OpenGeoSys-GEM Control File: *.gem

```
#GEM_PROPERTIES
  $GEM_THREADS
    8
  $GEM_INIT_FILE
    BC-dat.lst
  $FLAG_POROSITY_CHANGE
    1
  $MIN_POROSITY
    1.e-6
  $MAX_POROSITY
    1.0
  $FLAG_COUPLING_HYDROLOGY
    1
  $TEMPERATURE_GEM
    298.15
  $MAX_FAILED_NODES
     5
#STOP
```

(Example 01: Calcite-dolomite benchmark)

The control file *.gem contains the settings that are specific for the OpenGeoSys-GEM coupling. Other OpenGeoSys-GEM specific or important settings are in the *.mcp (Diffusion model), *.pcs (restart files), *.mfp (fluid density), *.mmp (porosity model) files.

Example 01 shows the control for the calcite-dolomite benchmark.

Keyword: **#GEM_PROPTERTIES**

Description: The #GEM_PROPTERTIES keyword indicates the beginning of the definitions. Definitions and data will be read until the file input terminator #STOP is reached.

Parameters: None

Sub keywords: $GEM_INIT_FILE, $GEM_THREADS, $FLAG_POROSITY_CHANGE, $MIN_POROSITY, $MAX_POROSITY, $FLAG_COUPLING_HYDROLOGY, $CALCULATE_BOUNDARY_NODES, $TEMPERATURE_GEM, $PRESSURE_GEM, $MAX_FAILED_NODES, $MY_SMART_GEMS, $KINETIC_GEM

Questions: Any?

Keyword: **$GEM_INIT_FILE**

Description: The keyword reads as parameter the GEMS3K input file (lst file) that contains the names of the GEMS data file (dch file), the GEMS numerical settings (ipm file) and the example setup (dbr file) used to initialize the GEMS3K kernel. The four files are created in GEM-SELEKTOR V3 by exporting a working setup for use with the GEMS3K

kernel. The user should make sure that the files are produced with a GEM-SELEKTOR version that is compatible to the GEMS3K version used in OpenGeoSys-GEM.

Parameters: The parameter is defined one line below the keyword. Only one parameter can be defined.

Sub keywords: None

ATTENTION: This keyword is inevitable.

Keyword: $GEM_THREADS

Description: The keyword $GEM_THREADS gives the number of threads that should be used in parallel to execute GEMS3K calculations. In case a parallel code with MPI tasks is executed, each MPI task spawns $GEM_THREADS. Using more than 1 thread may decrease greatly the computation time. It is possible to define an arbitrary number of threads, but it is recommended to match the number of threads with the number of CPUs (cores) that are available for running OpenGeoSys-GEMS.

Parameters: The parameter (int) must be written in the subsequent line after the keyword and must be greater zero. It is recommended to set it to the number of CPUs (cores) that should be used for calculations.

Sub keywords: None

Questions: Any?

Keyword: $FLAG_POROSITY_CHANGE

Description: The keyword $FLAG_POROSITY_CHANGE gives

Parameters: The parameter (int) must be written in the subsequent line after the keyword and must be zero (0) or one (1). If it is one (1), the porosity will be updated according to the result of the GEM calculation for each node. Node porosities will be interpolated to element porosities via calculation of the arithmetric mean. The amount of Fluid/Gas (including amount of dissolved species) will be adjusted to match the porosity. The excess volume can be accounted for by back-coupling to hydraulics via the keyword $FLAG_COUPLING_HYDRAULICS.

Sub keywords: None

Questions: Any?

Keyword: $MIN_POROSITY

Description: The keyword $FLAG_POROSITY_CHANGE gives

Parameters: The parameter (double) must be written in the subsequent line and must be greater than zero (0). Recommended value is “1.0e-6”. GEM can calculate zero porosities and chemical systems without fluid/gas

phase, but hydraulics/transport will not work with zero porosity. Porosities below $MIN_POROSITY are raised by adding fluid/gas to the system.

Sub keywords: None

Questions: Any?

Keyword: $MAX_POROSITY

Description: The keyword $FLAG_POROSITY_CHANGE gives

Parameters: The parameter (double) must be written in the subsequent line and must be smaller or equal to one (1.0). Recommended value is “1.0”.

Sub keywords: None

Questions: Any?

Keyword: $FLAG_COUPLING_HYDROLOGY

Description: The keyword $FLAG_POROSITY_CHANGE gives

Parameters: The parameter (int) must be written in the subsequent line after the keyword and must be zero (0) or one (1). It it is one, fluid volume changes after GEMS calculations (due to porosity changes, compositional changes, temperature changes ..) are back-coupled to hydraulics by adding appropriate source/sink terms for the next time step.

Sub keywords: None

Questions: Any?

Keyword: $CALCULATE_BOUNDARY_NODES

Description: The keyword $CALCULATE_BOUNDARY_NODES gives

Parameters: The parameter (int) must be written in the subsequent line after the keyword and must be zero (0) or one (1). If the flag is set to one, the chemical system is also calculated at boundary nodes (where concentrations are fixed). This might be necessary to change porosity at such nodes.

Sub keywords: None

Questions: Any?

Keyword: $TEMPERATURE_GEM

Description: The keyword $TEMPERATURE_GEM sets a temperature for GEMS calculations.

Parameters: The parameter (double) must be written in the subsequent line after the keyword and must be given in Kelvin.

Sub keywords: None

Questions: Any?

Keyword: $PRESSURE_GEM

Description: The keyword $PRESSURE_GEM allows to set a pressure for GEM independent from the hydraulic calculations.

Parameters: The parameter (double) must be written in the subsequent line after the keyword and must be given in Pascal.

Sub keywords: None

Questions: Any?

Keyword: $MAX_FAILED_NODES

Description: The keyword $PRESSURE_GEM allows to continue calculations even if GEM does not find a solution at a node.

Parameters: The parameter (int) must be written in the subsequent line after the keyword. Calculations are continued if up to $MAX_FAILED_NODES per GEMS thread are present.

Sub keywords: None

Questions: Any?

Keyword: $KINETIC_GEM

Description: The $KINETIC_GEM keyword enables to kinetically control precipitation/dissolution of solid phases.
An overview on the problems and uncertainties related to precipitation data is given by Palandri and Kharaka (2004) on pages 5 and 6. We implemented their approach which assumes that both dissolution and precipitation (forward and backward rates) must proceed by a single reversible mechanism. In literature kinetic rate laws that describe dissolution and precipitation of minerals are often given in a form similar to

$$\frac{dm}{dt} = SA * k * \left(a_{H^+}\right)^n * \left(1 - \Omega^p\right)^q , \qquad (1)$$

where *dm/dt* [mol/s] is the reaction rate in terms of change of mole amount *dm* per time *dt*. SA is the mineral reactive surface area [m^2], *k* is the rate constant [mol m^{-2} s^{-1}], a_{H^+} is the activity of H^+ ions [-], and *n*, *p*, *q*, are constants [-].

□ is the mineral saturation index [-]

$$\Omega = \frac{Q}{K}, \tag{2}$$

where Q stands for the activity quotient and K is the equilibrium constant for the reaction of interest. □ is dimensionless and has a value of 1 for equilibrium, less than 1 if the reactants are undersaturated (dissolution of products) and more than 1 if the reactants are oversaturated (precipitation of products).

Palandri and Kharaka (2004) map the majority of their data onto equation 3, in which they differentiate between reactions in pure H_2O (neutral pH) and those catalyzed by H^+ (acid) and OH^- (base)

$$\frac{dm}{dt} = -SA\left[\begin{array}{l} k_{acid}^{298.15\mathrm{K}} \exp\left(\frac{-E_{acid}}{R}\left(\frac{1}{T}-\frac{1}{298.15\mathrm{K}}\right)\right) a_{H+}^{n_1}\left(1-\Omega^{p_1}\right)^{q_1} \\ + k_{neutral}^{298.15\mathrm{K}} \exp\left(\frac{-E_{neutral}}{R}\left(\frac{1}{T}-\frac{1}{298.15\mathrm{K}}\right)\right)\left(1-\Omega^{p_2}\right)^{q_2} \\ + k_{base}^{298.15\mathrm{K}} \exp\left(\frac{-E_{base}}{R}\left(\frac{1}{T}-\frac{1}{298.15\mathrm{K}}\right)\right) a_{H+}^{n_3}\left(1-\Omega^{p_3}\right)^{q_3} \end{array}\right]. \tag{3}$$

T is the absolute temperature [K], and R the molar gas constant (R=8.31451070 J K^{-1} mol^{-1}). E_{acid} $E_{neutral}$ and E_{base} are (mineral specific) activation energies [J mol^{-1}]

It should be noted that the third term of equation 3 does not include the activity of OH^- ions, but instead is based on H^+ activity with a negative value for the order of the reaction rate.

For some minerals the reaction rate is not only described in terms of the activity of H^+, also other mechanisms may contribute. For such cases the activity of H^+ is replaced by the product of reaction activities where the n^i represent the reaction order with respect to species i

$$\prod a_i^{n^i}. \tag{4}$$

With inserting equation 3 into equation 4 the rates can be calculated in a quite general way

$$\frac{dm}{dt} = -SA\left[\begin{array}{l} k_{acid}^{298.15\mathrm{K}} \exp\left(\frac{-E_{acid}}{R}\left(\frac{1}{T}-\frac{1}{298.15\mathrm{K}}\right)\right)\prod a_i^{n_1^i} \quad \left(1-\Omega^{p_1}\right)^{q_1} \\ + k_{neutral}^{298.15\mathrm{K}} \exp\left(\frac{-E_{neutral}}{R}\left(\frac{1}{T}-\frac{1}{298.15\mathrm{K}}\right)\right)\prod a_i^{n_2^i} \quad \left(1-\Omega^{p_2}\right)^{q_2} \\ + k_{base}^{298.15\mathrm{K}} \exp\left(\frac{-E_{base}}{R}\left(\frac{1}{T}-\frac{1}{298.15\mathrm{K}}\right)\right)\prod a_i^{n_3^i} \quad \left(1-\Omega^{p_3}\right)^{q_3} \end{array}\right. \tag{5}$$

.

The above equation was implemented in OpenGeoSys and corresponding constraints on the masses of dependent components are passed to the GEMS3K kernel. In contrast to equation 3, the second term in equation 5 is multiplied with the product of reaction activities. Setting the reaction order to 0 ("zero") allows to remove the dependency on reaction activities from single terms.

Equation 5 is a very general implementation of a rate law. By setting appropriate parameter values, it is easily possible to mimic other (simpler) rate laws.

Currently only a very simple model for the calculation of the reactive surface area *SA* for a mineral *i* is implemented:

$$SA = V_i a_i \tag{6}$$

Where V_i is the volume of the mineral [m^3] and a_i is the relative surface area per volume [$m^2\ m^{-3}$].

Palandri, J. L., Kharaka, Y. K., 2004. A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical mdelling. U.S. Geological Survey Open File Report 2004-1068, Menlo Park, California, US.

Parameters:

first line: kinetic parameters
* name of phase which is controlled (from GEMS setup)
* number of kinetic model
* number of species activites used
* double E_acid,E_neutral,E_base; activation energies for temperature dependencies
* double k_acid, k_neutral,k_base; dissolution/precipitation rate constants
* double q1,p1,q2,q3,p2,p3; exponents for omega
* name of first species
* double n_1, n_2,n_3; exponents for acidic, neutral and base cases for species one
* name of next species
* .....three more exponents for each additional species

second line: reactive surface area
* number of model for calculation of reactive surface area
* model parameters for reactive surface area: e.g. specific reactive surface area

third line: additional parameters for kinetic model "5" (phase is solid solution that has end members with different stoichometry)
* number of end members

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* for each endmember a scaling factor for the specific reactive surface area
ATTENTION: July 2014: kinetics for solid solution is currently broken..do not use!

Example:

$KINETIC_GEM   ; phase for cation exchange which can dissolve, parameters from Palandri
 SS_Montmor 5 1 0.0 0.0 0.0 -10.98 -12.78 -16.52 1.0 1.0 1.0 1.0 1.0 1.0 H+ 0.34 0.0 -0.4
   1 3.0e+6         ; high reactive surface area
   6 2.0 2.0 1.0 2.0 1.0 2.0  ; scaling of end members according to Vanselow convention
  $KINETIC_GEM     ; like Palandri
   Gibbsite 1 1 0.0 0.0 0.0 -7.65 -11.50 -16.65 1.0 1.0  1.0 1.0  1.0 1.0  H+ 0.992 0.0 -0.784
   1 1.0e+2       ;
  $KINETIC_GEM     ; like zeolithes
   Phillipsite 5 1  0.0 0.0 0.0   0.0 -10.00 0.0  0.0 1.0  1.0 1.0  0.0 1.0  H+  0.0  0.0 0.0
   1 1.0e+2      ;
   3 2.0 1.0 1.0
```

Kinetic model	Remark
1	Implementation according to equation 5
2	Implementation according to equation 5, only dissolution is controlled
3	Implementation according to equation 5, only precipitation is controlled
4	Inactive (Implementation according to equation 5, but reactive surface area depends on initial porosity)
5	Implementation according to equation 5, but phase is a solid-solution which requires special treatment as endmembers have different stoichometry

Surface model	Remark
1	Implementation according to equation 6
2	Constant surface area given by parameter

3	As equation 6, but divided by porosity
4	As equation 6, but multiplied with porosity

Sub keywords: none

Questions: Any Questions or ToDos?

Keyword: $CONSTRAINT_GEMS

Description: With this keyword it is possible to set n dependent component to a specific initial amount. When initializing the system composition form values given in the IC files, it is necessary to pass mass constraints (upper and lower limits for mass balance calculation) to the GEM solver for each dependent component which is assumed out of equilibrium initially. This is normally associated with kinetic control of the corresponding phase.

Parameters: Example:
Sand 1245.0 1246.0 1 7 345.0 346.0
; dependent component name (chars), lower limit (double), upper limit (double), condition type (int), number of the independent component (int), lower limit (double), upper limit (double).

The parameters must be written in the subsequent line after the keyword. First the name of the dependent component, as defined in the GEM dch file, has to be given. Then two numbers (double) which are the lower and upper limit (dul and dll) for the initial gem calculations. It is possible to give the same number for dul and dll in order to fix it to a specific value. Otherwise the GEM algorithm will calculate an amount (which is in the given interval). The following four numbers are used to define for which nodes the constrain should apply. Currently only condition type '1' is implemented. For this condition type the constrain is applied to all nodes, for which the total amount of the independent component given is in the interval defined by the last two numbers(for a system with volume $1m^3$).

Sub keywords: None

Questions: ?

Keyword: #STOP

Description: This keyword indicates the end of the file. Everything written after file input terminator #STOP is unaccounted for input. However, users may write text and templates after #STOP as mnemonic or for blockwise copies and pastes.

Parameters: None
Sub keywords: None

Questions: What happens if I forget to write it and nothing comes after it?