersivity	Only required if number of control volumes in x-direction > 1
'transverse horizontal dispersivity'	α_{th} [m]	transverse horizontal thermal dispersivity	only required if number of control volumes in x- and y-direction > 1
'transverse vertical dispersivity'	α_{tv} [m]	transverse vertical thermal dispersivity	only required if number of control volumes in x- and z- or y- and z-direction > 1
'solid bulk density'	ρ_s [kg m ⁻³]	Solid bulk dry density	Required
Section Closing			Required/Optional
'done'			required
*All keyword headings must appear on a single line in the input file.			

3.14.3 EXAMPLE DATA FILE INPUT

```

! Section 10B: physical parameters - energy balance
! -----
!
!physical parameters - energy balance'
1

'specific heat of water'
4182.0d0

'specific heat of air'
1004.661d0

'number and name of zone'
1
'pepe rompe'

'specific heat of solid'
840.0d0

'water thermal conductivity in x-direction'
0.6d0

'water thermal conductivity in y-direction'
0.6d0

```

```

'water thermal conductivity in z-direction'
0.6d0

'solid thermal conductivity in x-direction'
3.5d0

'solid thermal conductivity in y-direction'
3.5d0

'solid thermal conductivity in z-direction'
3.5d0

'longitudinal dispersivity'
10.0d0

'transverse vertical dispersivity'
1.0d0

'transverse horizontal dispersivity'
1.0d0

'solid bulk density'
2650.0d0

'extent of zone'
0.0 1000.0d0 0.0 10.0 0.0 10.0

'end of zone'

```

3.14.4 DESCRIPTION OF EXAMPLE INPUT

The example provided for this data block contains only one material property zone ('pepe rompe') and provides the thermal parameters needed for a 3D-saturated heat transport problem. The thermal conductivities of the aqueous and solid phases are homogeneous and are identical in all directions. The longitudinal thermal dispersivity is 10 times higher than the transverse horizontal/vertical thermal dispersivities.

3.15 PHYSICAL PARAMETERS – REACTIVE TRANSPORT (DATA BLOCK 11)

3.15.1 DESCRIPTION OF DATA BLOCK

This data block specifies physical parameters affecting the reactive transport solution only. Parameters must be specified for each of the zones defined in Data block 9 ('physical parameters – porous medium', see Section 3.12) and are identified by the names of the zones. Parameters to be specified include diffusion coefficients and dispersivities.

3.15.2 DESCRIPTION OF INPUT PARAMETERS

3.15.2.1 'physical parameters – reactive transport'

A sub-block is required for each material property zone defined in the previous section ('physical parameters – porous medium'). Each material property zone is identified by the name of the zone as specified in the previous section. The input for each material property zone is ended with the

statement 'end of zone'. An exception to this format is diffusion coefficients, which are specified only once. All potential parameters are listed in Table 3.14.

3.15.2.2 'diffusion coefficients'

The specification of diffusion coefficients is only necessary once in this section, because diffusion coefficients are specified as free phase diffusion coefficients, which are independent of porous medium properties. If the solution domain is fully saturated, only a free phase diffusion coefficient in water needs to be specified. This diffusion coefficient is applied to all dissolved species. Species-specific diffusion coefficients are at the present time not considered in MIN3P-THCm. The free phase diffusion coefficient should therefore represent average diffusive transport behavior for the included species. If the solution domain is partially saturated, it is necessary to also specify an average free phase diffusion coefficient in air. The input of the diffusion coefficient is initiated with the subkeywords 'diffusion coefficients', followed by the values for the aqueous phase diffusion coefficient and, for the variably-saturated case, the gaseous phase diffusion coefficient.

3.15.2.3 'dispersivity'

Dispersivities are porous medium parameters, and need to be defined for each material property zone specified in Data block 9 of the input file ('physical parameters – porous medium'). The input for each zone is initiated by the name of the zone, as specified in Data block 9 of the input file. Dispersivities may be specified in longitudinal direction, and in transverse horizontal and transverse vertical directions. Dispersivities are initiated by the headers 'longitudinal dispersivity', 'transverse horizontal dispersivity' and 'transverse vertical dispersivity', followed by the appropriate dispersivity values. Only the relevant dispersivities need to be specified. Which dispersivities are required is a function of the active dimensions (in x, y and z-direction) in the solution domain (see Table 3.14 for the required dispersivities). The input for each zone is ended with the statement 'end of zone'.

3.15.2.4 'update gas density'

The sub-keyword 'update gas density' enables the option to update the gas density during the simulation. If this sub-keyword is not provided and no gas density is provided, the default value of gas density in 1.29 kg m^{-3} is used.

3.15.2.5 'constant gas density'

The sub-keyword 'constant gas density' enables the option to fix the gas density during the simulation. If this sub-keyword is provided, the gas density should be given in the next line and no gas density is provided in kg m^{-3} .

3.15.2.6 Gas viscosity models

There are three gas dynamic viscosity models available in MIN3P-THCm: Wilke, linear and constant viscosity models in [Pa s] by using the keywords 'wilke viscosity', 'linear viscosity' and 'constant viscosity', respectively. The Wilke viscosity model (Wilke 1950) calculates the viscosity of a gas mixture according to the viscosity, molar weight and molar fraction of each gas component. The input parameters are the viscosity of each gas component. For example:

```
'wilke viscosity'
2.04d-5           ;O2
1.46d-5           ;CO2
1.75d-5           ;N2
```

In the first line, the model name is provided. The following lines specify the gas viscosity values

of all gases in the same order as the gas names specified in data block 2: 'geochemical system'. The molar weight of each gas is provided in the database.

Similarly, the linear gas viscosity model, which calculates the viscosity of a gas mixture by the multiplication of the molar fraction of each gas and viscosity of each gas component, can be specified using the keyword 'linear viscosity' followed by the gas viscosity values of all gases in the same order as the gas names specified in data block 2: 'geochemical system'.

```
'linear viscosity'
2.04d-5           ;O2
1.46d-5           ;CO2
1.75d-5           ;N2
```

The constant viscosity model, which treats the gas mixture with a constant value, can be specified using the keyword 'constant viscosity' followed by one viscosity value of the gas mixture.

```
'constant viscosity'
1.84d-5           ;viscosity of the gas mixture
```

Table 3.14: Summary of input parameters for section 'physical parameters – reactive transport'

Keywords			Required/Optional	Typical Range of Values
'physical parameters – reactive transport'			required for any reactive transport simulation	
Subsection*	Parameter	Description	Required/Optional	
'diffusion coefficients'	D_a^0 [$m^2 s^{-1}$]	representative free phase diffusion coefficient in water	required for any reactive transport simulation	10^{-10} - 10^{-8}
	D_g^0 [$m^2 s^{-1}$]	representative free phase diffusion coefficient in air	only required if not fully-saturated	
N ^{noz} -zones	'longitudinal dispersivity'	α_l [m]	longitudinal dispersivity	only required if number of control volumes in x-direction > 1
	'transverse horizontal dispersivity'	α_{th} [m]	transverse horizontal dispersivity	only required if number of control volumes in x- and y-direction > 1
	'transverse vertical dispersivity'	α_{tv} [m]	transverse vertical dispersivity	only required if number of control volumes in x- and z- or y- and z-direction > 1
Section Closing			Required/Optional	
'done'			required	

*All keyword headings must appear on a single line in the input file.

3.15.3 EXAMPLE DATA FILE INPUT

An input example:

```
! Section 11: physical parameters - reactive transport
! -----
!
'physical parameters - reactive transport'

'diffusion coefficients'
2.0d-10                ;aqueous phase
2.0d-5                 ;gaseous phase

! -----
'aquifer'              ;name of zone

'longitudinal dispersivity'
0.5

'transverse vertical dispersivity'
0.005

'end of zone'

! -----
'tailings'            ;name of zone

'longitudinal dispersivity'
0.1

'transverse vertical dispersivity'
0.001

'end of zone'

'done'
```

3.15.4 DESCRIPTION OF EXAMPLE INPUT

The example input file contains the parameters for two zones of materials – the ‘aquifer’ and the ‘tailings’. Diffusion coefficients for the aqueous and gaseous phases are specified independently of these zones in the beginning of the section. The aqueous phase diffusion coefficient in the example section is $D_a^0 = 2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, and the gaseous phase diffusion coefficient is $D_g^0 = 2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. The two material property zones are initiated by the names of the zones ‘aquifer’ and ‘tailings’. (These names must be consistent with the names defined in the corresponding Data block 9 of the input file ‘physical parameters – porous medium’). For each of these zones dispersivities in longitudinal and transverse vertical direction are specified indicating that the section belongs to a simulation for a 2D-vertical cross section. The dispersivities for the material property zone ‘aquifer’ are 0.5m and 0.005m, respectively, while the dispersivities for the zone ‘tailings’ are 0.1 and 0.001m, respectively.

3.16 INITIAL CONDITION - VARIABLY-SATURATED FLOW

(DATA BLOCK 12)**3.16.1 DESCRIPTION OF DATA BLOCK**

This data block specifies the initial condition in the solution domain for the physical flow problem. The initial condition is defined for fully saturated flow by the hydraulic head and for variably-saturated flow by the pressure head distribution. The distribution of this parameter can be discretized across the model domain. These zones do not have to coincide with the material property zones defined in Data block 9-11 of the input file. It is also possible to base the initial condition on an existing solution, i.e., by providing a file with a hydraulic head or pressure head value for each spatial discretization point.

3.16.2 DESCRIPTION OF INPUT PARAMETERS**3.16.2.1 ‘initial condition – variably-saturated flow’**

A sub-block is required for each material property zone defined in the previous section (‘physical parameters – porous medium’). Each initial condition zone is identified by the name of the zone as specified in the previous section. The input for each material property zone is ended with the statement ‘end of zone’.

The zone number and a zone name are specified below the subkeywords ‘number and name of zone’ for each zone. The zone names may or may not be identical with the names specified for the material property zones. Table 3.15 provides a list of the related parameters.

3.16.2.2 ‘initial condition’

The next header ‘initial condition’ initiates the input of the initial condition in terms of hydraulic head or in terms of pressure head, as specified in Data Block 6 of the input file (‘control parameters – variably-saturated flow’ - if this section is not included, the input for the initial condition will be expected in terms of hydraulic head).

3.16.2.3 extent of zone’

The specified initial condition needs to be allocated to a specific area of the solution domain below the header ‘extent of zone’. MIN3P-THCm allows the simulation of flow and reactive transport in three spatial dimensions. The input in the following line defines the location of minimum and maximum coordinates in the x, y and z-directions for the initial condition to be allocated. If a 1D or 2D-simulation is conducted, the minimum and maximum coordinates for the excluded dimensions should be specified as 0.0 and 1.0, respectively. The input for each section is concluded with the statement ‘end of zone’. It is possible to overlay initial conditions. The input in the zone with the higher number replaces earlier input.

3.16.2.4 ‘read initial condition from file’

The initial conditions can be specified by reading from an external file with the extension prefix.ivs, which fits a pre-specified format (the same format as defined in the prefix_0.gsp files, which contains the flow solution). In this case, the statement ‘read initial condition from file’ needs to be included in the input data block ‘initial condition – variably-saturated flow’ instead of the number of zones and the zone-specific input. In addition a file with the name prefix.ivs must be provided containing the initial conditions. The required parameters in the file prefix.ivs depend on the flow processes as described below.

For isothermal saturated flow, the prefix.ivs should provide the x,y,z-coordinates of each control volume and the hydraulic head (h_w) [m] in the following format:

```
title = "dataset amd"
variables = "x", "y", "z", "h_w"
zone t = "initial condition " i = 40, j = 1, k = 1, f=point
  0.0000000E+00 0.0000000E+00 0.0000000E+00 0.5000000E-01
  0.0000000E+00 0.0000000E+00 0.5128205E-01 0.4811675E-01
  0.0000000E+00 0.0000000E+00 0.1025641E+00 0.4605224E-01
  0.0000000E+00 0.0000000E+00 0.1538462E+00 0.4377074E-01
  0.0000000E+00 0.0000000E+00 0.2051282E+00 0.4123221E-01
.....
```

For isothermal saturated density dependent flow, the prefix.ivs should provide the x,y,z-coordinates of each control volume, the hydraulic head (h_w) [m], and fluid pressure (P_w) [Pa] in the following format:

```
title = "dataset verif_sutra"
variables = "x", "y", "z", "h_w", "p_w"
zone t = "initial condition " i = 35, j = 10, k = 1, f=point
  0.0000000E+00 0.0000000E+00 0.0000000E+00 0.3324825E+02 0.3261653E+06
  0.1550000E+01 0.0000000E+00 0.0000000E+00 0.3247669E+02 0.3185963E+06
  0.2705000E+01 0.0000000E+00 0.0000000E+00 0.3220291E+02 0.3159105E+06
  0.3975500E+01 0.0000000E+00 0.0000000E+00 0.3201184E+02 0.3140361E+06
.....
```

For isothermal unsaturated flow, the prefix.ivs should provide the x,y,z-coordinates of each control volume, the hydraulic head (h_w) [m], fluid pressure (P_w) [Pa], aqueous phase saturation (S_a) [-], aqueous phase content ($\theta_a = \text{porosity} * S_a$) [-], gaseous phase saturation S_g [-] and gaseous phase content ($\theta_g = \text{porosity} * S_g$) [-] in the following format:

```
title = "dataset amd"
variables = "x", "y", "z", "h_w", "p_w", "s_a", "theta_a", "s_g", "theta_g"
zone t = "initial condition " i = 40, j = 1, k = 1, f=point
  0.0000000E+00 0.0000000E+00 0.0000000E+00 -0.5000000E-01 -0.5000000E-01 0.9991905E+00
  0.4995952E+00 0.8095380E-03 0.4047690E-03
  0.0000000E+00 0.0000000E+00 0.5128205E-01 -0.4811675E-01 -0.9939880E-01 0.9964679E+00
  0.4982340E+00 0.3532082E-02 0.1766041E-02
  0.0000000E+00 0.0000000E+00 0.1025641E+00 -0.4605224E-01 -0.1486163E+00 0.9916740E+00
  0.4958370E+00 0.8326019E-02 0.4163009E-02
.....
```

For isothermal unsaturated density dependent flow, the prefix.ivs should provide the x,y,z-coordinates of each control volume, the hydraulic head (h_w) [m], fluid pressure (P_w) [Pa], fluid pressure head (Ph_w) [m], aqueous phase saturation (S_a) [-], aqueous phase content ($\theta_a = \text{porosity} * S_a$) [-], gaseous phase saturation (S_g) [-], and gaseous phase content ($\theta_g = \text{porosity} * S_g$) [-] in the following format:

```
title = "dataset verif_sutra"
variables = "x", "y", "z", "h_w", "p_w", "ph_w", "s_a", "theta_a", "s_g", "theta_g"
zone t = "initial condition " i = 35, j = 10, k = 1, f=point
  0.0000000E+00 0.0000000E+00 0.0000000E+00 0.3324825E+02 0.3261653E+06 0.3375457E+02
  0.1000000E+01 0.3500000E+00 0.0000000E+00 0.0000000E+00
  0.1550000E+01 0.0000000E+00 0.0000000E+00 0.3247669E+02 0.3185963E+06 0.3297125E+02
  0.1000000E+01 0.3500000E+00 0.0000000E+00 0.0000000E+00 0.0000000E+00
  0.2705000E+01 0.0000000E+00 0.0000000E+00 0.3220291E+02 0.3159105E+06 0.3269330E+02
  0.1000000E+01 0.3500000E+00 0.0000000E+00 0.0000000E+00
  0.3975500E+01 0.0000000E+00 0.0000000E+00 0.3201184E+02 0.3140361E+06 0.3249933E+02
  0.1000000E+01 0.3500000E+00 0.0000000E+00 0.0000000E+00
.....
```

For non-isothermal saturated density dependent flow, the prefix.ivs should provide the x,y,z-coordinates of each control volume, the hydraulic head (h_w) [m], fluid pressure (P_w) [Pa], fluid pressure head (Ph_w) [m], aqueous phase density (ρ_a) [$kg\ m^{-3}$], aqueous phase saturation (S_a) [-], aqueous phase content (θ_a =porosity* S_a) [-], gaseous phase saturation (S_g) [-], gaseous phase content (θ_g =porosity* S_g) [-] and temperature [degC] in the following format:

```

title = "dataset verif_sutra"
variables = "x", "y", "z", "h_w", "p_w", "ph_w", "rho_a", "s_a", "theta_a", "s_g", "theta_g"
"temp_n"
zone t = "initial condition " i = 35, j = 10, k = 1, f=point
0.0000000E+00 0.0000000E+00 0.0000000E+00 0.3324825E+02 0.3261653E+06 0.3375457E+02
0.9850000E+03 0.1000000E+01 0.3500000E+00 0.0000000E+00 0.0000000E+00 0.6000000E+02
0.1550000E+01 0.0000000E+00 0.0000000E+00 0.3247669E+02 0.3185963E+06 0.3297125E+02
0.9850000E+03 0.1000000E+01 0.3500000E+00 0.0000000E+00 0.0000000E+00 0.6000000E+02
0.2705000E+01 0.0000000E+00 0.0000000E+00 0.3220291E+02 0.3159105E+06 0.3269330E+02
0.9850000E+03 0.1000000E+01 0.3500000E+00 0.0000000E+00 0.0000000E+00 0.6000000E+02
0.3975500E+01 0.0000000E+00 0.0000000E+00 0.3201184E+02 0.3140361E+06 0.3249933E+02
0.9850000E+03 0.1000000E+01 0.3500000E+00 0.0000000E+00 0.0000000E+00 0.6000000E+02
.....

```

Table 3.15: Summary of input parameters for section ‘initial condition – variably-saturated flow’

Keywords			Required/Optional
‘initial condition – variably-saturated flow’			required for any flow simulation
‘read initial condition from file’			optional, requires file prefix.ivs
N_i		number of zones	required, if initial condition not read from file
Subsection	Parameter	Description	Required/Optional
N_i zones	‘number and name of zone’	i_i number of zone	required, if initial condition not read from file
		name name of zone	
	‘initial condition’	h_i [m] p_i [m] initial hydraulic head or initial pressure head	
	‘extent of zone’	x_{min} [m] x_{max} [m] y_{min} [m] y_{max} [m] z_{min} [m] z_{max} [m] minimum and maximum coordinates defining zone in x-, y- and z-directions	
	‘end of zone’	- -	
Section Closing			Required/Optional
‘done’			required

3.16.3 EXAMPLE DATA FILE INPUT

a. Specified in Input File

```
'initial condition - variably-saturated flow'
2                               ;number of zones

! -----
'number and name of zone'
1
'upper aquifer'

'initial condition'
2.0

'extent of zone'
0.0 20.0 0.0 0.0 0.0 4.0

'end of zone'

! -----
'number and name of zone'
2
'lower aquifer'

'initial condition'
1.0

'extent of zone'
0.0 20.0 0.0 0.0 0.0 2.0

'end of zone'

'done'
```

b. Specified From an External File

```
'initial condition - variably-saturated flow'
'read initial condition from file'           ;read from file
```

Note: in such case, the file prefix.ivs containing the initial condition at each control volumes in the format of prefix.gsp should be provided. The first three lines as the tecplot header will be ignored by the code. For saturated flow, the initial hydraulic head or pressure is relevant. An example of the external file for saturated flow problem is:

```
title = "dataset comptran"
variables = "x", "y", "z", "h_w", "p_w", "s_w", "theta_a"
zone t = "Flow variables, initial condition" i = 41, j = 1, k = 1, f=point
0.0000000E+00 0.0000000E+00 0.0000000E+00 0.1000000E+01 0.1000000E+01 0.1000000E+01
0.3000000E+00
0.2500000E-01 0.0000000E+00 0.0000000E+00 0.1000000E+01 0.1000000E+01 0.1000000E+01
0.3000000E+00
0.5000000E-01 0.0000000E+00 0.0000000E+00 0.1000000E+01 0.1000000E+01 0.1000000E+01
0.3000000E+00
.....
```

For unsaturated flow, all parameters are relevant. An example of the external file for unsaturated flow problem is:

```
title = "dataset stedvs"
variables = "x", "y", "z", "h_w", "p_w", "s_w", "theta_a", "s_a", "theta_g"
zone t = "Flow variables, steady state" i = 21, j = 21, k = 1, f=point
0.0000000E+00 0.0 0.0 0.4565453E-01 0.4565453E-01 0.1000000E+01 0.1000000E+01
```

```

0.0000000E+00 0.0000000E+00
0.5000000E-01 0.0 0.0 0.4530134E-01 0.4530134E-01 0.1000000E+01 0.1000000E+01
0.0000000E+00 0.0000000E+00
0.1000000E+00 0.0 0.0 0.4423150E-01 0.4423150E-01 0.1000000E+01 0.1000000E+01
0.0000000E+00 0.0000000E+00
0.1500000E+00 0.0 0.0 0.4241359E-01 0.4241359E-01 0.1000000E+01 0.1000000E+01
0.0000000E+00 0.0000000E+00
.....

```

3.16.4 DESCRIPTION OF EXAMPLE INPUT

In the example a, the initial conditions for two zones are defined. The initial hydraulic head/pressure for the zone ‘upper aquifer’ is 2.0 m, and for the zone ‘lower aquifer’ is 1.0 m. The units for the initial condition need to be consistent with the ones specified in Data Block 6 of the input file (‘control parameters – variably-saturated flow’). We assume hydraulic head in this case. Initially, a hydraulic head in 2.0 m for the zone ‘upper aquifer’ is specified for the entire solution domain (i.e. $x=0$ to 20.0 m, $z=0$ to 4.0 m), but is later partially overwritten with the initial condition specified in the zone ‘lower aquifer’ (i.e. $x=0$ to 20.0 m, $z=0$ to 2.0 m) with a hydraulic head in 1.0 m.

3.16.5 ADDITIONAL COMMENTS

For steady state flow simulations, the initial condition is arbitrary, however, it may affect the efficiency of the solution, in particular for variably-saturated conditions. On the other hand, the initial condition for the flow problem has a direct impact for transient flow simulations and needs to be specified carefully. It may be of advantage to base a transient flow solution on an existing steady state flow solution. In this case the output of the steady state flow solution (prefix_1.gsp) can be copied to the file prefix.ivs, which is being read as the initial condition.

3.17 BOUNDARY CONDITIONS - VARIABLY-SATURATED FLOW (DATA BLOCK 13)

3.17.1 DESCRIPTION OF DATA BLOCK

In this data block, the flow boundary conditions for the solution domain are specified. By default, the boundaries of the solution domain are assigned as second type-Neumann boundaries with a specified flux of zero (no-flow boundary). Specific boundary conditions, which allow flow into and out of the domain, can be specified.

3.17.2 DESCRIPTION OF INPUT PARAMETERS

If no boundary conditions are specified, the domain boundary is assumed to be impermeable. To allow flux into and out of the solution domain, it is necessary to specify boundaries that are not of this type. The options for boundary types are:

Table 3.16: Boundary conditions for flow solution

Input Name	Boundary Type	Description	Mathematical
------------	---------------	-------------	--------------

			Expression
'first'	Dirichlet	Specified head boundary	$h = h_b$
'second'	Neumann	Specified flux boundary	$q = q_b$
'seepage'		Seepage face boundary	
'point'	Dirichlet	Specified head boundary	$h = h_b$
'atmospheric'	Neumann	Specified flux boundary	

The input data for flow boundary conditions follows the format previously described for other spatially distributed properties. However, unlike for the initial condition zones or for material property zones, boundary conditions can not be overlain on each other.

3.17.2.1 'boundary conditions - variably saturated flow'

The first required parameter is the number of boundary zones, which follows the keywords 'boundary conditions - variably saturated flow'. Each zone is defined by a zone number and zone name following the statement 'number and name of zone'. These zones are independent of those for physical material properties or the initial condition zones, but may have the same name.

3.17.2.2 'boundary type'

The statement 'boundary type' initiates the sub-block which defines what type of boundary condition is to be assigned. The actual boundary type and the numerical value of the boundary condition have to be specified immediately below this statement. The units of the numerical value for first type boundaries must coincide with those specified in Section 6 of the input file ('control parameters – variably-saturated flow': 'hydraulic head' or 'pressure head', both in meters). If a second type boundary condition is assigned a boundary flux needs to be specified in unit m s^{-1} . A seepage face boundary is a review boundary condition and requires the specification of an estimate for the elevation of the seepage face (steady state simulation), or an initial seepage face location which should coincide with the initial condition within the domain (transient simulation). An atmospheric boundary condition can be applied for flow to account for the interaction of the ground water flow with the atmospheric conditions (e.g. evaporation, rain runoff, rainfall). It is a special boundary condition as described in the MIN3P-THCm theory manual section 2.1.6 atmospheric boundary condition. Therefore, it is important to ensure that the evaporation function is activated (see section 3.8 'control parameters – energy balance').

3.17.2.3 'extent of zone'

The dimensions of the boundary zone are specified below the statement 'extent of zone'. As with other spatially distributed parameters, the precise dimensions of the boundary will be dependent on the grid spacing (See Data Block 3 of an input file). Since the model is capable of simulating flow and reactive transport in three dimensions, the specification of the boundaries must be provided in the x, y, and z-dimensions. The coordinates are also used to specify to which boundary face the boundary condition will be applied. This is of particular importance for second type (flux) boundary conditions. For example, the specification:

```
'extent of zone'
0.0 0.0  0.0 1.0  0.0 10.0
```

means that the boundary condition will be applied to the y-z plane of the solution domain at $x = 0.0$ covering an area from $y_{\min} = 0.0$ m to $y_{\max} = 1.0$ m and $z_{\min} = 0$ m to $z_{\max} = 10.0$ m. The model

formulation requires that this input structure is also obeyed for 1D- and 2D-simulations. For example, the specification of the left boundary of a 1D-simulation in x-direction would require the input:

```
'extent of zone'
0.0 0.0  0.0 1.0  0.0 1.0
```

The model can only handle boundary conditions on the surface (edges) of the solution domain. The input for each boundary zone is terminated with the statement 'end of zone'.

3.17.2.4 Transient boundary condition

It is also possible to specify transient boundary conditions for the flow through an additional file with extension: prefix.bcvs. To activate this function, additional keywords 'transient boundary conditions' must be added in the data block 13: 'boundary conditions - variably saturated flow'. This means that a regular data block 13 should be defined. The keywords 'transient boundary conditions' can be added before 'done' to activate the transient flow boundary conditions. In the file prefix.bcvs, the time and boundary conditions should be provided. **The number and order of the boundary conditions should be the same as specified in the file prefix.dat in the Data Block 13. The boundary types of each boundary condition are assumed the same as given in the data block 13 of the file prefix.dat and thus not given in the file prefix.bcvs.** In the MIN3P-THCm execution, the code starts to use the boundary conditions defined in the file prefix.dat for the first time step. After that, it will compare the time for the calculation (t_{exe}) and the time for the transient boundary conditions ($t_{trans,i}$). If $t_{exe} \leq t_{trans,i}$ the boundary condition values defined in the prefix.bcvs will be used.

An example for the activation of specifying transient flow boundary condition using the keywords:

```
! Data Block 13: boundary conditions - variably saturated flow
! -----
!
'boundary conditions - variably saturated flow'
2                               ;number of zones
! -----
'number and name of zone'
1
'inflow boundary'

'boundary type'
'second' 4.11d-5                ;flux

'extent of zone'
0.0 0.5  0.0 1.0  2.0 2.0

'end of zone'

! -----
'number and name of zone'
2
'outflow boundary'

'boundary type'
'first' 0.65d0                  ;hydraulic head

'extent of zone'
3.0 3.0  0.0 1.0  0.0 0.65

'end of zone'

'transient boundary conditions'
'done'
```

And the file prefix.bcvs should be as the following (**without header!**):

```
10.0  0.0      0.65d0
20.0  4.11d-5 0.65d0
```

The example defined two boundary zones for a 2D-vertical cross-section located in the x-z plane with dimensions 3 m (x-direction) by 2 m (z-direction). The first boundary condition ‘inflow boundary’ is defined at the top of the domain (x: from 0.0 to 0.5 meter, z = 2.0 m) with a flux of $4.11 \times 10^{-5} \text{ m s}^{-1}$ (second type boundary condition). The other boundary condition ‘outflow boundary’ is defined at the right boundary (x=3.0 m, and z: from 0.0 to 0.65 m) as constant hydraulic head in 0.65 m. The transient boundary condition is defined in the prefix.bcvs. At 10 hours (note: the time unit is defined in the Data block 4: time step control – global system), the flow into the domain is switched off (no flux for the ‘inflow boundary’), but the ‘outflow boundary’ keeps constant with a hydraulic head in 0.65 m. At 20 hours, the flow into the domain is switched on again with a flux in $4.11 \times 10^{-5} \text{ m s}^{-1}$, while the ‘outflow boundary’ keeps constant with a hydraulic head in 0.65 m.

Table 3.17: Summary of input parameters for section ‘boundary conditions – variably-saturated flow’

Keywords			Required/Optional	
‘boundary conditions – variably-saturated flow’			required for any flow simulation	
N_b		number of zones	required for any flow simulation	
Subsection	Parameter	Description	Required/Optional	
N_b zones	‘number and name of zone’	i_b	number of zone	required for any flow simulation
	‘boundary type’	name	name of zone	
		type	type of boundary condition: ‘first’ ‘second’ ‘seepage’	
	‘extent of zone’	h_b [m] p_b [m] q_b [m s^{-1}]	hydraulic head or pressure head, if type = ‘first’ or ‘seepage’ flux, if type = ‘second’	
		X_{\min} [m] X_{\max} [m] Y_{\min} [m] Y_{\max} [m] Z_{\min} [m] Z_{\max} [m]	minimum and maximum coordinates defining zone in x-, y- and z-directions	
	‘end of zone’	-	-	
Section Closing	Required /Optional			
‘done’			required for any flow simulation	

3.17.3 EXAMPLE DATA FILE INPUT

An input example:

```
'boundary conditions - variably-saturated flow'
3                                     ;number of zones

! -----
'number and name of zone'
1
'left boundary'

'boundary type'
'first' 10.0                          ;hydraulic head

'extent of zone'
0.0 0.0  0.0 1.0  0.0 3.5

'end of zone'

! -----
'number and name of zone'
2
'right boundary'

'boundary type'
'first' 9.53                          ;hydraulic head (m)

'extent of zone'
30.0 30.0  0.0 1.0  0.0 3.5

'end of zone'

! -----
'number and name of zone'
3
'top boundary'

'boundary type'
'second' 1.2d-8                       ;specified flux (m s-1)

'extent of zone'
13.5 30.0  0.0 1.0  3.5 3.5

'end of zone'

'done'

Example for SEEPAGE FACE BOUNDARY (benchmark shlomo):
! Data Block 13: boundary conditions - variably saturated flow
! -----
!
'boundary conditions - variably saturated flow'
3                                     ;number of zones

! -----
'number and name of zone'
1
'inflow boundary'

'boundary type'
'second' 1.20d-6                      ;flux

'extent of zone'
0.0 6.0  0.0 1.0  1.20 1.20

'end of zone'

! -----
```

```

'number and name of zone'
2
'outflow boundary'

'boundary type'
'first' 0.0d0                ;hydraulic head

'extent of zone'
0.0 0.0 0.0 0.0 0.0 0.0

'end of zone'
! -----
'number and name of zone'
3
'seepage face boundary'

'boundary type'
'seepage' 0.0d0              ;elevation of seepage face

'extent of zone'
0.0 0.0 0.0 1.0 0.01 1.20

'end of zone'

```

Example for transient flow boundary condition:

```

! Data Block 13: boundary conditions - variably saturated flow
! -----
!
'boundary conditions - variably saturated flow'
2                ;number of zones

! -----
'number and name of zone'
1
'inflow boundary'

'boundary type'
'second' 4.11d-5        ;flux

'extent of zone'
0.0 0.5 0.0 1.0 2.0 2.0

'end of zone'

! -----
'number and name of zone'
2
'outflow boundary'

'boundary type'
'first' 0.65d0          ;hydraulic head

'extent of zone'
3.0 3.0 0.0 0.0 0.0 0.65

'end of zone'

'transient boundary conditions'

'done'

And the transient boundary conditions file prefix.bcvs:

10.0 0.0 0.65d0
20.0 4.11d-5 0.65d0

```

3.17.4 DESCRIPTION OF EXAMPLE INPUT

The example data file contains three boundary zones for a 2D-vertical cross-section located in the x-z plane with dimensions 30 m (x-direction) by 3.5 m (z-direction). The left boundary and right boundary conditions are first type boundary conditions with a value of 10.0 and 9.53 m (hydraulic head or pressure head, as specified in the Section 5 of the corresponding input file). The third boundary condition at the top of the domain is a second type boundary condition specifying an influx (recharge) of $1.2 \times 10^{-8} \text{ m s}^{-1}$ (corresponding to 380 mm y^{-1}). This boundary condition does not extend over the entire top boundary, but only over a zone reaching from 13.5 to 30 m.

The second example defines a seepage face boundary condition (the last boundary condition 'seepage face boundary'. The elevation of the seepage face is assigned to be 0.0 m.

The third example defined two boundary zones for a 2D-vertical cross-section located in the x-z plane with dimensions 3 m (x-direction) by 2 m (z-direction). The first boundary condition 'inflow boundary' is defined at the top of the domain (x: 0.0 to 0.5 meter, z = 2.0 m) with a flux in $4.11 \times 10^{-5} \text{ m s}^{-1}$ (second type boundary condition). The other boundary condition 'outflow boundary' is defined at the right boundary (x=3.0 m, and z: 0.0 to 0.65 m) as constant hydraulic head in 0.65 m. The transient boundary condition is defined in the prefix.bcvs. At 10 hours (note: the time unit is defined in the Data block 4: time step control – global system), the flow into the domain is switched off (no flux for the 'inflow boundary'), but the 'outflow boundary' keeps constant with a hydraulic head in 0.65 m. At 20 hours, the flow into the domain is switched on again with a flux in $4.11 \times 10^{-5} \text{ m s}^{-1}$, while the 'outflow boundary' keeps constant with a hydraulic head in 0.65 m.

3.18 INITIAL CONDITION – ENERGY BALANCE (DATA BLOCK 12B)

3.18.1 DESCRIPTION OF DATA BLOCK

This data block defines the initial condition for the heat transport problem. As for the heat transport problem, the specification of several zones specified in the section 3.14 ('physical parameters – energy balance') is necessary.

3.18.2 DESCRIPTION OF INPUT PARAMETERS

3.18.2.1 'initial condition - energy balance'

The number of zones needs to be specified after the keywords 'initial condition - energy balance'. In the following, a zone number and a zone name have to be provided below the subkeywords 'number and name of zone' for each zone. The zone names may or may not be identical with the names specified for the material property zones or the initial conditions for the flow problem.

The initial condition can be specified through the sub-keyword 'initial condition' followed by the temperature value of the zone. For vertically linearly distributed initial condition, the initial condition can be specified through the sub-keyword 'geothermic gradient' followed by two parameter values: the temperature gradient in [$^{\circ}\text{C m}^{-1}$] and the temperature on the top of the domain in [$^{\circ}\text{C}$].

3.18.2.2 'extent of zone'

As for the heat transport problem, the specified initial condition needs to be allocated to a specific area of the solution domain below the subkeywords 'extent of zone'. MIN3P-THCm allows the simulation of flow, heat transport and reactive transport in three spatial dimensions. Detailed descriptions of the initial condition specification can be found in 3.21.12.

3.18.2.3 'read initial condition from file'

If the keywords 'read initial condition from file' are provided in the Data Block 'initial condition - energy balance', MIN3P-THCm will read the initial aqueous phase density distribution and initial temperature distribution from the external file prefix.ivs. However, this function is only valid for non-isothermal density dependent flow. The format of the file prefix.ivs is described in section 3.16.2.4.

3.18.3 EXAMPLE DATA FILE INPUT

An example input:

```
! Data Block 12B: initial condition - energy balance
! -----
'initial condition - energy balance'
1                               ;number of zones

!'geothermic gradient'
!0.03d0      ! geothermic gradient [oC m-1]
!17.0d0      ! temperature in the top

'number and name of zone'
1
'pepe rompe'

'initial condition'
20.0d0

'extent of zone'
0.0 1000.0d0 0.0 1.0   0.0 10.0

'end of zone'
'done'
```

3.18.4 DESCRIPTION OF EXAMPLE INPUT

The example data file contains one zone for a 2D-vertical cross-section located in the x-z plane with dimensions 1000 m (x-direction) by 10 m (z-direction). The initial temperature is 20°C for the entire domain.

The alternative method for the initial condition specification through 'geothermic gradient' commented out by adding "!" in front of the keyword and the following two parameters - the thermal gradient in 0.03°C m⁻¹, and the temperature on the top of the domain in 17°C.

3.19 BOUNDARY CONDITIONS – ENERGY BALANCE (DATA

BLOCK 13B)

3.19.1 DESCRIPTION OF DATA BLOCK

The boundary conditions for the heat transport problem are specified through the keywords 'boundary conditions - energy balance'.

3.19.2 DESCRIPTION OF INPUT PARAMETERS

The input data for heat transport boundary conditions follows the format previously described for other spatially distributed properties. Similar to the input for flow boundary conditions, boundary types cannot be overlain on each other.

The first required parameter is the number of boundary zones, which follows the keywords 'boundary conditions - energy balance'.

Each zone is defined by a zone number and zone name following the statement 'number and name of zone'. These zones are independent of those for physical material properties or the initial condition zones, but may have the same name.

Four types of boundary conditions can be specified below the subsection identifier 'boundary type':

Table 3.18: Boundary conditions for energy balance

Type	Name	Description
'first'	Dirichlet	specified temperature
'second'	Neumann	specified heat flux
'point'	Neumann	specified heat flux
'free'	Neumann	free exit boundary
'gradient'	Dirichlet	Linear distributed boundary with specified temperature

If the boundary type 'gradient' is specified, three parameters are needed: axis indicator (x-, y- or z-axis), the temperature at coordinate 0.0 on the specified axis (T_0), temperature gradient (dT). The temperature at the i^{th} boundary control volume ($T_b(i)$) can be interpolated:

$$T_b(i) = T_0 + dT[X(i) - X(0)] \quad \text{Equation 3-47}$$

Where $X(i)$ is the coordinate of the specified axis at the i^{th} control volume, $X(0)$ is the reference coordinate (e.g. 0.0).

3.19.3 EXAMPLE DATA FILE INPUT

```
!
! Data Block 13B: boundary conditions - energy balance
! -----
!
```

```
'boundary conditions - energy balance'
2

'number and name of zone'
1
'inflow'

'boundary type'
'free' 60.0d0

'extent of zone'
0.0d0 0.0d0 0.0 1.0 0.0d0 30.0d0

'end of zone'

'number and name of zone'
2
'hydrostatic'

'boundary type'
'free' 20.0d0

'extent of zone'
246.0d0 246.0d0 0.0 1.0 0.0d0 30.0d0
'end of zone'

'done'
```

3.19.4 DESCRIPTION OF EXAMPLE INPUT

The example data file contains one zone for a 2D-vertical cross-section located in the x-z plane with dimensions 246 m (x-direction) by 30 m (z-direction). The first zone specifies the line ($x=0.0$, $z=0.0 - 30.0$ m) with 'free' boundary condition and temperature in 60.0°C . The second zone specifies the other line ($x=246.0$, $z=0.0 - 30.0$ m) with 'free' boundary condition and temperature in 20.0°C .

3.20 INITIAL CONDITION – BATCH REACTIONS (DATA BLOCK 14)

3.20.1 DESCRIPTION OF DATA BLOCK

This data block is used to define the problem-specific chemical parameters for geochemical batch simulations. This section specifies the masses, volumes and rates of reaction for the components and reactions previously specified in Data Block 2 of the input file ('geochemical system'). Parameters specified in this section include the concentrations of each component present in the aqueous phase, surface site characteristics for pH dependent sorption and complexation, volume fraction of mineral phases present and information to control the rates of mineral phase dissolution and precipitation.

Types of batch simulations that can be conducted using this data block include: speciation calculations, kinetic batch simulations, speciation and determination of exchanger or surface site composition with specified water composition, and speciation for fixed total concentrations involving aqueous and surface complexation reactions.

For example, if you wish to calculate saturation indices for a water sample, the components and reactions of interest would be specified in data block 'geochemical system' and the amounts of the

dissolved species would be specified in this data block. Alternatively, if you wish to simulate kinetically controlled dissolution of calcite, the components (Ca^{2+} , CO_3^{2-} , H^+ , etc.) and the mineral phase calcite would be specified in the data block 'geochemical system', but the initial aqueous and solid phase concentrations would be specified in this data block. The parameters related to the rate of calcite dissolution would also be specified here.

Transient data can be generated for kinetic batch simulations. The output file (prefix_*.lb*) will contain data describing the transient evolution of the geochemical composition versus time. In addition to monitoring changes with time, it is also possible to monitor changes with pH (under equilibrium conditions). These pH-sweep calculations will produce output to this file (prefix_*.lb*) that can be used for the construction of pC-pH diagrams.

It is possible to carry out an unlimited number of batch problems with different geochemical assemblages in a single simulation. For example, if you had a series of water samples you wish to specify, the specific concentrations for each sample can be specified in a separate sub-block and all the calculations would be made in a single simulation. Alternatively, one can conduct a variety of separate batch problems involving different processes (e.g. kinetically controlled precipitation/dissolution, complexation, or simple speciation) in a single simulation. The tables (from Table 3.19 to Table 3.22) summarize the related parameters described in the following subsection.

3.20.2 DESCRIPTION OF INPUT PARAMETERS

3.20.2.1 'initial condition – local geochemistry'

The chemical conditions for the batch reaction simulation are initiated with the data block header ('initial condition – local geochemistry') followed by the number of simulations that are to be conducted. The simulation-specific input is initiated using the statement 'number and name of zone' followed by the number and the name (up to 72 characters) identifying the simulation.

3.20.2.2 'kinetic batch simulation'

If kinetically-controlled dissolution-precipitation reactions are to be considered in the simulation, the statement 'kinetic batch simulation' needs to be included in this input section. If a kinetic batch simulation is conducted, the transient evolution of all species involved will be reported to the output files prefix_x.lb*, where x corresponds to the number of the simulation (for content of files see file prefix_o.fls, generated at run-time). The geochemical composition at the end of the simulation is reported to the generic output file prefix_o.gen. The following parameters define the initial time step and the final solution time for the kinetic batch simulation. The initial time step should be set to a small value and will be automatically adjusted during the course of the simulation. The magnitude of the initial time increment will be determined by the time scale of the fastest kinetic process. Time unit is the same as specified in the Data Block 5 – 'control parameters – local geochemistry'.

```
'kinetic batch simulation'
1.0d-2          ;initial time step (local chemistry)
8.00d2         ;final solution time
```

3.20.2.2.1 'kinetically controlled dissolution-precipitation reactions'

Another method for the kinetically-controlled dissolution-precipitation reactions can be considered in the simulation by using the statement 'kinetically controlled dissolution-precipitation reactions' in this input section. Two parameters have to be provided: logical parameter for the output of

transient data, and the initial time step for the kinetic reaction. The difference of this method to the previous one lies in that no final simulation time is needed. The program will stop the simulation when the SI is over 0.99.

```
'kinetically controlled dissolution-precipitation reactions'
.true.                ;output of transient data
1.0d-2               ;initial time step (local chemistry)
```

3.20.2.3 Concentration Input

The next input block describes the unspciated water composition. An input value must be provided for each component specified in Data block 2 of the input file ('geochemical system') maintaining the same order as defined in Data block 2.

3.20.2.3.1 Input Types

Input can be provided in various ways and is controlled by the type-specification following the concentration input. Potential input units are:

- total aqueous component or total component concentrations: 'free'
- fixed activities: 'fixed'
- Use for charge balance: 'charge'
- pH (only for component H⁺): 'ph'
- pH-sweep calculations (only for component H⁺): 'ph_sweep'
- pe, Eh (only for redox master variable and for fixed pH). 'pe', 'eh'
- fixed partial pressure (pCO₂ and pO₂ only, if pH is fixed): 'pco2', 'po2', 'pn2'

Total aqueous component concentrations correspond to total analytical concentrations for most components. These concentrations have to be provided in the input units specified in Data block 2 ('geochemical system') of the input file. Alternatively, a fixed activity can be specified for a specific component. The units of chemical compositions are provided in the input units specified in the Data Block 2: 'geochemical system'). For the component H⁺, a fixed pH can be specified alternatively, or a pH-sweep calculation can be conducted. Additional input is required for the pH-sweep simulations. The first value in the input line is the starting-pH of the pH-sweep, while the value following the type specification 'ph_sweep' is the final pH of the pH-sweep calculations. The last parameter in the input line defines the number of steps for the pH-sweep calculations. If a pH-sweep calculation is conducted, output for the construction of pC-pH-diagrams will be written to the output files prefix_x.lb*, where x corresponds to the number of the simulation (for content of files see file prefix_o.fl, generated at run-time). The number of steps should be set to 50 or greater to facilitate the generation of well resolved pC-pH-diagrams. A pH-sweep calculation can only be conducted for a pure equilibrium system.

Alternatively, fixed partial pressures can be specified to constrain selected components (O₂(aq), N₂(aq) and CO₃²⁻). At the present time these calculations are only accurate for a temperature of 25°C, but may also be used as approximations for higher or lower temperatures. Partial pressures are to be provided in terms of atm, independent of the input units specified in Data block 2 ('geochemical system').

It is also possible to use pe or Eh to constrain the value of the standard redox master variable O₂(aq). As for pCO₂, this specification can only be used in conjunction with a fixed pH. The calculations are only exact for 25 °C.

Alternatively, any charged component can be used to satisfy the charge balance in the equilibrated solution, provided this is physically possible. In this case it is necessary to provide an estimate for

the total aqueous component concentrations.

If a component is not in the database (for example a specific organic compound), it can be added to the database comp.dbs. Section 4.1.1 describes the content of comp.dbs and provides information on how to add additional components.

3.20.2.4 'sorption parameter input'

If ion exchange or surface complexation reactions are included in the simulation (as specified in section 'geochemical system'), the appropriate input parameters have to be provided for each simulation under the keywords 'sorption parameter input'. The required input differs between ion-exchange and surface complexation reactions. For ion-exchange reactions, it is necessary to provide the cation exchange capacity (CEC) and the bulk density of the porous medium (rhobulk). For surface complexation reactions, it is necessary to specify the name of the surface site (as previously defined in Data block 2: 'geochemical system'), along with the mass, the surface area and the site density. Alternatively, the current MIN3P-THCm (starting from version V1.0.106) provides the option to specify the ion exchange parameters in the current data block using the keywords 'sorption parameter input of ion-exchange', and the surface complexation parameters using 'sorption parameter input of surface-complex'. The corresponding components are defined in Data Block 2: 'geochemical system' under keywords 'sorbed species of ion-exchange' or 'sorbed species of surface-complex'. However, if both ion exchange and surface complexation reactions are included in the same simulation (as specified in section 'geochemical system'), the appropriate input parameters have to be provided for each simulation (zone) under the keywords 'sorption parameter input of ion-exchange' and 'sorption parameter input of surface-complex' followed by the required parameters. The required input units for all ion exchange and surface complexation parameters are specified in Table 3.20. The model assumes by default that the initial total concentrations of the components provided in the input file are the sum of the aqueous and the sorbed parts. During the initialization calculations, the code will determine the fractions in the aqueous and the sorbed components (i.e. as the exchanger or the surface complexes) based on the initial total component concentrations and the specified cation exchange capacity or surface complexation parameters.

In the practice, chemical analysis often obtains the total concentrations of the pore water, which can be assumed to be in equilibrium with the solid phase. However, the concentration of the sorbed components are normally not analyzed. In such cases, MIN3P-THCm has the function to calculate the sorbed component concentration by fixing the concentrations of the aqueous components under the assumption of equilibrium between sorbed and aqueous phases. In the case of ion exchange or surface complexation reactions this can be realized by using the statement 'equilibrate with fixed solution composition' to implicitly consider the surface sites in the mass balance calculations. If both ion exchange and surface complexation reactions have to be considered in the same calculation, both statements 'equilibrate with fixed solution composition of ion-exchange' and 'equilibrate with fixed solution composition of surface-complex' have to be included (valid only for MIN3P-THCm version 1.0.106 and newer). The following three examples demonstrate the usage of this function.

An example of the input parameters for a case considering the surface complexation reaction:

```
-----
'number and name of zone'
1
'background chemistry - aquifer'

'concentration input'
8.000      'ph'                ; 'h+1'
5.147d-4   'charge'           ; 'so4-2'
1.0d-7     'free'             ; 'zn+2'
1.0d-7     'free'             ; 'pb+2'
1.0d-10    'free'             ; 'ca+2'
```



```

'number and name of zone'
1
'background chemistry - aquifer'

'concentration input'
8.015      'ph'                ; 'h+1'
5.147d-4   'charge'           ; 'so4-2'
1.0d-7     'free'             ; 'zn+2'
1.0d-7     'free'             ; 'pb+2'
1.0d-10    'free'             ; 'ca+2'
1.0d-5     'free'             ; 'mg+2'
1.0d-5     'free'             ; 'k+1'
1.0d-3     'free'             ; 'na+1'

'sorption parameter input of surface-complex'
'=feoh(s)' 100.0d0 10.0d0 6.02228d0 ;surface site, mass, area, site density

'sorption parameter input of ion-exchange'
0.7333                ;cation exchange capacity
1.875d0               ;dry bulk density

'equilibrate with fixed solution composition of ion-exchange'

'equilibrate with fixed solution composition of surface-complex'

'extent of zone'
0.0 0.0 0.0 0.0 0.00 16.0

'end of zone'

'done'

```

This example includes the parameters of surface complexation reactions: the surface site is '=feoh(s)'. Its mass is 100.0 g solid (L H₂O)⁻¹, surface area is 10.0 m² (g solid)⁻¹ and the site density is 6.02228 sites nm⁻²; and the parameters of the ion exchange reactions: the CEC is 0.7333 meq (100g solid)⁻¹, the dry bulk density is 1.875 g cm⁻³.

3.20.2.5 'CEC fraction of multisite ion exchange'

If multisite ion exchange model is activated through the keyword 'surface sites of ion-exchange' in the Data Block 2, the initial CEC (Cation Exchange Capacity) fractions of each site type can be specified in the current data block using the keyword 'CEC fraction of multisite ion exchange'. An example for that is:

```

'CEC fraction of multisite ion exchange'
0.0025                ; '-FES'
0.20                  ; '-II'
0.7975                ; '-PS'

```

In the example, three ion exchange sites are defined: site -FES with a fraction of 0.25 %, site -II with a fraction of 20 %, and site -PS with a fraction of 79.75 % (Xie et al. 2014b). The fractions should sum up to 100%.

3.20.2.6 'mineral input'

If mineral phases have been specified in Data block 2 ('geochemical system') and the string 'kinetically-controlled dissolution-precipitation reactions' has been included in the current data block, it is necessary to specify a set of mineralogical parameters under the keyword 'mineral input'. Two lines (6 parameters in total) are required if the update type is 'constant', 'twothird', 'linear' or 'exponent', three lines (9 parameters in total) are required for the update type 'geometric'. A 'constant' update type means that the mineral reactivity remains constant during the course of a

simulation. This specification is most commonly used and must be applied for secondary mineral phases, i.e. mineral phases, which are not present initially. The update type-specification ‘exponent’ implies that the reactivity is updated according to the following equation:

$$k_i^{m,t} = k_i^{m,0} \left(\frac{\varphi_i^t}{\varphi_i^0} \right)^\alpha \quad \text{Equation 3-48}$$

In which, i is an indicator for the i^{th} minerals, m denotes mineral related parameters, α is user defined coefficient (dimensionless). In this relationship, $k_i^{m,0}$ and φ_i^0 define the initial effective rate constant and mineral volume fraction, respectively. $k_i^{m,t}$ and φ_i^t define the effective rate constant and mineral volume fraction at the present solution time t . It is important to note that the initial mineral volume fraction φ_i^0 cannot be set as 0.0 according to Equation 3-48. To avoid this problem, a very small value (e.g. 10^{-10}) can be specified.

The update type-specification ‘twothird’ implies that a twothird-power:

$$k_i^{m,t} = k_i^{m,0} \left(\frac{\varphi_i^t}{\varphi_i^0} \right)^{\frac{2}{3}} \quad \text{Equation 3-49}$$

is used to update the mineral reactivity (Lichtner, 1996). In some cases, such as secondary minerals that initially do not exist ($\varphi_i^0 = 0.0$), or a mineral that can completely dissolve, numerical instability might emerge. To avoid that, the update type ‘twothird-mix’ can be used instead, which basically using the same Equation 3-49 as the type ‘twothird’. The difference between them is: an additional parameter – the volume fractions of mineral for nucleation threshold φ_i^{nuc} , is required for the update type ‘twothird-mix’. If $\varphi_i^t < \varphi_i^{nuc}$, $k_i^{m,t} = k_i^{m,0}$; otherwise, $k_i^{m,t}$ is calculated according to Equation 3-49.

The update type ‘linear’ implies that the reactivity is updated according to (Perko et al. 2015):

$$k_i^{m,t} = k_i^{m,ref} \left(\frac{\varphi_i^t}{\varphi_i^{nuc}} \right), \quad \text{if } \varphi_i^t \geq \varphi_i^{nuc} \quad \text{Equation 3-50}$$

$$k_i^{m,t} = k_i^{m,ref}, \quad \text{if } \varphi_i^t < \varphi_i^{nuc}$$

Similar to the update type ‘twothird-mix’, the volume fractions of mineral for nucleation threshold φ_i^{nuc} is required to calculate the reference effective rate constant $k_i^{m,ref}$ according to Equation 3-51.

$$k_i^{m,ref} = k_i^{m,0} S^0 \left(\frac{\varphi_i^{nuc}}{\varphi_i^0} \right) = k_i^{m,0} S^{nuc} \quad \text{Equation 3-51}$$

In which S^0 is the initial mineral surface area, S^{nuc} is the mineral surface area relative to the nucleation threshold. If $\varphi_i^t < \varphi_i^{nuc}$, $k_i^{m,t} = k_i^{m,ref}$; otherwise, $k_i^{m,t}$ is calculated according to Equation 3-51.

The effective rate constant may be either specified directly in the input file (default option with the standard database), or it is alternatively possible to specify the reactive surface area instead. This is only meaningful, if an intrinsic rate constant for the mineral phase is specified in the database file mineral.dbs. Additional information on the content of the database file mineral.dbs and on how to add rate expressions to the database is provided in Section 4.7 of this document. The use of the update type ‘geometric’ is not recommended, however, it is required for transport-controlled

dissolution reactions described by the shrinking core model (for detailed information on this topic, the reader is referred to see the Theory Manual).

The first input parameter is the mineral volume fraction, i.e. the volume of bulk aquifer occupied by the specific mineral phase divided by the bulk volume of the aquifer. This quantity has been chosen, since it is convenient for reactive transport simulations. For batch simulations, the volume of water is always one liter. The volume fraction has therefore to be determined based on:

$$\varphi_i = \frac{V_i}{1 + \sum_{k=1}^{N_m} V_k} \quad \text{Equation 3-52}$$

where φ_i is the volume fraction of the *i*th mineral to be provided for the input file, and V_i (V_k) are the volumes of minerals in contact with 1L H₂O. It is planned to include additional options for input units in future model versions, which are more convenient for batch simulations [mol L⁻¹ H₂O or g L⁻¹ H₂O]. The mineral volume [L] can be determined from the mineral weight using:

$$V_i = 10^3 \frac{G_i}{\gamma_i} \quad \text{Equation 3-53}$$

where G_i is the mineral mass [g] and γ_i is the density [g cm⁻³] of the *i*th mineral phase and 10³ is a conversion factor [cm³ L⁻¹]. The densities for common minerals are included in the database mineral.dbs and are summarized in section 4.7. If the mineral content is provided in moles, the conversion can be performed using:

$$V_i = 10^3 \frac{M_i GFW_i}{\gamma_i} \quad \text{Equation 3-54}$$

where M_i is the mineral mass in moles and GFW_i is the gram formula weight of the mineral phase [g mol⁻¹]. The following input parameter (minequil) is a logical statement defining if the specific mineral phase is allowed to react in the batch simulation. If this statement is set to .true., the specific mineral phase may dissolve or precipitate, otherwise the mineral phase will not participate actively in the simulation (the saturation indexes SIs are calculated nevertheless). The last parameter in the first input line defines the update_type, which was introduced previously. In the second line, a minimum mineral volume fraction has to be specified. This parameter can be set to 0.0 if the update type is 'constant'. If the update type is 'twothird', a value of 0.0 will prohibit the re-formation of a mineral phase, after it has been dissolved completely. It is therefore recommended to specify a small value for the minimum mineral volume fraction. This value should be chosen small enough ($\leq 10^{-10}$) that the geochemical evolution is not affected notably by the mineral mass which has not been reacted. The minimum mineral volume fraction must also be set to a small value, if the update type is 'geometric'.

For the default database mineral.dbs, the next parameter defines the effective rate constant in units [mol L⁻¹ bulk s⁻¹] for a zero order reaction. The units for higher order reactions, which depend on aqueous concentrations, are given by [mol⁽¹⁻ⁿ⁾ Lⁿ H₂O L⁻¹ bulk s⁻¹], where *n* defines the overall reaction order (see also Table 3.22). Alternatively, laboratory derived rate constants (per unit surface area) may be inserted into the database. The units for these rate constants are specified in Table 3.22. In this case, the reactive surface area [m² mineral L⁻¹ bulk] needs to be specified in the problem specific data file in place of the effective rate constant. For transport-controlled reactions, this parameter is simply a scaling factor, which includes the tortuosity of the leached layer/protective surface layer on the dissolving mineral phase. The last parameter in this row is not

used at the moment and must be set to 0.0.

If a geometric update of the mineralogical parameters is specified (required for transport controlled reactions), it is necessary to specify 3 additional parameters in a new line, which depend on the average grain size. The first parameter in the additional line is the radius of a mineral particle with average grain size specified in meters. The next parameter defines the radius of the unreacted portion of the mineral [m], which must be smaller than the radius of the mineral grains specified previously in case of transport controlled reactions. (The formulation of the shrinking core model requires that the mineral particles are partially reacted initially). The last parameter defines the minimum radius for the mineral grains, which must be set to a small value.

Table 3.19: Summary of input parameters for section ‘initial condition – local chemistry’, Part 1.

Keywords			Required/Optional	
‘initial condition – local geochemistry’			required for any batch simulation	
nzone	number of simulations		required for any batch simulation	
Subsection	Parameter	Description	Required/Optional	
‘number and name of zone’	izone	number of simulation	required for any batch simulation	
	name	name of simulation		
‘kinetic batch simulation’	delt	initial time step for local chemistry calculations	required for any kinetic batch simulation	
	tfinal	final solution time for local chemistry calculations		
‘concentration input’	conc	concentration input, as specified by type	required for all components specified in input section ‘geochemical system’	
	type	‘free’		specified total concentration units as specified in section ‘geochemical system’
		‘fixed’		fixed species activity, units as specified in section ‘geochemical system’
		‘po2’		fixed pO ₂ [atm]
		‘pn2’		fixed pN ₂ [atm]
		‘pco2’		fixed pCO ₂ [atm]
		‘ph’		fixed pH
		‘ph_sweep’		sweep over specified pH-range
		‘pe’		fixed pe
		‘eh’		fixed Eh [mV]
‘charge’	use component to satisfy charge balance estimate in units [mol L ⁻¹ H ₂ O]			

Table 3.20: Summary of input parameters for section ‘initial condition – local chemistry’, Part 2.

Subsection	Parameter	Description	Required/Optional
------------	-----------	-------------	-------------------

N _i zones	'sorption parameter input'	cec	cation exchange capacity [meq (100g soil) ⁻¹]	required for ion exchange reactions
		rhobulk	dry bulk density [g cm ⁻³]	
		surface site	name of surface site	required for surface complexation reactions
		mass	mass of surface site [g solid L ⁻¹ H ₂ O]	
		area	surface area of surface site [m ² g ⁻¹ solid]	
		site density	site density [sites nm ⁻²]	
	'sorption parameter input of ion-exchange'	cec	cation exchange capacity [meq (100g soil) ⁻¹]	required for ion exchange reactions
		rhobulk	dry bulk density [g cm ⁻³]	
	'sorption parameter input of surface-complex'	surface site	name of surface site	required for surface complexation reactions
		mass	mass of surface site [g solid L ⁻¹ H ₂ O]	
		area	surface area of surface site [m ² g ⁻¹ solid]	
		site density	site density [sites nm ⁻²]	

Table 3.21: Summary of input parameters for section ‘initial condition – local chemistry’, Part 3.

	Subsection	Parameter	Description	Required /Optional	
Ni zones		phi	initial mineral volume fraction [m ³ mineral m ⁻³ bulk]	required for all mineral specified in section ‘geochemical system’ (only if string ‘kinetically-controlled dissolution-precipitation reactions’ is specified)	
		minequil	equilibrate with mineral phases		
		type	‘constant’		no update of rate constant (surface area)
			‘twothird’		update of rate constant (surface area) based on two-thirds power law
			‘twothird-mix’		update of rate constant (surface area) based on two-thirds power law with threshold value
			‘linear’		update of rate constant (surface area) based on linear function
			‘exponent’		update of rate constant (surface area) based on the exponent defined by user
			‘geometric’		update of rate constant (surface area) based on geometric update
		phi_min	minimum mineral volume fraction [m ³ mineral m ⁻³ bulk]		
		k_eff	effective rate constant in [mol l ⁻¹ bulk s ⁻¹], (if rate constant in database is set to unity)		
		or	or		
		area	reactive surface area in [m ² mineral L ⁻¹ bulk], (if rate constant specified in database)		
		or	or		
		factor	scaling factor (for type ‘geometric’)		
		sat	level of supersaturation, set to 0.0		
α	Coefficient for type ‘linear’				
phinuc	Mineral volume fraction for nucleation threshold				
rad_init	initial radius of mineral grain [m], only for type ‘geometric’				
rad_surf	initial radius of unreacted portion of mineral grain [m], only for type ‘geometric’				
rad_min	minimum radius of mineral grain [m], only for type ‘geometric’				
‘end zone’	of	-	-		

Section Closing	Required /Optional
'done'	required

Table 3.22: Units for effective rate constants dependent on rate expression

Reaction type	rate expression	units for $k_i^{m,t}$
zero order default option using standard database	$R_i^m = -k_i^{m,t}$ $R_i^m = -k_i^{m,t} \left(1 - \frac{IAP_i^m}{K_i^m} \right)$	mol l ⁻¹ bulk s ⁻¹
n th order	$R_i^m = -k_i^{m,t} (T_j^a)^n$ $R_i^m = -k_i^{m,t} (T_j^a)^n \left(1 - \frac{IAP_i^m}{K_i^m} \right)$	mol ¹⁻ⁿ l ¹⁻ⁿ H ₂ O L ⁻¹ bulk s ⁻¹
Monod	$R_i^m = -k_i^{m,t} \left[\frac{T_j^a}{K_j^{a,mo} + T_j^a} \right]$	mol l ⁻¹ bulk s ⁻¹

In Table 3.22, R_i^m is the reaction rate, $k_i^{m,t}$ is the effective rate constant, T_j^a is the total aqueous component concentration, K_i^m is the equilibrium constant, IAP_i^m is the ion activity product, $K_j^{a,mo}$ is the half saturation constants. K_i^m and $K_j^{a,mo}$ are provided in the database mineral.dbs, while $k_i^{m,t}$ is calculated according to Equation 3-48 or Equation 3-49.

3.20.3 EXAMPLE DATA FILE INPUT

Example 1: Speciation and kinetic batch simulation

```
! Data Block 14: initial condition - local geochemistry
! -----
!
! 'initial condition - local geochemistry'
2                               ;number of simulations
! -----
! 'number and name of zone'
1
! 'Sierras speciation calculation'

'concentration input'
1.0d-3  'free'                  ;conc,   type      - ca2+
1.0d-7  'free'                  ;conc,   type      - na+
1.0d-3  'free'                  ;conc,   type      - co32-
1.0d-7  'free'                  ;conc,   type      - h4sio4
```

```

1.0d-7  'free'                ;conc,   type    - al3+
5.0     'ph'                  ;conc,   type    - h+

'end of zone'

! -----
! 'number and name of zone'
2
! 'kinetically-controlled dissolution of calcite and albite'

'kinetic batch simulation'
1.0d-2                ;delt
1.0d0                  ;tfinal

'concentration input'
1.7d-5  'free'                ;conc,   type    - ca2+
1.0d-6  'free'                ;conc,   type    - na+
2.0d-5  'free'                ;conc,   type    - co32-
1.0d-6  'free'                ;conc,   type    - h4sio4
1.0d-6  'free'                ;conc,   type    - al3+
5.0     'pH'                  ;conc,   type    - h+

'mineral input'
5.0d-4  .true.  'constant'    ;phi,    minequil, type - calcite
1.0d-10 1.0d-8  0.0          ;phi_min, k_eff,  sat
5.0d-1  .true.  'constant'    ;phi,    minequil, type - albite
1.0d-10 1.0d-13 0.0         ;phi_min, k_eff,  sat
0.0d0   .false. 'constant'    ;phi,    minequil, type - al(oh)3(am)
1.0d-10 1.0d-8  0.0         ;phi_min, k_eff,  sat
0.0d0   .false. 'constant'    ;phi,    minequil, type - sio2(am)
1.0d-10 1.0d-8  0.0         ;phi_min, k_eff,  sat

'end of zone'

```

Example 2: Surface complexation

```

! Data Block 14: initial condition - local geochemistry
! -----
!
! 'initial condition - local geochemistry'
2
!                                     ;number of zones

! -----
! 'number and name of zone'
1
! 'pH-sweep from 0-14, fixed total metal concentration'

'concentration input'
0.0     'ph_sweep'  14.0  50          ;conc type  ph_final  steps - 'h+1'
1.0d-7  'free'      ;conc type                    - 'me+2'

'sorption parameter input'
'=soh'  1.0d0  10.0d0  6.02228d0      ;surface site, mass, area, site density

'end of zone'

! -----
! 'number and name of zone'
2
! 'ph-sweep from 0-14, fixed solution composition'

'concentration input'
0.0     'ph_sweep'  14.0  50          ;conc type  ph_final  steps - 'h+1'
1.00d-7 'free'      ;conc type                    - 'me+2'

'sorption parameter input'
'=soh'  1.0d0  10.0d0  6.02228d0      ;surface site, mass, area, site density

'equilibrate with fixed solution composition'

```

```
'end of zone'
```

```
'done'
```

Example 3: Ion exchange

```
! Section 14: initial condition - local geochemistry
```

```
! -----
```

```
!
```

```
'initial condition - local geochemistry'
```

```
1 ;number of zones
```

```
! -----
```

```
'number and name of zone'
```

```
1
```

```
'background chemistry - aquifer'
```

```
'concentration input'
```

```
1990.0d0 'free' ;conc type - 'na+1'
```

```
100.0d0 'free' ;conc type - 'k+1'
```

```
436.0d0 'free' ;conc type - 'mg+2'
```

```
444.0d0 'free' ;conc type - 'ca+2'
```

```
5700.0d0 'free' ;conc type - 'cl-1'
```

```
7.0d0 'ph' ;conc type - 'h+1'
```

```
'sorption parameter input'
```

```
10.0d0 ;cec
```

```
1.875d0 ;rhob
```

```
'end of zone'
```

```
'done'
```

Example 4: pH-sweep calculations

```
! Data Block 14: initial condition - local geochemistry
```

```
! -----
```

```
!
```

```
'initial condition - local geochemistry'
```

```
1 ;number of zones
```

```
! -----
```

```
'number and name of zone'
```

```
1
```

```
'pH-sweep from 0-14 '
```

```
'concentration input'
```

```
0.0 'ph_sweep' 14.0 50 ;h+1
```

```
1.00d-4 'free' ;seo4-2
```

```
'end of zone'
```

```
'done'
```

Example 5: specification of mineral update types

```
'mineral input'
```

```
0.20 .true. 'linear' ;phim, minequil, update_type - calcite
```

```
1.d-10 5.0d-5 0.00d0 1.0d-7 ;phimin, areanuc, supsatm, phinuc
```

```
0.15 .false. 'twothird-mix' ;phim, minequil, update_type - gypsum
```

```
1.d-10 200.0 0.00d0 1.0d-7 ;phimin, areanuc, supsatm, phinuc
```

```
5.00d-1 .true. 'geometric' ;phim, minequil, update_type - albite-ph-d
```

```
1.00d-7 0.1d0 0.00d0 ;phimin, scalfac, supsatm
```

```
1.50d-4 1.50d-4 3.00d-7 ;radi, rads, radmin
```

```
1.0d-10 .false. 'exponent' ;phim, minequil, update_type - dolomite
```

1.d-10 200.0 0.80d0 ;phimin, areanuc, alpha

3.20.4 DESCRIPTION OF EXAMPLE INPUT

Example 1 provides the initial conditions for two batch reactions. For the first batch reaction 'Sierras speciation calculation', no minerals are considered. Only the initial total concentrations of five components plus pH are provided. For the second batch reaction 'kinetically-controlled dissolution of calcite and albite', in addition to the initial concentrations of the primary components, the parameters for the kinetic reactions of minerals calcite, albite.

Example 2 specifies the initial conditions for two batch reactions (pH-sweep from 0.0 to 14.0) considering surface complexation. The difference of the two reactions lies in the methods of the initial chemical speciation concerning the sorbed species. For the first batch reaction, the total solution composition is provided and assumed as fixed total concentration. MIN3P-THCm will calculate the concentrations of the aqueous and sorbed species. The other batch reaction used the keywords 'equilibrate with fixed solution composition'. The initialization calculation will determine the sorbed species concentration while the aqueous component concentration provided in the input file remains unchanged.

Example 3 specifies the initial conditions for a batch reaction considering ion exchange reactions. The related sorption parameters of the soil are: CEC in $10.0 \text{ meq (100g solid)}^{-1}$, the dry bulk density in 1.875 g cm^{-3} .

Example 4 demonstrates the initial condition setup for pH-sweep calculation for the specification of selenium components depending on pH value spanning from 0.0 to 14.0.

Example 5 demonstrates the specification of the mineral update types and related parameters. The update type 'linear' of the mineral calcite is specified in the first two lines. The initial volume fraction of calcite (φ_i^0) is 0.20. The volume fraction of calcite for nucleation threshold φ_i^{nuc} is 10^{-7} . The initial mineral surface area is $100.0 \text{ m}^2 \text{ L}^{-1} \text{ bulk}$. The reference S^{nuc} can be calculated according to Equation 3-51: $100.0 \times 1.0^{-7} / 0.2 = 5.0 \times 1.0^{-5} \text{ m}^2 \text{ L}^{-1} \text{ bulk}$, which is the 2nd input parameter in the second line. The minimum volume fraction is 10^{-10} (1st parameter in the 2nd line). The supersaturation parameter is 0.0 (the 3rd parameter in the 2nd line).

The update type 'twothird-mix' is specified to gypsum in the 3rd and 4th lines. The φ_i^0 of gypsum is 0.15. The initial mineral surface area is $200.0 \text{ m}^2 \text{ L}^{-1} \text{ bulk}$. The volume fraction of calcite for nucleation threshold φ_i^{nuc} is 10^{-7} . The minimum volume fraction is 10^{-10} (1st parameter in the 2nd line). The supersaturation parameter is 0.0 (the 3rd parameter in the 2nd line).

The following three lines is to specify the update type 'geometric' to albite. The φ_i^0 of gypsum is 0.50. The minimum volume fraction is 10^{-10} . The scale factor is 0.10. The supersaturation parameter is 0.0. The initial radius of mineral grain is $1.50 \times 10^{-4} \text{ [m]}$. The initial radius of unreacted portion of mineral grain is also $1.50 \times 10^{-4} \text{ [m]}$. The minimum radius of mineral grain is $3.00 \times 10^{-7} \text{ [m]}$

The last two lines specifies the update type 'exponent' to dolomite. The φ_i^0 of gypsum is 0.15. The minimum volume fraction is 10^{-10} . The initial mineral surface area is $200.0 \text{ m}^2 \text{ L}^{-1} \text{ bulk}$. The coefficient α is 0.8.

3.20.5 ADDITIONAL COMMENTS

MIN3P-THCm provides various forms to simulate kinetic reactions of minerals (see section 4.7).

Some of the required parameters are provided in the database mineral.dbs. Additional parameters are provided in the input file.

3.21 INITIAL CONDITION – REACTIVE TRANSPORT (DATA BLOCK 15)

3.21.1 DESCRIPTION OF DATA BLOCK

This data block defines the initial condition for the reactive transport problem. As for the flow problem, the specification of several zones is necessary. The input structure is consistent with the one for section ‘initial condition - local chemistry’ with some restrictions:

- Kinetic batch simulations cannot be conducted (use batch option of model).
- pH-sweep calculations cannot be conducted (use batch option of model).
- An additional input section is required defining the extent of the zone in the solution domain covered by the specified initial condition.

3.21.2 DESCRIPTION OF INPUT PARAMETERS

3.21.2.1 ‘initial condition – reactive transport’

The number of zones needs to be specified after the keywords ‘initial condition – reactive transport’. In the following, a zone number and a zone name have to be provided below the sub-keywords ‘number and name of zone’ for each zone. The zone names may or may not be identical with the names specified for the material property zones or the initial conditions for the flow problem.

The initial condition can be specified through the sections ‘concentration input’, ‘mineral input’ and ‘sorption parameter input’ in the same way as described in section ‘initial condition - local chemistry’.

3.21.3 ‘READ INITIAL AQUEOUS COMPONENT CONCENTRATIONS FROM FILE’

The initial distributed total component concentrations for reactive transport can be specified through an external file prefix.aqt. To activate this function, the keywords ‘read initial aqueous component concentrations from file’ should be provided in the Data Block ‘initial condition - reactive transport’. In such case, **the number of zones should be 1 no matter how many zones the domain includes. The order of the aqueous components must be the same as defined in the Data Block 2: ‘geochemical system’.** The file provides the x,y,z-coordinates and the total concentrations of each primary component in [mol L⁻¹] in each control volume. This file has exact the same format of the output file prefix_0.gst.

3.21.4 ‘READ INITIAL MINERAL VOLUME FRACTIONS FROM FILE’

The distributed initial mineral volume fractions and porosity can be specified through an external file prefix.min. To activate this function, the keywords ‘read initial mineral volume fractions from file’ should be provided in the Data Block ‘initial condition - reactive transport’. The file provides the x,y,z-coordinates, the initial mineral volume fractions in [m³ m⁻³] and the porosity for each control volume. **The order of the minerals must be the same as defined in the Data Block 2:**

'**geochemical system**'. This file has exact the same format of the output file prefix_0.gsv.

3.21.5 'READ CEC FROM FILE'

The distributed parameters CEC (cation exchange capacity) and dry bulk density can be specified through an external file prefix.cec. To activate this function, the keywords 'read cec from file' should be provided in the Data Block 'initial condition - reactive transport'. The file provides the x,y,z-coordinates, CEC in [meq (100 g solid)⁻¹] and the dry bulk density in [g cm⁻³] for each control volume. An example of the prefix.cec file:

```
title = "dataset basin"
variables = "x", "y", "z", "cec", "rho"
zone t = "field", i = 1000, j = 150, k = 1, f=point
  0.0000000E+00 0.0000000E+00 0.0000000E+00 0.1000000E+01 0.2750000E+01
  0.4404404E+03 0.0000000E+00 0.0000000E+00 0.1000000E+01 0.2750000E+01
  0.8808806E+03 0.0000000E+00 0.0000000E+00 0.1000000E+01 0.2750000E+01
  0.1321321E+04 0.0000000E+00 0.0000000E+00 0.1000000E+01 0.2750000E+01
  0.1761762E+04 0.0000000E+00 0.0000000E+00 0.1000000E+01 0.2750000E+01
.....
```

3.21.6 'READ INITIAL MINERAL AREAS FROM FILE'

The distributed initial mineral surface area of each mineral in each control volume can be specified through an external file prefix.surf. To activate this function, the keywords 'read initial mineral areas from file' should be provided in the Data Block 15: 'initial condition - reactive transport'. The file provides the x,y,z-coordinates, the initial surface area of each mineral in [m² mineral (L bulk)⁻¹] for surface controlled reaction and in [m mineral (m³ bulk)⁻¹] for transport controlled reaction. **The order of the minerals must be the same as defined in the Data Block 2: 'geochemical system'**. This file has exact the same format of the output file prefix_0.gsv.

3.21.7 'READ MINERAL VOLUME FRACTIONS NUCLEATION THRESHOLDS FROM FILE'

The mineral volume fractions nucleation threshold (φ_{min}) in [m³ m⁻³] is a parameter defined for the calculation of mineral reaction rate R till mineral approaching disappearance according to:

$$R = S' \frac{\varphi}{\varphi_0 + \varphi_{min}} \quad \text{Equation 3-55}$$

In which φ_0 and φ refer to the initial and current mineral volume fraction [m³ m⁻³], S' is the reference mineral surface area. To use the parameter, the mineral update type should be 'linear'.

The distributed mineral volume fractions nucleation thresholds as nodal values at each control volume can be specified through an external file prefix.vnuc. To activate this function, the keywords 'read mineral volume fractions nucleation thresholds from file' should be provided in the Data Block 'initial condition - reactive transport'. The file provides the x,y,z-coordinates, the mineral volume fractions nucleation thresholds in [m³ m⁻³]. **The order of the minerals must be the same as defined in the Data Block 2: 'geochemical system'**. The prefix.vnuc file has the same format of the output file prefix_0.gsv but without porosity.

3.21.8 'READ NUCLEATION THRESHOLD REFERENCE SURFACE AREA FROM

FILE'

The distributed nucleation threshold reference surface area as nodal values at each control volume can be specified through an external file prefix.anuc. To activate this function, the keywords 'read nucleation threshold reference surface area from file' should be provided in the Data Block 'initial condition - reactive transport'. The file provides the x,y,z-coordinates, the nucleation threshold reference surface area. **The order of the minerals must be the same as defined in the Data Block 2: 'geochemical system'.**

3.21.9 INITIAL CONDITION FOR ISOTOPE COMPONENTS

Input parameters for the initial condition for isotope components (data block 15) are essentially the same as for non-isotope simulations although ensure that inputs for component concentration and mineral inputs include all isotopes that were includes in the component and mineral sections in data block 2. In addition, the ratio of isotope component concentrations needs to be such that the initial isotopic ratio of the solution is represented.

3.21.10 'LINEAR SORPTION INPUT'

The dimensionless linear sorption coefficient K_s (defined in section 3.3.2.7) can be specified using the keyword 'linear sorption input' as the following:

```
'linear sorption input'
'sr_85+2'    14.535
'co_60+2'    1377.0
```

3.21.11'SALINITY DEPENDENT REACTION RATE OF MINERALS'

Additionally, the section 'salinity dependent reaction rate of minerals' can be added to this block to activate the function accounting the salinity dependent sulfur reducing bacterial (SRB) reaction. To use the model, please follow the steps:

1. Add the keywords 'salinity dependent reaction rate of minerals' to the data block 'initial condition - reactive transport' followed by the number of the mineral(s) to be considered for the model;
2. Add the name of the first mineral plus the keyword 'equation', and the number and the values of the coefficients (f_i) of a function to calculate the salinity inhibition factor k_{sal} (in [-]) depending on the salinity S (in [g/L]) based on the experimental data:

$$k_{sal} = \sum_{i=0}^n f_i S^i \quad \text{Equation 3-56}$$

3. Add the minimum salinity & related k_{sal} , and the maximum salinity & related k_{sal} for the first mineral to ensure no negative k_{sal} will be calculated according to the above equation;
4. If more than one minerals are considered, follow the steps 2 and 3 for the rest of the minerals;
5. The other properties of the minerals (e.g. kinetics) remain unchanged.).

The input format is demonstrated in the example 3 (section 3.21.13).

3.21.12 'EXTENT OF ZONE'

As for the flow problem, the specified initial condition needs to be allocated to a specific area of the solution domain below the subkeywords 'extent of zone'. MIN3P-THCm allows the simulation of flow and reactive transport in three spatial dimensions. The following input defines the location of minimum and maximum coordinates in the x, y and z-directions for the initial condition to be allocated. If a 1D or 2D-simulation is conducted, the minimum and maximum coordinates for the excluded dimensions should be specified as 0.0 and 1.0, respectively. The input for each section is concluded with the statement 'end of zone'. It is possible to overlay initial conditions. The input in the zone with the higher number replaces earlier input. The input zones do not have to coincide with the material property zones or initial condition zones specified in Data Blocks 9-12 of the input file.

3.21.13 EXAMPLE DATA FILE INPUT

Example 1: input is as the following:

```
! Section 15: initial condition - reactive transport
! -----
!
'initial condition - reactive transport'
1                               ;number of zones

! -----
'number and name of zone'
1
'aquifer'

'concentration input'
1.7d-5  'free'                ;conc,   type   - ca2+
1.0d-6  'free'                ;conc,   type   - na+
2.0d-5  'free'                ;conc,   type   - co32-
1.0d-6  'free'                ;conc,   type   - h4sio4
1.0d-6  'free'                ;conc,   type   - al3+
5.0     'pH'                  ;conc,   type   - h+

'mineral input'
5.0d-4  .true.  'constant'    ;phi,    minequil, type - calcite
1.0d-10 1.0d-8  0.0          ;phi_min, k_eff,  sat
5.0d-1  .true.  'constant'    ;phi,    minequil, type - albite
1.0d-10 1.0d-13 0.0          ;phi_min, k_eff,  sat
0.0d0   .false. 'constant'    ;phi,    minequil, type - al(oh)3(am)
1.0d-10 1.0d-8  0.0          ;phi_min, k_eff,  sat
0.0d0   .false. 'constant'    ;phi,    minequil, type - sio2(am)
1.0d-10 1.0d-8  0.0          ;phi_min, k_eff,  sat

'extent of zone'
0.0 1.0 0.0 1.0 0.0 4.0

'end of zone'

'done'
```

Example 2: combine mineralogical parameters (see section 3.3.2.18)

```
! Section 15: initial condition - reactive transport
! -----
'initial condition - reactive transport'
3                               ;number of zones
... ..
'number and name of zone'
3
'background chemistry - reactive barrier'
```

```

'concentration input'
6.29      'ph'          'h+1'
4.04d-3   'free'         'cl-1'
1.95d-3   'free'         'co3-2'
1.44d-3   'free'         'so4-2'
5.29d-20  'free'         'hs-1'
5.32d-4   'free'         'ca+2'
2.53d-13  'free'         'fe+2'
4.72d-12  'free'         'fe+3'
9.84d-5   'free'         'cro4-2'
1.52d-7   'free'         'cr(oh)2+'
1.98d-6   'free'         'tce'
1.37d-6   'free'         'cis-1,2-dce'
1.73d-7   'free'         'vc'
2.99d-6   'free'         'ethane'
1.98d-31  'free'         'h2(aq)'

'mineral input'
0.50d0    .false.      'twothird' ;phim, minequil, update_type - fe_0_h2o_1
1.00d-10  1.94d2      0.00d0    ;phimin, area, supsatm
0.50d0    .false.      'twothird' ;phim, minequil, update_type - fe_0_cr
1.00d-10  1.94d2      0.00d0    ;phimin, area, supsatm
0.50d0    .false.      'twothird' ;phim, minequil, update_type - fe_0_tce
1.00d-10  1.94d2      0.00d0    ;phimin, area, supsatm
0.50d0    .false.      'twothird' ;phim, minequil, update_type - fe_0_cdce
1.00d-10  1.94d2      0.00d0    ;phimin, area, supsatm
0.50d0    .false.      'twothird' ;phim, minequil, update_type - fe_0_vc
1.00d-10  1.94d2      0.00d0    ;phimin, area, supsatm
0.50d0    .false.      'twothird' ;phim, minequil, update_type - fe_0_so4_2
1.00d-10  1.94d2      0.00d0    ;phimin, area, supsatm
0.00d0    .false.      'constant' ;phim, minequil, update_type - calcite
1.00d-10  7.3030d-10  0.00d0    ;phimin, k_eff, supsatm
0.00d0    .false.      'constant' ;phim, minequil, update_type - siderite(d)
1.00d-10  1.1574d-10  0.00d0    ;phimin, k_eff, supsatm
0.00d0    .false.      'constant' ;phim, minequil, update_type - fe(oh)2(s)
1.00d-10  1.1574d-9   0.00d0    ;phimin, k_eff, supsatm
0.00d0    .false.      'constant' ;phim, minequil, update_type - cr(oh)3(a)
1.00d-10  1.1574d-10  0.00d0    ;phimin, k_eff, supsatm
0.00d0    .false.      'constant' ;phim, minequil, update_type - mackinawite
1.00d-10  1.1574d-10  0.00d0    ;phimin, k_eff, supsatm
0.00d0    .false.      'constant' ;phim, minequil, update_type - ferrihydrite
1.00d-10  1.1574d-9   0.00d0    ;phimin, k_eff, supsatm

'extent of zone'
1.8 2.4 0.0 0.0 0.00 3.20

'end of zone'

'done'
!
```

Example 3: salinity dependent reaction rate of minerals

```

! Data Block 15: initial condition - reactive transport
! -----
!
'initial condition - reactive transport'
1                               ;number of zones
! -----
'number and name of zone'
1
'inflow'

'concentration input'
6000.00 'free' 'ca+2'
10900.00 'charge' 'na+1'
2800.00 'free' 'mg+2'
450.00 'free' 'k+1'
31000.00 'free' 'cl-1'
1240.00 'free' 'so4-2'
5.95 'ph' 'h+1'
```

```

303.00 'free' 'co3-2'
1.0d-10 'free' 'hs-1'
-200.00 'eh' 'o2(aq)'

'mineral input' ;bottom
1.00d-10 .false. 'constant' ;ch2o-h2s
1.00d-10 6.9d-9 0.00d0 ;
1.00d-10 .false. 'constant' ;calcite
1.00d-10 4.0d-8 0.00d0 ;
0.50d-10 .false. 'constant' ;anhydrite
0.50d-10 4.0d-9 0.00d0 ;
0.50d-10 .false. 'constant' ;halite
0.50d-10 1.16d-8 0.00d0 ;

'salinity dependent reaction rate of minerals'
1 ;number of minerals
ch2o-h2s ;name of minerals
'equation' 4 ;type of relation (=equation), no of parameters
-2.716E-01 2.11E-02 -9.455E-05 -3.20E-08 ;coefficients
15.0 3.0E-02 ; minimum salinity [g/L], k_sal [-]
225.0 0.046e-4 ; maximum salinity [g/L], k_sal [-]

'extent of zone'
0.0 20.0 0.0 1.0 0.0 1.0

'end of zone'

```

3.21.14 DESCRIPTION OF EXAMPLE INPUT

Example 1 provides the initial conditions for a 1D vertical reactive transport problem ($z=0.0$ to 4.0 m). There is only one zone named 'background chemistry - reactive barrier'. Following the zone name is the section 'concentration input', which specifies the total aqueous concentrations and types of six components in the following six lines provided in the same order as defined in the Data Block 2 ('geochemical system'). The section 'mineral input' provides the parameters for the kinetic reactions of minerals calcite, albite, $\text{Al}(\text{OH})_3(\text{am})$ and $\text{SiO}_2(\text{am})$. The mineral update type of all four minerals is 'constant'. Initially, the solid phases is composed dominantly of albite with a volume fraction in 0.50 [$\text{m}^3 \text{m}^{-3}$], and of tracer amount of calcite in 5.0×10^{-4} [$\text{m}^3 \text{m}^{-3}$]. The other two minerals are secondary minerals. The minimum volume fractions of all four minerals are 10^{-10} [$\text{m}^3 \text{m}^{-3}$], while the effective rate constants are 10^{-13} [$\text{mol L}^{-1} \text{bulk s}^{-1}$] for albite and 10^{-8} [$\text{mol L}^{-1} \text{bulk s}^{-1}$] for the rest.

Example 2 provides one of the three initial conditions for a 2D vertical reactive transport problem ($x=1.8$ to 2.4 m, $z=0.0$ to 3.20 m) using the function 'combine mineralogical parameters' (see section 3.3.2.18). The zone name to be specified is 'background chemistry - reactive barrier'. Similar to the example 1, the section 'concentration input' specifies the total aqueous concentrations and types of 15 components, while the section 'mineral input' provides the parameters for the kinetic reactions of all minerals. It is important to note that the first six minerals are treated as combined, which indicates the representation of the same material Fe^0 participates in six dissolution/precipitation reactions. Therefore, the initial total volume fraction of the Fe^0 in 0.5 [$\text{mol L}^{-1} \text{bulk s}^{-1}$] is specified to the first six minerals. The update types are 'twothird' for the first six minerals and 'constant' for the rest. The reactive surface area of the Fe^0 is 194.0 [$\text{m}^2 \text{mineral L}^{-1} \text{bulk}$]. The minimum volume fractions of all minerals are 10^{-10} [$\text{m}^3 \text{m}^{-3}$]. The effective rate constants for calcite, siderite, $\text{Fe}(\text{OH})_2$, $\text{Cr}(\text{OH})_3$, mackinawite and ferrihydrite are 7.303×10^{-10} , 1.1574×10^{-10} , 1.1574×10^{-9} , 1.1574×10^{-10} , 1.1574×10^{-10} , 1.1574×10^{-9} [$\text{mol L}^{-1} \text{bulk s}^{-1}$], respectively.

Example 3 demonstrates the input formats for the specification of initial conditions considering salinity dependent sulfate reduction. The parameters under sections 'concentration input' and 'mineral input' are defined in the exact same way as described in example 1. An additional section

'salinity dependent reaction rate of minerals' defines the parameters required for the salinity dependent sulfate reduction model based on experimental data. This example applied the model for one mineral $\text{ch}_2\text{o-h}_2\text{s}$ using the function (Brandt et al. 2001):

$$k_{sal} = -0.2716 + 0.0211 S - 9.455 \times 10^{-5} S^2 - 3.20 \times 10^{-8} S^3$$

Equation 3-57

The minimum salinity is 15.0 g L^{-1} and the k_{sal} is 0.03, which means if the salinity lower than 15.0 g L^{-1} , 0.03 will be used for the calculation. The maximum salinity is 225.0 g L^{-1} , and the k_{sal} is 4.6×10^{-6} . When the salinity is higher than 225.0 g L^{-1} , the k_{sal} is 4.6×10^{-6} .

3.22 BOUNDARY CONDITIONS - REACTIVE TRANSPORT (DATA BLOCK 16)

3.22.1 DESCRIPTION OF DATA BLOCK

In the last section of the problem-specific input file, the boundary conditions for the reactive transport problem need to be specified. The input is as defined in the section of 'initial condition – local chemistry' with the following exceptions:

- Kinetic batch simulations cannot be conducted (use batch option of model).
- pH-sweep calculations cannot be conducted (use batch option of model).
- the subsections 'mineral input' and 'sorption parameter input' are not needed.
- an additional input section is required defining the type of boundary condition.
- an additional input section is required defining the extent of the zone in the solution domain covered by the specified initial condition.

It is also possible to specify transient boundary conditions for the simulation of boundary conditions changing with time. To realize it, an additional block 'update boundary conditions' has to be specified followed by one or several boundary conditions.

3.22.2 DESCRIPTION OF INPUT PARAMETERS

The input data for reactive transport boundary conditions follows the format previously described for other spatially distributed properties. Similar to the input for flow boundary conditions, boundary types cannot be overlain on each other.

The first required parameter is the number of boundary zones, which follows the keywords 'boundary conditions – variably-saturated flow'.

Each zone is defined by a zone number and zone name following the statement 'number and name of zone'. These zones are independent of those for physical material properties or the initial condition zones, but may have the same name.

Four types of boundary conditions can be specified below the subsection identifier 'boundary type':

Table 3.23: Boundary conditions for reactive transport

Type	Name	Description
'first'	Dirichlet	specified concentration (fixed)
'second'	Neumann	free advective mass outflux for aqueous phase
'third'	Cauchy	advective mass influx for aqueous phase
'mixed'	Dirichlet/Cauchy	advective mass influx and free diffusive mass influx for aqueous and gaseous phases

The subsection 'concentration input' is only required for first, third and mixed-type boundary conditions. For additional information on input requirements and options in this section see section 'initial condition – local chemistry'.

The dimensions of the boundary zone are specified below the statement 'extent of zone'. As with other spatially distributed parameters, the precise dimensions of the boundary will be dependent on the grid spacing (See Section 3 of input file). Since the model is capable of simulating reactive transport in three dimensions, the specification of the boundaries must be provided in the x, y, and z-dimensions. The coordinates are also used to specify to which boundary face the boundary condition will be applied. This is of particular importance for third, second and mixed type boundary conditions. For example the specification

```
'extent of zone'
0.0 0.0  0.0 1.0  0.0 10.0
```

means that the boundary condition will be applied to the y-z plane of the solution domain at $x = 0$ covering an area from $y_{\min} = 0$ m to $y_{\max} = 1$ m and $z_{\min} = 0$ m to $z_{\max} = 10.0$ m. The model formulation requires that this input structure is obeyed also for 1D- and 2D-simulations. For example, the specification of the left boundary of a 1D-simulation in x-direction would require the input:

```
'extent of zone'
0.0 0.0  0.0 1.0  0.0 1.0
```

At the present time, the model can only handle boundary conditions on the surface (edges) of the solution domain. The input for each boundary zone is terminated with the statement 'end of zone'.

3.22.3 TRANSIENT BOUNDARY CONDITION

For the specification of transient boundary conditions, the keyword 'update boundary conditions', followed by the number and starting time of boundary conditions to be updated, has to be added to the initial boundary conditions. The detailed boundary conditions are given in the following blocks between a pair of keywords - 'start of target read time input' and 'end of target read time input'. The chemical compositions can be updated with time, but the boundary types cannot be changed. If BCs to be updated are more than one, they must be placed in the same order as defined in the initial boundary conditions. Example 2 demonstrates the format for the specification of transient boundary conditions.

3.22.4 USE BACKGROUND CHEMISTRY FOR BOUNDARY ZONE

It is also possible to specify a boundary condition with a chemical composition specified in the initial condition. This is only applicable when the first type boundary condition is assigned. The keyword for that is 'use background chemistry for boundary zone'. This is useful to specify 2D

boundary conditions with local injections. Example 3 in the next subsection demonstrates its usage.

3.22.5 EXAMPLE DATA FILE INPUT

Example 1: Input data for second and third type boundary conditions for a 1D reactive transport problem:

```
! Data Block 16: boundary conditions - reactive transport
! -----
!
'boundary conditions - reactive transport'
2                               ;number of zones

! -----
'number and name of zone'
1
'infiltrating fluid'

'boundary type'
'third'

'concentration input'
3.0      'ph'                ;'h+1'
1.0d-10  'free'              ;'fe+3'
2.5d-3   'free'              ;'so4-2'
1.0d-3   'free'              ;'zn+2'
1.0d-5   'free'              ;'fe+2'
1.0d-3   'free'              ;'cu+2'

'extent of zone'
0.0 1.0  0.0 1.0  0.0 0.0

'end of zone'

! -----
'number and name of zone'
2
'outflow boundary'

'boundary type'
'second'

'extent of zone'
0.0 1.0  0.0 1.0  16.0 16.0

'end of zone'

'done'
```

Example 2: Input data for transient boundary conditions for a 1D reactive transport problem:

```
! Data Block 16: boundary conditions - reactive transport
! -----
!
'boundary conditions - reactive transport'
2                               ;number of zones
!
! zone 1
! -----
!
'number and name of zone'
1
'inflow boundary'
```

```

'boundary type'
'first'

'concentration input'
2.00d-2      'free'          ;h+1
1.00d-2      'free'          ;co3-2

'guess for ph'
5.0

'extent of zone'
0.0 0.0  0.0 0.0  0.0 0.0

'end of zone'

! -----
'number and name of zone'
2
'outflow boundary'

'boundary type'
'second'

'extent of zone'
0.0 0.0  0.0 0.0  0.20 0.20

'end of zone'

! -----
'update boundary conditions'
2                                ;number of target read times
0.25                            ;target read times
0.50
!
! target read time 1
! -----
!
'start of target read time input'
1
!
! zone 1
! -----
!
'number and name of zone'
1
'inflow boundary'

'concentration input'
2.00d-2      'free'          ;h+1
1.00d-2      'free'          ;co3-2

'guess for ph'
5.0

'end of zone'

'end of target read time input'

!
! target read time 2
! -----
!
'start of target read time input'
2
!
! zone 1
! -----
!
'number and name of zone'
1
'inflow boundary'

```

```
'concentration input'
2.00d-7      'free'           ;h+1
1.00d-7      'free'           ;co3-2

'guess for ph'
5.0

'end of zone'

'end of target read time input'

'done'
```

Example 3: Use background chemistry for boundary zone

```
! Data Block 16: boundary conditions - reactive transport
! -----
!
'boundary conditions - reactive transport'
3                               ;number of zones

! -----
'number and name of zone'
1
'source'

'boundary type'
'third'

'concentration input'
2.00d-4      'free'           ;h+1
1.00d-4      'free'           ;co3-2
1.00d-8      'free'           ;ca+2

'guess for ph'
5.0

'extent of zone'
0.0 0.02 0.0 0.0 0.0 0.0

'end of zone'

! -----
'number and name of zone'
2
'inflow boundary'

'boundary type'
'first'

'use background chemistry for boundary zone'

'extent of zone'
0.021 0.1 0.0 0.0 0.0 0.0

'end of zone'

! -----
'number and name of zone'
3
'outflow boundary'

'boundary type'
'second'

'extent of zone'
0.0 0.1 0.0 0.0 0.20 0.20

'end of zone'
```

'done'

3.22.6 DESCRIPTION OF EXAMPLE INPUT

Example 1 specifies the boundary conditions (BCs) for 1D vertical reactive transport problem (domain length 16.0 m). At $z=0.0$ m, a third type boundary condition is defined together with the solution compositions of six components under section 'concentration input'. The boundary solution is low in pH (3.0) containing SO_4^{2-} , Fe^{2+} , Fe^{3+} , Zn^{2+} and Cu^{2+} . A second type BC is specified at the outflow boundary ($z=16.0$ m), indicating free advective mass outflux for the aqueous phase.

Example 2 specifies transient boundary conditions for reactive transport including two switches of BCs at 0.25 days and 0.5 days, respectively. These boundary conditions can be divided into two parts: the initial BCs and the BCs to be switched to. The initial BCs are assigned in the same way as those in example 1. They consist of two boundary conditions: first type BC for the inflow, and second type BC for the outflow. Both initial boundary conditions will be applied from the beginning of the simulation. The second part starts from the statement 'update boundary conditions' followed by two numbers (i.e. 0.25 and 0.50) in two separate lines, indicating the boundary conditions will be updated at 0.25 and 0.50 time units (e.g. days, which is defined in Data Block 4). The corresponding BCs to be updated at both time intervals are specified in the rest part of the input file between each pairs of statements '**start of target read time input**' and '**end of target read time input**'. The boundary condition to be updated at 0.25 days is provided between the first pair of the statement, which is the same as initial BC. This implies the BC is updated at 0.25 days, but actually remains unchanged. Similarly, the other BC to be updated at 0.5 days is specified between the next pairs of the statements. The solution at the boundary is changed to a solution with much lower concentrations of the components than those in the BC at 0.25 days. The last BC will be applied until the end of the simulation. Important is to keep the boundary types and required parameters consistent with the initial BCs. Best practice is to copy the initial boundary conditions into the pairs of statements, and modify the concentration at the corresponding switch time.

Example 3 specifies the BCs for a 2D vertical reactive transport problem. Three BCs are specified. The 1st one is a first type BC - the 'source' boundary, which is specified using the keywords 'boundary type', 'first' and 'concentration input' followed by the concentrations and types of all aqueous components. This BC leads to the connection of the 'source' boundary solution to the domain within the region from $x=0.0$ to 0.02 m at the bottom boundary ($z=0.0$). The rest of the bottom boundary is assigned with a first type BC named 'inflow boundary'. This boundary solution has the same chemical compositions as the initial condition through the application of the statement 'use background chemistry for boundary zone'. The top boundary of the domain ($x=0.0$ to 0.1 m, $z=0.2$ m) is assigned with a second type boundary named the 'outflow boundary'.

3.22.7 ADDITIONAL COMMENTS

Boundary condition types and parameters for isotope components (data block 16) are essentially the same as for simulations without isotopes.

3.23 ICE SHEET LOADING/UNLOADING (DATA BLOCK 17)

3.23.1 DESCRIPTION OF DATA BLOCK

For the simulation of the glaciation induced hydrogeomechanic coupling simulation, a simplified ice sheet 1D loading/unloading model can be used to specify the boundary conditions. The parameters are specified in a separate Data Block with the header 'ice sheet loading/unloading' (see the input example in section 3.23.3).

3.23.2 DESCRIPTION OF INPUT PARAMETERS

The parameters can be grouped into two parts: general properties and the ice sheet evolution stage parameters (see the example in the following section).

The general properties: The first logical parameter is to specify the status of the ice sheet. If it is true, the thickness of the ice sheet remains constant during the simulation. If it is false, the thickness will change with the glaciation/deglaciation processes. Similar to Bense and Person (2008), the thickness of the ice sheet ($h_{ice}(x, t)$, [L]) and the imposed hydraulic head beneath the ice sheet ($h_w(x, t)$, [L]) are computed as a function of distance and time according to Van der Veen (1999):

$$h_{ice}(x, t) = H_{ice}(t) \left[1 - \left(\frac{x}{L(t)} \right)^a \right]^{1/b} \quad \text{Equation 3-58}$$

$$h_w(x, t) = \alpha h_{ice}(x, t) \quad \text{Equation 3-59}$$

where $H_{ice}(t)$ [L] is the specified maximum ice sheet thickness, $L(t)$ [L] is the corresponding horizontal length of the ice sheet, x [L] is the distance from the ice sheet origin (i.e. starting point), a and b are constants [-], and α defines the ratio between the hydraulic head at the base of the ice sheet and the ice sheet thickness (Bea et al. 2011). Additional parameters are: the hydraulic conductivities of the ice sheet, ice density, and fresh water density.

The ice sheet evolution stage parameters are: The number of the glaciation/deglaciation stages, bool parameter for specifying the flow boundary condition (i.e. .true. – considered as flow boundary condition, .false. – non flow boundary condition, for example during glaciation period), factor for water pressure, factor for ice pressure, start and end time of the stage, horizontal position of the ice front, ice sheet thickness at the start and end time of the stage.

3.23.3 EXAMPLE DATA FILE INPUT

An example is provided below (Bea et al., 2011):

```
! Data Block 17: Ice Sheet loading/unloading
! -----
!
'ice sheet loading/unloading'
.false.                ! isconstant
440000.0d0             ! Ice Sheet point source (x)
4000.0d0               ! Ice Sheet point source (z)
2.5d0                 ! a
1.0d0                  ! b
```

```

-50.0d0          ! logkxx - hydraulic conductivity of ice
-50.0d0          ! logkyy
-50.0d0          ! logkzz
1.0d3           ! ice density
1.0d3           ! fresh water density
3               ! number of stages
1               ! istage
.false.
0.0d0           ! Factor for pw
1.0d0           ! Factor for pice
0.0d0 12500.0d0 ! time(1,i),time(2,i)
0.0d0 439950.0d0 ! l(1,i),l(2,i)
0.0d0 2000.0d0  ! h(1,i),h(2,i)
0.0d0 0.0d0     ! l1perm(1,i),l1perm(2,i)
0.0d0 0.0d0     ! l2perm(1,i),l2perm(2,i)
0.0d0 0.0d0     ! thickperm(1,i),thickperm(2,i)
2               ! istage
.false.
0.0d0           ! Factor for pw
1.0d0           ! Factor for pice
12500.0d0 17500.0d0 ! time(1,i),time(2,i)
439950.0d0 439950.0d0 ! l(1,i),l(2,i)
2000.0d0 2000.0d0  ! h(1,i),h(2,i)
0.0d0 0.0d0     ! l1perm(1,i),l1perm(2,i)
0.0d0 0.0d0     ! l2perm(1,i),l2perm(2,i)
0.0d0 0.0d0     ! thickperm(1,i),thickperm(2,i)
3               ! istage
.true.
0.95d0          ! Factor for pw
1.0d0           ! Factor for pice
17500.0d0 22500.0d0 ! time(1,i),time(2,i)
439950.0d0 0.0d0    ! l(1,i),l(2,i)
2000.0d0 0.0d0     ! h(1,i),h(2,i)
0.0d0 0.0d0     ! l1perm(1,i),l1perm(2,i)
0.0d0 0.0d0     ! l2perm(1,i),l2perm(2,i)
0.0d0 0.0d0     ! thickperm(1,i),thickperm(2,i)

!'compute permafrost'

'done'

```

3.23.4 DESCRIPTION OF EXAMPLE INPUT

The example data file contains 2D xz-plane ($x=0$ to 440 km, $z=0$ to 4 km) ice sheet loading/unloading parameters in three stages. The general parameters indicate: the thickness of the ice sheet changes with time. The ice sheet extends up to 440 km horizontally, and up to $z=4000$ m. The coefficients of a and b are 2.5 and 1.0, respectively, which are used for the ice thickness calculations. The hydraulic conductivity of the ice sheet are 10^{-50} m/s, the densities of ice and water are assumed to 1000 kg m^{-3} .

The glaciation/deglaciation processes include three stages: During the stage 1 (from 0 to 12500 years), the ice sheet develops and the ice front reaches 439950 m. The ice sheet thickness increased up to 2000 m. During the stage 2 (from 12500 to 17500 years), the ice sheet remains unchanged. During the stage 3, the deglaciation process results in the complete retreat of the ice sheet. The melted ice provides water source on the top of the soil. In this case, a factor of water pressure with 0.95 is applied. More detailed description is referred to the base case simulation in Bea et al. (2011).

3.23.5 ADDITIONAL PARAMETERS

Skempton coefficients at all control volumes are specified through a separate file 'prefix.skempton' in the following format.

```
title = "dataset basin"
variables = "x", "y", "z","skempton"
zone t = "field",i = 450, j = 100, k = 1, f=point
0.0000000E+00 0.0000000E+00 0.0000000E+00 0.9518758E+00
0.9799555E+03 0.0000000E+00 0.0000000E+00 0.9518758E+00
0.1959911E+04 0.0000000E+00 0.0000000E+00 0.9518758E+00
0.2939866E+04 0.0000000E+00 0.0000000E+00 0.9518758E+00
```

To facilitate this input, the keyword 'read skempton coefficient from file' should be included in the data block 10: 'physical parameters - variably saturated flow'. This parameter is applied to calculate the pore water pressure owing to the loading of the ice sheet.

4 DATABASE

The geochemical database is derived from the database of MINTEQA2 (Allison et al., 1991). Because MIN3P-THCm allows the simulation of open or partially open systems (in contact with the atmosphere) and the inclusion of kinetically-controlled reactions, the half-reaction approach (i.e. the use of the electron as a component and redox master variable) could not be used in MIN3P-THCm. The electron is eliminated by combining all half reactions in the MINTEQA2-database with the $O_2(aq)/H_2O$ half reaction.

The MIN3P-THCm geochemical database also allows the specification of kinetically-controlled intra-aqueous and dissolution-precipitation reactions. Default values for ion-exchange and surface complexation reactions are also provided and were taken from the database of PHREEQC2 (Parkhurst and Appelo, 1999).

4.1 COMPONENTS

4.1.1 COMP.DBS

The database file for the primary components is named comp.dbs. Two types of components can be specified in the database file: aqueous components and non-aqueous components (currently limited to surface sites for surface complexation reactions).

4.1.1.1 aqueous components

The entry for the aqueous component Ba^{2+} is given by:

```
ba+2      2.0    5.00  .00      137.34000  0.0
```

where ba+2 is the name of the component, 2.0 is the charge, 5.00 and .00 are the Debye-Huckel constants a and b. 137.34000 defines the gram formula weight and 0.0 is the alkalinity factor.

4.1.1.1.1 Alkalinity factor

The alkalinity factor is used to determine the alkalinity value of the water. It is defined as the proton uptake capacity of the species when titrated to the carbonate alkalinity end point. By definition, the alkalinity factor of CO_3^{2-} equals two (2).

4.1.1.1.2 Isotope components

The isotope components should be included in the database in the same format as other components. The following data block defines the sulfur isotope components as sulfate and hydrosulfide:

```
so4-2      -2.0    4.00  -.04    95.95173    .00
34so4-2    -2.0    4.00  -.04    97.94753    .00
hs-1       -1.0    3.50  .00     33.07200    .00
34hs-1     -1.0    3.50  .00     34.97586    .00
```

In the example, the components including the master isotope (^{32}S) are represented by so4-2 and hs-1; while the components including the heavy isotope (^{34}S) are 34so4-2 and 34hs-1. The properties of the same components including master or heavier/lighter isotopes are the same except the molar weight.

4.1.1.2 non-aqueous components

The entry for the non-aqueous component $\equiv\text{FeOH}$ is given by:

```
=feoh      0.0      .00  .00      .00000  0.0
```

where =feoh is the name of the component on the surface site. The next value defines the charge of the surface species. All remaining values are arbitrary for surface complexation reactions and are set to 0.0.

4.1.2 ADDING NEW COMPONENTS

If components are added to the database, the name of the new component must be different than the name of any existing component. If the alkalinity factor or the Debye-Huckel parameters are not known, 0.00 should be specified. When no Debye-Huckel parameters are specified, the Davies Equation is used. All other parameters are required to allow the consideration of the new component. When adding additional components the following format must be obeyed:

```
Line 1: format (a12, f4.1, 4x, f5.2, f5.2, 8x, f11.5, f7.2)
```

This data format is based on that used in MINTEQA2 (e.g. a12 indicates a string of 12 characters, f4.1 indicates a real number that contains up to four (4) digits, of which one digit places to the right of the decimal point (i.e. 673.8), 4x indicates four (4) blank spaces).

4.1.3 COMPONENTS FOR MULTICOMPONENT DIFFUSION

If multicomponent diffusion model is applied (see section 3.2.2.6), the molecular diffusion coefficient (in $\text{m}^2 \text{s}^{-1}$) is species dependent. This parameter is required to be attached at the end of each entry as the following:

```
ca+2      2.0      6.00  .17      40.08000  .00  0.792d-9
```

This parameter for the relevant components should be verified before the simulation.

4.2 COMPLEXATION REACTIONS

The database file for aqueous complexation reactions is named complex.dbs. As an example the database entry for the association reaction



is given by:

```
h3sio4-   6.1200  -9.8300      -1.00  4.00  .00  95.1070  .00
  2  h4sio4   1.000  h+1      -1.000
```

4.2.1 LINE 1

The first line begins with the name of the aqueous complex (h3sio4-), 6.1200 is the enthalpy change,

-9.8300 is the equilibrium constant for 25°C. The following value (-1.00) defines the charge of the species, while 4.00 and .00 define the Debye-Huckel constants a and b. 95.1070 is the gram formula weight of the aqueous complex, and the last value in the first input line (.00) defines the alkalinity factor for h3sio4-.

The MIN3P-THCm database uses association reaction for complexation reaction. The sign of the equilibrium constants $\log K_{25}$ should be turned around if the reactions are expressed as dissociation reactions.

$$K_{25} = [H_3SiO_4^-] \cdot [H^+] \cdot [H_4SiO_4]^{-1}$$

4.2.2 LINE 2

The second line defines the chemical reaction mentioned above. The number of components, as well as the pairs of name and stoichiometric coefficient of the associated components, are specified. In the example, the aqueous complex consists of 2 components (h4sio4 and h+1) with stoichiometric coefficients of 1.000 and -1.000, respectively.

4.2.3 ADDING COMPLEXES

Additional complexes can be specified. The only requirement is that the complex can be formed from the components included in the database file comp.dbs. If the numerical values for the enthalpy change, the Debye-Huckel parameters or the alkalinity factor are not known, 0.00 should be specified. All other parameters must be known to allow the consideration of the aqueous complex. At the present time, the following format must be obeyed, if additional complexes are specified in the database:

```
Line 1: format(a12,2x,2f10.4,16x,3f5.2,f9.4,f7.2)
Line 2: format(6x,i1,3x,5(a12,1x,f7.3,1x))
```

The formats are the same as used in MINTQA2 (e.g. a12 indicates a character string 12 characters long, f5.1 indicates a real number that contains up to five (5) digits of which one (1) places to the right of the decimal point, 4x indicates four (4) blank spaces, and i1 is a one (1) digit integer).

4.2.4 ISOTOPE COMPLEXES

Analogous to the complex database, entries are required for each secondary aqueous species that contains one of the isotope components.

For example the entry including the master sulfur isotope (^{32}S):

```
khso4(aq)          .0000          0.8136          .00 .00 .00      136.1716          .00
   3 h+1           1.000 k+1         1.000 so4-2          1.000
```

requires a corresponding entry for the ^{34}S component:

```
kh34so4(aq)        .0000          0.8136          .00 .00 .00      138.1716          .00
   3 h+1           1.000 k+1         1.000 34so4-2        1.000
```

4.2.5 COMPLEXES FOR MULTICOMPONENT DIFFUSION

If multicomponent diffusion model is applied (see section 3.2.2.6), the molecular diffusion

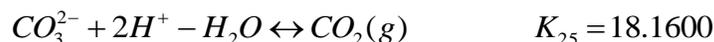
coefficient (in $[m^2 s^{-1}]$) is species dependent. This parameter for all chemical complexes is required to be placed at the end of each entry to the first line as the following:

```
oh-          13.3620  -13.9980          -1.00 3.50  .00  17.0074  1.00  5.273d-9
  2  h2o          1.000 h+1          -1.000
```

This parameter for the relevant complexes should be verified before the simulation.

4.3 GAS EXCHANGE REACTIONS

The database file for gas exchange reactions is named gases.dbs. As an example the database entry for the formation of $CO_2(g)$



is given by:

```
co2(g)      - .5300  18.1600          41.0100
  3  co3-2          1.000 h+1          2.000 h2o          -1.000
```

where co2(g) defines the name of the gas, -.5300 is the enthalpy change of the reaction, 18.1600 is the equilibrium constant and 41.0100 is the gram formula weight of the gas. The second line defines the chemical reaction mentioned above for the formation of $CO_2(g)$. The first parameter defines the number of components comprising the gas (in this case 3). In the following the pairs of name and stoichiometric coefficient of the components are specified. The three components in the example are co3-2, h+1 and h2o with stoichiometric coefficients of 1.000, 2.000 and -1.000, respectively.

```
Line 1: format (a12,2x,2f10.4,31x,f9.4/6x,i1,3x,5(a12,1x,f7.3,1x))
```

The MIN3P-THCm database uses association reaction for gas exchange reaction. The sign of the equilibrium constants $\log K_{25}$ should be turned around if the reactions are expressed as dissociation reactions.

$$K_{25} = [CO_2(g)] \cdot [H^+]^{-2} \cdot [CO_3^{2-}]^{-1}$$

4.4 ION EXCHANGE AND SORPTION REACTIONS

Component species involved in ion exchange and surface complexation reactions are defined in the comp.dbs file (see above section on component species). This section refers to the database file sorption.dbs, which contains secondary exchanged/adsorbed species and parameters of their formation reactions.

In the default database, ion exchange and adsorption reactions were taken from the database of PHREEQC2 (Parkhurst and Appelo, 1999).

An example for database entries for the exchange of calcium with sodium is given by:



```
'ca-x(na)'      0.0000  0.7959          2.00  40.0800
  2  'ca+2'      1.000  'na+1' -2.000
```

where ca-x(na) defines the name of surface species, 0.0000 is the enthalpy change of the reaction, 0.7959 is the equilibrium constant (Gaines-Thomas), 2.00 is the electrical charge of the exchanged component (here Ca^{2+}), and 40.0800 is the gram formula weight of the exchanged aqueous component (Ca).

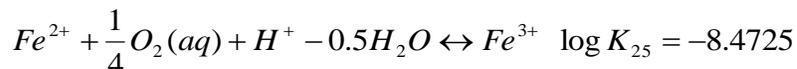
The second line defines the ion exchange reaction mentioned above. The first parameter defines the number of associated components (in this case 2) followed by the pairs of name and stoichiometric coefficient of the components. The two components in this example are ca+2 and na+1 with stoichiometric coefficients of 1.000 and -2.000, respectively. All the components should be included in the database file comp.dbs.

The MIN3P-THCm database uses association reaction for ion exchange and sorption reactions. The sign of the equilibrium constants $\log K_{25}$ should be turned around if the reactions are expressed as dissociation reactions.

$$K_{25} = [\text{Ca} - X(\text{Na})] \cdot [\text{Na}^+]^2 \cdot [\text{Ca}^{2+}]^{-1}$$

4.5 EQUILIBRIUM REDOX REACTIONS AND KINETICALLY-CONTROLLED INTRA-AQUEOUS REACTIONS

Equilibrium redox reactions and kinetically-controlled intra-aqueous reactions can be specified in the database file redox.dbs. The default database contains only equilibrium redox reactions as defined in the MINTEQA2-database (Allison et al., 1991). The database entry for the reaction:



is given by:

```
'fe+3'
4 'fe+2'    1.000 'o2(aq)'    0.250 'h+1'    1.000 'h2o'    -.500
'equilibrium' -8.4725    23.4570
```

where fe+3 is the secondary component of the redox couple, (i.e. this component will be treated in a similar way as an aqueous complex). The second line defines the redox reaction as mentioned above. The number of components comprising the secondary redox species is defined, followed by the pairs of name and stoichiometric coefficient of these components. This example has 4 components, with the names fe+2, o2(aq), h+1, and h2o and the stoichiometric coefficients 1.000, .250, 1.000 and -.500, respectively. In the third line, the keyword 'equilibrium' identifies the reaction as an equilibrium redox reaction. The equilibrium constant for the reaction (-8.4725) and the enthalpy change (23.4570) of the reaction are also specified.

Unlike for the database files comp.dbs, complex.dbs, gases.dbs and sorption.dbs, the input in redox.dbs is format-free. Each line starting with ! is considered a comment line. Additional redox reaction can be entered.

4.6 KINETICALLY-CONTROLLED INTRA-AQUEOUS REACTIONS

The MIN3P-THCm database redox.dbs uses association reaction for equilibrium redox reactions

and kinetically-controlled intra-aqueous reactions. The sign of the equilibrium constants $\log K_{25}$ should be turned around if the reactions are expressed as dissociation reactions because the equilibrium constant for the chemical reaction described in the previous section 4.5 as formation reaction is defined as the following:

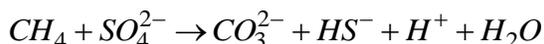
$$K_{25} = [Fe^{3+}][Fe^{2+}]^{-1} \cdot [O_2(aq)]^{-1/4} \cdot [H^+]^{-1}$$

It is also possible to specify irreversible, kinetically-controlled reactions in this database file. In general, the database-structure allows calculating rate expressions including fractional order terms, Monod-type terms and inhibition terms:

$$R_i^a = -k_i^a \left[\prod_{j=1}^{N_c} (T_j^a)^{o_{ij}^{a,t}} \prod_{\substack{j=1, \\ K_{ij}^{a,mo} > 0}}^{N_c} \left(\frac{T_j^a}{K_{ij}^{a,mo} + T_j^a} \right)^{o_{ij}^{a,mo}} \right. \\ \left. * \prod_{\substack{j=1, \\ K_{ij}^{a,in} > 0}}^{N_c} \left(\frac{K_{ij}^{a,in}}{K_{ij}^{a,in} + T_j^a} \right)^{o_{ij}^{a,in}} \prod_{\substack{j=1, \\ K_{ij}^{a,m,in} > 0}}^{N_c} \left(\frac{K_{ij}^{a,m,in}}{K_{ij}^{a,m,in} + \varphi_i} \right)^{o_{ij}^{a,m,in}} \right] \quad \text{Equation 4-1}$$

where R_i^a is the reaction rate of the i^{th} intra-aqueous component, k_i^a is the rate constant T_j^a are the total concentrations of the aqueous or biomass components. $o_{ij}^{a,t}$, $o_{ij}^{a,mo}$ and $o_{ij}^{a,m,in}$ define the reaction orders with respect to the total aqueous component concentrations, the Monod-type term and the inhibition term, respectively. $K_{ij}^{a,mo}$ are the half saturation constants, $K_{ij}^{a,in}$ are inhibition constants for aqueous components and $K_{ij}^{a,m,in}$ are inhibition constants due to the presence of minerals. φ_i are the volume fractions of the inhibiting minerals.

Most commonly used are Monod-type rate expressions. For example, a reaction describing the reduction of methane by sulfate:



which is inhibited in the presence of $O_2(aq)$, NO_3^- and goethite is defined by the database entry:

```
!
! ch4-oxidation - sulfate reduction - Monod-kinetics
! inhibition by O2, nitrate, and goethite
!
'ch4-so4'
6 'ch4(aq)' -1.000 'so4-2' -1.000 'h2o' 1.000 'co3-2' 1.000 'hs-1' 1.000 'h+1' 1.000
'irreversible'

'hyperbolic T^a' 4
'so4-2' 1.6d-3 1.0d0
'ch4(aq)' 1.0d-5 1.0d0
'so4-2' 1.0d-10 2.0d0
'ch4(aq)' 1.0d-10 2.0d0

'inhibition T^a' 2
'o2(aq)' 3.125d-5 1.0d0
'no3-1' 1.600d-5 1.0d0

'inhibition phi^m' 1
```

```
'goethite'      1.00d-06  1.0
```

Here 'ch4-so4' is the name of the reaction (defined by the user, up to 12 characters). The second line defines the reaction stoichiometry of the reaction, starting with the number of components involved and followed by the components and the stoichiometric coefficients. The key word 'irreversible' identifies the reaction as a kinetic reaction. The number of Monod and threshold terms is specified after the key word 'hyperbolic T^a'. Threshold terms have the same form as Monod terms and may be included for numerical reasons (i.e. to turn the reaction off, if the concentrations of reacting species become very small). In each line, first the name of the component is specified, followed by the half saturation constant [mol L⁻¹] and the exponent $o_{ij}^{a,mo}$. This exponent should be set to 1.0 for all Monod-type expressions, but may be set to a higher value for the threshold terms (resulting in a more rapid deactivation of the reaction when concentrations fall below the threshold limit).

The number of inhibition and toxicity terms due to the presence of aqueous components is specified after the key word 'inhibition T^a'. It is followed by the entries for these terms in the next lines. These entries consist of the names of the inhibiting components and the inhibition constants [mol L⁻¹].

The number of inhibition and toxicity terms due to the presence of mineral phases is specified after the key word 'inhibition phi^m'. It is followed by the entries for these terms in the next lines. These entries consist of the names of the inhibiting minerals and the inhibition constants [mol L⁻¹].

The specification of the fraction order term in the general rate expressions mentioned above, the keywords 'fractional T^a' can be specified.

4.7 MINERAL DISSOLUTION-PRECIPITATION REACTIONS

Mineral dissolution-precipitation reactions are described as kinetically-controlled reactions in MIN3P-THCm in the database file mineral.dbs.

4.7.1 SURFACE-CONTROLLED RATE EXPRESSIONS

The default database entry for each reaction is based on the simple rate expression:

$$R_i^m = -k_i^m S_i \left[1 - \left(\frac{IAP_i^m}{K_i^m} \right) \right]$$

where R_i^m is the reaction rate of the 5th mineral, k_i^m is the rate constant, IAP_i^m is the ion activity product and K_i^m is the equilibrium constant for the reaction. The default database entry for the reaction



is defined by:

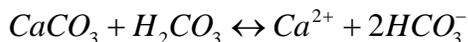
```
'calcite'
'surface'
100.0894  2.7100
2  'ca+2'  1.000  'co3-2'  1.000
'reversible'  8.4750  2.5850
```

where 'calcite' is the name of the mineral phase, 'surface' identifies the reaction as a surface-controlled reaction (other options are discussed below). The entries in the 3rd input line define the gram formula weight (100.0894) [g mol⁻¹] and the density (2.7100) [g cm⁻³] of calcite. The next line defines the reaction as mentioned above. The first entry in the line defines the number of components, the names of the components and the corresponding stoichiometric coefficients. The key word 'reversible' identifies the reaction as a reversible reaction. It is followed by the equilibrium constant $\log_{10}K_{25}$ of the reaction and the enthalpy change (2.5850), in [kcal mol⁻¹]. Other options of reaction types are: 'dissolution_to_equilibrium', 'precipitation_to_equilibrium' and 'raoult'. The same parameters (i.e. $\log K_{25}$ and enthalpy change) should be provided.

The MIN3P-THCm database uses association reaction for mineral dissolution-precipitation reactions. The sign of the equilibrium constants $\log K$ should be turned around if the reactions are expressed as dissociation reactions.

$$K_i^m = [CaCO_3] \cdot [Ca^{2+}]^{-1} \cdot [CO_3^{2-}]^{-1} = [Ca^{2+}]^{-1} \cdot [CO_3^{2-}]^{-1}$$

It is also possible to use the database to include more complex dissolution-precipitation reactions. An alternative description for the dissolution of calcite follows the reaction pathways proposed by Chou et al. [1989]:



which is described by the rate expression:

$$R_i^m = -S_i [k_{i1}^m \{H_2O\} + k_{i2}^m \{H_2CO_3\} + k_{i3}^m \{H^+\}] \left(1 - \frac{IAP_i^m}{K_i^m} \right)$$

The appropriate database entry is (rate data from Chou et al., 1989):

```
'calcite-ch'
'surface'
100.0894 2.710
2 'ca+2' 1.000 'co3-2' 1.000
'reversible' 8.4600 2.585

'parallel reaction pathways' 3

'pathway' 1
'log rate constant' -0.051
'activation energy' 2.000
'fractional C^c' 1
'h+1' 1.000
'end pathway'

'pathway' 2
'log rate constant' -6.187
'activation energy' 2.000
'fractional C^c' 1
'h2o' 1.000
'end pathway'

'pathway' 3
'log rate constant' -3.301
'activation energy' 2.000
'fractional C^x' 1
'h2co3aq' 1.000
'end pathway'
```

In addition to the standard database entry, the activation energy is defined (2.000, Plummer et al., 1978). The three parallel reaction pathways are included. The first and second pathways are dependent on the activity of protons and water (dependent on one component as species in solution; 'fractional C^c'), while the entry for the third reaction pathway is set to 'fractional C^x', because the reaction shows a dependence on the aqueous complex 'h2co3aq' (a secondary species in the MIN3P-THCm notation). The rate constants for the reactions are also provided (mass units: mol, time units: seconds) per unit surface area of the mineral (m²) with the key word 'log rate constant'. The activation energy is also specified, by means of the key word 'activation energy'.

The irreversible, pH-dependent dissolution of albite can be defined by the rate expression:

$$R_i^m = -\max \left\{ S_i \left[(k_{i1}^m \{H^+\}^{0.49} + k_{i2}^m + k_{i3}^m \{OH^-\}^{-0.30}) \left(1 - \frac{IAP_i^m}{K_i^m} \right) \right], 0 \right\}$$

The appropriate database entry is:

```
'albite-ph-d'
'surface'
262.2250 2.620
5 'na+1' 1.000 'al+3' 1.000 'h4sio4' 3.000 'h+1' -4.000 'h2o' -4.000
'irreversible dissolution - log K control ' -2.5920 17.400

'parallel reaction pathways' 3

'pathway' 1
'log rate constant' -9.690
'activation energy' 13.900
'fractional C^c' 1
'h+1' 0.490
'end pathway'

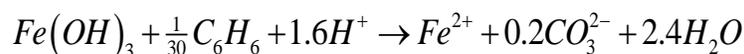
'pathway' 2
'log rate constant' -14.150
'activation energy' 13.900
'fractional C^x' 1
'oh-1' -0.300
'end pathway'

'pathway' 3
'log rate constant' -12.100
'activation energy' 13.900
'end pathway'
```

where the statement 'irreversible dissolution - logK control' is used to avoid albite precipitation under low temperature conditions. The other database entries follow the same format as was described for calcite dissolution-precipitation.

The dissolution of albite may also be described as a far from equilibrium reaction by using the string 'irreversible dissolution'.

Mineral dissolution reactions can also be described using a Monod-type formulation, similar to intra-aqueous kinetics. This is particularly useful for reductive dissolution reactions of Mn and Fe-oxides and hydroxides. The reductive dissolution of ferrihydrite in the presence of benzene for example can be described by the reaction stoichiometry:



The corresponding rate expression is:

$$R_{Fe(OH)_3-C_6H_6} = -k_{Fe(OH)_3-C_6H_6} \left[\frac{[C_6H_6]}{K_{Fe(OH)_3-C_6H_6, C_6H_6}^s + [C_6H_6]} \right] \left[\frac{K_{Fe(OH)_3-C_6H_6, NO_3}^i}{K_{Fe(OH)_3-C_6H_6, NO_3}^i + [NO_3^-]} \right] \left[\frac{K_{Fe(OH)_3-C_6H_6, O_2}^i}{K_{Fe(OH)_3-C_6H_6, O_2}^i + [O_{2(aq)}]} \right]$$

The form of the rate expression is based on the assumption that the reaction is first order with respect to ferrihydrite and takes into account substrate limitation as well as inhibition of the reaction in the presence of dissolved oxygen and nitrate. This reaction can be described with the database entry:

```
'feoh3-c6h6'
'surface'
104.8692  4.3713
5  'c6h6' -0.0333  'h+1' -1.600  'co3-2' 0.200  'fe+2' 1.000  'h2o' 2.400
'irreversible dissolution'

'hyperbolic T^a' 2
'c6h6'  1.0d-3  1.000
'c6h6'  1.d-10  2.000

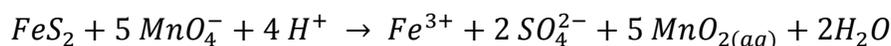
'inhibition T^a' 2
'o2(aq)' 3.125d-6  1.000
'no3-1'  8.000d-6  1.000

'log rate constant' 1.477d0
```

Entries for the gram formula weight of the mineral phase, the density, the number of components, the names of the components and the corresponding stoichiometric coefficients are defined as before. The reaction type is defined by the string 'irreversible dissolution'.

It is to note that there are two sets of parameters defined under 'hyperbolic T^a'. The second one is set to avoid the numerical issue when the concentration of C_6H_6 approaching zero.

It is also possible to use a general rate expression in the same way as Equation 4-1 to define the mineral kinetic reaction. The equation for the pyrite oxidation by MnO_4^- is:



It is defined as an irreversible dissolution reaction and the reaction rate is dependent on the MnO_4^- concentration as defined in the database mineral.dbs as the following:

```
!
! pyrite-mno4
! pyrite oxidation by mno4-1
! gram formula weight from MINTEQA2
! density from Manual of Mineralogy (1993)
!
'pyrite-mno4'
'surface'
119.9750  5.0200
6  'mno4-1' -5.000  'h+1' -4.000  'fe+3' 1.000  'so4-2' 2.000  'mno2(aq)' 5.000  'h2o' 2.000
'irreversible dissolution'

'fractional T^a' 1
'mno4-1' 1.000

'hyperbolic T^a' 1
'mno4-1' 1.0d-10 1.000
```

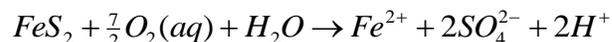
In this example, the lines begins with '!' are comments, documenting the origin of the data. The

name 'pyrite-mno2' is the mineral reaction name, representing the chemical formula FeS_2 in the chemical reaction equation. This reaction is surface controlled as defined in the next line. The rest of the data provided in the data block is the same as the other examples mentioned above except the keywords 'fractional T^a', which is for the specification of the fraction order term of the total concentration of MnO_4^- in the general rate expressions in Equation 4-1. The reaction order is 1.000.

4.7.2 DIFFUSION-CONTROLLED RATE EXPRESSION

All reactions discussed up to now were surface-controlled reactions. MIN3P-THCm also allows the use of the shrinking core model to describe mineral dissolution reactions. These reactions are identified in the database file for minerals by the string 'transport' in replacement of the string 'surface'.

Due to the accumulation of alteration products on the mineral surface, the oxidation of pyrite by dissolved oxygen may be described using the shrinking core model. The reaction stoichiometry for this reaction is:



A rate expression based on the shrinking core model can be expressed as:

$$R_i^m = -10^3 S_i \frac{r_i^p}{(r_i^p - r_i^r)r_i^r} \frac{D_{il}^m}{v_{il}^m} [\text{O}_2(\text{aq})]$$

In this rate expression 10^3 is a conversion factor [L m^{-3}], S_i is a scaling factor including the tortuosity of the surface coating or altered rim on the mineral surface, r_i^p is the radius of the particle, r_i^r is the radius of the unreacted portion of the particle, D_{il}^m is the free phase diffusion coefficient of the primary reactant in water (in this case $\text{O}_2(\text{aq})$), and v_{il}^m is the stoichiometric coefficient of oxygen in the reaction equation. The parameters S_i , r_i^p , and r_i^r are specified in the problem specific input file (see Data blocks 14 or 15). The remaining parameters are not problem specific and therefore defined in the database. The database entry for the oxidative dissolution of pyrite described by the shrinking core model is:

```
'pyrite-sc'
'transport'
119.9750 5.020
5 'fe+2' 1.000 'so4-2' 2.000 'h+1' 2.000 'h2o' -1.000 'o2(aq)' -3.500
'irreversible dissolution'

'fractional C^c' 1
'o2(aq)' 1.000
'shrinking core parameters' 2.41d-9 3.500
```

Transport controlled reactions can only be described as irreversible reactions. The other database entries follow the same format as was described in the previous examples.

Additional parameters are required after the key word 'shrinking core parameters'. These are the free phase diffusion coefficient of the primary reactant in water (D_{il}^m in $\text{m}^2 \text{s}^{-1}$), which is $2.41 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for the example; and the stoichiometric coefficient of oxygen in the reaction equation (v_{il}^m), which is 3.5.

4.8 KINETICAL REACTIONS CONTAINING ISOTOPES

The definition of the geochemical database for kinetic reactions containing isotopes are basically in the same way as mentioned in the previous sections. Generally, additional keywords are required to define the master and dependent isotopes. The following example showed the definition of sulfate reduction reaction by organic matter containing the master isotope (i.e. ^{32}S in SO_4^{2-}):

```
'ch2o-h2s-m'
'surface'
30.000 0.8786
4 'co3-2' 1.000 'hs-1' 0.500 'so4-2' -0.500 'h+1' 1.500
'irreversible dissolution'
'hyperbolic sum T^a' 2
2 'so4-2' '34so4-2' 1.62d-3 1.0d0
2 'so4-2' '34so4-2' 2.4d-6 2.0d0
'isotopic fractionation_master' 1
2 'so4-2' '34so4-2'
0.9616
```

The first five lines define the reaction as surface controlled irreversible intra-aqueous reaction. The keyword, 'hyperbolic sum T^a' in line 6 specifies that the reaction rate is dependent on the total sulfate concentration (i.e the sum of two sulfate isotope components 'so4-2' and '34so4-2'). The number "2" in line 6 indicates two lines are following providing parameters for the dependence – each line one term as the hyperbolic term in Equation 4-1. The following two lines denote the number of isotopic components to be summed, the name of the components, the half saturation constant, and the exponent (see section 4.5).

The next line provides the entry with the relevant parameters to determine isotopic fractionation as described by Equations 2-128 to 2-132 in the theory manual. The keyword 'isotopic fractionation_master' is followed by the number of isotope sets in the reaction. For example if both carbon and sulfur isotopes were to be simulated the number would be 2. The following lines describe the number of isotopes in the set, the name of the isotope components starting with the 'master component' as described for data block 8, followed on the next lines by the fractionation factor for each isotope component starting with the second in the list of name. To clarify, the master component is the isotope that the other isotopes are compared to, to get a ratio and delta value, and therefore does not have a fractionation factor.

In the example, the keyword 'isotopic fractionation_master' in line 9 is followed by the number "1". This indicates that the current reaction contains one set of isotope(s) (i.e. the sulfur isotopes: ^{32}S and ^{34}S in the components 'so4-2' and '34so4-2', respectively). The fractionation factor of '34so4-2' is 0.9616.

The corresponding entry for the same intra-aqueous kinetic reaction (i.e. the sulfate reduction by organics components) containing isotope ^{34}S is:

```
'ch2o-34h2s-m'
'surface'
30.000 0.8786
4 'co3-2' 1.000 '34hs-1' 0.500 '34so4-2' -0.500 'h+1' 1.500
'irreversible dissolution'
'hyperbolic sum T^a' 2
2 'so4-2' '34so4-2' 1.62d-3 1.0d0
2 'so4-2' '34so4-2' 2.4d-6 2.0d0
'isotopic fractionation' 'ch2o-h2s-m'
```

where the keyword 'isotopic fractionation' and the name of the reaction/mineral 'ch2o-h2s-m' in the last line of the data block define that the isotope fractionation parameters that determine the reaction

rate are included with the mineral 'ch2o-h2s-m' as the corresponding reaction/mineral containing the master isotope. In this way, the isotope fractionation parameters are described with only one mineral, and then the other corresponding minerals just refer to the master mineral.

If the mineral is reversible then a third line is needed under the 'isotopic fractionation_master' keyword to identify the other minerals with isotopes in the set to properly determine mineral solubilities. For example gypsum dissolution/precipitation would be represented by the following entries;

```
'gypsum_iso'
'surface'
172.1722 2.3200
3 'ca+2' 1.000 'so4-2' 1.000 'h2o' 2.000
'reversible' 4.5800 0.1090
'isotopic fractionation_master' 1
2 'so4-2' '34so4-2'
1
1 '34gypsum_iso'
```

```
'34gypsum_iso'
'surface'
172.1722 2.3200
3 'ca+2' 1.000 '34so4-2' 1.000 'h2o' 2.000
'reversible' 4.5800 0.1090
'isotopic fractionation' 'gypsum_iso'
```

As a further example, the entries for the mineral k2cro4 in the four isotope Cr system would include;

```
'50k2cro4'
'surface'
194.1902 1.0000
2 '50cro4-2' 1.000 'k+1' 2.000
'reversible' -0.0073 -4.2500
'isotopic fractionation' '52k2cro4'
```

```
'52k2cro4'
'surface'
194.1902 1.0000
2 'cro4-2' 1.000 'k+1' 2.000
'reversible' -0.0073 -4.2500
'isotopic fractionation_master' 1
4 'cro4-2' '50cro4-2' '53cro4-2' '54cro4-2'
1 1 1
3 '50k2cro4' '53k2cro4' '54k2cro4'
```

```
'53k2cro4'
'surface'
194.1902 1.0000
2 '53cro4-2' 1.000 'k+1' 2.000
'reversible' -0.0073 -4.2500
'isotopic fractionation' '52k2cro4'
```

```
'54k2cro4'
'surface'
194.1902 1.0000
2 '54cro4-2' 1.000 'k+1' 2.000
'reversible' -0.0073 -4.2500
'isotopic fractionation' '52k2cro4'
```

In these entries of minerals, the keywords 'isotopic fractionation_master' defines the master isotope mineral '52k2cro4', which is a surface controlled reversible reaction. The equilibrium constant $\log_{10}K_{25}$ (-0.0073) of the reaction and the enthalpy change (-4.2500), in [kcal mol⁻¹]. The other three related isotopic minerals are '50k2cro4', '53k2cro4' and '54k2cro4', which are defined in separate blocks as surface controlled reversible reactions in the same way as described in section 4.7.1

except the last line. The last line closes the definition of each isotopic minerals by using the keywords 'isotopic fractionation' followed by the associated isotopic fractionation master, i.e. the mineral '52k2cro4'.

4.9 PITZER VIRIAL COEFFICIENTS DATABASE

The activity coefficients of aqueous species in highly saline solutions are calculated based on Pitzer equations (Pitzer, 1973). The HMW (Harvie-Møller-Weare) activity model (Harvie et al. 1984) that is equivalent to the original Pitzer equation was implemented in MIN3P-THCm (Bea et al., 2010, 2011). The HMW model consists of a set of polynomial equations for water activity (a_w), the osmotic coefficient (ϕ), the activity coefficients of cations (γ_C), anions (γ_A), and neutral species (γ_N), which have to be determined using the Pitzer parameters: $\beta(0)$, $\beta(1)$, $\beta(2)$, C^ϕ , θ , λ and ψ . A special xml data file pitzer.xml is required to provide the Pitzer parameters.

In the file, the interaction parameters used in the model are provided, including:

A^ϕ - the one third Debye-Hückel slope ($A^\phi = 0.392$ at 25°C, Pitzer and Mayorga, 1973) (see equation B-2 in Appendix B.1 of the theory manual) in the form:

```
<aphi>
  <coeff value="0.3915d0"/>
</aphi>
```

$\beta(0)$ – ion-interaction parameter, α_1 and α_2 (see equation B-18 to B-22 in Appendix B.1 of the theory manual). When either ion in a pair of ion couple is monovalent, $\alpha_1 = 2$. For 2–2 or higher valence pairs, $\alpha_1 = 1.4$. For all electrolytes $\alpha_2 = 12$.

```
<b0>
  <coeff sps1="na+1" sps2="cl-1" value="7.45618073E-02" alpha1="2.0d0" alpha2="12.0d0" />
  <coeff sps1="k+1" sps2="cl-1" value="0.0477811552" alpha1="2.0d0" alpha2="12.0d0" />
  <coeff sps1="ca+2" sps2="so4-2" value="0.15" alpha1="1.4d0" alpha2="12.0d0" />
  ....
</b0>
```

$\beta(1)$ - ion-interaction parameter, (see equation B-18 to B-20 in Appendix B.1 of the theory manual).

```
<b1>
  <coeff sps1="al+3" sps2="so4-2" value="18.53"/>
  <coeff sps1="na+1" sps2="cl-1" value="2.75240690E-01"/>
  <coeff sps1="k+1" sps2="cl-1" value="2.15510997E-01"/>
  .....
</b1>
```

$\beta(2)$ - ion-interaction parameter, (see equation B-18 to B-20 in Appendix B.1 of the theory manual).

```
<b2>
  <coeff sps1="al+3" sps2="so4-2" value="-500.0"/>
  <coeff sps1="mg+2" sps2="so4-2" value="-35.25877546"/>
  <coeff sps1="sr+2" sps2="so4-2" value="-41.8"/>
  <coeff sps1="fe+2" sps2="so4-2" value="-42.0"/>
  <coeff sps1="mn+2" sps2="so4-2" value="-40.0"/>
  <coeff sps1="ca+2" sps2="oh-" value="-5.72"/>
</b2>
```

C^ϕ - ion-interaction parameter, (see equation B-30 in Appendix B.1 of the theory manual).

```
<cfi>
  <coeff sps1="al+3" sps2="so4-2" value="-0.0911"/>
```

```

<coeff sps1="na+1" sps2="cl-1" value="1.53693372E-03"/>
<coeff sps1="k+1" sps2="cl-1" value="-7.48604891d-4"/>
... ..
</cfi>

```

θ_{ij} - ionic interaction parameter between cation-cation or anion-anion, (see equation B-23 to B-25 in Appendix B.1 of the theory manual).

```

<theta>
<coeff sps1="k+1" sps2="na+1" value="-3.20349317E-03"/>
<coeff sps1="k+1" sps2="fe+2" value="-0.07"/>
<coeff sps1="mg+2" sps2="na+1" value="0.07"/>
<coeff sps1="ca+2" sps2="na+1" value="5.00000000E-02"/>
<coeff sps1="h+1" sps2="na+1" value="0.036"/>
<coeff sps1="ca+2" sps2="k+1" value="1.15600000E-01"/>
<coeff sps1="h+1" sps2="k+1" value="0.005"/>
<coeff sps1="ca+2" sps2="mg+2" value="0.007"/>
<coeff sps1="h+1" sps2="mg+2" value="0.1"/>
<coeff sps1="h+1" sps2="ca+2" value="0.092"/>
<coeff sps1="so4-2" sps2="cl-1" value="7.03278797E-02"/>
<coeff sps1="hso4-" sps2="cl-1" value="-0.006"/>
<coeff sps1="hso4-" sps2="so4-2" value="-1.16842489E-01"/>
<coeff sps1="oh-" sps2="cl-1" value="-0.05"/>
... ..
</theta>

```

Ψ – ion-interaction parameter of ternary terms (see equation B-31 in Appendix B.1 of the theory manual).

```

<psi>
<coeff sps1="na+1" sps2="k+1" sps3="cl-1" value="-3.69149429E-03"/>
<coeff sps1="na+1" sps2="k+1" sps3="br-1" value="-0.0022"/>
<coeff sps1="na+1" sps2="k+1" sps3="so4-2" value="7.32101065E-03"/>
<coeff sps1="na+1" sps2="k+1" sps3="hco3-" value="-0.003"/>
<coeff sps1="na+1" sps2="k+1" sps3="co3-2" value="0.003"/>
<coeff sps1="na+1" sps2="ca+2" sps3="cl-1" value="-3.00000000E-03"/>
... ..
<coeff sps1="hco3-" sps2="co3-2" sps3="na+1" value="0.002"/>
<coeff sps1="hco3-" sps2="co3-2" sps3="k+1" value="0.012"/>
</psi>

```

λ – ion – neutral species interaction parameters (see equation B-11 and B16 in Appendix B.1 of the theory manual).

```

<lambda>
<coeff sps1="cl-1" sps2="co2(aq)" value="-0.005"/>
<coeff sps1="na+1" sps2="h2co3" value="0.1"/>
<coeff sps1="k+1" sps2="h2co3" value="0.051"/>
<coeff sps1="mg+2" sps2="h2co3" value="0.183"/>
<coeff sps1="ca+2" sps2="h2co3" value="0.183"/>
... ..
</lambda>

```

5 REFERENCES:

(See the references in the theory manual)

Bea, S.A., J. Carrera, C. Ayora and F. Batlle. 2010. Pitzer Algorithm: Efficient implementation of Pitzer equations in geochemical and reactive transport models. *Computers & Geosciences*, 36, 526-538.

Harvie, C.E., N. Moller and J.H. Weare. 1984. The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system to high ionic strengths at 25°C. *Geochimica et Cosmochimica Acta*, 48, 723-751.

MacInnes, D.A. 1919. The activities of the ions of strong electrolytes: *Journal American Chemical Society*, v. 41, p. 1086-1092.

Molins, S., J. Greskowiak, C. Wanner and K. U. Mayer. 2015. A benchmark for microbially mediated chromium reduction under denitrifying conditions in a biostimulation column experiment, *Computational Geosciences*, DOI: 10.1007/s10596-014-9432-0.