

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 was 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 solutions. 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, facilitating the investigation of the interactions between reaction and transport processes. The model can also be used as a batch model for equilibrium speciation problems, kinetic batch problems or for generating pC-pH-diagrams.

MIN3P-THCm is characterized by a high degree of flexibility concerning the definition of the geochemical reaction network to facilitate the model's application to a wide range of hydrogeological and geochemical problems. The 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 for considering the 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. However, 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.

Parallelization of MIN3P-THCm (ParMIN3P-THCm) was achieved through the domain decomposition method based on PETSc (Portable Extensible Toolkit for Scientific Computation) libraries. PETSc was also used as the parallel solver package and for data structure and message communication. A hybrid MPI and OpenMP parallel programming approach was implemented in the code to take advantage of leadership-class supercomputers that combine both shared memory and distributed memory architectures.

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1 INSTALLING AND RUNNING MIN3P-THCM

The following assumes that the program will be installed on a PC with WINDOWS OS. The package can be installed on any drive. This guide assumes 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,” which contains a number of subdirectories.

The “bin” directory includes the MIN3P-THCm executable. The “database” directory includes the database files and the “benchmarks_standard” directory includes a set of working examples. The “simulations” directory is empty and is dedicated to 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-clicking on the program will launch a new DOS-window (Figure 1.1). Now provide the name of the input file without extension and return.

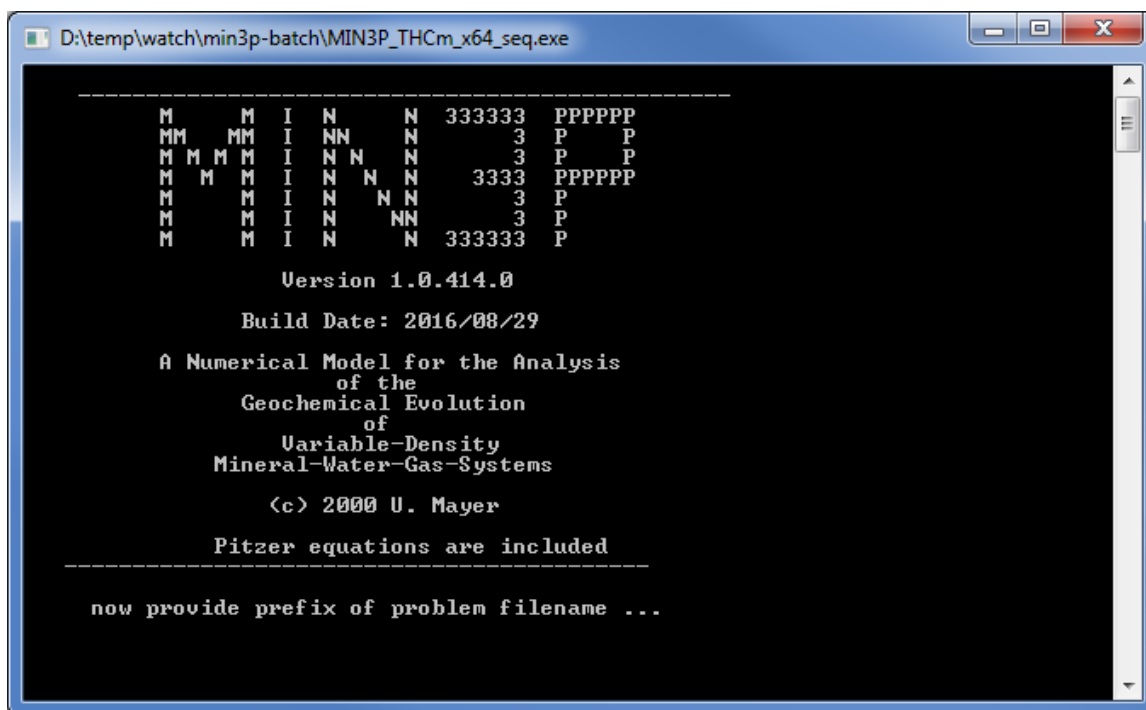


Figure 1.1: The DOS window while launching the MIN3P-THCm program

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

As a result of the potentially large number of output files generated by the program, it is highly

recommended that a directory is created 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 the output files generated are ASCII text files by default. Most output files have a Tecplot header that can be read by various post-processing programs (Section 2.2). Alternatively, binary output is available when the MPI parallel version is used.

IMPORTANT: If you want to run the simulations apart from in the “simulations” directory, you must 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.

The users for the parallel version (ParMIN3P-THCm) are referred to the <MIN3P-THCm User Manual for Parallel Configuration> by Su et al. (2018).

2 FILE STRUCTURE

The 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 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) may 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 prefix.tem (**tem**perature) and prefix.ivs (**ini**tial condition **vari**ably **satur**ated flow) files. If the root water uptake option is used, the file prefix soi must be provided for the daily evaporative budget. Depending on the way the root is simulated, optional files prefix.rld, paramAS.txt, paramRT.txt, sol.txt or volrac.txt can be required. 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
	prefix.aqt	Distributed initial condition for aqueous component concentrations	Optional
	restart.dat	restart file	Optional
	prefix soi	Time distribution of parameters needed for the evaporative budget	Optional
	prefix.rld	Spatial distribution of the RSD of a stationary root structure	Optional
	paramAS.txt	Root structure parameters for ArchiSimple use	Optional
	paramRT.txt	Root structure parameters for Root Typ use	Optional
	sol.txt	Effects of the soil constraints on the root growth (for Root Typ and ArchiSimple use)	Optional
	volrac.txt	Daily root volume for ArchiSimple use	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
sit.dbs	Specific ion interaction theory (SIT)	Optional

2.2 OUTPUT FILES

A brief summary of all output files can be found in the file prefix_o.flc, which gives new users a helpful overview of the output files. This file contains the file names, provides a brief description of the files' contents 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 prefix_o.flc, in which the parameters and units of almost all output files are described.

The files prefix_o.gen and prefix.log document 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 files.

Table 2.2: Output files – general model output

File name	Description	TECPLOT Header
prefix_o.gen	General problem-specific output, contains feedback from the 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 troubleshooting 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 the 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 transport	N

prefix_o.aqt	Record of the spatial distribution of all component concentrations before batch reactions.	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 = g lobal/ s patial/ p ressure	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 = v elocities	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 = m ass and liquid filled v olumes	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 = m ass v olume c hange	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 = m ass balance (v olume) e rrors	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 = g lobal/ s patial/ t otal 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 = g lobal/ s patial/ s pecies 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 = g lobal/ s patial/ i ntra-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 = g lobal/ s patial/ m aster 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 g as 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: gsgr – global/spatial/de g assing/ r ates	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/sor b ed 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.gsac	Activity coefficient for primary and secondary aqueous species at output time x (0 = initial condition) – contour data Output format: x,(y),(z), parameter values Suffix meaning: gss – global/spatial/ a ctivity coefficient	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/ b alance/ t ime	Y
prefix_x.gmf	Total flux of each aqueous component for multicomponent diffusion (MCD) - contour data Output format: x,(y),(z), parameter values Suffix meaning: cbt – globe/ m ass/ f lux	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 m ass of a queous c omponents	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/ d issolution-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 = global/breakthrough/total aqueous component concentrations	Y
prefix_x.gbc	Aqueous species concentrations at output location x – transient data Output format: time, parameter values Suffix meaning: gbc = global/breakthrough/species 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 = global/breakthrough/intra-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 = global/breakthrough/master variables	Y
prefix_x.gbg	Partial gas pressures at output location x – transient data Output format: time, parameter values Suffix meaning: gbg = global/breakthrough/partial gas pressures	Y
prefix_x.gbgr	Degassing rates at output location x – transient data Output format: time, parameter values Suffix meaning: gbgr = global/breakthrough/degassing/rates	Y
prefix_x.gbv	Mineral volume fractions at output location x – transient data Output format: time, parameter values Suffix meaning: gbv = global/breakthrough/volume fractions	Y
prefix_x.gbb	Surface species at output location x – transient data Output format: time, parameter values Suffix meaning: gbb = global/breakthrough/sorbed species	Y
prefix_x.gbs	Mineral saturation indices at output location x – transient data Output format: time, parameter values Suffix meaning: gbs = global/breakthrough/saturation indices	Y
prefix_x.gbd	Mineral dissolution-precipitation rates at output location x – transient data Output format: time, parameter values Suffix meaning: gbd = global/breakthrough/dissolution - 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.gbjs	Isotope data at output location x – transient data Output format: time, parameter values Suffix meaning: gbjs = g lobal/ b reakthrough/ i sotope fractionation	Y
Prefix_x.gbac	Activity coefficient for primary and secondary aqueous species at output location x – transient data Output format: time, parameter values Suffix meaning: gbx = g lobal/ b reakthrough/ a ctivity coefficient	
prefix_o.mas	Total mass (in moles) of all aqueous components – transient data Output format: time, parameter values Suffix meaning: mas = total mass of a queous 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 m ineral 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 g as 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 s orbed s pecies	N
prefix_o.ebal	System energy balance Output format: time, energy, water filled volume and air filled volume Suffix meaning: ebal = e nergy b alance	Y
prefix_o.ebalc	Energy balance contributions Output format: time, total energy inflow, out flow, and the change in storage Suffix meaning: ebal = e nergy b alance contributions	Y
prefix_o.ebale	Energy balance error Output format: time, total energy inflow, out flow, and the change in storage Suffix meaning: ebal = e nergy b alance contributions	Y
prefix.evap	Climate output Output format: time, parameter values Suffix meaning: evap = e vaporation 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 owing to the specified geochemical reactions. The total system mass for aqueous phase components, minerals, gases, and surface species are reported in 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.flc 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 runtime.

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 by reason of the specified heat transport conditions. The total system energy evolution is reported in the prefix_o.ebal, prefix_o.ebalc, and prefix_o.ebale files. 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 prefix.evap file. This file includes the solution time [days], evaporation rate [kg s⁻¹ m⁻²], temperature [°C], relative humidity [-], wind [m s⁻¹], rainfall rate [kg s⁻¹ m⁻²], runoff rate [kg s⁻¹ m⁻²], rain – runoff [kg s⁻¹ m⁻²], vapour density (r_v) [kg m⁻³], vapour pressure (P_v) [Pa], solar radiation (R_n) [J s⁻¹ m⁻²], latent heat of evaporation (L_w) [J s⁻¹ m⁻²], sensible heat (H_s) [J s⁻¹ m⁻²], and total energy balance at the atmospheric boundary surface [J s⁻¹ 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/v olume 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
Prefix_x.lbac	Activity coefficient for primary and secondary aqueous species, local geochemistry – transient data Output format: time, parameter values Suffix meaning: lbx = local/ breakthrough/activity coefficients	

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 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 17 data blocks.

Table 3.1: Data blocks for the 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. 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: 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 modelling 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 over time	As above but with conditions changing over 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, certain subsections and even entire sections are optional. Table 3.3 summarizes the input section requirements for each simulation type (R = required, O = optional, N = not used):

Table 3.3: Input requirements of data blocks 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 necessary. When the program reads the input file, it searches for the required parameter(s). If found, the program reads the required parameters before moving 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 begin with “;”. The user can use any symbols to distinguish them 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 THE DATA BLOCK

In this data block, the problem title is read and the type of simulation 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 DESCRIPTIONS OF THE 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 the type of simulation to be performed, four true/false statements must be specified in the following four input lines (see the example in section 3.2.3):

3.2.2.2 varsat_flow

This statement determines if a flow simulation is to be performed. If .true. is provided, flow simulation will be activated. Note: varsat_flow is a logical variable in the code. In the example in section 3.2.3, varsat_flow is placed as comment to remind the user. The program reads only the value (either .true. or .false.) at the beginning of the first line under the keyword 'global control parameters'. Similar treatment apply to the following three lines as described in the following three subsections.

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 root_uptake

This statement specifies if the simulation is to involve root water uptake. This root water uptake option is available only for the variably saturated case.

3.2.2.7 Additional keywords

Additional keywords can be added to invoke additional capabilities:

`'multicomponent diffusion'`: This keyword activates multicomponent diffusion. `'hybrid multicomponent diffusion'`: This keyword activates hybrid multicomponent diffusion. In such cases, the database files (comp.dbs, complex.dbs) must include the free aqueous diffusion coefficient (D_0) for each species (see section 4.1.3).

`'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 function's parameters must be provided in an additional data block (Data Block 17) with the keywords `'ice sheet loading/unloading'` (see section 3.23).

`'energy balance'`: This activates 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) is used to control the frequency of backing up intermediate calculation results. These data can be used for restarting a simulation. The default value is 10. Generally, there are two files to save the previous results: restart.tmp1 and restart.tmp2. Restart.tmp1 saves at the given number of time steps (N_t) while restart.tmp2 documents the results double the number of specified time steps ($2*N_t$). The documented results include all the spatial data needed for restarting 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) and pointer to next output time for contour data. From the second line, 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': This keyword activates 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 (usually renamed from the restart.tmp1 or restart.tmp2, whichever is the latest generated), is needed. The simulation will continue from the time recorded in the restart.dat file. However, it should be noted that the transient output is overwritten when simulation is restarted. To avoid loss of transient output when simulation is restarted, user can use additional keywords (see below) to resume output from breaking point when simulation is restarted.

There are two restart files generated during MIN3P simulation, with breaking point t1 and t2. When simulation is restarted, user can choose one restart file to restart simulation. The results can be appended in two different methods: the normal results appending and the legacy results appending.

'append results' and 'append results in legacy mode': The former one appends results immediately after the breaking point while the latter one appends results after it reaches the second breaking point. For example, assuming $t_1 < t_2$, if results are appended in normal mode and t1 is chosen as restart time, the code removes the old transient output data after t1 and appends the new results; if results are appended in legacy mode, user can only choose the earlier restart file (t1). The code keeps the old transient output before t2 and appends the new results after t2. When simulation is restarted, there is loss of significance during I/O that may cause blips in the transient output at the first few time steps (e.g., storage change over time). In this case, user can use legacy mode to avoid such a problem.

When 'append results' or 'append results in legacy mode' is used, user will find the following information in the prefix_o.flr file, indicating the results afterward are appended results to the previous simulations. The simulation can be restarted consecutively.

+++++

output of appended results

+++++

or

+++++

output of appended results in legacy mode

+++++

If the results files are generated by the old code, the transient output data may be not completed (last record earlier than the last breaking point). In this case, the last record is before restarting time, an warning information is given in prefix_o.flr file, as shown below.

warning - last data record in file prefix_x.abc is before restarted time

When 'append results' or 'append results in legacy mode' is used but the results of transient output in the previous simulation do not exist, the outputs of initial condition (time = 0.0) in the transient result is skipped. Other than that, the results output are the same as normal 'restart'. At the restart point, the effect of 'time steps between output' is ignored. Compared to the previous code, this will cause some difference in the transient output if 'number of skipped output times' is larger than 1, due to extra output at restart point.

The accumulative mass balance and accumulative relative mass balance error are recalculated based on the breaking point (restarted time) saved in the transient output file. If the last record is before breaking point, last record is used instead of breaking point record and there will be numerical error in the accumulative relative error as the results before the breaking point are not completed.

3.2.3 EXAMPLE DATA INPUT FILE

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'

!'append results'                ;Append results after the first restart time
!'append results in legacy mode' ;Append results after the second restart time
```

```
'multicomponent diffusion'
```

```
'done'
```

3.2.4 DESCRIPTION OF THE 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 restart.tmp1 will be generated at every 20 time steps and restart.tmp2 at 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 modelling 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 easier.

3.3 GEOCHEMICAL SYSTEM (DATA BLOCK 2)

3.3.1 DESCRIPTION OF THE 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 DESCRIPTIONS OF THE INPUT PARAMETERS

3.3.2.1 'geochemical system'

The data block 'geochemical system' comprises a series of sub-blocks. The sub-block 'components' is required for all simulations. 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
'define sorption type'	Specify the sorption type		N
'specify output unit for SCM sorbed species concentration'	Define the output unit for the concentration of sorbed species using the SCM model		N
'linear sorption'	Linear sorption model (K_d concept)	-	N
'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
'use sit model'	Use the SIT model based on the specific ion interaction theory	sit.dbs	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 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 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 isotope 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) sulphur isotopes can be defined as:

```
'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 eight components including four isotope components of sulphur: 'so4-2,' '34so4-2,' and 'hs-1,' '34hs-1.' 'So4-2' and 'hs-1' represent the components containing light (^{32}S) isotopes and '34so4-2' and '34hs-1' include the heavy (^{34}S) 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 component for surface complexation reactions.

3.3.2.4 'biomass components'

This sub-block requires specifying 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 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'

```

Seven biogeochemical reactions are considered in the calculation. The first six reactions are the microbially mediated reactions (for a detailed description, refer 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.

Simulating 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 simulating sulphur 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 sulphur such as 'caso4aq', 'ca34so4aq', 'h2saq', and 'h234saq'. The species 'caso4aq' and 'h2saq' represent the light ³²S isotopes and 'ca34so4aq' and 'h234saq' represent the heavy 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 nine minerals, of which six contain sulphur 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 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 the amount in solution per unit volume of solution, R is the retardation factor, θ is porosity [-], and 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 (⁸⁵Sr²⁺ and ⁶⁰Co²⁺) obeying the linear sorption model is:

```
'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 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 cation exchange capacity (CEC) 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 is set out below:

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

Above, 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 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 highlight 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, the keywords ‘sorbed species’ cannot be used for the case when both surface complexation and ion exchange reactions must be considered simultaneously. To overcome this problem, both the keywords ‘sorbed species of surface-complex’ and ‘sorbed species of ion-exchange’ must be defined as described in the following sections.

‘sorbed species of surface-complex’

This sub-block requires 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 is set out below:

```
'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 above, five surface complexation species are defined, which implies a 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 is that it can be combined with the sub-block ‘sorbed species of ion-

exchange’ to include both ion exchange and surface complexation reactions simultaneously.

3.3.2.9 ‘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. For 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 above, 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.

3.3.2.10 ‘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 use 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 site should be specified through the keyword ‘CEC fraction of multisite ion exchange’ (in Data Block 14: initial condition - reactive transport).

3.3.2.11 ‘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, such as:

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

It is important to ensure 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 and in the file complex.dbs for secondary species).

Below is an example of 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 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 the D_0 of the secondary species OH^- is $5.273 \times 10^{-9} m^2 s^{-1}$.

If Pitzer's model is required because of the high salinity in the solution, the file Pitzer.xml is needed.

3.3.2.12 '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'
```

3.3.2.13 'define input units'

By default, the program assumes all aqueous component concentrations will be provided in $mol L^{-1} H_2O$. 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 $mg L^{-1}$.

3.3.2.14 'define temperature'

By default, standard temperature of $25^\circ C$ is assumed for all geochemical calculations. This is implied if the temperature is not explicitly provided. If the environmental temperature is different, it can be specified using 'define temperature' followed by the temperature in $^\circ C$. For example, the following information specifies $10^\circ C$ as the environmental temperature:

```
'define temperature'
10.0
```

3.3.2.15 '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 increment for reading the next temperature, z_1 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 by reason of seasonal changes by specifying only one yearly temperature cycle.

3.3.2.16 'define sorption type' and 'specify output unit for SCM sorbed species concentration'

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, the 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 specifying 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'
```

An example of specifying 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'

```

An example of specifying 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') and 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.

Add keyword 'specify output unit for SCM sorbed species concentration' in Data Block 2: geochemical system after the keyword 'define sorption type' and parameter 'surface-complex'. The keyword has only effect on the output unit for the SCM sorbed species concentration. The default unit for the sorbed species concentration is 'mol/L H₂O.' Optional unit is 'mol/L bulk,' which is more suitable for unsaturated porous media. Example:

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

'specify output unit for SCM sorbed species concentration'
'mol/L bulk'           !optional unit
```

In this example, the output unit for the concentration of sorbed species using the surface complexation model (SCM) is specified as mol/L bulk.

3.3.2.17 'combine mineralogical parameters'

If a solid mineral can react with different reactants (e.g., Fe⁰(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 be 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., Fe⁰(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 3.21.4 example 2). The reaction stoichiometry and reaction constants of all minerals must 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 six ‘minerals’ defined in the first parts represent six different chemical reactions in which 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 represent other reactions defined in 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 is 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.

3.3.2.18 ‘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.

3.3.2.19 ‘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 of geochemical system 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'
... ..
```

3.3.2.20 ‘use sit model’

This sub-keyword defines the activity correction of the aqueous species according to the specific ion interaction theory (SIT) model, which was first suggested by Brønsted (1922), and further developed by Guggenheim (1955), Scatchard (1936), and Ciavatta (1980). In such case, the corresponding database sit.dbs should be provided.

3.3.3 EXAMPLE DATA INPUT FILE

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

Example 1: Geochemical system including nine 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 THE EXAMPLE INPUT

The first example input includes nine components. The Fe(II)/Fe(III) redox couple is assumed to be at equilibrium. The problem also includes 26 secondary aqueous species, two gases, and five minerals. The saturation indices of two additional minerals are calculated. Sulphate reduction is specified to be a kinetically controlled reaction. The location of the database to be used, wall2, is specified. The temperature is 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, as 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 THE DATA BLOCK

In this data block, the simulation's dimensions are specified (1D, 2D or 3D) and the domain's geometry in Cartesian or cylindrical coordinates is defined. The model's spatial discretization is based on a control volume (block centred 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 the grid coordinates will correspond to the actual size of the solution domain.

3.4.2 DESCRIPTIONS OF THE 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 uniform, this value is "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 "1" for the number of zones and number of cells (control volumes) and 0.0 and 1.0 for min and max values, respectively. The orientation of your particular problem within the xyz-coordinate system is flexible. However, when modelling 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, coordinates. It is easy to specify spatial discretization in radial coordinates by 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 INPUT FILE

An example of a two-dimensional Cartesian coordinate discretization (xz-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 of 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 THE EXAMPLE INPUT

The first example input file is for a 2D simulation in the xz-plane because the numbers of control volumes in x and z axis are greater than 1. However, the number of control volume in y-axis is 1, which is the default value indicating no discretization in 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 the 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 the 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. Compared to the first example, the specification of the spatial data is the same except for the additional inclusion of the keyword 'radial coordinates', which enables the code to treat the first coordinate as the radial coordinate.

3.4.5 ADDITIONAL NOTES

The decision of how many zones and the degree of discretization 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 advantageous to specify this zone when defining the spatial discretization. This allows for 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 compared to the internal cells. In such case, the centroid points of the cells at the boundaries are located exactly 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 THE DATA BLOCK

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

The code includes an adaptive time stepping scheme, which only requires specifying a minimum and 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 small minimum time step should be chosen to avoid failure of program execution. The maximum time step may affect the accuracy of the model's 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 for very large time steps. As the model is based on a fully-implicit method, there is practically no limit for the maximum time step size.

3.5.2 DESCRIPTIONS OF THE 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 the input parameters for the 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 ensure 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 runtime.

3.5.2.2 ‘threshold of failed timestep ratio’

This is an optional keyword to terminate the simulation when the ratio of the failed timestep over total timestep exceeds the specified ratio. This is generally used in running batch jobs. Some of the jobs may be difficult to converge with a lot of timestep reducing, causing the delay for all the other jobs. In this case, the jobs can be terminated and returned to the user to check. To use this feature, user needs to add the following keyword and parameter in DataBlock: ‘time step control - global system’.

```
'threshold of failed timestep ratio'
0.5                               ;failed timestep ratio
```

3.5.2.3 ‘periodic maximum time step’

This is an optional keyword to use different maximum time steps in the specified time ranges. For a long-term simulation, the simulation conditions may change significantly. In this case, the system needs to reduce time steps a lot if given a big maximum time step. With this option, user can set a smaller maximum time step during that time range. It is also useful to control transient output when ‘time steps between output’ is used.

3.5.3 EXAMPLE DATA INPUT FILE

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

'threshold of failed timestep ratio'
0.5
```

```
'periodic maximum time step'
3                               ;number of time step list
10.0    20.0    0.001         ;time start, time end, maximum time step
100.0    200.0    0.0001      ;time start, time end, maximum time step
1000.0    1020.0    0.01      ;time start, time end, maximum time step

'done'
```

3.5.3.1 Description of the 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 timescale.

3.6 CONTROL PARAMETERS—LOCAL CHEMISTRY (DATA BLOCK 5)

3.6.1 DESCRIPTION OF THE 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's performance or if convergence problems occur.

3.6.2 DESCRIPTIONS OF THE INPUT PARAMETERS

3.6.2.1 'control parameters - local geochemistry'

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

3.6.2.2 'newton iteration settings'

In this sub-block, an increment for numerical differentiation and 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, unrealistic values for ionic strength may 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 the 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 the update technique for activity coefficients for local chemistry. Two options are currently 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 the minimum reaction rate of minerals for local chemical reaction calculations. The parameter cannot be zero. The default value in the code is 1.0e-300.

3.6.2.10 ‘sparse block matrices’ and ‘dense block matrices’

These 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 INPUT FILE

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 ensure 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 THE 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's performance or if convergence problems occur.

3.7.2 DESCRIPTIONS OF THE 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 prefix_o.mve. Additional information about these files' content can be found in the file prefix_o.fls, which is created at run-time.

3.7.2.3 'run steady state flow in transient mode'

For some steady state flow, because of transient effect, the simulation may encounter convergence problem if using steady state flow directly. In this case, transient flow can be used until flow reaches steady state condition. To use this feature, please set flow to transient flow.

To determine whether the flow has reached steady state, user can specify the tolerance for steady state by using relative difference value and absolute difference value divided by time step. By default, these tolerance is preset to 1.0d-6 for both relative difference and absolute difference. These parameters can be modified using the following command and parameter after keyword 'run steady state flow in transient mode'.

'tolerance for steady state'

rtol

atol

where rtol is the relative difference divided by time step (day) for hydraulic head between current time step and previous time step and atol is the absolute difference divided by time step (day) for hydraulic head between current time step and previous time step.

User can also control if the heat transport has reached steady state by adding following keyword to data block 'control parameters - energy balance'.

'tolerance for steady state'

rtol

atol

where rtol is the relative difference divided by time step (day) for temperature between current time step and previous time step and atol is the absolute difference divided by time step (day) for temperature between current time step and previous time step

3.7.2.4 '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.

3.7.2.5 '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 medium's hydraulic conductivity uses the unit for permeability [m²], as described in the following subsection. An example is set out below:

```
! 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.

3.7.2.6 ‘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).

3.7.2.7 ‘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, centred spatial weighting will be used instead. This setting will have an effect only if partially-saturated conditions exist in the solution domain. For 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 is calculated according to:

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

3.7.2.8 ‘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 applying the under-relaxation factor is larger than the maximum specified update, the update is locally set to the specified maximum update. This approach ensures intermediate computed hydraulic head values remain in a physically reasonable range, which enhances convergence.

3.7.2.9 ‘newton iteration settings’

This sub-block allows for specifying a number of parameters affecting the Newton-Raphson iteration loop. The first parameter identifies the increment used for constructing 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.

3.7.2.10 water freezing/thawing feature

This feature control the hydraulic conductivity change when temperature drops below the specified freezing point. To use this feature, user need to add the following keywords and parameters into Data Block 'control parameters - variably saturated flow' to activate water freezing/thawing module for flow problem.

```
'water freezing temperature'
-1.0                               ;water freezing point in Celsius
'water freezing conductivity'
```

1.0d-30

;hydraulic conductivity after water freezing in m/s

User can also specify a fitting curve to represent relative conductivity change over the temperature change. This fitting curve can smooth the hydraulic change when water freezing/thawing process is used. The relative conductivity is then estimated based on the provided curve when temperature is between the specified minimum temperature and maximum temperature. To use this feature, user needs to add the following keywords and parameters into Data Block 'control parameters - variably saturated flow'. Make sure keyword 'water freezing conductivity' is removed, otherwise, it will use fixed 'water freezing conductivity' instead. The output of temperature - fitted relative conductivity is exported in the gen file.

```
'water freezing relative conductivity curve'
0.01273 22.47 2.002 1.002 ;parameter a, b, c and d for relative
                           ;conductivity curve relcond=d+(a-d)/
                           ;(1.0+((temperatureC+2.0)/c)^b)
-1.0 1.0 0.01 1.0        ;temperature min and max, relative conductivity min and max
```

3.7.2.11 'enable divergence check'

Add support of nonlinear solver divergence check for Newton iterations. Without this option, if the solver diverges, it will continue until the maximum number of Newton iteration is reached. With divergence check, the Newton solver skips the unnecessary computing and reduce timestep when divergence in Newton iteration is detected. For highly nonlinear problem, do not use this option. To use this option, please add keyword 'enable divergence check' into current block.

3.7.2.12 '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 as non-convergent. In this case, it will be necessary to either increase the maximum number of iterations or the factorization level (improve the quality of the solution procedure), or to decrease the maximum allowed update (decrease the difficulty of the problem). The solver information level specifies how much information will be written to the prefix.log file and to the screen. Three different levels are available:

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

By default, the information level is set to 1. The next two parameters define the solver's residual tolerance and the solver's 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'	-	-	-	-
'compute underrelaxation factor'	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 INPUT FILE

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

'enable divergence check'

'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 THE EXAMPLE INPUT

In the example input section, mass balance calculations are performed, a hydraulic head is used as the input unit for initial and boundary conditions, and centred 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 THE 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 DESCRIPTIONS OF THE INPUT PARAMETERS

3.8.2.1 'energy balance'

The sub-keyword 'energy balance' should be given if the 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: the Diersch model and the 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):

$$f_T^\mu = \frac{10^{\left(\frac{248.37}{T+133.15}\right)}}{10^{\left(\frac{248.37}{T_f+133.15}\right)}} \quad \text{Equation 3-13}$$

where T_f is the reference temperature. This model is used in the code SUTRA and is, 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 the 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 a 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 the temperature in Kelvin. The relation is valid for $373.15\text{K} < T < 593.15\text{K}$.

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 as:

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

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 $\text{W m}^{-1} \text{ } ^\circ\text{C}^{-1}$ 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 is 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 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, equal to the one for the variably-saturated flow problem, as described in Section 3.7.2.12.

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 INPUT FILE

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 THE EXAMPLE INPUT

In the first example, an energy balance calculation is performed. The code uses centred 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, meaning that the viscosity change as a result of solutes 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 kg m⁻³ °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 five 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's residual and update tolerance have been specified three orders of magnitude more stringent than the convergence tolerance.

In the second example, 'model 2' is selected for calculating 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 substance	10^{-20}	-	-
'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 (dρ/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 for calculating 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 calculating 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 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 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 as sinusoidal functions, is depicted in Figure 3.1.

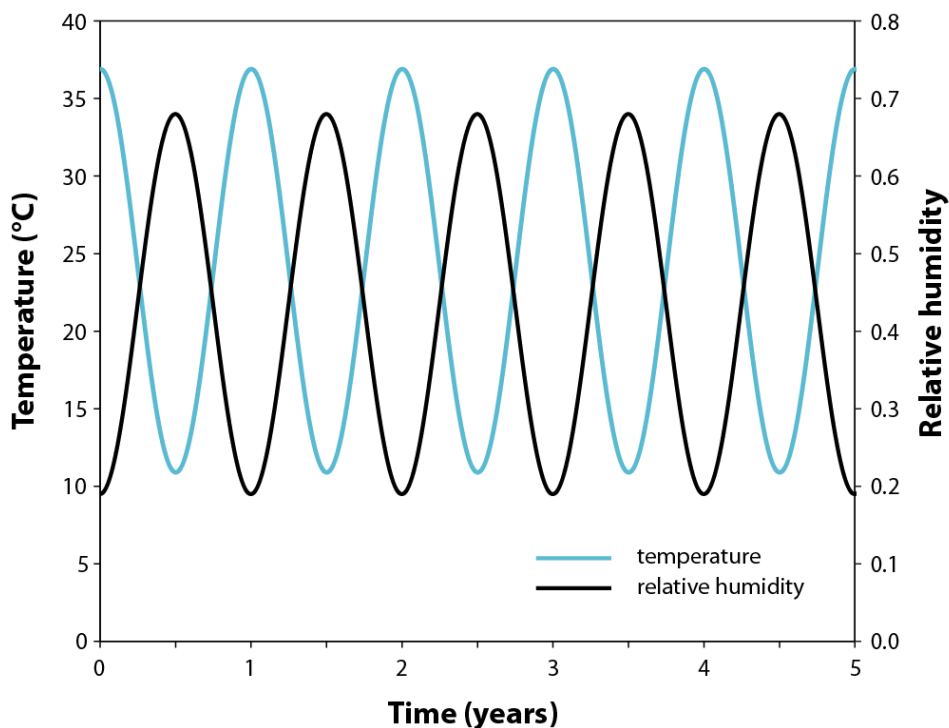


Figure 3.1: MIN3P-THCm output example when a sinusoidal function for climate variables is employed.

3.9.1 DESCRIPTION OF THE DATA BLOCK

In this section, control parameters affecting the evaporation model are defined using the header ‘control parameters – evaporation.’ It is noteworthy that the keyword ‘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 DESCRIPTIONS OF THE 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, runoff etc.) in the file prefix.evap.

3.9.2.2 ‘vapour density model’

If the sub-block ‘vapour density model’ is specified, the vapour 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 vapour density models are available: the default model and the Saito et al.

(2006) model.

The default model is the vapour density is calculated as:

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

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

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

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 (which equals 7 in Nimmo and Miller's (1986) study).

3.9.2.5 'reference vapor diffusivity'

The parameter 'reference vapor diffusivity' specifies the reference vapour 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 (an 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 the model's name specifies the model to account for 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) as:

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

The formulation of model 2 is defined as:

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

The formulation of the model 3 is defined as:

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

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

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

In which r_0 is the surface resistance [s m-1], which should theoretically be equal to the resistance to molecular diffusion across 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’ allows for calculating 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 calculating diffusive vapour flow transport. The default model is:

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

Alternatively, Millington’s model (‘millington’) and no tortuosity model (‘not consider’) can be specified. Millington’s model is defined as:

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

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 how the parameters should be 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:

- Average relative humidity of the atmosphere $\overline{H_r}$ [-]
- Annual 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 depend on units of the problem]
- Time during the day when relative humidity is maximum t_{dmax} [time units depend 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 atmospheric temperature. The data structure is the same as the previous section's relative humidity parameters. A sinusoidal function with both daily and annual cycles may be specified in Data Block 6B for atmospheric 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 previously described.

3.9.2.13 'solar radiation parameters'

The keyword 'solar radiation parameters' leads to the specification of parameters for 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 located in the northern part of the earth and a negative value otherwise.
- Time till when January begins. 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 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 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 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 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 options 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 representative of natural wind speed variations.

$$v_a = \overline{v_a} + \Delta v_{ay} \cos \left[\frac{2\pi(t - t_{ymax})}{365} \right] + \Delta v_{ad} \cos[2\pi(t - t_{dmax})]$$

Equation 3-37

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

- Average wind speed $\overline{v_a}$ 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 INPUT FILE

The following example demonstrates use 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 THE 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 clay content (f_c) of 2.0%, and an empirical constant (a) of 15.

As nothing is specified for calculating the saturated vapour density (ρ_{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 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 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, which 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 2.1.6 titled "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 (ρ_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 **Error! Reference source not found.** 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.' The 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 $^\circ\text{C}$. 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. An 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 five-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 six significant digits (i.e., 9240.08 days). Certain editing programs will truncate significant digits. Therefore, the user must check over the 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 0.0000000E+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 parameters' descriptions and are skipped by the program. From the fourth line on, the required parameters must be provided in the following 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 THE 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's performance or potentially correct convergence problems.

3.10.2 DESCRIPTIONS OF THE 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 owing 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.

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:

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

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 , and $v_{a,kl}$ defines the Darcy flux from control volume k to l . For centred weighting, the interfacial concentrations are defined based on:

$$T_{j,kl}^a = \frac{T_{j,k}^a + T_{j,l}^a}{2}$$

Equation 3-39

If centred weighting is used, the Peclet criterion must be followed to ensure convergence. The following requirements must be obeyed:

$$Pe = \frac{v_{a,kl} \Delta x}{D_{a,kl}} < 2$$

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:

$$T_{j,kl}^a = T_{j,k}^a + \sigma(r_{kl}) \frac{T_{j,k}^a + T_{j,l}^a}{2}$$

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:

$$Cr = \frac{v_{a,kl} \Delta t}{\Delta x} < 1$$

Equation 3-42

where Δt defines the time increment. Neither the Courant nor the Peclet restrictions apply to 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’ or ‘no-update’ under the sub-block ‘activity update settings.’ By default, the activity coefficients are updated after the completion of each time step (‘time lagged’ or ‘time_lagged’ or ‘time-lagged’) (Lichtner, personal communication, 1997). Alternatively, the option ‘double update’ or ‘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 six options: 'millington', 'archie', 'assigned tau', 'no correction', 'millington-quirk experimental' and 'fix diffusion'. 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 follows:

```
! 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's 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 vapour (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 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 is set out below:

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
2.0           ;alpha, tortuosity update factor
```

The example input defines that the tortuosity is updated according to 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.

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 an 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.

Another option for the update of tortuosity is ‘millington-quirk experimental’. The tortuosity in the aqueous and gas phase is calculated based on the relationship defined as

$$\tau = S_p^{b_{mq}} \phi^{a_{mq}+1} \quad \text{Equation 3-45}$$

Where a_{mq} and b_{mq} are the given parameters. To use ‘millington-quirk experimental’, user needs to add the following keywords and parameters.

```
'tortuosity correction'
'millington-quirk experimental'
2.0d0      ; a_mq
4.2d0      ; b_mq
```

The last option for the update of tortuosity is ‘fix diffusion’. In this case, the free diffusion coefficient is used. To use ‘fix diffusion’, user needs to add the following keywords and parameters.

```
'tortuosity correction'
'fix diffusion'
```

3.10.2.5 Gas tortuosity correction

By default, the same tortuosity correction method is used for both aqueous phase and gas phase.

If ‘gas tortuosity correction’ is set to ‘manual’, the old prefix.gvs file is used as gas tortuosity data. If ‘gas tortuosity correction’ is set to ‘assigned tau’, user needs to specify gas tortuosity after specifying aqueous tortuosity, an example is given below.

```
'number and name of zone'
1
```

```
'background1'
0.25                ;porosity
0.50                ;tortuosity for aqueous phase
0.50                ;tortuosity for gas phase
'extent of zone'
0.0 0.20  0.0 1.0  0.0  1.0
'end of zone'
```

If 'gas tortuosity correction' is set to 'assigned tau' and external file (prefix.torgas) is used as gas tortuosity, user needs to add keyword 'read gas tortuosity field from file' in the block 'physical parameters - porous medium', example input is

```
'physical parameters - porous medium'
1                ;number of property zones
'read tortuosity field from file'
'read gas tortuosity field from file'
```

3.10.2.6 'spatial averaging - diffusion'

The effective diffusion coefficient (D_e) is a physical parameter of each control volume. To calculate the diffusive flux between two connected control volumes, a representative D_e must be calculated using the parameters of both control volumes. For example, if the control volumes have different sizes, spatially weighted averaged D_e might be more reasonable. Considering the D_e is calculated based on 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 calculating the representative D_e or calculating 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 (default), the arithmetic D_e averaging method, and the harmonic averaging method.

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

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

The arithmetic D_e averaging method (using the keyword 'arithmetic D_e '): first calculate the D_e of each control volume using the corresponding effective porosity and tortuosity, then calculate 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 the keyword 'harmonic'): first calculate the D_e of each control volume using the corresponding effective porosity and tortuosity, then calculate 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'
```

3.10.2.7 'gas advection'

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

3.10.2.8 'cumulative mole fractions'

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

3.10.2.9 'enable gravity for gas phase'

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

3.10.2.10 '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]
```

3.10.2.11 'update porosity'

The sub-block 'update porosity' allows for keeping track of porosity changes attributable to dissolution-precipitation reactions. If this statement is enabled, porosity is calculated based on:

$$\phi^{t+\Delta t} = \phi^t - \sum_{i=1}^{N_m} \phi_i^{t+\Delta t} - \phi_i^t \quad \text{Equation 3-46}$$

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 completing a time step. Usually, porosity changes are relatively slow and this simplification does not lead to significant inaccuracies.

3.10.2.12 '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.

3.10.2.13 'pore clogging'

When the sub-block 'pore clogging' is specified, the code will evaluate the porosity reduction attributable to mineral precipitation. If porosity in a control volume is reduced to a threshold value that can be provided by the user by adding the keywords 'porosity threshold minimum' followed by the value, the code will stop chemical reaction in this control volume and the mass transport between the connected control volumes. The default value of the 'porosity threshold minimum' in 1.0e-6 is set if not provided.

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

'spatial weighting'
'upstream'

'activity update settings'
'time_lagged'

'update porosity'
'update permeability'

'pore clogging'
'porosity threshold minimum'
1.0d-4
```

To use the function, the 'update porosity' and 'update permeability' functions should be turned on.

3.10.2.14 'water freezing reaction rate'

Reduce reaction rate to zero or very small value when temperature drops to a specified threshold. This feature should be used together with water freezing feature in variably saturated flow. To use 'water freezing reaction rate', user needs to add the following keyword and parameter.

```
'water freezing reaction rate'

1.0d-30 ;reaction rate when water is frozen
```

3.10.2.15 'enable divergence check'

Add support of nonlinear solver divergence check for Newton iterations. Without this option, if the solver diverges, it will continue until the maximum number of Newton iteration is reached. With divergence check, the Newton solver skips the unnecessary computing and reduce timestep when divergence in Newton iteration is detected. For highly nonlinear problem, do not use this option. To use this option, please add keyword 'enable divergence check' into current block.

3.10.2.16 '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 three 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 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).

3.10.2.17 ‘solver settings’

The solver package WatSolv (VanderKwaak et al., 1997) is also used for solving 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 INPUT FILE

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

'enable divergence check'

'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 THE 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 the 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 one log concentration cycle while the maximum update is locally restricted to two 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's residual and 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 the ‘control parameters – reactive transport’ section

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’	-	-	-	-
‘pore clogging’	-	-	-	10^{-6} - 10^{-4}
‘porosity threshold minimum’	Minimum porosity	10^{-6}	-	
‘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 THE 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 would typically 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 DESCRIPTIONS OF THE 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 four output times can be specified per line. If the number of output times exceeds four, the values for the output times must be specified in the next line. The time units used are the same as those specified in Section 3.5 ('time step control'). Spatial data is written to the files prefix_*.gs*, as described in Section 2.2 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 three 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 four output locations can be specified per line. If the number of output locations exceed four, the values for the output locations must 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 the section ‘spatial discretization’ (Section 3.4). Numbering of the grid is performed in x-direction first, then in the y-direction, and, finally, in the z-direction (Figure 3.2).

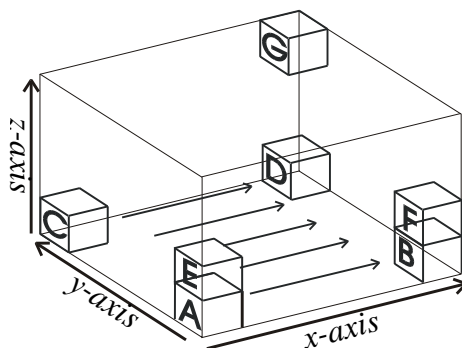


Figure 3.2: Spatial discretization and numbering principle

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 occurs 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 before 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 elevation’s prior coordinate transformation and to depth values after transformation is completed.

3.11.2.5 Output in binary format

The output in binary format is possible only for parallel computing (not the OpenMP version) through adding the keywords ‘use binary format’ within Data Block 8: ‘output control.’ In such case, most of the output files except *.log and *.gen will be written in binary format.

By default, if ‘use binary format’ is specified, transient output will also be in binary format. If you want to use binary data format for spatial output but ASCII data format for the transient output, please add the following command in the output control section: ‘use ascii data format for transient output,’

3.11.2.6 ‘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 sulphate (i.e., ‘so4-2’ as the master isotope component, followed by the isotope component ‘34so4-2’) and the other is sulphide (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 sulphur. The R_{std} values for both sets are 4.5005E-2 as the accepted sulphur isotope ratio of the standard Canyon Diablo troilite (CDT) reference material (Gibson et al. 2011).

3.11.2.7 ‘output activity coefficients’

The output of activity coefficients is optional. By default, the activity coefficients are not exported to files during simulation. To use this feature, user needs to add keyword 'output activity coefficients' in Data Block 8: 'output control'. The output file format is gsac for global output, gbac for transient output and lbac for batch reaction output.

3.11.2.8 'output of mass through specified boundary'

This command adds support for mass output through the specified boundary, including water (*_i.b.mvc), aqueous phase (*_ic_i.b.mac) and gas phase (*_ig_i.b.mgc). Here i is the index of specified boundary, ic is the index of aqueous component and ig is the index of gas. The format of these three files are similar to *_o.mvc, *_ic.mac, *_ig.mgc except that the storage terms and other source sink terms are not included. Please look at gen file and fls file for detail.

To use this feature, please add the keyword 'output of mass through specified boundary' followed by number of specified boundary and boundary zone definition, as shown below.

'output of mass through specified boundary'

2 ;total number of specified boundary

'number and name of zone'	;keyword for zone
1	;number of specified boundary
'boundary-1'	;name of specified boundary
'extent of zone: boundary nodes only'	;keyword for zone selection
0.0 0.1 0.0 0.0 0.0 0.0	;coordinates for zone selection
'end of zone'	;end of current zone

'number and name of zone'	;keyword for zone
2	;number of specified boundary
'boundary-2'	;name of specified boundary
'extent of zone: boundary nodes only'	;keyword for zone selection
0.1 0.1 0.0 0.0 0.15 0.20	;coordinates for zone selection
'end of zone'	;end of current zone

3.11.3 EXAMPLE DATA INPUT FILE

An example is as follows:

```
! -----
'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'

'output activity coefficients'

'done'
```

3.11.4 DESCRIPTION OF THE EXAMPLE INPUT

In the sample input file spatial output will be written at the specified six output times: 1.0, 2.0, 5.0, 10.0, 20.0 and 50.0 time units. Six spatial output files will be generated. Breakthrough curves will be generated for the specified four 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 THE DATA BLOCK

This data block is used to specify the zones used to discretize various 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 the physical parameters specific to variably-saturated flow or reactive transport.

3.12.2 DESCRIPTIONS OF THE 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 sub-keywords '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 is reproduced exactly in future input sections.

The third parameter is the zone's porosity. This value is specified directly below the property zone name.

The fourth parameter is the zone's tortuosity. 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 should material properties be accidentally overwritten. 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)

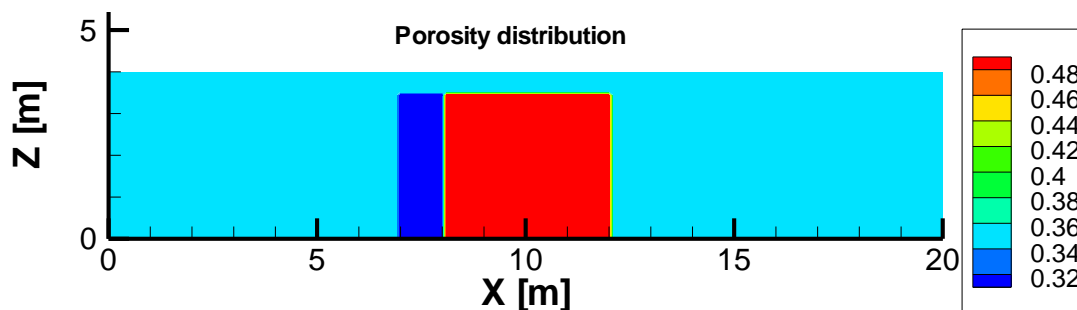


Figure 3.3: Allocation of material properties to discretized solution domain.

3.12.3 EXAMPLE DATA INPUT FILE

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 THE EXAMPLE INPUT

In the example file, the number of material property zones is three. 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 ranges from 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 second 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 as the scenario is 2D) and 0.0 to 3.5 m in the z-direction. This zone overlays 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- and z-coordinates 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 discretizes 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 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 with 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, and z-coordinates plus the corresponding porosity for each control volume should be provided, with 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 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 THE DATA BLOCK

This data block only specifies physical parameters affecting the flow solution. 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. For 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 defining a specific storage coefficient.

3.13.2 DESCRIPTIONS OF THE 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 ends 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 specifying ‘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 sub-keywords ‘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:

$$S_g = 1 - S_w + S_g^r \quad \text{Equation 3-47}$$

Table 3.12: Summary of the input parameters for section ‘physical parameters – variably-saturated flow’

Keywords				Required/ Optional
‘physical parameters – variably-saturated flow’				required
Subsection*	Parameter	Description		Required/ Optional
N ^{mz} -zones	‘hydraulic conductivity in x-direction’	K_{xx} [m d ⁻¹]	Hydraulic conductivity in x-direction	Only required if the 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 the 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 the 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 INPUT FILE

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 THE 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 xz-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.spsstor through the keywords ‘read specific storage coefficient from file’ in 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, and z-coordinates and the specific storage coefficient of each control volume as follows:

```
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 provide 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 or read from zone selection.

```
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 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. To read skempton coefficients from zone, user needs to add the following keyword and parameter into Data block 'control parameters – variably saturated flow'

```
'specific skempton coefficient'
0.9518758E+00
```

3.14 PHYSICAL PARAMETERS - ENERGY BALANCE (DATA

BLOCK 10B)**3.14.1 DESCRIPTION OF THE 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 DESCRIPTIONS OF THE 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'). It is suggested each material property zone is identified by the name of the zone, as specified in 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 ends 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 the 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 on 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 specifying '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 zone. Thermal dispersivities may be specified in longitudinal, 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 the 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 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-, and z-coordinates, the thermal capacity in [$\text{J kg}^{-1} \text{K}^{-1}$], thermal conductivity for water in x-, y- and z-coordinates in [$\text{J s}^{-1} \text{m}^{-1} \text{K}^{-1}$], thermal conductivity for solids in x-, y- and z-coordinates in [$\text{J s}^{-1} \text{m}^{-1} \text{K}^{-1}$], 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 the 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 [$\text{J kg}^{-1} \text{°C}^{-1}$]	Specific heat of the aqueous phase	Required for any heat transport simulation
‘specific heat of air’	C_g^0 [$\text{J kg}^{-1} \text{°C}^{-1}$]	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 ^{nu} -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 the 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 the 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 the 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 the 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 the 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 the number of control volumes in z-direction > 1
	‘longitudinal dispersivity’	α_l [m]	Longitudinal thermal dispersivity	Only required if the number of control volumes in x-direction > 1
	‘transverse horizontal dispersivity’	α_{th} [m]	Transverse horizontal thermal dispersivity	Only required if the number of control volumes in x- and y-direction > 1
	‘transverse vertical dispersivity’	α_{tv} [m]	Transverse vertical thermal dispersivity	Only required if the 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 INPUT FILE

```
! 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 THE 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 THE 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 DESCRIPTIONS OF THE 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 ends 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 presently not considered in MIN3P-THCm. The free-phase diffusion coefficient should, therefore, represent average diffusive transport behaviour 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. The dispersivities required are a function of the active dimensions (in the x-, y- and z directions) 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's 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
```

3.15.2.7 Hybrid component diffusion

If the hybrid component diffusion model is activated (see Data Block 1), additional parameters are required in this data block. These parameters are the correction factors of effective porosity and tortuosity for each primary and secondary species (see the "Multicomponent diffusion model" section in the theory manual). If no data is provided, the default value of 1.0 will be applied, which means no modification. The specification of these parameters is as follows:

1. The correction factors of effective porosity of primary species are provided through the keyword 'porosity correction factor of primary species for hMCD diffusion' followed by the factors of each primary species in the same order as the components defined in Data Block 2: 'geochemical system' under 'components.'
2. The correction factors of effective porosity of secondary species are provided through the keyword 'porosity correction factor of secondary species for hMCD diffusion' followed by the factors of each secondary species in the same order as the species defined in Data Block 2: geochemical system under 'secondary aqueous species.'
3. The correction factors of effective tortuosity of primary species are provided through the keyword 'tortuosity correction factor of primary species for hMCD diffusion' followed by the factors of each primary species in the same order as the components defined in Data Block 2: geochemical system under 'components.'

4. The correction factors of effective tortuosity of secondary species are provided through the keyword 'tortuosity correction factor of secondary species for hMCD diffusion' followed by the factors of each secondary species in the same order as the species defined in Data Block 2: 'geochemical system' under 'secondary aqueous species.'
5. Example (see example 2 in the following subsection): In the example, there are four materials: the circulation chamber, filter, gap and clay ('background 1'). The hMCD model is applied only for the clay. The number of primary species is 17, while the number of secondary species is 23.

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 [$\text{m}^2 \text{s}^{-1}$]	Representative free phase diffusion coefficient in water	Required for any reactive transport simulation	10^{-10} - 10^{-8}
	D_g^0 [$\text{m}^2 \text{s}^{-1}$]	Representative free phase diffusion coefficient in air	Only required if not fully-saturated	
N ^{mz} -zones	'longitudinal dispersivity'	α_l [m]	Longitudinal dispersivity	Only required if the number of control volumes in x-direction > 1
	'transverse horizontal dispersivity'	α_{th} [m]	Transverse horizontal dispersivity	Only required if the number of control volumes in x- and y-direction > 1
	'transverse vertical dispersivity'	α_{tv} [m]	Transverse vertical dispersivity	Only required if the number of control volumes in x- and z- or y- and z-direction > 1
	'porosity correction factor of primary species for hMCD diffusion'	$f_{\phi,j}^c$ [-]	Effective porosity correction factor for components Optional	Between 0 to 1.0, default 1.0

	'tortuosity correction factor of primary species for hMCD diffusion'	$f_{\tau,j}^c$ [-]	Effective tortuosity correction factor for components	Optional	Between 0 to 1.0, default 1.0
	'porosity correction factor of secondary species for hMCD diffusion'	$f_{\phi,j}^x$ [-]	Effective porosity correction factor for secondary species	Optional	Between 0 to 1.0, default 1.0
	'tortuosity correction factor of secondary species for hMCD diffusion"	$f_{\tau,j}^x$ [-]	Effective tortuosity correction factor for secondary species	Optional	Between 0 to 1.0, default 1.0
	Section Closing				Required/Optional
	'done'			Required	
*All keyword headings must appear on a single line in the input file.					

3.15.3 EXAMPLE DATA INPUT FILE

Input examples:

Example 1:

```
! 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'
```

Example 2:

```
! Data Block 11: physical parameters - reactive transport
```

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

```
!
```

```
'physical parameters - reactive transport'
```

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

```
'circulation chamber'
```

```
'longitudinal dispersivity'
```

```
0.0
```

```
'transverse horizontal dispersivity'
```

```
0.0
```

```
'transverse vertical dispersivity'
```

```
0.0
```

```
'end of zone'
```

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

```
!
```

```
'filter'
```

```
'longitudinal dispersivity'
```

```
0.0
```

```
'transverse horizontal dispersivity'
```

```
0.0
```

```
'transverse vertical dispersivity'
```

```
0.0
```

```
'end of zone'
```

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

```
!
```

```
'gap'
```

```
'longitudinal dispersivity'
```

```
0.0
```

```
'transverse horizontal dispersivity'
```

```
0.0
```

```
'transverse vertical dispersivity'
```

```
0.0
```

```
'end of zone'
```

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

```
!
```

```
'clay'
```

```
'longitudinal dispersivity'
```

```
0.0
```

```
'transverse horizontal dispersivity'
```

```
0.0
```

```
'transverse vertical dispersivity'
```

```
0.0
```

```
'porosity correction factor of primary species for hMCD diffusion'
```

```
1.0 ; 'cs+'
```

```
1.0 ; 'na+1'
```

```
1.0 ; 'k+1'
```

```
1.0 ; 'mg+2'
```

```
1.0 ; 'ca+2'
```

```
1.0 ; 'sr+2'
```

```
0.667 ; 'cl-1'
```

```
1.0 ; 'h+1'
```

```
1.0 ; 'o2(aq)'
```

```
0.667 ; 'so4-2'
```

```
0.667 ; 'co3-1'
```

```

0.533 ;'i-1' =0.08/0.15, effective porosity of I- is 0.08
0.667 ;'br-1' 0.1/0.15, effective porosity of Br- is 0.10
1.0   ;'HTO'
1.0   ;'co_60+2'
1.0   ;'eu+3'
1.0   ;'sr_85+2'
1.0   ;'soh(s)'
1.0   ;'soh(w)'
1.0   ;'toh'

'tortuosity correction factor of primary species for hMCD diffusion'
11.1  ;'cs+'
1.0   ;'na+1'
1.0   ;'k+1'
1.0   ;'mg+2'
1.0   ;'ca+2'
1.0   ;'sr+2'
1.0   ;'cl-1'
1.0   ;'h+1'
1.0   ;'o2(aq)'
1.0   ;'so4-2'
1.0   ;'co3-1'
0.55  ;'i-1'
0.38  ;'br-1'
1.0   ;'HTO'
3.0   ;'co_60+2'
1.0   ;'eu+3'
2.8   ;'sr_85+2'
1.0   ;'soh(s)'
1.0   ;'soh(w)'
1.0   ;'toh'

'porosity correction factor of secondary species for hMCD diffusion'
1.0   ;'khso4(aq)'
1.0   ;'h2so4(aq)'
1.0   ;'oh-'
1.0   ;'mgoh+'
1.0   ;'mgco3aq'
1.0   ;'mghco3+'
1.0   ;'mgso4aq'
1.0   ;'caoh+'
1.0   ;'cahco3+'
1.0   ;'caco3aq'
1.0   ;'caso4aq'
1.0   ;'cahso4+'
1.0   ;'naco3-'
1.0   ;'nahco3aq'
1.0   ;'naso4-'
1.0   ;'kso4-'
1.0   ;'sroh+'
1.0   ;'hco3-'
1.0   ;'h2co3aq'
1.0   ;'hso4-'
1.0   ;'cscl(aq)'
1.0   ;'csi(aq)'
1.0   ;'csbr(aq)'

'tortuosity correction factor of secondary species for hMCD diffusion'
1.0   ;'khso4(aq)'
1.0   ;'h2so4(aq)'
1.0   ;'oh-'
1.0   ;'mgoh+'
1.0   ;'mgco3aq'
1.0   ;'mghco3+'
1.0   ;'mgso4aq'
1.0   ;'caoh+'
1.0   ;'cahco3+'
1.0   ;'caco3aq'
1.0   ;'caso4aq'
1.0   ;'cahso4+'
1.0   ;'naco3-'

```

```

1.0      ; 'nahco3aq'
1.0      ; 'nasO4-'
1.0      ; 'kso4-'
1.0      ; 'sroh+'
1.0      ; 'hco3-'
1.0      ; 'h2co3aq'
1.0      ; 'hso4-'
1.0      ; 'cscl (aq) '
1.0      ; 'csi (aq) '
1.0      ; 'csbr (aq) '

```

```
'end of zone'
```

```
'done'
```

3.15.4 DESCRIPTION OF THE EXAMPLE INPUT

Example 1: 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 ‘aquifer’ are 0.5m and 0.005m, respectively, while the dispersivities for the zone ‘tailings’ are 0.1 and 0.001m, respectively.

Example 2: In the example, the domain includes four materials, in which only the material “clay” applies the hybrid component diffusion model. The additional four data blocks provide the correction factors of effective porosity and tortuosity for each primary and secondary species. The code will read the data blocks according to the keywords. Therefore, the order of the data blocks is not fixed. However, the parameters for each components or secondary species must be provided in the same order as specified in Data Block 2: ‘geochemical system.’ The correction factors of anions can be calculated if experimental data for the anions and neutral species (such as HTO) are obtained. For example, the measured effective porosity values of the clay are 0.15 for HTO, 0.10 for Br^- and 0.8 for I^- , respectively. Thus the correction factors of effective porosity are $0.10/0.15 = 0.667$ for Br^- , and $0.8/0.15 = 0.533$ for I^- .

3.16 INITIAL CONDITION - VARIABLY-SATURATED FLOW (DATA BLOCK 12)

3.16.1 DESCRIPTION OF THE 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 variablysaturated flow by the pressure-head distribution. The distribution of this parameter can be discretized across the model’s 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 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, and 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- and 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- and 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 ($\theta_a = \text{porosity} \cdot S_a$) [-], gaseous phase saturation S_g [-], and gaseous phase content ($\theta_g = \text{porosity} \cdot S_g$) [-] 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 ($\theta_a = \text{porosity} \cdot S_a$) [-], gaseous phase saturation (S_g) [-], and gaseous phase content ($\theta_g = \text{porosity} \cdot S_g$) [-] 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 ($\theta_a = \text{porosity} \cdot S_a$) [-], gaseous phase saturation (S_g) [-], gaseous phase content ($\theta_g = \text{porosity} \cdot S_g$) [-] 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 the ‘initial condition – variably-saturated flow’ section

Keywords			Required/Optional
‘initial condition – variably-saturated flow’			Required for any flow simulation
‘read initial condition from file’			Optional; requires the file prefix.ivs
N_i		Number of zones	Required if the initial condition is not read from the file
Subsection	Parameter	Description	Required/Optional
N_i zones	‘number and name of zone’	i_i Number of zone	Required if the initial condition is not read from the file
	‘initial condition’	name h_i [m] p_i [m]	
	‘extent of zone’	x_{min} [m] x_{max} [m] y_{min} [m] y_{max} [m] z_{min} [m] z_{max} [m]	
	‘end of zone’	-	
	Section Closing		
‘done’			Required

3.16.3 EXAMPLE DATA INPUT FILE

a. Specified in the 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 volume 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 the 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 the 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 THE EXAMPLE INPUT

In the example, the initial conditions for two zones are defined. The initial hydraulic head/pressure for the zone ‘upper aquifer’ is 2.0 m; for the zone ‘lower aquifer,’ it is 1.0 m. The units for the initial condition need to be consistent with those 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 of 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 of 1.0 m.

3.16.5 ADDITIONAL COMMENTS

For steady-state flow simulations, the initial condition is arbitrary; however, it may affect the solution’s efficiency, particularly for variably-saturated conditions. On the other hand, the initial condition for the flow problem has a direct impact on transient flow simulations and must 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 THE 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 boundary-type options 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	$q = q_b$
‘free-drainage’	Neumann	Calculated flux boundary, where the gradient of total head is equal to 1 and the gradient of the pressure head is equal to 0.	$q = q_b$

'seepage'		Seepage face boundary	
'point'	Dirichlet	Specified head boundary	$h = h_b$
'atmospheric'	Neumann	Specified flux boundary	
'tracer'	-	Mark the tracer location	

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 material property zones, boundary conditions cannot be overlain.

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 that defines the type of boundary condition to be assigned. The actual boundary type and numerical value of the boundary condition must 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 groundwater 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 on the atmospheric boundary condition. Therefore, it is important to ensure the evaporation function is activated (see Section 3.8 'control parameters – energy balance').

Please note the 'tracer' boundary condition for flow problem only marks the zone where tracer will be applied. It does not change the flow in the domain.

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 depend on the grid spacing (see Data Block 3 of an input file). As the model is capable of simulating flow and reactive transport in three dimensions, the boundaries' specification 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 yz-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's 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, the additional keyword 'transient boundary conditions' must be added in 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 Data Block 13. The boundary types of each boundary condition are assumed to be the same as given in Data Block 13 of the file prefix.dat and, thus, not given in the file prefix.bcvs.** In MIN3P-THCm's 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.

Below is 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 flo'
2                                     ;number of zones
! -----
!                                     'number and
name of zon'
1 'inflow boundar'
'boundary typ' 'secon' 4.11d-5          ;flux
3.0 'extent of zon' 0.5 0.0 1.0 2.0 2.0
'end of zon'

! -----
!                                     'number and
name of zon'
2 'outflow boundar'
'boundary typ' 'firs' 0.65d0          ;hydraulic head
'extent of zon'
3.0 3.0 0.0 1.0 0.0 0.65
'end of zon'
'transient boundary condition' 'don'
```

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 xz-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 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 INPUT FILE

```

3  An input example: 'boundary conditions-- variably-saturated flo' ;number of zones
! ----- 'number and
name of zon'
1 'left boundar'
'boundary typ' 'firs' 10.0 ;hydraulic head
3.0 'extent of zon' 0.0 0.0 1.0 0.0 3.5
'end of zon'

! ----- 'number and
name of zon'
2 'right boundar'

```

```

''boundary typ''''firs'' 9.53                      ;hydraulic head (m)
''extent of zon''
30.0 30.0 0.0 1.0 0.0 3.5
''end of zon''

! -----''number and
name of zon''
3''top boundar''
''boundary typ''''secon'' 1.2d-8                    ;specified flux (m s-1)
''extent of zon''
13.5 30.0 0.0 1.0 3.5 3.5
''end of zon''
''don''

```

Example for SEEPAGE FACE BOUNDARY (benchmark shlomo):

! Data Block 13: boundary conditions-- variably saturated flow

```

! -----
3 !''boundary conditions-- variably saturated flo'' ;number of zones

! -----''number and
name of zon''
1''inflow boundar''
''boundary typ''''secon'' 1.20d-6                    ;flux
3.0 ''extent of zon'' 6.0 0.0 1.0 1.20 1.20
''end of zon''

! -----''number and
name of zon''
2''outflow boundar''
''boundary typ''''firs'' 0.0d0                      ;hydraulic head
3.0 ''extent of zon'' 0.0 0.0 0.0 0.0 0.0
''end of zon''

! -----''number and
name of zon''
3''seepage face boundar''
''boundary typ''''seepag'' 0.0d0                    ;elevation of seepage face
3.0 ''extent of zon'' 0.0 0.0 1.0 0.01 1.20
''end of zon''

```

Example for transient flow boundary condition:

! Data Block 13: boundary conditions-- variably saturated flow

```

! -----
!''boundary conditions-- variably saturated flo''
2                      ;number of zones

! -----''number and
name of zon''
1''inflow boundar''
''boundary typ''''secon'' 4.11d-5                    ;flux
3.0 ''extent of zon'' 0.5 0.0 1.0 2.0 2.0
''end of zon''

! -----''number and
name of zon''
2''outflow boundar''
''boundary typ''''firs'' 0.65d0                      ;hydraulic head
''extent of zon''
3.0 3.0 0.0 0.0 0.0 0.65
''end of zon''
''transient boundary condition''
''don''

```

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 THE EXAMPLE INPUT

The example data file contains three boundary zones for a 2D-vertical cross-section located in the xz-plane with dimensions 30 m (x-direction) by 3.5 m (z-direction). The left 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 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 xz-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 Data Block 4: 'time step control – global system'), the flow in 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 THE 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 DESCRIPTIONS OF THE 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 must 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 the 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 3.21.2.11.

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 INPUT FILE

An example input:

```
! Data Block 12B: initial condition-- energy balance
  3                                     ! -----
                                     -----'initial    condition--    energy
                                     balanc'' ;number of zones

''geothermic gradien''
!0.03d0      ! geothermic gradient [oC m-1]
!17.0d0      ! temperature in the top
''number and name of zon''
1''pepe romp''
''initial conditio''
20.0d0
''extent of zon''
0.0 1000.0d0 0.0 1.0    0.0 10.0
''end of zon'' ''don''
```

3.18.4 DESCRIPTION OF THE EXAMPLE INPUT

The example data file contains one zone for a 2D-vertical cross-section located in the xz-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 THE DATA BLOCK

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

3.19.2 DESCRIPTIONS OF THE 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 overlaid.

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	Linearly 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), and the temperature gradient (dT). The temperature at the i^{th} boundary control volume ($T_b(i)$) can be interpolated:

$$T_b(i) = T_0 + dT[X(i) - X(0)] \quad \text{Equation 3-48}$$

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

3.19.3 EXAMPLE DATA INPUT FILE

```
!
! Data Block 13B: boundary conditions-- energy balance
! -----
! ''boundary conditions-- energy balanc''
2

''number and name of zon''
1
''inflo''

''boundary typ''
''fre'' 60.0d0

''extent of zon''
0.0d0 0.0d0 0.0 1.0 0.0d0 30.0d0

''end of zon''
```

```

''number and name of zon''
  2
''hydroestati''

''boundary typ''
''fre'' 20.0d0

''extent of zon''
 246.0d0 246.0d0 0.0 1.0 0.0d0 30.0d0
''end of zon''
''don''

```

3.19.4 DESCRIPTION OF THE EXAMPLE INPUT

The example data file contains one zone for a 2D-vertical cross-section located in the xz-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 THE 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 the 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. Parameters relating 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 constructing 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 various 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 DESCRIPTIONS OF THE 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 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 file prefix_x.lb*, where x corresponds to the number of the simulation (for the content of files, see the prefix_o.fls file 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 simulation. The magnitude of the initial time increment will be determined by the time scale of the fastest kinetic process. The time unit is the same as specified in 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 must be provided: a logical parameter for the output of transient data and the initial time step for the kinetic reaction. The difference between this method and 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 reaction'
.true.           ;output of transient data
1.0d-2           ;initial time step (local chemistry)
```

3.20.2.3 Concentration Input

The next input block provides the total concentration of each component in the same order as specified in Data Block 2: 'geochemical system' of the input file.

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 the 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 must 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 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 constructing pC-pH-diagrams will be written to the output files prefix_x.lb*, where x corresponds to the number of the simulation (for the content of files see the prefix_o.flb file, which is 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⁻). Currently, 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). For pCO₂, this specification can only be used along 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 the section 'geochemical system'), the appropriate input parameters must 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) allows for

specifying 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 the 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 the 'geochemical system' section), the appropriate input parameters must 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. By default, the model assumes 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 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 sorbed components' concentration is normally not analyzed. In such cases, MIN3P-THCm has a function for calculating the sorbed component concentration by fixing the concentrations of the aqueous components under the assumption of equilibrium between sorbed and aqueous phases. For 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' must be included (valid only for MIN3P-THCm version 1.0.106 and newer). The following three examples demonstrate use of this function.

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

```
'number and name of zon'
1 'background chemistry-- aquife'
'concentration input'
8.000      'p'      'h+'
5.147d-4   'charg'   'so4-'
1.0d-7     'fre'     'zn+'
1.0d-7     'fre'     'pb+'
1.0d-10    'fre'     'ca+'
1.0d-5     'fre'     'mg+'
1.0d-5     'fre'     'k+'
1.0d-3     'fre'     'na+'
'sorption parameter input' '=feoh(s)' 100.0d0 10.0d0 6.02228d0 ;surface site, mass,
area, site density
'equilibrate with fixed solution composition'
3.0 'extent of zon' 1.0 0.0 1.0 0.00 6.0
'end of zon'
'don'
```

This example considers 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.

An example of the input parameters for a case considering the ion exchange reaction:

```
! Data Block 14: initial condition-- reactive transport
! -----
3                               ! 'initial condition-- reactive transport' ;number of
                               zones
```

```

! -----''number and
name of zon''
1''background chemistry-- aquife''
''concentration input''
1.0d-3 ''fre'' ''na+''
2.0d-4 ''fre'' ''k+''
1.0d-8 ''fre'' ''ca+''
1.0d-8 ''fre'' ''cl-''
7.0d0 ''p'' ''h+''
12.5 ''p'' ''o2(aq)''
1.2d-3 ''fre'' ''no3-''
''sorption parameter input''
2.93d-2 ;cation exchange capacity [meq/100 g solid]
1.875d0 ;dry bulk density [g/cm^3]
''equilibrate with fixed solution composition''
3.0 ''extent of zon'' 0.0 0.0 0.0 0.00 0.8
''end of zon''
''don''

```

This example includes the parameters of the ion exchange reactions: the CEC is 2.93×10^{-2} meq (100g solid)⁻¹ and the dry bulk density is 1.875 g cm^{-3} .

An example of the input parameters for the case including both ion exchange and surface complexation reactions is set out below:

```

! Data Block 14: initial condition-- reactive transport
! -----
3 ''initial condition-- reactive transport'' ;number of
zones

! -----''number and
name of zon''
1''background chemistry-- aquife''
''concentration input''
8.015 ''p'' ''h+''
5.147d-4 ''charg'' ''so4-''
1.0d-7 ''fre'' ''zn+''
1.0d-7 ''fre'' ''pb+''
1.0d-10 ''fre'' ''ca+''
1.0d-5 ''fre'' ''mg+''
1.0d-5 ''fre'' ''k+''
1.0d-3 ''fre'' ''na+''

''sorption parameter input of surface-comple'' '=feoh(s'' 100.0d0 10.0d0
6.02228d0 ;surface site, mass, area, site density
''sorption parameter input of ion-exchang''
0.7333 ;cation exchange capacity
1.875d0 ;dry bulk density
''equilibrate with fixed solution composition of ion-exchang''
''equilibrate with fixed solution composition of surface-comple''
3.0 ''extent of zon'' 0.0 0.0 0.0 0.00 16.0
''end of zon''
''don''

```

This example includes the parameters of surface complexation reactions: the surface site is '=feoh(s)'. Its mass is $100.0 \text{ g solid (L H}_2\text{O)}^{-1}$, surface area is $10.0 \text{ m}^2 \text{ (g solid)}^{-1}$, and the site density is $6.02228 \text{ sites nm}^{-2}$. For the parameters of the ion exchange reactions: the CEC is $0.7333 \text{ meq (100g solid)}^{-1}$ and the dry bulk density is 1.875 g cm^{-3} .

3.20.2.5 'CEC fraction of multisite ion exchange'

If the multisite ion exchange model is activated through the keyword 'surface sites of ion-exchange' in 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 of that is:


```

''CEC fraction of multisite ion exchange''
0.0025      ''-FE''
0.20        ''-I''
0.7975      ''-P''

```

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 (six parameters in total) are required if the update type is ‘constant,’ ‘twothird,’ ‘linear,’ or ‘exponent.’ Three lines (nine parameters in total) are required for the update type ‘geometric.’ A ‘constant’ update type means 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 the reactivity is updated according to the following equation:

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

in which, i is an indicator for the i^{th} minerals, m denotes mineral-related parameters, and α is a 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 3-49. 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:

$$k_i^{m,t} = k_i^{m,0} \left(\frac{\varphi_i^t}{\varphi_i^0} \right)^{\frac{2}{3}} \quad \text{Equation 3-50}$$

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 uses the Equation 3-50 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 3-50.

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

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

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

Equation 3-51

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-

52.

$$k_i^{m,ref} = k_i^{m,0} S^0 \left(\frac{\varphi_i^{nuc}}{\varphi_i^0} \right) = k_i^{m,0} S^{nuc} \quad \text{Equation 3-52}$$

In which S^0 is the initial mineral surface area and 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 3-52.

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, because it is convenient for reactive transport simulations. For batch simulations, the volume of water is always one liter. The volume fraction must, therefore, be determined based on:

$$\varphi_i = \frac{V_i}{1 + \sum_{k=1}^{N_m} V_k} \quad \text{Equation 3-53}$$

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. Inclusion of additional options for input units is planned for 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:

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

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:

$$V_i = 10^3 \frac{M_i GFW_i}{\gamma_i} \quad \text{Equation 3-55}$$

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 (nevertheless, the saturation indexes (Sis) are calculated). 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. Therefore, it is recommended that a small value for the minimum mineral volume fraction is specified. This value should be small enough ($\leq 10^{-10}$) that the geochemical evolution is not notably affected by the mineral mass that 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 $[\text{mol L}^{-1} \text{ bulk s}^{-1}]$ for a zero order reaction. The units for higher order reactions, which depend on aqueous concentrations, are given by $[\text{mol}^{(1-n)} \text{ L}^n \text{ H}_2\text{O L}^{-1} \text{ bulk s}^{-1}]$, 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 $[\text{m}^2 \text{ mineral L}^{-1} \text{ bulk}]$ 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 that 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 three 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 the ‘initial condition – local chemistry’ section, 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	
I _i zones	'number and name of zone'	izone	Number of the simulation			Required for any batch simulation
		name	Name of the 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 the input section 'geochemical system'
		type	'free'	Specified total concentration units as specified in the 'geochemical system' section		
			'fixed'	Fixed species activity, units as specified in the 'geochemical system' section		
			'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 the component to satisfy the charge balance estimate in units [mol L ⁻¹ H ₂ O]		

Table 3.20: Summary of input parameters for the ‘initial condition – local chemistry’ section, 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 the surface site	Required for surface complexation reactions
		mass	Mass of the surface site [g solid L ⁻¹ H ₂ O]	
		area	Surface area of the 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 the surface site	Required for surface complexation reactions
		mass	Mass of the surface site [g solid L ⁻¹ H ₂ O]	
		area	Surface area of the surface site [m ² g ⁻¹ solid]	
		site density	Site density [sites nm ⁻²]	

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

	Subsection	Parameter	Description		Required /Optional
N _i zones	'mineral input'	phi	Initial mineral volume fraction [m ³ mineral m ⁻³ bulk]		required for all minerals specified in the 'geochemical system' section (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 the 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 the rate constant in the database is set to unity)		
		or	or		
		area	reactive surface area in [m ² mineral L ⁻¹ bulk], (if the 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 the type 'geometric'				
rad_surf	Initial radius of unreacted portion of mineral grain [m], only for the type 'geometric'				
rad_min	Minimum radius of mineral grain [m], only for the type 'geometric'				

	'end of zone'	-	-	
	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, and $K_j^{a,mo}$ 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 3-49 or Equation 3-50.

3.20.3 EXAMPLE DATA INPUT FILE

Example 1: Speciation and kinetic batch simulation

```
! Data Block 14: initial conditio- - local geochemistry
! -----
!
'initial conditio- - local geochemist'y'
2                               ;number of simulations

! -----
'number and name of zo'e'
!
'Sierras speciation calculati'n'
'concentration inp't'
1.0d-3   'fr'e'                ;conc,   type      - ca2+
1.0d-7   'fr'e'                ;conc,   type      - na+
```

```

1.0d-3  \ 'fr'e'                ;conc,   type      - co32-
1.0d-7  \ 'fr'e'                ;conc,   type      - h4sio4
1.0d-7  \ 'fr'e'                ;conc,   type      - al3+
5.0     \ 'h'                   ;conc,   type      - h+'
'end of zo'e'

! -----
'number and name of zo'e'
\
'kinetically-controlled dissolution of calcite and albi'e''
'kinetic batch simulati'n'
1.0d-2                ;delt
1.0d0                 ;tfinal\
'concentration inp't'
1.7d-5  \ 'fr'e'                ;conc,   type      - ca2+
1.0d-6  \ 'fr'e'                ;conc,   type      - na+
2.0d-5  \ 'fr'e'                ;conc,   type      - co32-
1.0d-6  \ 'fr'e'                ;conc,   type      - h4sio4
1.0d-6  \ 'fr'e'                ;conc,   type      - al3+
5.0     \ 'H'                   ;conc,   type      - h+'
'mineral inp't'
5.0d-4  .true. \ 'consta't'      ;phi,    minequil, type - calcite
1.0d-10 1.0d-8 0.0              ;phi_min, k_eff,  sat
5.0d-1  .true. \ 'consta't'      ;phi,    minequil, type - albite
1.0d-10 1.0d-13 0.0             ;phi_min, k_eff,  sat
0.0d0   .false.' 'consta't'      ;phi,    minequil, type - al(oh)3(am)
1.0d-10 1.0d-8 0.0              ;phi_min, k_eff,  sat
0.0d0   .false.' 'consta't'      ;phi,    minequil, type - sio2(am)
1.0d-10 1.0d-8 0.0              ;phi_min, k_eff,  sat\
'end of zo'e'

```

Example 2: Surface complexation

```

! Data Block 14: initial conditio- - local geochemistry
! -----
\
'initial conditio- - local geochemist'y'
2                                ;number of zones

! -----
'number and name of zo'e'
\
'pH-sweep from 0-14, fixed total metal concentrati'n''
'concentration inp't'
0.0     \ 'ph_swe'p' 14.0 50      ;conc type ph_final steps \ 'h'1'
1.0d-7  \ 'fr'e'                ;conc type                        \ 'me'2''
'sorption parameter inp't'
's'h' 1.0d0 10.0d0 6.02228d0      ;surface site, mass, area, site density\
'end of zo'e'

! -----
'number and name of zo'e'
\
'ph-sweep from 0-14, fixed solution compositi'n''
'concentration inp't'
0.0     \ 'ph_swe'p' 14.0 50      ;conc type ph_final steps \ 'h+1'
1.00d-7 \ 'fr'e'                ;conc type                        \ 'me'2''
'sorption parameter inp't'
's'h' 1.0d0 10.0d0 6.02228d0      ;surface site, mass, area, site density\
'equilibrate with fixed solution compositi'n''
'end of zo'e''
'do'e'

```

Example 3: Ion exchange

```

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

```



```

3                                     'initial condition - local geochemist'y ;number of zones

! -----
'number and name of zo'e'
\
'background chemistr- - aquif'r''
'concentration inp't'
1990.0d0 \ 'fr'e'           ;conc   type   \ 'na'1'
100.0d0  \ 'fr'e'           ;conc   type   \ 'k'1'
436.0d0  \ 'fr'e'           ;conc   type   \ 'mg'2'
444.0d0  \ 'fr'e'           ;conc   type   \ 'ca'2'
5700.0d0 \ 'fr'e'           ;conc   type   \ 'cl'1'
7.0d0    \ 'h'              ;conc   type   \ 'h'1''
'sorption parameter inp't'
10.0d0           ;cec
1.875d0          ;rhob\
'end of zo'e'\
'do'e'

```

Example 4: pH-sweep calculations

```

! Data Block 14: initial conditio- - local geochemistry
! -----
3                                     'initial conditio- - local geochemist'y ;number of zones

! -----
'number and name of zo'e'
\
'pH-sweep from 0-1' ''
'concentration inp't'
0.0      \ 'ph_swe'p' 14.0  50 ;h+1
1.00d-4  \ 'fr'e'           ;seo4-2\
'end of zo'e'\
'do'e'

```

Example 5: Specification of mineral update types

```

'mineral inp't'
0.20      .true\ 'line'r' ;phim, minequil, update_type - calcite
1.d-10    5.0d-5  0.00d0  1.0d-7 ;phimin, areanuc, supsatm, phinuc
0.15      .false\ 'twothird-m'x' ;phim, minequil, update_type - gypsum
1.d-10    200.0   0.00d0  1.0d-7 ;phimin, areanuc, supsatm, phinuc
5.00d-1   .true\ 'geometr'c' ;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\ 'expone't' ;phim, minequil, update_type - dolomite
1.d-10    200.0   0.80d0 ;phimin, areanuc, alpha

```

Example 6: Combine mineralogical parameters (see Section 3.3.2.17)

```

! -----
'number and name of zo'e'
\
'background chemistr- - reactive barri'r''
'concentration inp't'
6.29      \ 'h'              \ 'h'1'
4.04d-3   \ 'fr'e'           \ 'cl'1'
1.95d-3   \ 'fr'e'           \ 'co3'2'
1.44d-3   \ 'fr'e'           \ 'so4'2'
5.29d-20  \ 'fr'e'           \ 'hs'1'
5.32d-4   \ 'fr'e'           \ 'ca'2'
2.53d-13  \ 'fr'e'           \ 'fe'2'
4.72d-12  \ 'fr'e'           \ 'fe'3'
9.84d-5   \ 'fr'e'           \ 'cro4'2'
1.52d-7   \ 'fr'e'           \ 'cr(oh)'+
1.98d-6   \ 'fr'e'           \ 't'e'
1.37d-6   \ 'fr'e'           \ 'cis-1,2-d'e'

```

```

1.73d-7 \ 'fr'e' \ 'c'
2.99d-6 \ 'fr'e' \ 'etha'e'
1.98d-31 \ 'fr'e' \ 'h2(a')'
'mineral inp't'
0.50d0 .false. \ 'twothi'd' ;phim, minequil, update_type - fe_0_h2o_1
1.00d-10 1.94d2 0.00d0 ;phimin, area, supsatm
0.50d0 .false. \ 'twothi'd' ;phim, minequil, update_type - fe_0_cr
1.00d-10 1.94d2 0.00d0 ;phimin, area, supsatm
0.50d0 .false. \ 'twothi'd' ;phim, minequil, update_type - fe_0_tce
1.00d-10 1.94d2 0.00d0 ;phimin, area, supsatm
0.50d0 .false. \ 'twothi'd' ;phim, minequil, update_type - fe_0_cdce
1.00d-10 1.94d2 0.00d0 ;phimin, area, supsatm
0.50d0 .false. \ 'twothi'd' ;phim, minequil, update_type - fe_0_vc
1.00d-10 1.94d2 0.00d0 ;phimin, area, supsatm
0.50d0 .false. \ 'twothi'd' ;phim, minequil, update_type - fe_0_so4_2
1.00d-10 1.94d2 0.00d0 ;phimin, area, supsatm
0.00d0 .false. \ 'consta't' ;phim, minequil, update_type - calcite
1.00d-10 7.3030d-10 0.00d0 ;phimin, k_eff, supsatm
0.00d0 .false. \ 'consta't' ;phim, minequil, update_type - siderite(d)
1.00d-10 1.1574d-10 0.00d0 ;phimin, k_eff, supsatm
0.00d0 .false. \ 'consta't' ;phim, minequil, update_type - fe(oh)2(s)
1.00d-10 1.1574d-9 0.00d0 ;phimin, k_eff, supsatm
0.00d0 .false. \ 'consta't' ;phim, minequil, update_type - cr(oh)3(a)
1.00d-10 1.1574d-10 0.00d0 ;phimin, k_eff, supsatm
0.00d0 .false. \ 'consta't' ;phim, minequil, update_type - mackinawite
1.00d-10 1.1574d-10 0.00d0 ;phimin, k_eff, supsatm
0.00d0 .false. \ 'consta't' ;phim, minequil, update_type - ferrihydrite
1.00d-10 1.1574d-9 0.00d0 ;phimin, k_eff, supsatm
'extent of zo'e'
1.8 2.4 0.0 0.0 0.00 3.20
'end of zo'e'
'do'e'
!
```

3.20.4 DESCRIPTION OF THE 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 and albite are considered. The minerals al(oh)3(am) and sio2(am) are secondary minerals.

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 $10.0 \text{ meq (100g solid)}^{-1}$ and the dry bulk density is 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 the 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 3-52: $100.0 \times 1.0^{-7} / 0.2 = 5.0 \times 1.0^{-5} \text{ m}^2 \text{ L}^{-1} \text{ bulk}$, 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 third and fourth 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 are 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 specify 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.

Example 6 demonstrates the parameter inputs required as initial conditions for minerals to be combined. All the parameters are in line with Example 1 as described above. The only difference is the volume fraction of the first five minerals to be combined should be the same as the total amount 0.5.

3.20.5 ADDITIONAL COMMENTS

MIN3P-THCm provides various forms to simulate minerals’ kinetic reactions (see Section 4.7). Some of the required parameters are provided in the database mineral.db. Additional parameters are provided in the input file.

3.21 INITIAL CONDITION – REACTIVE TRANSPORT (DATA BLOCK 15)

3.21.1 DESCRIPTION OF THE 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 the ‘initial condition – local chemistry’ section, with some restrictions:

- Kinetic batch simulations cannot be conducted (use the batch option of the model).
- pH-sweep calculations cannot be conducted (use the batch option of the 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 DESCRIPTIONS OF THE INPUT PARAMETERS

3.21.2.1 'initial condition – reactive transport'

The number of zones needs to be specified after the keyword 'initial condition – reactive transport.' In the following, a zone number and a zone name must 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 the 'initial condition – local chemistry' section.

3.21.2.2 'Read initial aqueous component concentrations from file'

The initial distributed total component concentrations for reactive transport can be specified through an external file called prefix.aqt. To activate this function, the keyword '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 Data Block 2: 'geochemical system.'** The file provides the x-, y- and z-coordinates and the total concentrations of each primary component in [mol L⁻¹] in each control volume. This file has the same format as the output file prefix_0.gst.

Tip: The user can generate a file prefix.aqt by running a simulation first. The code will generate a file prefix_0.gst and a file prefix_o.aqt (after version MIN3P-THCm.V1.0.549). The user can rename the prefix_o.aqt (or the file prefix_0.gat) to prefix.aqt. The difference between prefix_o.aqt and prefix_0.gst is that the concentration in the latter file is after batch reaction. When non-aqueous components are excluded, there is very small difference in the concentrations of components between prefix_o.aqt and prefix_0.gst. The user can use either file. However, when non-aqueous components are included, the difference is significant and prefix_o.aqt has to be used.

3.21.2.3 '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- and 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 Data Block 2: 'geochemical system.'** This file has the same format of the output file prefix_0.gsv.

3.21.2.4 '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- and 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 is below:

```
title " "dataset bas"n"
variables <<  >>x"<  >>y"<  >>z >>,"c >>c >>,"r >>o"
zone t " "fie"d",i = 1000, j = 150, k = 1, f=point
0.000000E+00 0.000000E+00 0.000000E+00 0.100000E+01 0.275000E+01
0.440444E+03 0.000000E+00 0.000000E+00 0.100000E+01 0.275000E+01
0.880888E+03 0.000000E+00 0.000000E+00 0.100000E+01 0.275000E+01
0.132132E+04 0.000000E+00 0.000000E+00 0.100000E+01 0.275000E+01
```

0.1761762E+04 0.0000000E+00 0.0000000E+00 0.1000000E+01 0.2750000E+01
.....

3.21.2.5 ‘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 Data Block 15: ‘initial conditio— - reactive transport.’ The file provides the x-, y- and z-coordinates, the initial surface area of each mineral in [m² mineral (L bulk)⁻¹] for surface-controlled reactions and in [m mineral (m³ bulk)⁻¹] for transport-controlled reactions. **The order of the minerals must be the same as defined in Data Block 2: ‘geochemical system.’** This file has the same format of the output file `prefix_0.gsv`.

3.21.2.6 ‘Read mineral volume fractions nucleation thresholds from file’

The mineral volume fractions nucleation threshold (φ_{nuc}) in [m³ m⁻³] is a parameter defined for limiting the mineral reactive surface area S from updating, till the mineral approaches disappearance according to:

$$S = S_0 \left(\frac{\varphi}{\varphi_0} \right)^{2/3}, \text{ if } \varphi > \varphi_{nuc}$$

$$S = S_0, \text{ if } \varphi \leq \varphi_{nuc}$$
Equation 3-56

In which φ_0 and φ refer to the initial and current mineral volume fraction [m³ m⁻³]. S_0 is the reference mineral surface area. To use the parameter, the mineral update type should be ‘twothird-mix.’

To use the parameter for the mineral update type of ‘linear’, it must be used in combination with the keyword ‘Read nucleation threshold reference surface area from file’ described in the subsection follows.

$$S = S_{nuc} \frac{\varphi}{\varphi_{nuc}}, \text{ if } \varphi \geq \varphi_{nuc}$$

$$S = S_{nuc}, \text{ if } \varphi < \varphi_{nuc}$$
Equation 3-57

In which S_{nuc} is the nucleation threshold reference surface area.

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 conditio— - reactive transport.’ The file provides the x-, y- and z-coordinates and the mineral volume fractions nucleation thresholds in [m³ m⁻³]. **The order of the minerals must be the same as defined in Data Block 2: ‘geochemical system.’** The `prefix.vnuc` file has the same format of the output file `prefix_0.gsv` but without porosity.

3.21.2.7 ‘Read nucleation threshold reference surface area from file’

The distributed nucleation threshold reference surface area S_{nuc} 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 conditio— - reactive transport.’ The file provides the x-, y- and z-coordinates and the nucleation threshold reference surface area. **The order of the minerals must be the same as defined in Data Block 2: ‘geochemical system.’**

3.21.2.8 '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 included 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.

3.21.2.9 '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 follows: '

```
'linear sorption inp't'
'sr_85'2'    14.53'
'co_60'2'    1377.0
```

3.21.2.10 'salinity dependent reaction rate of minerals'

The section 'salinity dependent reaction rate of minerals' can be added to this block to activate the function accounting for the salinity-dependent sulphur-reducing bacterial (SRB) reaction by organic substances. To use the model, please follow the following:

1. Add the keywords 'salinity dependent reaction rate of minerals' to 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 type of functions to describe the model. Currently, there are two options:
 - (a) Polynomial function using 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:

$$k_{sal} = \sum_{i=0}^n f_i S^i \quad \text{Equation 3-58}$$

(3)

Add the minimum salinity and the corresponding value of k_{sal_min} , and the maximum salinity and the corresponding value of k_{sal_max} for the first mineral to ensure no negative k_{sal} will be calculated according to the above equation.) Cosine function using keyword 'strong inhibition by one component.' This model uses one component (e.g., Cl⁻), which is normally the most abundant component in a saline solution and linearly correlated to the salinity, to simulate the strong inhibition effect of salinity on the biogenic sulfate reduction reaction according to:

$$k_{sal} = \begin{cases} 1 & , \text{if } S < C_L \\ [\cos(a * S + b) + 1]/2 & , \text{if } C_L \leq S \leq C_H \\ 0 & , \text{if } S > C_H \end{cases} \quad \text{Equation 3-59}$$

where S is the concentration of Cl⁻ in [mol L⁻¹]. The coefficients a and b can be determined based on Cl⁻ concentration levels C_H and C_L . Below concentration C_L , there is no inhibition of sulphate

reduction while above concentration C_H , sulphate reduction is completely inhibited. The rate of biogenic sulphate reduction between these two concentration values is assumed to follow a cosine function, with the parameters a and b defined according to Equation 3-60 and Equation 3-61:

$$a = \frac{180}{C_H - C_L} \quad \text{Equation 3-60}$$

$$b = -aC_L \quad \text{Equation 3-61}$$

3. If more than one minerals are considered, follow steps 2 and 3 for the rest of the minerals.
4. The other properties of the minerals (e.g., kinetics) remain unchanged.

The input format is demonstrated in Example 3 (Section 3.21.3).

3.21.2.11 'extent of zone'

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 for 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' and 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.

3.21.3 EXAMPLE DATA INPUT FILE

Example 1: input is as follows:

```
! Section 15: initial condition - reactive transport
! -----
\
    3                                'initial condition - reactive transpo't ;number of zones

! -----
'number and name of zo'e'
\
'aquif'r'\
'concentration inp't'
1.7d-5   \ 'fr'e'                      ;conc,   type      - ca2+
1.0d-6   \ 'fr'e'                      ;conc,   type      - na+
2.0d-5   \ 'fr'e'                      ;conc,   type      - co32-
1.0d-6   \ 'fr'e'                      ;conc,   type      - h4sio4
1.0d-6   \ 'fr'e'                      ;conc,   type      - al3+
5.0      \ 'H'                        ;conc,   type      - h+\
'mineral inp't'
5.0d-4   .true. \ 'consta't'           ;phi,     minequil, type - calcite
1.0d-10   1.0d-8  0.0                 ;phi_min, k_eff,   sat
5.0d-1    .true. \ 'consta't'           ;phi,     minequil, type - albite
1.0d-10   1.0d-13 0.0                 ;phi_min, k_eff,   sat
0.0d0     .false.' 'consta't'          ;phi,     minequil, type - al(oh)3(am)
1.0d-10   1.0d-8  0.0                 ;phi_min, k_eff,   sat
```

```

0.0d0      .false.' 'consta't'      ;phi,      minequill, type - sio2(am)
1.0d-10    1.0d-8      0.0          ;phi_min, k_eff,      sat`
'extent of zo'e'0 1.0  0.0 1.0  0.0 4.0`
'end of zo'e'`
'do'e'

```

Example 2: combining the mineralogical parameters (see Section 3.3.2.17)

```

! Section 15: initial condition - reactive transport
! -----
      3      'initial condition - reactive transpo't ;number of zones
... `
'number and name of zo'e'
`
'background chemistr- - reactive barri'r'`
'concentration inp't'
6.29      ` 'h'          ` 'h'1'
4.04d-3    ` 'fr'e'      ` 'cl'1'
1.95d-3    ` 'fr'e'      ` 'co3'2'
1.44d-3    ` 'fr'e'      ` 'so4'2'
5.29d-20   ` 'fr'e'      ` 'hs'1'
5.32d-4    ` 'fr'e'      ` 'ca'2'
2.53d-13   ` 'fr'e'      ` 'fe'2'
4.72d-12   ` 'fr'e'      ` 'fe'3'
9.84d-5    ` 'fr'e'      ` 'cro4'2'
1.52d-7    ` 'fr'e'      ` 'cr(oh)'+`
1.98d-6    ` 'fr'e'      ` 't'e'
1.37d-6    ` 'fr'e'      ` 'cis-1,2-d'e'
1.73d-7    ` 'fr'e'      ` 'c'
2.99d-6    ` 'fr'e'      ` 'etha'e'
1.98d-31   ` 'fr'e'      ` 'h2(a')`
'mineral inp't'
0.50d0     .false.  ` 'twothi'd' ;phim, minequill, update_type - fe_0_h2o_1
1.00d-10   1.94d2   0.00d0      ;phimin, area, supsatm
0.50d0     .false.  ` 'twothi'd' ;phim, minequill, update_type - fe_0_cr
1.00d-10   1.94d2   0.00d0      ;phimin, area, supsatm
0.50d0     .false.  ` 'twothi'd' ;phim, minequill, update_type - fe_0_tce
1.00d-10   1.94d2   0.00d0      ;phimin, area, supsatm
0.50d0     .false.  ` 'twothi'd' ;phim, minequill, update_type - fe_0_cdce
1.00d-10   1.94d2   0.00d0      ;phimin, area, supsatm
0.50d0     .false.  ` 'twothi'd' ;phim, minequill, update_type - fe_0_vc
1.00d-10   1.94d2   0.00d0      ;phimin, area, supsatm
0.50d0     .false.  ` 'twothi'd' ;phim, minequill, update_type - fe_0_so4_2
1.00d-10   1.94d2   0.00d0      ;phimin, area, supsatm
0.00d0     .false.  ` 'consta't' ;phim, minequill, update_type - calcite
1.00d-10   7.3030d-10 0.00d0      ;phimin, k_eff, supsatm
0.00d0     .false.  ` 'consta't' ;phim, minequill, update_type - siderite(d)
1.00d-10   1.1574d-10 0.00d0      ;phimin, k_eff, supsatm
0.00d0     .false.  ` 'consta't' ;phim, minequill, update_type - fe(oh)2(s)
1.00d-10   1.1574d-9  0.00d0      ;phimin, k_eff, supsatm
0.00d0     .false.  ` 'consta't' ;phim, minequill, update_type - cr(oh)3(a)
1.00d-10   1.1574d-10 0.00d0      ;phimin, k_eff, supsatm
0.00d0     .false.  ` 'consta't' ;phim, minequill, update_type - mackinawite
1.00d-10   1.1574d-10 0.00d0      ;phimin, k_eff, supsatm
0.00d0     .false.  ` 'consta't' ;phim, minequill, update_type - ferrihydrite
1.00d-10   1.1574d-9  0.00d0      ;phimin, k_eff, supsatm`
'extent of zo'e'
1.8 2.4  0.0 0.0  0.00 3.20`
'end of zo'e'`
'do'e'
!

```

Example 3: salinity-dependent reaction rate of minerals

```

! Data Block 15: initial conditio- - reactive transport
! -----
      3      'initial conditio- - reactive transpo't ;number of zones
! -----

```



```

'number and name of zo'e'
\
'infl'w'\
'concentration inp't'
6000.0\ 'fr'e' 'ca'2'
10900.0\ 'char'e' 'na'1'
2800.0\ 'fr'e' 'mg'2'
450.0\ 'fr'e' 'k'1'
31000.0\ 'fr'e' 'cl'1'
1240.0\ 'fr'e' 'so4'2'
5.9\ 'h' 'h'1'
303.0\ 'fr'e' 'co3'2'
1.0d-1\ 'fr'e' 'hs'1'
-200.0\ 'h' 'o2(a)'\
'mineral inp't' ;bottom
1.00d-10 .false. \ 'consta't' ;ch2o-h2s
1.00d-10 6.9d-9 0.00d0 ;
1.00d-10 .false. \ 'consta' ' ;calcite
1.00d-10 4.0d-8 0.00d0 ;
0.50d-10 .false. \ 'consta' ' ;anhydrite
0.50d-10 4.0d-9 0.00d0 ;
0.50d-10 .false. \ 'consta' ' ;halite
0.50d-10 1.16d-8 0.00d0 ;\
3 'salinity dependent reaction rate of minera's' ;number
of minerals
ch2o-h2s ;name of minerals\
'equati'n' 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 zo'e' 20.0 0.0 1.0 0.0 1.0\
'end of zo'e'

```

Example 4: Data input for initial conditions – reactive transport considering the salinity-dependent biogenic sulphate reduction reaction – option (b)

```

! Data Block 14: initial conditio- - reactive transport
! -----
\
3 'initial conditio- - reactive transpo't ;number of zones
! -----
'number and name of zo'e'
\
'background chemistr- - aquif'r'\
'concentration inp't'
9600.00\ 'fr'e' 'ca'2' in [mg/L]
94000.00\ 'char'e' 'na'1'
3400.00\ 'fr'e' 'mg'2'
2600.00\ 'fr'e' 'k'1'
193000.00\ 'fr'e' 'cl'1'
600.00\ 'fr'e' 'so4'2'
5.95\ 'h' 'h'1'
76.00\ 'fr'e' 'co3'2'
1.5d-10\ 'fr'e' 'hs'1'
-200.00\ 'h' 'o2(a)'\
'mineral inp't'
1.00d-1 .false. \ 'consta't' ;ch2o-h2s
1.00d-10 6.9d-9 0.00d0 ;
1.00d-1 .false. \ 'consta' ' ;calcite
1.00d-10 4.0d-8 0.00d0 ;
0.32d-0 .false. \ 'consta' ' ;Anhydrite
0.50d-10 4.0d-9 0.00d0 ;
0.30d-0 .false. \ 'consta' ' ;halite
0.50d-10 1.16d-8 0.00d0 ;\
3 'salinity dependent reaction rate of minera's' ;number of
mineral\
'ch2o-h's' ;name of minerals\
'strong inhibition by one compone't' 1 ;type of relation (f=cos(a*x+b))\

```

```
'cl'1'          ; Name of the component
0.076          ; component concentration when the reaction rate is the highest (f=1.0).
1.41          ; component concentration when the reaction rate is the lowest (f=0.0).
'extent of zo'e0 1.0 0.0 1.0 0.00 16.0'
'end of zo'e'
```

Example 5: Initial conditions through external input file(s)

```
! Data Block 15: initial condition- - reactive transport
! -----
\
  3          'initial conditio- - reactive transpo't ;number of zones
! -----
'read initial aqueous component concentrations from fi'e' ; *.aq\
'read initial mineral volume fractions from fi'e' ; *.mi\
'read cec from fi'e' ; *.cec
! -----
'number and name of zo'e'
\
'background'2'\
'concentration inp't' ; From Hobbs et al. (2011), Table A-3, Sample ID: CFN-161
0.6240E-03 \ 'fr'e' ;ca
0.5220E-03 \ 'char'e' ;na
0.8230E-03 \ 'fr'e' ;'mg'2'
0.6400E-04 \ 'fr'e' ;'k'1'
0.2915E-02 \ 'fr'e' ;'cl'1'
0.2600E-03 \ 'fr'e' ;'so4'2'
7.0 \ 'h' 'h'1'
0.1722E-04 \ 'fr'e' ;'co3'2'
1.0d-1 \ 'fr'e' ;'hs'1'
1.0E-2 \ 'fr'e' ;'o2(a')'\
'mineral inp't' ;reactive
2.80E-03 .false \ 'consta't' ;ch2o-h2s
1.00d-10 6.9d-9 0.00d0 ;
9.30E-02 .false \ 'consta't' ;calcite
1.00d-10 4.0d-8 0.00d0 ;
1.00E-07 .false \ 'consta't' ;anhydrite
0.50d-10 4.0d-9 0.00d0 ;
1.00E-07 .false \ 'consta't' ;halite
0.50d-10 1.16d-8 0.00d0 ;
1.00E-12 .false \ 'twothi'd' ;phim, minequil, update_type - dolomite
1.0d-7 1.0d-5 0.00d0 ;phimin, scalfac, supsatm
1.00E-12 .false \ 'twothi'd' ;phim, minequil, update_type \ 'pyrite-serg'o'
1.0d-7 6.0d-3 0.00d0 ;phimin, scalfac, supsatm\
'sorption parameter inp't'
17.5d0 ;cation exchange capacity [meq/100 g solid]
1.0d0 ;dry bulk density [g/cm^3]\
'equilibrate with fixed solution composition'

'extent of zone'
0.0 440000.0 0.0 1.0 0.0 4000.0

'end of zone'

'done'
```

3.21.4 DESCRIPTION OF THE 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 Data Block 2 ('geochemical system'). The section 'mineral input' provides the parameters for the

kinetic reactions of the 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 are composed dominantly of albite with a volume fraction of $0.50 [\text{m}^3 \text{m}^{-3}]$ and of tracer amount of calcite of $5.0 \times 10^{-4} [\text{m}^3 \text{m}^{-3}]$. The other two minerals are secondary minerals. The minimum volume fraction of all four minerals is $10^{-10} [\text{m}^3 \text{m}^{-3}]$ while the effective rate constant is $10^{-13} [\text{mol L}^{-1} \text{bulk s}^{-1}]$ 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 3.3.2.17). The zone name to be specified is 'background chemistry - reactive barrier.' Similar to 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} and $1.1574 \times 10^{-9} [\text{mol L}^{-1} \text{bulk s}^{-1}]$, respectively.

Example 3 demonstrates the input formats for specifying initial conditions considering salinity-dependent sulphate 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 sulphate 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):

$$k_{sal} = -0.2716 + 0.0211 S - 9.455 \times 10^{-5} S^2 - 3.20 \times 10^{-8} S^3 \quad \text{Equation 3-62}$$

The minimum salinity is 15.0 g L^{-1} and the k_{sal} is 0.03, which means if the salinity is 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} .

Example 4: This example is similar to Example 2, considering the salinity-dependent biogenic sulphate-reduction model but using the cosine function, as defined using the sub-keyword 'strong inhibition by one component' followed by the component 'cl-1' and its threshold concentrations: the C_L in 0.076 mol L^{-1} , and C_H in 1.41 mol L^{-1} . The k_{sal} is calculated according to Equation 3-59. The initial conditions for 10 components and four minerals are provided in the same manner as Example 1.

Example 5 defines the initial conditions of reactive transport for a 2D vertical basin scale domain (horizontal in 440km and vertical in 4 km). The model is, thus, very complex. Therefore, the initial conditions are provided at each control volume through three external files: a file prefix.aqt for the concentration distributions of 10 components, a file prefix.min for the volume fractions of six minerals and the porosity and a file prefix.cec for the cation exchange capacity (CEC) of the porous media. It is important to provide the same parameters as described in Example 1, even though they are replaced with the data provided by the external files.

3.22 BOUNDARY CONDITIONS - REACTIVE TRANSPORT (DATA

BLOCK 16)**3.22.1 DESCRIPTION OF THE 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 on ‘initial condition – local chemistry’ with the following exceptions:

- Kinetic batch simulations cannot be conducted (use the batch option of the model).
- pH-sweep calculations cannot be conducted (use the batch option of the 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 DESCRIPTIONS OF THE 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 overlaid.

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 and free advective mass outflux for aqueous phase.
‘mixed’	Dirichlet/Cauchy	Advective mass influx and free diffusive mass influx for aqueous and gaseous phases and free advective mass outflux for aqueous phase.
‘third-evap’	Cauchy	Advective mass influx for aqueous phase but no outflow mass flux. Mass is retained in the domain for outflow boundary.
‘mixed-evap’	Dirichlet/Cauchy	Advective mass influx and free diffusive mass influx for aqueous and gaseous phases but no outflow mass flux. Mass is retained in the domain for outflow boundary.
‘tracer’	Cauchy	Advective mass influx for aqueous phase. The total mass transported is calculated based on the

		specified tracer concentration and the flux through the control volume.
--	--	---

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 the ‘initial condition – local chemistry’ section.

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 depend on the grid spacing (see Section 3 of the input file). As 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 yz-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
```

Currently, 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 the 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 the 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 the 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 specifying transient boundary conditions.

3.22.4 USE BACKGROUND CHEMISTRY FOR BOUNDARY ZONE

It is also possible to stipulate 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 use.

3.22.5 EXAMPLE DATA INPUT FILE

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 the 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 THE 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 BCs for the inflow and second-type BCs 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. It is important the boundary types and required parameters are kept 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 first 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 THE DATA BLOCK

For simulating the glaciation induced hyrogeomechanic 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 THE 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 ice sheet’s status. If it is true, the ice sheet’s thickness 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 ice sheet’s thickness ($h_{ice}(x, t)$, [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):

$$h_{ice}(x, t) = H_{ice}(t) \left[1 - \left(\frac{x}{L(t)} \right)^a \right]^{1/b} \quad \text{Equation 3-63}$$

$$h_w(x, t) = \alpha h_{ice}(x, t) \quad \text{Equation 3-64}$$

where $H_{ice}(t)$ [L] is the specified maximum ice sheet’s thickness, $L(t)$ [L] is the corresponding horizontal length of the ice sheet, x [L] is the distance from the ice sheet’s origin (i.e., the 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’s 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 the flow boundary condition, .false. – the non-flow boundary condition, for example during the glaciation period), factor for water pressure, factor for ice pressure, start and end time of the stage, horizontal position of the ice front, and the ice sheet’s thickness at the start and end time of the stage.

The chemical composition of melt water can be optionally specified using the keyword ‘concentration input’ within Data Block 17: ‘ice sheet loading/unloading.’ The required data and format are demonstrated in the following example. The order of the component should be the same as specified in Data Block 2: ‘geochemical system.’

3.23.3 EXAMPLE DATA INPUT FILE

An example is provided below (Bea et al., 2011):

```
! Data Block 17: Ice Sheet loading/unloading
! -----
!
```

```

'ice sheet loading/unloading'
.false.                                ! is constant
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                          ! llperm(1,i),llperm(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                          ! llperm(1,i),llperm(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                          ! llperm(1,i),llperm(2,i)
0.0d0  0.0d0                          ! l2perm(1,i),l2perm(2,i)
0.0d0  0.0d0                          ! thickperm(1,i),thickperm(2,i)

'concentration input'
10                                     ! number of chemical components
0.2915E-02      'charge' ;c1
0.4000E-04      'free'  ;br
0.5220E-03      'free'  ;na
0.6400E-04      'free'  ;k
6.0             'ph'    ;h
0.1722E-04      'free'  ;hco3
0.6240E-03      'free'  ;ca
0.8230E-03      'free'  ;mg
0.2600E-03      'free'  ;so4
1.0d0           'po2'   ;o2(aq)

!'compute permafrost'

'done'

```

3.23.4 DESCRIPTION OF THE 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 be 1000 kg m^{-3} . The glaciation/deglaciation processes include three stages. During 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 stage 2 (from 12500 to 17500 years), the ice sheet remains unchanged. During stage 3, the deglaciation process results in the complete retreat of the ice sheet. The melted ice provides a water source on the top of the soil. In this case, a factor of water pressure with 0.95 is applied. The chemical compositions of the melting water at the top boundary during the glacier melting phase are provided. The melting water is normally higher in $\text{O}_2(\text{aq})$.

A 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 Data Block 10: 'physical parameters - variably saturated flow.' This parameter is applied to calculate the pore water pressure owing to the ice sheet's loading.

3.24 PLANT TRANSPIRATION AND PASSIVE/REJECTIVE

UPTAKE (DATA BLOCK 18)

3.24.1 DESCRIPTION OF THE DATABLOCK

This data block is used to specify the parameters and options needed to compute the root water uptake in each control volumes, for the variably saturated case. The use of this option requires the prefix.soi file that contains five columns : time (day), potential evapo transpiration (m/s), rate of water interception by the plant canopy (m/s), crop factor representing the rate at which intercepted water evaporates (dimensionless) and a scale tree growth (scale factor accounting for the influence of tree growth on transpiration). These parameters allow the computation of the evaporative budget at each time step.

The simulation of the root is expressed in root surface densities (RSD) for each control volumes, which is modeled in different ways :

- RSD constant in time with a spatial distribution given in an prefix.rld file read during initialization (in 1D only, along depth)
- RSD constant in time and set in the different material property zones (all dimensions)
- RSD evolving in time and depth according to a 1D model along depth, obtained from the PhD study of Amandine Germon, CIRAD.

Where a, b, c and d have to be provided by the user. This model has been obtained from studies on eucalyptus plantations in Itatinga, Bresil (PhD of Amandine Germon, CIRAD).

- RSD evolving in time and depth, computed by the root architecture functions 'ArchiSimple' (1D or 2D) and 'Root Typ' (2D). These functions currently coupled to MIN3P are initially developed in stand alone programs by Loïc Pagès, INRA. Those functions are licensed under license Apache V2.0. In the current configuration, ArchiSimple allows to simulate a root architecture on a maximum of 201 time steps and on a domain with 3 m depth maximum (see explanations below).

Note that the number of dimensions considered is automatically detected from the coordinates of the MIN3P domain. By default, ArchiSimple and Root Typ compute the root architecture in 3D, but :

- if the MIN3P domain is in 1D, only RSD in 1D are transferred from ArchiSimple to MIN3P, there is no possibility of using Root Typ in that case
- if the MIN3P domain is in 2D, only RSD in 2D are transferred from ArchiSimple or Root Typ to MIN3P.

3.24.2 DESCRIPTION OF THE INPUT PARAMETERS**'read root length density from file'**

The activation of this statement allows the consideration of a steady root architecture for a 1D study, along the depth profile. The root surface densities are read in a `prefix.rld` file that must be provided when using this option. This file contains a first line « variables = "x", "y", "z", "rld" » and four columns : the x,y,z domain coordinates (even if it's used only for a 1D study) and the root surface densities values.

'update - internal'

This option allows to compute the root surface densities profile in 1D according to the equation :

$$rld(ivol) = \exp(a + b * \sqrt{z(ivol)}) + c * time + d * \sqrt{z(ivol) * time}$$

The parameters a, b, c and d are user dependant, so they have to be indicated in the following line in the format 'a b c d'. For eucalyptus plantation study in Itatinga, Brasil (A. Germon, PhD) the parameter values are : a = -12.48, b = 1.725, c = 0.0017 and d = 0.0003961.

'update - coupled - AS'

When using this option, the root surface densities are daily computed by ArchiSimple function and transferred by coupling to MIN3P. ArchiSimple represents the root system as a set of small segments and computes the root surface densities (RSD) in each control volume of the domain of MIN3P. If the MIN3P domain is in 1D, the RSD are transferred in 1D and if the MIN3P domain is in 2D, the RSD are transferred in 2D. Although the RSD are computed in 3D by ArchiSimple, this kind of simulation coupled to MIN3P is not available yet.

When using ArchiSimple function, please refer to and cite *Pages et al. (2014) Calibration and evaluation of ArchiSimple, a simple model of root system architecture. Ecol. Model. 290:76-84.*

The use of this ArchiSimple function requires three files describing the root and soil characteristics : `volrac.txt`, `paramAS.txt` and `sol.txt`.

The file `paramAS.txt` is a list of 23 parameters allowing the root developmental processes such as emission, elongation, branching, radial growth and self-pruning (*Pages et al., 2014*). In ArchiSimple, units are in days and millimeters :

0.5 # *X position of the seed (in MIN3P domain, meters)*
 0 # *Y position of the seed (in MIN3P domain, meters)*
 1 # *Z position of the seed (in MIN3P domain, meters)*
 1 # *Emission rate of primary roots (nb of root / day)*
 1 # *Maximum number of primary roots*
 100 # *Age of emission of adventitious roots*
 30 # *Maximum distance from origin of adventitious roots (mm)*
 0.5 # *Emission rate of adventitious roots (nb of root / day)*
 1 # *Initial diameter of adventitious roots (mm)*
 5 # *Maximum number of adventitious roots*
 0.2 # *Threshold tip diameter below which there is no possible elongation (diameter of the finest root in mm)*
 1 # *Threshold tip diameter above which there is no possible elongation (diameter of the thickest root in mm)*
 25 # *Slope of the potential elongation rate versus tip diameter (mm/mm/day)*
 1 # *Gravitropism type (0 :plagio, -1 and +1 : geo, -2 and +2 : exo)*
 0.005 # *Gravitropism intensity*
 5.3 # *Lag time between initiation and emergence of roots : maturity age of tip (day)*
 7 # *Inter-primordium distance (mm)*
 0.18 # *Average ratio of the diameter of the daughter root to that of the mother root (dimensionless)*
 0.17 # *Relative variation of the daughter root diameter (dimensionless)*
 0.1 # *Root tissue density (g/cm3)*
 1000.0 # *Coefficient of the growth duration (day mm-2)*
 8000 # *Coefficient of the life duration (day mm g-1)*
 0.4 # *Proportionality coefficient between section area of the segment and the sum of distal section areas (dimensionless)*

The file `volrac.txt` shows one column corresponding to the maximum root volume for each time step (mm3) :

100000.0
 100000.0
 100000.0
 100000.0
 100000.0

The maximum number of time steps is currently set to 201, so if a simulation with more timesteps is required, please contact Frederic Gerard, INRA (Frederic.Gerard@inra.fr) to modify the parameter NBPASMAX in ArchiSimple. This maximum biomass volume value is used because the demand for root biomass of all roots is accumulated throughout the root system for calculating the total root demand. A satisfaction coefficient is then calculated at each time step as the ratio of the supply to the demand. Actual growth is calculated from potential growth using this coefficient. (Pages *et al.*, 2014).

The file `sol.txt` displays informations linked to the soil characteristics, for each soil horizon :

Croiss Ramif ICMeca Direction contr. (0 : isotrope, 1 verticale)

```
1.0 1.0 0.0002 0
1.0 1.0 0.0002 0
1.0 1.0 0.0002 0
1.0 1.0 0.0002 0
```

One soil horizon has a thickness of 5 cm and the maximum number of horizons is set to 60, allowing the root growth in a soil domain of 3 meters maximum. If the number of horizons (NBHORMAX) or thickness of horizon (epaissHor) must be modified, please contact Frederic Gerard, INRA (Frederic.Gerard@inra.fr).

The first column 'Croiss' refers to a coefficient between 0 and 1 accounting for the heterogeneities of growth in soil horizons (1 correspond to a fast growth and 0 to a slow growth). Indeed, root growth can be dependant of soil characteristic such as humidity, so this coefficient is applied on the elongation of the root segments. It can be used to simulate the effects of humidity by reducing the growth rate of the root.

The second column 'Ramif' corresponds to a coefficient greater than 0 for the modulation of branching density. For small values, distances between the root branches decreases, and for large 'Ramif' values the distances between the root branches increases. This coefficient regulates the inter-branch distance.

The third column 'ICMeca' is an index of soil mechanical constraints. This dimensionless number allows defining the way the root shape is affected by the resistance of the soil, by modifying the position of the root segments. When ICMeca has high values, the root branching pattern is smooth and when ICMeca has low values, the root branching pattern is tortuous.

Finally, the last column 'Direction contr. (0 : isotrope, 1 verticale)' allows to define if the soil

mechanical constraint acts in the vertical direction (if set to 1) or in all the directions (isotropic, if set to 0). It is an indicator of the mechanical constraint.

'update - coupled - RT'

When using this option, the root surface densities are daily computed by Root Typ function and transferred by coupling to MIN3P. Root Typ considers that root tips can take various states, coded by numbers of types. Each root type is given a set of parameters to qualify and quantify how the morphogenetic processes operate in a given type. Root Typ represents the root system as a set of nodes and computes the root surface densities (RSD) in each control volume of the domain of MIN3P. Although the RSD are computed in 3D by Root Typ, this kind of simulation coupled to MIN3P is not available yet. The RSD are then transferred to MIN3P in 2D.

When using Root Typ function, please refer to and cite *Pages et al. (2004) Root Typ: a generic model to depict and analyse the root system architecture. Plant and Soil. 258:103-119.*

The use of this Root Typ function requires two files describing the root and soil characteristics : `paramRT.txt` and `sol.txt`.

The file '`sol.txt`' is the same file than for ArchiSimple option (see description on the section above).

The file '`paramRT.txt`' contains the following structure with units in days and centimeters :

70 *Duration of the simulation (not considered)*
 1 *Number of transplanted axis*
 9 *Number of reiteration phases*
 5000 6000 7000 8000 9000 9100 9200 9300 9400 *Dates of reiteration*
Radial growth coefficient

TYPE 0 (BASE DE LA TIGE)

3.1416 0.02 *Average of the insertion angle on the previous type (average, standard deviation)*
 0.7 0.05 *Insertion angle parameters during a reiteration (average, standard deviation)*
 1.0 *Duration before emergence (days)*
 200.0 0.1 *Average of the maximal length (average, standard deviation)*
 0.0 0.0 *Growth rate parameters (average, standard deviation)*
 0.2 0.0 *Inter-branch distance parameters (average, standard deviation)*

-1 Indicator of tropism type (0 : plagio, - or +1 : geo - or +, 2 : exo)

0.1 Tropisme intensity

0.0 Sensitivity to mechanical constraint

2.0 Apical diameter (cm)

8000.0 Necrosis duration since the growth stop (days)

0.0 Probability of reiteration at the reiteration dates

0 1 Min and max number of reiterated roots

1000.0 Age from which transformation may happen

0.0 Daily probability of transition

-1 Sens of transition (-1 -> lower type, +1 -> higher type)

0.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 Proportion of types among the branches

Note that the 18 previous lines of the datablock « TYPE 0 » can be duplicate with several parameters modifications to simulation a second root Typ. Up to 8 different types can be considered that way.

'random generator seed - RT' and **'random generator seed - AS'**

If one of the two sections 'random generator' is indicated, the following line must contain a random seed value. This option of fixing a constant seed is usefull for comparison of a same root for debugging purposes. By default these sections do not appear and the seed of the random generator is initialized on the time of the launch of the simulation.

If none of the previous options **'read root length density from file'**, **'update - internal'**, **'update - coupled - AS'** and **'update - coupled - RT'** is activated, the root surface densities considered are specified for each material zones, in the **'root water uptake'** section.

The two following sections correspond to parameters set for all the MIN3P domain. For more informations, please refer to *Mayer et al., (2011) Reactive Transport Modeling in Variably Saturated Media with MIN3P : Basic Model Formulation and Model Enhancements. Groundwater Reactive Transport Models, 187-212.*

'transpiration global parameters'

This section contains three lines indicating :

- the relative extractable water at 50% of maximum extraction capacity (fitting parameter).
- A fitting parameter for root water uptake function
- A canopy evaporation factor

'correction method for water stress'

This section contains one indicator value indicating which option is used to account for the negative effects of water stress (*Mayer et al., 2011*). If the indicator is set to 1, the reduction function for water stress is averaged across the entire spatial domain. If the indicator is set to 2, the reduction function is calculated separately for each control volume, and if the indicator is set to 3, the reduction factor is equal to 1.

The following sections and parameters are indicated for each material zones, between the tags 'name of zones' and 'end of zone'.

'root water uptake'

These keywords are followed by three lines indicating :

- the water pressure at wilting point (absolute value in m),
- the water pressure at field capacity (absolute value in m),
- the root surface density assigned to all control volumes located in the given material property zone.

'passive solute uptake'

This parameter set to 1.0 is not used in the current version.

3.24.3 EXAMPLE DATA INPUT FILE

```

! Data Block 18: plant transpiration and passive/rejective uptake
! -----
!
'plant transpiration and passive/rejective uptake'
! -----
!NB :If none of these options is activated, the root length densities considered are those
!NB :specified in the 'root water uptake' section. In the 'update-internal' option, ivol
!NB :refers to the control volume ID.
!'read root length density from file'; 1D
!'update - internal' ; 1D model: rld(ivol)=exp(a+b*sqrt(z(ivol))+c*time+d*sqrt(z(ivol))*time)
!-12.48 1.725 0.0017 0.0003961; a, b, c, d parameters of the model for 'update - internal'
!'update - coupled - AS' ; 1D/2D (automatic detection)
'update - coupled - RT' ; 2D

'transpiration global parameters'
2.0 ;rew_0
-2.0 ;p1
0.1 ;f_i
'correction method for water stress'
1

'A'

'root water uptake'
160.0 ;water pressure wilting point
1.0 ;water pressure field capacity
0.1 ;root length density

'passive solute uptake'
1.0
'end of zone'

'B'

'root water uptake'
160.0 ;water pressure wilting point
1.0 ;water pressure field capacity
1.0 ;root length density

'passive solute uptake'
1.0
'end of zone'

'done'

```

3.24.4 DESCRIPTION OF THE EXAMPLE INPUT

In the example file, the number of material property zones is 2. The names for the two zones in the example file are 'A' and 'B', they both have a water pressure at wilting point value of 160 and a water pressure at field capacity of 1. Although root length density values are set for each of the two material property zones (value of 0.1), they are not considered because the option 'update - coupled - RT' is activated, allowing the computation of the root architecture by Root Typ function at each time step of the simulation. Note that the lack of the keyword '**random generator seed - RT**' or '**random generator seed - AS**' implies that the root architecture simulation is different at each launch (normal mode, not suitable for debug). Indeed, in that case the random seed is initialized based on the random computer time at which the run has been launched. For all the spatial domain, the transpiration global parameters are :

- a relative extractable water at 50% of maximum extraction capacity of 2,
- a fitting parameter for root water uptake function of -2,

- and a canopy evaporation factor of 0.1,

and the reduction function for water stress is averaged over the entire spatial domain.

4 DATABASE

The geochemical database is derived from the MINTEQA2 database (Allison et al., 1991). Because MIN3P-THCm allows for simulating open or partially open systems (in contact with the atmosphere) and including kinetically-controlled reactions, the half-reaction approach (i.e., 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 $\text{O}_2(\text{aq})/\text{H}_2\text{O}$ half-reaction.

The MIN3P-THCm geochemical database also allows for specifying 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 PHREEQC2 database (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 and 5.00 and .00 are the Debye-Hückel 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 endpoint. 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 sulphur isotope components as sulphate and hydrosulphide:

```
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-Hückel parameters are not known, 0.00 should be specified. When no Debye-Hückel parameters are specified, the Davies equation is used. All other parameters are required to allow for considering 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), and 4x indicates four (4) blank spaces).

4.1.3 COMPONENTS FOR MULTICOMPONENT DIFFUSION

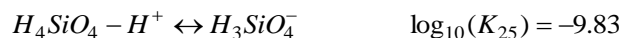
If the multicomponent diffusion model is applied (see Section 3.2.2.7), the molecular diffusion coefficient (in $\text{m}^2 \text{s}^{-1}$) is species-dependent. This parameter is required to be attached at the end of each entry as follows:

```
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

and -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-Hückel 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 constant $\log K_{25}$ 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 two 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 and the Debye-Hückel parameters or the alkalinity factor are not known, 0.00 should be specified. All other parameters must be known to allow for considering the aqueous complex. Currently, 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 MINTEQA2 (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 sulphur 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 the multicomponent diffusion model is applied (see Section 3.2.2.7), the molecular diffusion

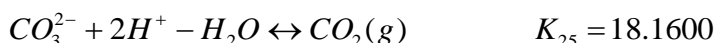
coefficient (in $[m^2 s^{-1}]$) is species-dependent. This parameter for all chemical complexes is required to be placed at the end of each entry to the first line as follows:

```
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

Gases.db is the database file for gas exchange reactions. 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 $CO_2(g)$ formation. 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 reactions for gas exchange reactions. The sign of the equilibrium constant $\log K_{25}$ should be turned around if the reactions are expressed as dissociation reactions.

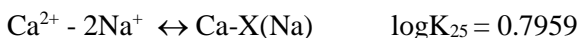
$$K_{25} = [CO_2(g)] \cdot [H^+]^{-2} \cdot [CO_3^{2-}]^{-1}$$

4.4 ION EXCHANGE AND SORPTION REACTIONS

Component species involved in ion exchange and surface complexation reactions are defined in the comp.db file (see the section above on component species). This section refers to the database file sorption.db, 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 PHREEQC2 (Parkhurst and Appelo, 1999) database.

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).

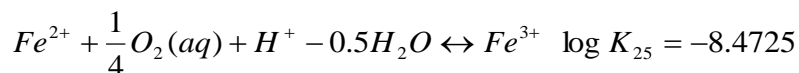
The second line defines the ion exchange reaction mentioned above. The first parameter defines the number of associated components (in this case, 2) followed by the pairs of name and stoichiometric coefficient of the components. The two components in this example are ca+2 and na+1 with stoichiometric 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 constant $\log K_{25}$ 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 similarly to 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 four 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 reactions 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 constant $\log K_{25}$ should be turned around if the reactions are expressed as dissociation reactions because the equilibrium constant for the chemical reaction described in Section 4.5 as a formation reaction is defined as follows:

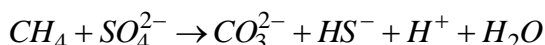
$$K_{25} = [Fe^{3+}][Fe^{2+}]^{-1} \cdot [O_2(aq)]^{-1/4} \cdot [H^+]^{-1}$$

It is also possible to specify irreversible, kinetically controlled reactions in this database file. In general, the database structure allows for calculating rate expressions including fractional order terms, Monod-type terms and inhibition terms:

$$R_i^a = -k_i^a \left[\prod_{j=1}^{N_c} (T_j^a)^{o_{ij}^{a,t}} \prod_{\substack{j=1, \\ K_{ij}^{a,mo} > 0}}^{N_c} \left(\frac{T_j^a}{K_{ij}^{a,mo} + T_j^a} \right)^{o_{ij}^{a,mo}} \right. \\ \left. * \prod_{\substack{j=1, \\ K_{ij}^{a,in} > 0}}^{N_c} \left(\frac{K_{ij}^{a,in}}{K_{ij}^{a,in} + T_j^a} \right)^{o_{ij}^{a,in}} \prod_{\substack{j=1, \\ K_{ij}^{a,m,in} > 0}}^{N_c} \left(\frac{K_{ij}^{a,m,in}}{K_{ij}^{a,m,in} + \phi_i} \right)^{o_{ij}^{a,m,in}} \right] \quad \text{Equation 4-1}$$

where R_i^a is the reaction rate of the i^{th} intra-aqueous component, k_i^a is the rate constant and 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 regarding 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 owing 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 sulphates:



which is inhibited in the presence of $O_2(aq)$, NO_3^- and goethite, 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 stoichiometry of the reaction, starting with the number of components involved and followed by the components and the stoichiometric coefficients. The keyword 'irreversible' identifies the reaction as a kinetic reaction. The number of Monod and threshold terms is specified after the keyword '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 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 owing to the presence of aqueous components is specified after the keyword '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 by reason of the presence of mineral phases is specified after the keyword '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].

For specification of the fraction order term in the general rate expressions mentioned above, the keyword '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 i^{th} mineral in [mol (L bulk)⁻¹ s⁻¹], k_i^m is the rate constant in [mol m⁻² s⁻¹], S_i is the surface area of the mineral in [m² (L bulk)⁻¹]. 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
```

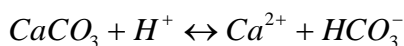
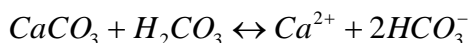
where 'calcite' is the name of the mineral phase and 'surface' identifies the reaction as a surface-controlled reaction (other options are discussed below). The entries in the third input line define

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 keyword 'reversible,' identifies the reaction as a reversible reaction. It is followed by the equilibrium constant log₁₀*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 reactions 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 calcite dissolution 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'
```

Besides 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 depend on the

activity of protons and water (dependent on one component as species in the 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 (m²L⁻¹ bulk) with the keyword 'log rate constant.' The activation energy is also specified by means of the keyword '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 Cc' 1
'h+1' 0.490
'end pathway'

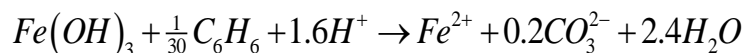
'pathway' 2
'log rate constant' -14.150
'activation energy' 13.900
'fractional Cx' 1
'oh-1' -0.300
'end pathway'

'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 described for calcite dissolution-precipitation.

The dissolution of albite may also be described as a far-from-equilibrium reaction 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 regarding ferrihydrite and considers 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

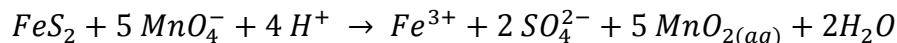
'inhibition T^a' 2
'o2(aq)' 3.125d-6  1.000
'no3-1'  8.000d-6  1.000

'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 approaches zero.

It is also possible to use a general rate expression in the same way as Equation 4-1 to define the minerals' kinetic reaction. The equation for the pyrite oxidation by MnO_4^- is:



It is defined as an irreversible dissolution reaction and the reaction rate depends on the MnO_4^- concentration, as defined in the database mineral.dbs as follows:

```
!
! pyrite-mno4
! pyrite oxidation by mno4-1
! gram formula weight from MINTQA2
! 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
```

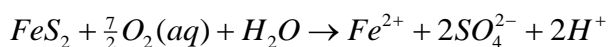
In this example, the lines beginning with '!' are comments, documenting the origin of the data. The name 'pyrite-mno2' is the mineral reaction name, representing the chemical formula FeS_2 in the

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 keyword '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 till now were surface-controlled reactions. MIN3P-THCm also allows 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.'

As a result of 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:

$$R_i^m = -10^3 S_i \frac{r_i^p}{(r_i^p - r_i^r) r_i^r} \frac{D_{il}^m}{\nu_{il}^m} [O_2(aq)]$$

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, $O_2(aq)$) and ν_{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 are, 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 described in the previous examples.

Additional parameters are required after the keyword 'shrinking core parameters.' These are the free-phase diffusion coefficients of the primary reactant in water (D_{il}^m in $m^2 s^{-1}$), which is $2.41 \times 10^{-9} m^2 s^{-1}$, for example, and the stoichiometric coefficient of oxygen in the reaction equation (ν_{il}^m), which is 3.5.

4.8 KINETICAL REACTIONS CONTAINING ISOTOPES

The definition of the geochemical database for kinetic reactions containing isotopes is basically as mentioned in the previous sections. Generally, additional keywords are required to define the

master and dependent isotopes. The following example shows the definition of sulphate reduction reactions 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 a 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 sulphate concentration (i.e., the sum of two sulphate 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 sulphur 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 in the next lines by the fractionation factor for each isotope component starting with the second in the list of names. 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 sulphur 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 sulphate 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. Consequently, 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:

```
'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), which 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 must 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>
```

$\beta(0)$ — the ion interaction parameter, α_1 and α_2 (see equations 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 equations 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 equations 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 equations 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} — ion interaction parameter between cation-cation or anion-anion (see equations 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 equations 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>
```

4.10 SIT DATABASE

The activity coefficients of aqueous species in moderately saline solutions can be calculated based on the specific ion interaction theory (Guggenheim and Turgeon, 1955; Ciavatta, 1980). The general idea of SIT theory is that the activity coefficient γ_j of the j th ion in the solution can be expressed as

$$\log \gamma_j = -z_j^2 \frac{0.51\sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_k \varepsilon_{jk} c_k$$

where z_j is the electrical charge of the j th ion, I is the ionic strength and c_k is the molal concentration of the k th ion. ε_{jk} refers to the interaction coefficient between the j th and the k th ions,

which is provided in the database sit.dbs in the form:

```
!SIT model
!-epsilon parameters from SIT.dat (PHREEQC)
Cd+2 Cl- 0.16
Cd+2 NO3- 0.09
CdCl+ Cl- 0.127
CdCl+ ClO4- 0.25
CdI+ Cl- 0.136
CdI+ ClO4- 0.27
```

The last term in each line provides the interaction coefficient ε_{jk} between the ions in the first two terms.

4.11 EXPONENTIAL DECAY FOR KINETIC REACTION

To use exponential decay function for kinetic reactions, user needs to modify redox database to add 'exponential T^a' term. Example is shown below.

```
'exponential T^a' 2
'biomass1' 0.5
'biomass1' 0.3
```

5 REFERENCES:

(See more references in the theory manual to avoid repetition)

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.

Guggenheim, E.A.; Turgeon, J.C. 1955. "Specific interaction of ions". *Trans. Faraday Soc.* 51: 747-761. doi:10.1039/TF9555100747.

Ciavatta, L. 1980. "The specific interaction theory in the evaluating ionic equilibria". *Ann. Chim. (Rome)*. 70: 551-562.