

piChem
A FEFLOW Plugin for Advanced Geochemical Reactions
User Guide



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1 Introduction and Acknowledgement

DHI-WASY GmbH acknowledges Dr. Laurin Wissmeier for developing the piChem plugin. piChem is a plugin for FEFLOW for the calculation of advanced geochemical reactions together with aqueous phase flow and transport. piChem employs the interface version of PHREEQC [1] as a reaction engine, which enhances FEFLOW's built-in reaction capabilities with the full set of geochemical reactions in PHREEQC [2,3].

2 Program Capabilities

The reaction capabilities of piChem include:

- Activity corrected solution speciation (using various activity corrections, as well as the Pitzer [4] or SIT [5] ion association models),
- Mineral dissolution/precipitation reactions,
- Solid solution reactions,
- Ion exchange reactions,
- Surface complexation reactions with optional diffuse double layer calculations (Dzombak & Morel DDL [6] and CD_MUSIC [7,8]),
- Gas phase exchange reactions,
- Temperature and pressure dependent reactions [9],
- Advanced calculations of solution density from ion composition, and
- Kinetic reactions with possible dependency on solution speciation using PHREEQC's scripting capabilities and rate integrators [10].

Immediate access to comprehensive geochemical databases is provided. Functionality to extend these databases with user-defined components and reactions is an integral part of PHREEQC.

piChem defines geochemical reactions through PHREEQC input scripts. These can be produced using one of PHREEQC's graphical user interfaces:

(http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html)

or a text editor (<http://www.hydrochemistry.eu/>).

User-defined geochemical output is imported into FEFLOW for graphical display using FEFLOW's integrated visualisation tools. In addition, PHREEQC output is saved with the DAC/DAR-files for later post-processing.

3 User Guide

3.1 Operating Instructions

1. Set up the FEFLOW model for water flow and mass transport.

Define a non-reactive placeholder species for mass transport in FEFLOW. If more than one mass transport species is present in the simulation, the placeholder species has to be named “**p4f**”.

- a. Define transport properties (porosity, molecular diffusion, dispersivities) for the placeholder species. These properties will be used for all PHREEQC components. Due to the transport of solution species in terms of elements, all species must have the same transport properties.
- b. Define constant concentration boundary conditions for the placeholder species. All nodes with the same numeric value for constant concentration boundaries of the placeholder species will be associated with a PHREEQC input model. In order to conceptualise different boundary conditions assign different numeric values to the concentration of the constant concentration boundaries of the placeholder species. The associated PHREEQC models define the concentrations of geochemical components at the respective boundary after all speciation calculations.

Only fixed concentration boundaries and zero-gradient boundaries can be used with piChem. *Mathematical formulation of transport equation in Transport Settings* in the *FEFLOW Problem Settings* has to be set to **Convective form**.

2. Define a nodal distribution named “**p4f**” in the *User Data* section of the *Data Panel* for the assignment of geochemical properties.

Different numeric values of the nodal distribution are used to identify different geochemical domains, and all nodes with the same value are associated with the same PHREEQC model. In order to conceptualise geochemically heterogeneous domains, assign different values to the nodes in different parts of the domain (see section *Geochemically Heterogeneous Domains*). The PHREEQC models also define the initial concentrations of the geochemical components at the associated nodes after speciation calculations.

3. Define a time series named “**p4f**” for the iteration between reactions and transport in *Edit... -> Time Series*.

Reaction steps are defined by the time steps in this time series. The absolute simulation time, which is accessible via *FEFLOW Problem Settings -> Simulation - Time Control* is added to the time steps in this time series during the simulation.

Time variable boundary conditions can be implemented by setting the numerical value of time steps where a change in boundary conditions occurs to -1 (*minus one*). One set of boundary files has to be associated with every time steps for which a change in boundary conditions is defined (see section *Time-Variable Boundary Conditions*).

The FEFLOW model without the plugin has to be a fully functional flow and transport model.

4. Open the Plug-ins Panel (->View->Panels->Plug-ins Panel), attach and enable piChem.
5. Open the file association editor to associate PHREEQC files with the FEFLOW model using the button *Edit plugin properties*.
 - a. Select the “**p4f**” time series if it is to be used to define reaction time steps. If not, reactions are calculated every n^{th} transport step.
 - b. Define the number n of transport steps which are skipped between reaction calculations. With $n = 0$, reactions are calculated after every transport step. If the “**p4f**” time series is selected for the definition of the reaction times this number has no effect.
 - c. Define the PHREEQC database file. This database is used for all subsequent PHREEQC calculations.
 - d. Associate one PHREEQC input file with every occurring numerical value of the constant concentration boundaries for the placeholder mass transport species and for every time step for which a change in boundary conditions is defined in the “**p4f**” time series (see section PHREEQC Input Files for Boundary Conditions).

The property indicator for boundary conditions is of the form
`BC(boundary_concentration_value, change_time)`.

- e. Associate one PHREEQC input file with every numeric value of the nodal distribution named “**p4f**” (see section PHREEQC Input Files for Initial Conditions).

The property indicator for initial conditions is of the form `IC(user_data_value)`. **All PHREEQC input files have to be fully functional PHREEQC models in combination with the selected database.**

File associations can be redefined any time before the start of the simulation using the *Edit plugin properties* button in the *Plug-ins* Panel. When the FEFLOW fem file is saved, file associations are stored as relative paths.

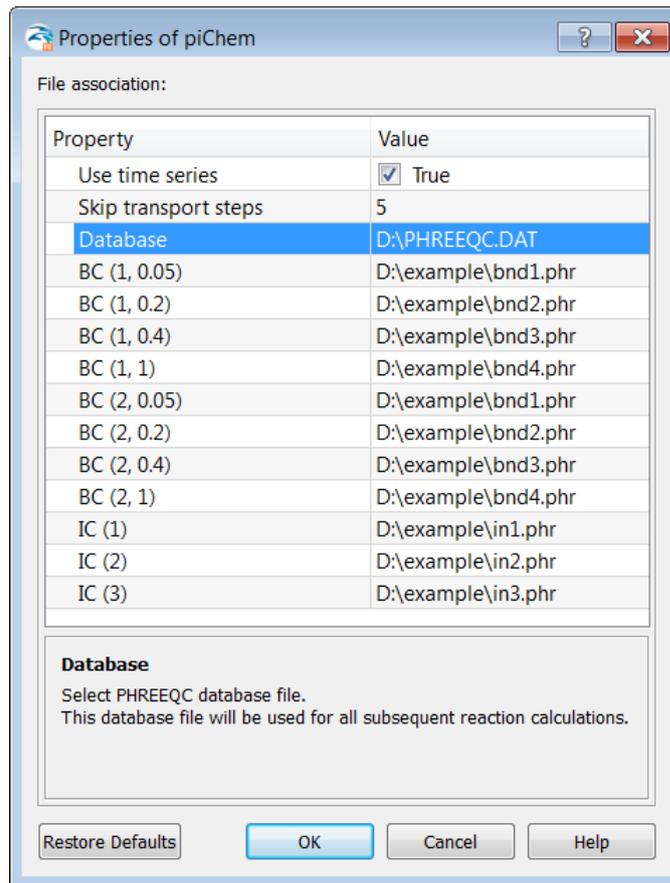


Figure 3.1 File association editor

- Start the simulation using the *Start* button.
 If **not** all boundary conditions and nodal distribution values are associated with valid PHREEQC input files at the beginning of a simulation run, the simulation is automatically stopped.

3.2 PHREEQC Input Files for Boundary Conditions

These files define the component concentrations at the associated boundary as result of PHREEQC reaction calculation. The SOLUTION with the highest cell number in the input file defines the component concentrations at the associated FEFLOW boundary.

3.3 PHREEQC Input Files for Initial Conditions

These files not only define the initial component concentrations at the associated nodes as result of PHREEQC speciation calculations but all geochemical reactions and reactants (EQUILIBRIUM_PHASES, SURFACE, EXCHANGE etc.). For geochemically heterogeneous domains, different numeric values can be attributed to the user-defined nodal distribution, and with this, parts of the geochemical domains can be associated with different PHREEQC models. The SOLUTION with the highest cell number and its reactants define the initial and geochemical conditions at the associated nodes. The

volume of solution is adjusted to the product of saturation and porosity after the initial speciation calculation. To avoid changes in solid phase properties during the initial model run before the solution volume is adjusted to the initial moisture content the initial solution should be set up in equilibrium with the solids.

Solid phase properties such as exchangers, mineral phases and reactive surfaces have to be entered as per litre of soil!

3.4 Result Visualisation and Storage

Output from SELECTED_OUTPUT/USER_PUNCH keyword combinations in any of the PHREEQC input files is transferred to FEFLOW as nodal distributions in the *User Data* section of the *Data Panel*. The nodal distributions are updated after every reactions step and can be visualised using any of FEFLOW's visualisation tools. In addition, they are saved to DAC and DAR files if the simulation is recorded. Only the last loaded definition is considered if multiple SELECTED_OUTPUT/USER_PUNCH definitions with the same index number are encountered. In order to define multiple SELECTED_OUTPUT/USER_PUNCH sections use different indices even if these sections are defined within different PHREEQC input files. To suppress default output from PHREEQC, use the SELECTED_OUTPUT keyword with the flag – *reset false*.

SELECTED_OUTPUT/USER_PUNCH definitions with index 0 (zero) are reserved for the coupling procedure!

3.5 PHREEQC Supplementary Reactions and Database Amendments

Supplementary reaction definitions and redefinitions of reactions in the loaded database (_MASTER_SPECIES, _SPECIES, PHASES, RATES-keywords etc.) should be placed in the first loaded PHREEQC input file (= first PHREEQC file after the database file in the file association dialog).

3.6 PHREEQC Keyword Restrictions

The use of the ADVECTION, DATABASE, INVERSE_MODELLING, RUN_CELLS, TRANSPORT keywords in initial conditions files is not permitted. The use of COPY, DELETE, REACTION, REACTION_TEMPERATURE, REACTION_PRESSURE, MIX and SAVE keywords as well as any _MODIFY keywords in the PHREEQC input files is depreciated.

3.7 Time-Variable Boundary Conditions

The time series “**p4f**” in the FEFLOW model is not only used to define the iteration between transport and reaction calculations (see section Split Operator) but also to implement time-variable boundary conditions. A change in boundary concentrations occurs at every time step where the numerical value of the time series is set to -1 (*minus one*). PHREEQC model files have to be associated with the corresponding boundary nodes for every change of boundary conditions. PHREEQC input file can be associated

multiple times if certain boundary conditions do not change at time steps that indicate a changes.

3.8 Geochemically Heterogeneous Domains

Geochemical reactions may take place only in certain parts of the domain or with different geochemical parameters such as reaction kinetics, CEC, amount of mineral phases etc. In order to conceptualise geochemically heterogeneous domains, different numerical values in the user-defined nodal distribution are associated with different PHREEQC model files.

Since, ever condition has to be defined by a separate PHREEQC model, continuous changes in boundary conditions or geochemical reaction properties throughout the domain are not feasible.

3.9 Temperature Dependence

For FEFLOW problems that involve heat transport, temperature in °C is automatically transferred to PHREEQC prior to each reaction step in order to account for the temperature dependence of speciation reactions. Consult the PHREEQC manual for details on the mode of temperature dependence of reactions.

3.10 Variable Liquid Phase Saturation

For FEFLOW problems that involve variable liquid phase saturation (Richards' equation), the solution volume in PHREEQC is updated prior to each reaction step. The solution volume in PHREEQC corresponds to the moisture content in FEFLOW times the default cell volume of 1L. Convergence problems in PHREEQC may be more frequent in situations with very low moisture contents. Thus, reasonable moisture contents should be maintained also in very dry situations through the adjustment of residual saturation in the soil moisture retention (*unsaturated flow model*).

3.11 Charge Balance Requirements

Although not strictly required, PHREEQC input models should produce charge-balanced solutions. Use the -charge identifier with the appropriate property in the SOLUTION keyword to ensure charge balance. Since minor charge imbalances may be introduced by SURFACE reactions if the ion composition in the diffuse layer is not explicitly calculated, charge imbalance (in equivalents) is transported in the FEFLOW calculations as an additional component.

4 Coupling Procedure

4.1 Theoretical Background

The coupling of geochemistry and hydrology in piChem is based on the assumption that aqueous phase flow, be it fully saturated or variably saturated, can be expressed as the transport of the individual components that constitute the aqueous phase [11,12]. Thus following Wissmeier and Barry [13], the classical advection diffusion/dispersion equation is employed for multi-component transport [14-16],

$$\frac{\partial \theta c_i}{\partial t} = -\nabla \cdot (\mathbf{q} c_i) + \nabla \cdot (\theta \bar{\mathbf{D}} \nabla c_i) + S \quad (4.1)$$

where θ is the relative liquid phase saturation ($\text{m}^3 \text{m}^{-3}$), c_i (kg m^{-3}) is the concentration of solution species i , \mathbf{q} (m s^{-1}) is the Darcy flux, $\bar{\mathbf{D}}$ ($\text{m}^2 \text{s}^{-1}$) is the hydrodynamic dispersion tensor, and S ($\text{kg m}^{-3} \text{s}^{-1}$) is a source-sink term. Since the liquid phase is composed of solution species according to

$$\theta = \frac{\sum_i n_i m_i}{\rho} \quad (4.2)$$

where n_i (mol m^3) is the moles of solution species i in a control volume with a molar weight m_i (kg mol^{-1}), the application of Eq. 1 to all solution species in the liquid phase effectively yields phase mass balance according to

$$\frac{\partial \rho \theta}{\partial t} = -\nabla \cdot \rho \theta \mathbf{v} \quad (4.3)$$

here \mathbf{v} is the barycentric mass flow velocity of the liquid phase [17]. This implies that the net mass flux induced by diffusion/dispersion [18] can be neglected, which is a common assumption [19-22] that is warranted using a single species independent diffusion coefficient.

With the separation of aqueous phase flow, component transport and geochemical reactions (see section Operator Splitting

The split-operator scheme decouples the simultaneous and dependent processes of solute transport and geochemical reactions into independent, sequentially solved calculation steps [29-35]. piChem employs a non-iterative sequential approach (SNIA) for operator splitting with user-defined splitting time steps Δt . At every reaction step, the solution composition in terms of ion species is reconstructed from the transported element assembly and the charge balance before it is speciated with the solid and gaseous phases. After the reaction step, the transport equations are updated with the resulting element concentrations in the aqueous phase. In the current version, liquid phase saturation is not updated after reactions.

The numerical error introduced by operator splitting is on the order of $O(\Delta t)$ [11, 13]. The effect of operator splitting on numerical accuracy also in unsaturated conditions has been thoroughly investigated by the authors in [26-32]. In practical cases, the error can be oftentimes reduced by constraining the time step by the performance index, which is the product of the grid Courant and Péclet numbers [32]. However, the performance index can only be calculated as a posteriori analysis in the current version.

The influence of the splitting time step in the sequential non-iterative approach is very problem-specific. Similarly, to mesh convergence, comparative studies with variations of the splitting time-step are required to prove time step convergence for the aspired solution accuracy.

Program Flow), the number of transport equations that need to be solved can be greatly reduced by a basis switch to chemical elements [23-25]. In this case, the predominant components that constitute the aqueous phase are hydrogen and oxygen, which need to be included in the transport process. A small charge imbalance in the solution may be induced by surface complexation reactions where the diffuse layer composition is not explicitly calculated. In order to account for this, charge balance is transported as an additional component [27, 28].

4.2 Operator Splitting

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4.3 Program Flow

When the simulation is started, piChem checks whether the file association is consistent with the current boundary conditions and nodal reference distribution and stops the simulation otherwise. If the check was successful, piChem analyses all user-defined PHREEQC model files and calculates their component concentrations. Then, piChem adds the set of PHREEQC components that participate in any reaction to FEFLOW's mass transport species by copying the user-defined placeholder species. As a result, all PHREEQC components have the same transport properties as the placeholder species. Subsequently, an independent geochemical cell is created for every FEFLOW node in the simulation domain. The geochemical properties of the cells are assigned according to the user-defined nodal reference and the association of PHREEQC model files. Next, piChem adjusts the boundary and initial concentrations of FEFLOW's mass transport components according to the PHREEQC boundary models. Finally, an additional nodal reference

distribution is constructed for all PHREEQC output parameters according to SELECTED_OUTPUT/USER_PUNCH definitions.

Whenever piChem encounters a split operator time step, component concentrations in PHREEQC's cell solutions are adjusted according to the current FEFLOW mass transport concentrations and reactions are calculated in PHREEQC for the period since the last split operator time step. If the split operator time step is labeled as boundary change time step, boundary concentrations in FEFLOW are reset according to the designated PHREEQC boundary model files. After updating the FEFLOW component concentrations and nodal reference distributions with the result of the reaction calculations, flow and transport simulations proceed until the next split operator time step.

4.4 Negative Component Concentrations

Finite element solutions of solute transport frequently lead to oscillatory behavior with negative concentrations near sharp concentration fronts [19, 33-35]. Even though oscillations can be opposed by various numerical amendments [36, 37], non-negative concentrations in the entire domain can be generally not guaranteed. Obviously, geochemical reaction calculations in PHREEQC are only meaningful for physical, that is, positive input concentrations as PHREEQC defines solutions in terms of moles of elements.

Therefore, negative concentrations from transport calculations are set to zero during reaction calculations. After the reaction step, negative concentrations from the previous transport step are added to the output concentrations from the reaction step. This procedure remedies significant mass balance errors that would otherwise result from the repeated adjustment of negative output from transport calculations to zero. Nevertheless, it is recommended to avoid oscillations in transport calculations through appropriate domain discretisation [38, 39].

4.5 Offset Components

Since FEFLOW employs one error norm for all primary variables as convergence criterion, components with a large concentration offset are calculated with lower relative accuracy [36]. This is particularly relevant for the components oxygen and hydrogen, whose concentrations are generally in the range of 55.3 and 110.6 mol/L, respectively. Despite their large absolute concentrations, minor inaccuracies in the transport of these components may have intolerable consequences on solution pe and pH. In order to improve the numerical accuracy for oxygen and hydrogen, their pure water concentrations are subtracted prior to transport and added again before reaction calculations. Offset components are marked by an asterisk (*) in their FEFLOW species name.

5 Application Examples

5.1 Pesticide Infiltration with Degradation Chain: *Pesticide*

This example simulates the transient infiltration of a pesticide containing solution into an initially dry, layered soil together with the decomposition of the pesticide into toxic daughter products. The simulation is inspired by but does not exactly duplicate the application example no. 7 of the software packages SWMS-2D [40] and HYDRUS-2D [41]. Because of FEFLOW's built-in capabilities to calculate kinetic degradation chains, this example can be regarded as a verification of the coupling procedure. For direct comparison, reactions are calculated for one set of solutes by PHREEQC and for another set by FEFLOW, where flow and transport is always calculated by FEFLOW.

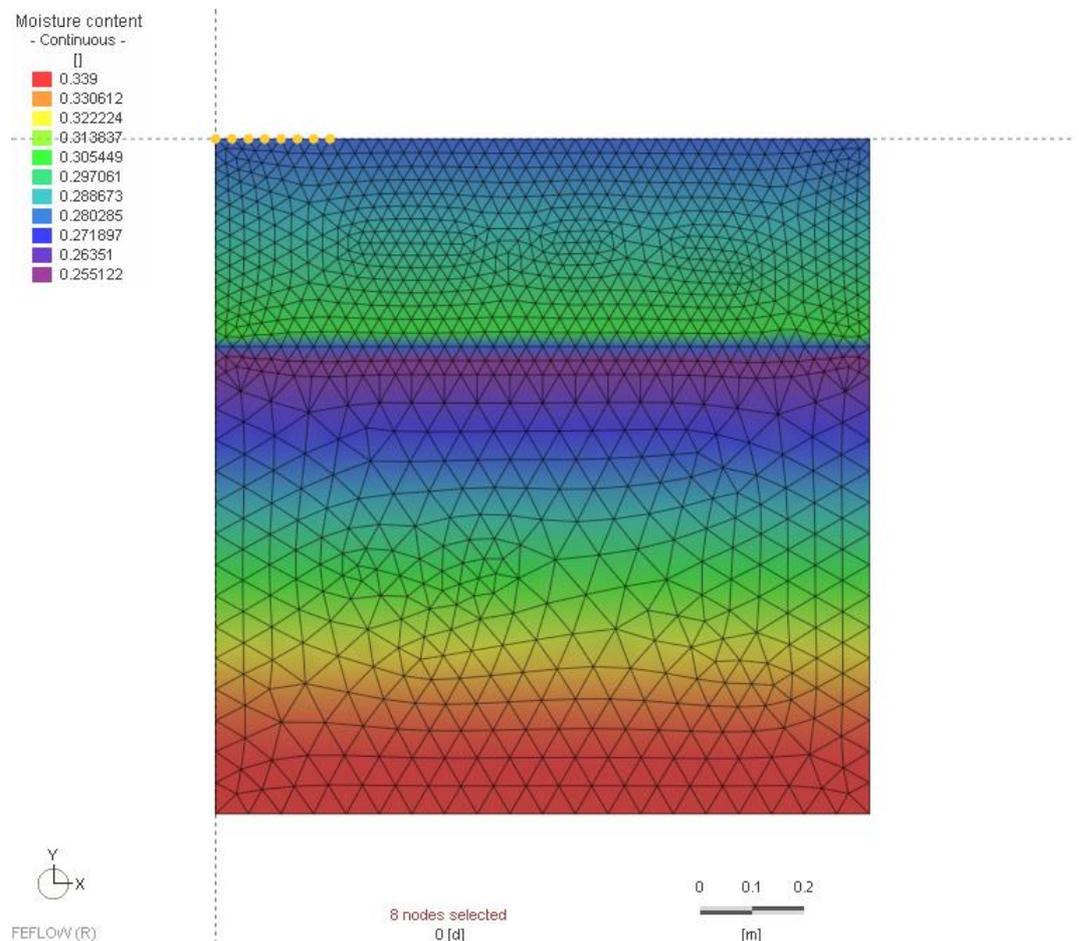


Figure 5.1 Radially symmetric simulation domain of the pesticide simulation with finite element mesh and initial moisture content. The source zone is indicated by the highlighted nodes at $y = 0$

The radially symmetric simulation domain with 1109 nodes is displayed in Figure 5.1. The soil is divided into two subdomains with different hydraulic properties, i.e., higher conductivity and lower saturated water content below $y = -0.4$ m. The initial hydraulic head h (m) of the simulation is set to -1.2 m. The resulting moisture content (in colour in Figure 5.1) shows a discontinuity at the layer boundaries.

The pesticide *Aldicarb* enters the unsaturated soil via a constant concentration boundary at the top in the region $y = 0$ m, $0 \text{ m} \leq x \leq 0.2 \text{ m}$ (marked by highlighted nodes in Figure 5.1). Transformations between *Aldicarb* and its breakdown products are governed by first-order rates according to Eqs. (4-9), where n_i denotes moles of the chemical in the control volume (mol L^{-1}), $k_1 - k_5$ are reaction constants (s^{-1}), c_i denote total molal concentrations ($\text{mol kg}_{\text{water}}^{-1}$) and w stands for the kilograms of water in the control volume (kg L^{-1}).

$$\text{Aldicarb (a):} \quad \frac{\partial n_a}{\partial t} = -(k_1 c_a + k_2 c_a)w \quad (5.1)$$

$$\text{Aldicarb Oxime (ao):} \quad \frac{\partial n_{ao}}{\partial t} = k_1 c_a w \quad (5.2)$$

$$\text{Aldicarb Sulfoxide (asx):} \quad \frac{\partial n_{asx}}{\partial t} = (k_2 c_a - k_3 c_{asx} - k_4 c_{asx})w \quad (5.3)$$

$$\text{Aldicarb Sulfoxide Oxime (asxo):} \quad \frac{\partial n_{asxo}}{\partial t} = k_3 c_{asx} w \quad (5.4)$$

$$\text{Aldicarb Sulfone (asn):} \quad \frac{\partial n_{asn}}{\partial t} = -(k_4 c_{asn} + k_5 c_{asn})w \quad (5.5)$$

$$\text{Aldicarb Sulfone Oxime (asno):} \quad \frac{\partial n_{asno}}{\partial t} = k_5 c_{asn} w \quad (5.6)$$

The reaction chains together with first-order rate constants are displayed schematically in Figure 5.2.

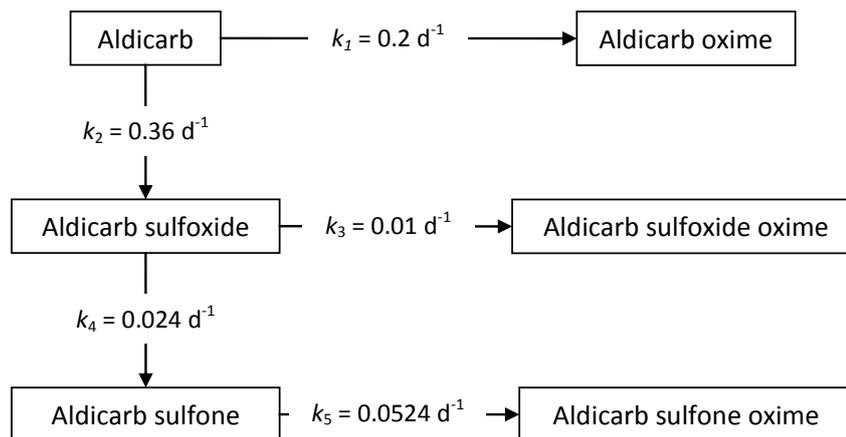


Figure 5.2 Aldicarb reaction chain.

The simulation uses the database file *pesti.dat* that only contains the minimum species definitions for water together with the necessary reaction definitions for Aldicarb and its daughter products. The coupling time step Δt was set to 0.02 days during the first day and increased to 0.2 days for the remaining 7 days of the simulation period.

In order to verify the coupling procedure, mass concentrations are compared along the centerline ($x = 0$) for simulations where reactions were computed using the coupling (PiCHEM) and using the fully implicit method in FEFLOW (Figure 5.3). Small differences in chemical concentrations can be attributed to the splitting error. The magnitude of these differences decreases linearly with Δt . It has to be noted that the difference between the coupled and the fully implicit method is largest directly after a reaction step. The presented results are recorded after half a transport step.

If negative concentrations from the previous transport step were not summed to the concentrations after transport, an obvious mass balance error with overestimation of all pesticide species would be produced. Thus, the results prove the accuracy of the coupling procedure and particularly the successful suppression of significant mass balance errors that would result from the uncompensated adjustment of concentrations to positive values during reaction calculations (see section Operator Splitting).

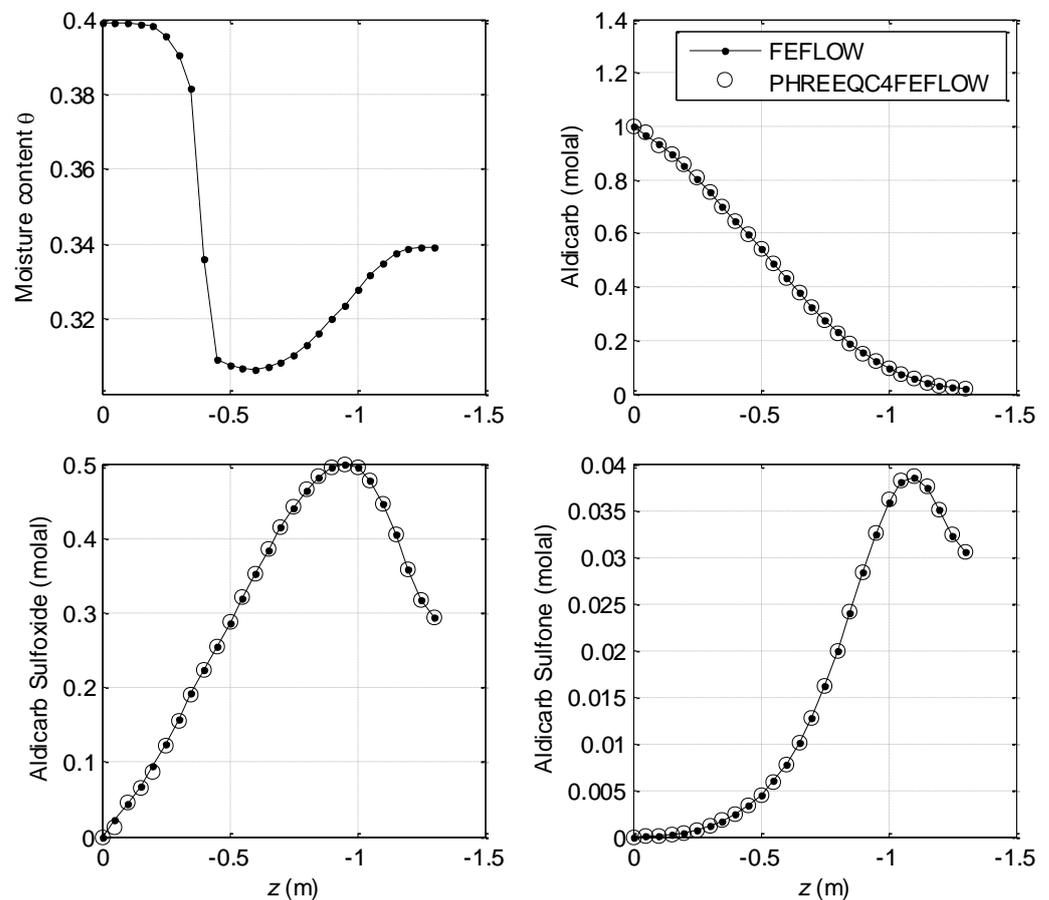


Figure 5.3 Comparison of concentrations from the coupling procedure and FEFLOW alone 8 d after start of the infiltration experiment

5.2 Reactive Transport Benchmark: *MoMaS_modi*

This example follows the reactive transport benchmark MoMaS [42, 43] for the definition of the simulation domain and the hydraulic properties for flow and transport. However, artificial reaction networks are used by the original benchmark. In the presented application, complex reactions based on activity corrected solution speciation and the default PHREEQC database *phreeqc.dat* were introduced to demonstrate the capabilities of piChem in natural environments. The geochemical model combines the simulation of the snow-plough effect [44-46] induced by cation exchange with the kinetic dissolution and precipitation of calcite (CaCO_3^s) according to the sophisticated rate expression by Plummer et al. [47].

The domain consists of a two-dimensional rectangular box discretised into 14212 triangular elements (7266 nodes). The domain has two inlet sections and an outlet. At the two inlets, a flux of intensity 0.0225 m s^{-1} is assigned, and a hydraulic head of 1 m is prescribed at the outlet. Aqueous phase flow is set up for fully saturated conditions so that in combination with the constant boundary conditions a steady flow field evolves. In analogy to a typical clay material, the vertical subdomain wall in the centre of the domain (Medium B) has lower permeability, a higher porosity and dispersivity, and a four times as high cation exchange capacity compared to the rest of the domain (Medium A).

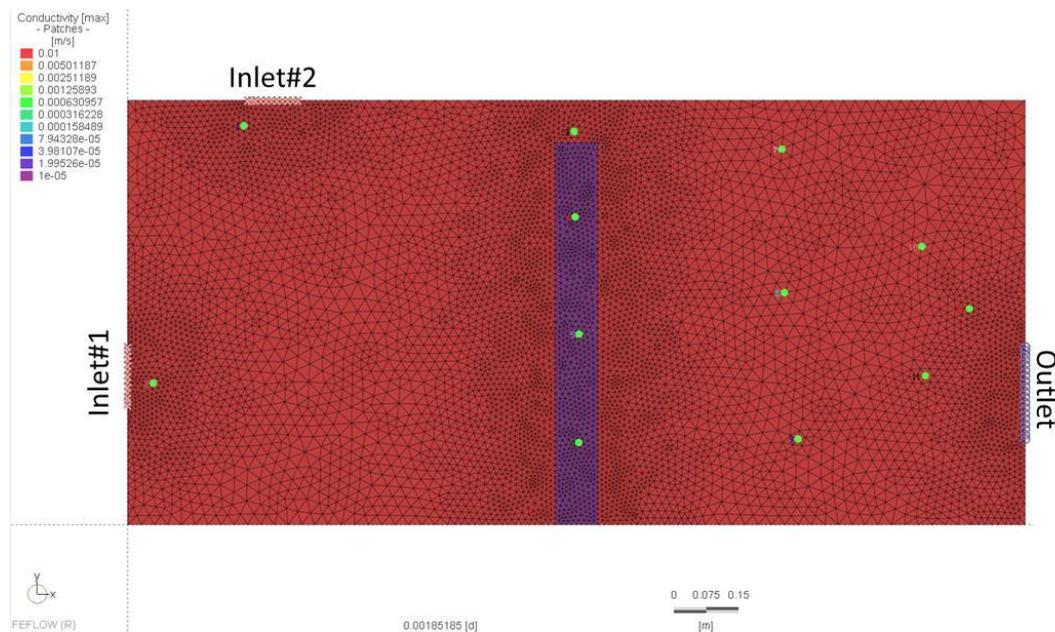


Figure 5.4 Simulation domain of *MoMaS_modi* with finite element mesh and hydraulic conductivity. Medium A is red; Medium B is purple

Table 5.1 Hydro-dispersive parameters of the *MoMaS_modi* problem

	Medium A	Medium B
Porosity [-]	0.25	0.50
Hydraulic conductivity [m/s]	10^{-2}	10^{-5}
Longitudinal dispersivity [m]	10^{-2}	6×10^{-2}
Transverse dispersivity [m]	10^{-3}	6×10^{-3}

Figure 5.4 shows the simulation domain of MoMaS_modi with its finite element discretisation. The conductivity field, shown in colour, depicts the low-permeability zone in the centre of the domain. The hydro-dispersive parameters are given in Table 5.1.

The initial solution in the both subdomains is in equilibrium with calcite and atmospheric CO₂ at a partial pressure of 10^{-3.5} atm. Since Ca⁺² is the only exchanging ion, all exchange sites are initially occupied by calcium.

At boundary 1, a solution in equilibrium with highly soluble natron (Na₂CO₃·10H₂O) and atmospheric oxygen at 10^{-0.7} atm is introduced. Due to the equilibration with natron, the boundary solution has a pH of 11.51, a sodium concentration of 2.61 mol L⁻¹ and an equally high alkalinity.

The inflowing solution at boundary 2 is equilibrated with 1 mole of magnesite (MgCO₃) as well as atmospheric CO₂ and oxygen while maintaining a pH of 4 through the titration with HCl. In addition, a non-reactive tracer is declared using the SOLUTION_MASTER_SPECIES and SOLUTION_SPECIES keywords, and entered into the solution at a concentration of 1 mmol L⁻¹.

When the inflowing solution at boundary 1 equilibrates with the initial exchanger, the intruding sodium almost entirely replaces initially sorbed calcium since the concentration effect overrides the higher affinity of the exchanger for calcium ions [48]. Together with the large concentration of carbonate ions in the inflow, desorption of calcium leads to an oversaturation with respect to calcite behind the infiltration front. In this fast flowing system, the kinetics of calcite precipitation act on the same time scale as transport (as indicated by the Damköhler numbers [19, 49, 50]). As a result of this time-dependency, calcite precipitates as a ring around the inlet (see Figure 5.5). Similarly, magnesium in the inflowing solution at boundary 2 exchanges against calcium. Since the pH of the solution is acidic, oversaturation with respect to calcite as result of the exchange process is not as pronounced as with the inflowing solution 1 (see Figure 5.5).

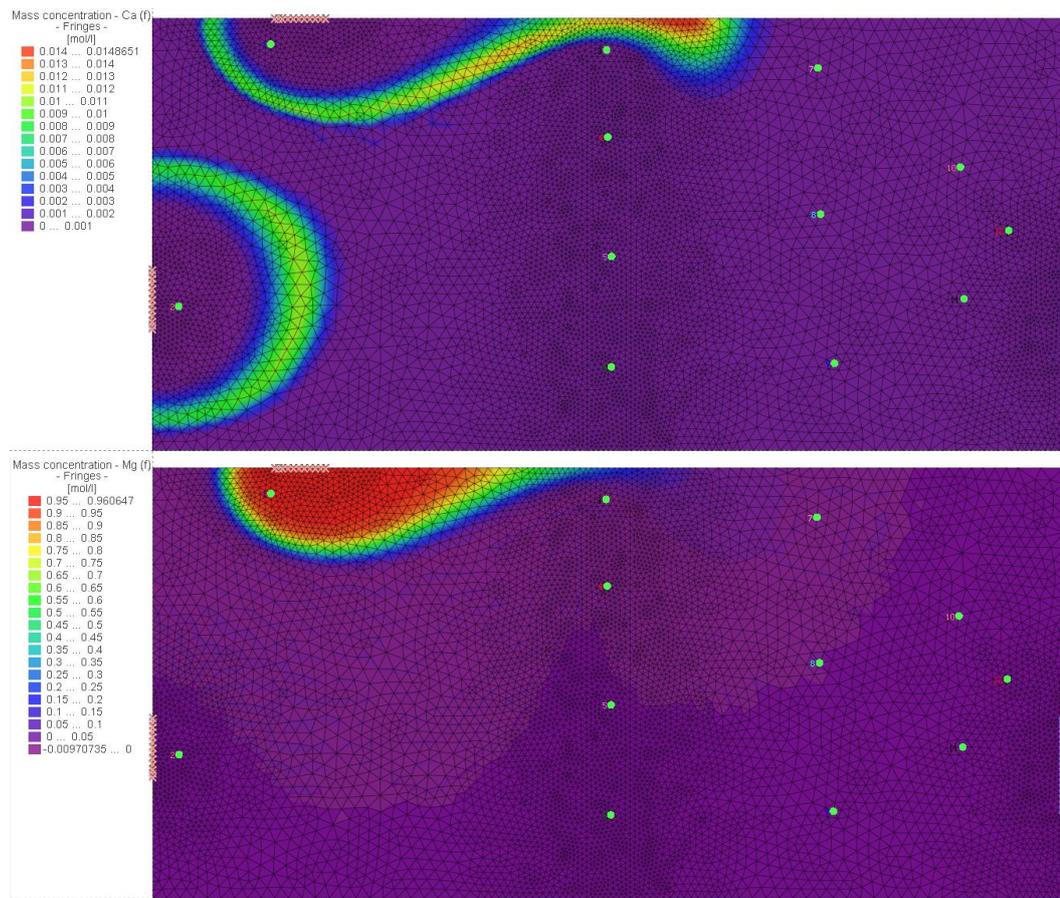


Figure 5.5 Calcite and Magnesium distribution at time 0.0001 days

5.3 3D Aquifer Simulation with Heavy Metal Spill and Surface Complexation: *Spill_3D_modi*

The model *spill_3D_modi.fem* extends the example *spill_3D.fem* from FEFLOW's collection of demo applications by including the geochemistry of a heavy metal spill with detailed ion speciation and retention due to surface adsorption. The simulated processes are mineral dissolution/precipitation, cation exchange and surface complexation with variably charged surfaces. The contaminant enters the aquifer in a source zone that is conceptualised via a constant concentrations boundary in the top layer of the aquifer, where the contamination site is in contact with the aquifer. The aquifer is divided vertically into three compartments where the top and the bottom compartment have the same hydraulic and geochemical properties. Water flow is driven by the hydraulic gradient from the eastern to the western boundary. In addition, several multi-layered wells are distributed in the domain, which alter the flow field through the addition or removal of water to or from different aquifer layers.

The contaminating solution contains a mixture of the heavy metals cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn). For simplicity, inflow concentrations are set to 1 mmol L^{-1} for all heavy metals. The anion species *Charge_dummy* is declared using the SOLUTION_MASTER_SPECIES and SOLUTION_SPECIES keywords. Its concentration is adjusted to balance the charge of the positive heavy metal ions. After the initial speciation, the pH in the inflowing solution is adjusted to 4 using hydrochloric acid.

Within the aquifer compartments, the solution is equilibrated with a cation exchanger at 1 mmol L^{-1} soil. In addition, the solution is in equilibrium with a calcite phase and the kinetic dissolution and precipitation of a large amount of quartz in the aquifer is considered [51,52]. In the middle aquifer compartment with lower conductivity and dispersivity, the heavy metals are additionally adsorbed by charged surfaces with pH and ionic strength dependent charge density according to the surface complexation model by Dzombak and Morel [6]. Furthermore, the initial amount of calcite is set to 1 mol L^{-1} soil.

The reaction zones in the layered aquifer are displayed in Figure 5.6. From top to bottom, the following reaction zones are differentiated.

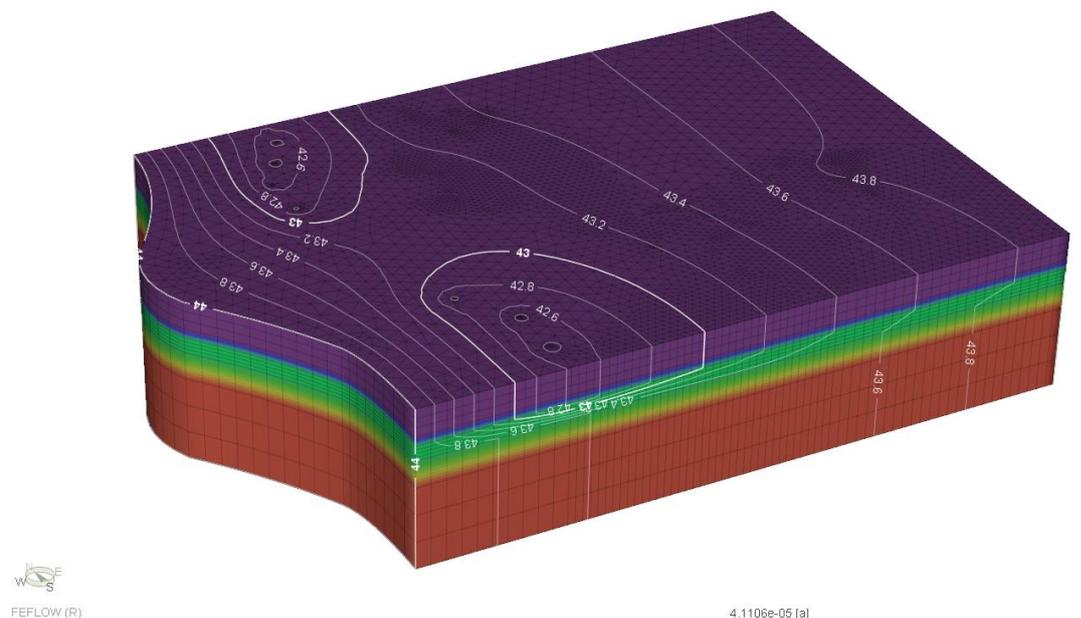


Figure 5.6 Reaction zones and flow field of the *Spill_3D_modi* problem

Reaction zone 1:

- Cation exchanger
- Calcite (equilibrium phase)
- Quartz (kinetic phase)
- Initial equilibrium with Calcite, atmospheric O₂ and CO₂

Reaction zone 2:

- No Calcite
- Surface complexation on Ferrihydrite

Reaction zone 3:

- Quartz (kinetic phase)

6 References

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