Porosity & Permeability evolution plug-in for FeFlow

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1 Conceptual model

Water flow with specific chemical properties modifies can modify the geometry of pores in porous media. Mineral precipitation obstructs or reduces the radius of pores. Mineral dissolution enlarges pore radius or increases the connectivity between pores. The macroscopic effects of these pore scale processes are changes in porosity and permeability at the Darcy scale.

The input to simulate porosity and permeability evolution in porous media is the mass of products resulting from the reaction between the liquid phase (reactants) and the solid phase (porous media). FeFlow is used as the mainstay for simulating flow and mass transport in porous media. The mass of reactants to estimate changes in porosity and permeability may come from FeFlow Reaction Kinetics editor or PiChem plug in.

Add here intro to FeFlow kinetics editor….

PiChem (**ref**) is a FeFlow plug-in that allows access to PHREEQC code. PHREEQC is an iterative solver of reactions in liquid phase (**ref**). It can simulate equilibrium and kinetic reactions that occur in porous media.
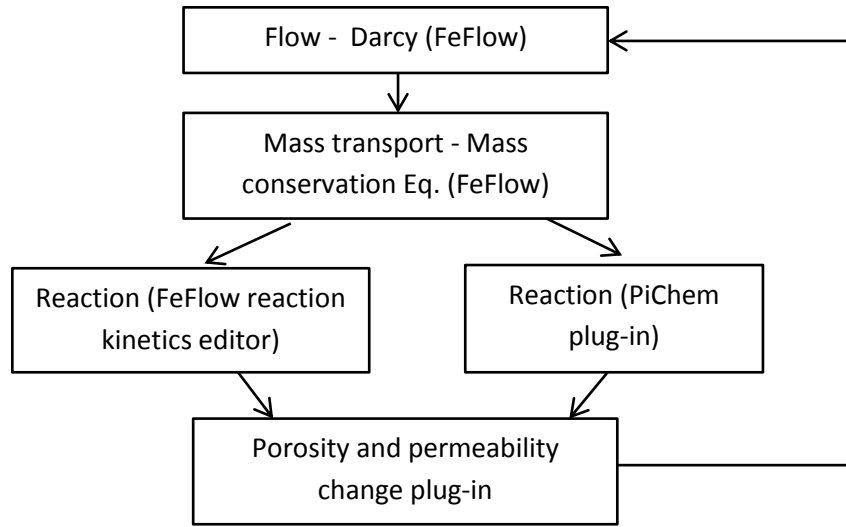

Figure 1. phi/K evolution plug-in position in simulation environment

1.1 Porosity evolution by mass conservation equation

Lichtner (1988) proposed a continuum representation of mass transport in a porous medium comprising reacting minerals and fluid. Homogeneous reactions between aqueous species are assumed to be sufficiently rapid to maintain local equilibrium within the fluid phase. Conversely, heterogeneous reactions involving minerals and fluid are described through kinetic rate laws where equilibrium is just a special case.

Chemical equations can be arranged as matrix of stoichiometric coefficients corresponding to aqueous complexes and minerals.

$$\sum_{j=1}^{N} v_{ji} A_j \rightleftarrows A_i \qquad \text{eq 1}$$

$$\sum_{j=1}^{M} v_{jr} A_j \rightleftarrows A_r \qquad \text{eq 2}$$

Aqueous species are noted by $\{A_j\}$(j = 1,…,N) and minerals as $\{A_r\}$(r=1,…,M), both considered primary species while aqueous complexes are noted by symbol A_i and are considered secondary species. v_{ji} and v_{jr} refer to stoichiometric reaction matrices. The reaction between aqueous species and aqueous complexes is described by Eq 1 and the reaction between mineral species and aqueous species is described by eq 2 (**Lichtner, 1988**)

Continuum mass conservation equation for the primary species can be expressed in the following system of partial differential equations:

$$\frac{d}{dt}(\phi\,\psi_j) + \nabla \cdot \Omega_j = -\sum_{r=1}^{M} v_{jr}\,\frac{\delta\Xi_r}{\delta t} \qquad (j = 1, \dots, N)$$

eq. 3

$$\frac{d}{dt}\left(\frac{\phi_r}{\overline{V}_r}\right) = \frac{\delta\Xi_r}{\delta t} \qquad (j = 1, \dots, M)$$

eq 4

N refers to aqueous species and M to mineral species (solid). ϕ is the porosity of the porous medium, ψ_j is generalized concentration and Ω_j generalized flux for the $j$thprimary species. ϕ_r is the volume fraction of mineral, Ξ_r is the reaction progress density of the rth mineral volume with molar volume $\overline{V}_r$. Right hand side of equations 3 and 4 display the source/sink terms describing the irreversible reaction of minerals and fluid with reaction rates $\delta\Xi_r/\delta t$ (**Lichtner, 1988**).

Since molar volume $\overline{V}_r$ of a mineral is constant, equation 4 that deals with changes in porosity over time can be rewritten as:

$$\frac{d\phi_r}{dt} = \overline{V}_r\,\frac{\delta\Xi_r}{\delta t}$$

eq 5

Integrating equation 5 with respect to time while assuming reaction rate is constant at a certain point of infinitesimal length of the whole reaction time yields a linear dependence of volume fraction $\phi_r$on time according to eq 6 (**Lichtner, 1988**).

$$\phi_r(t + \Delta t) = \phi_r(t) + \overline{V}_r \cdot I_r \cdot \phi(t = 0) \cdot \Delta t$$

Eq 6

$\phi(t = 0)$: initial porosity
$\phi_r(t + \Delta t)$: mineral volume fraction in time $t + \Delta t$
$\phi_r(t)$: mineral volume fraction in previous timestep (Mineral species volume / Total Volume)
$\overline{V}_r$: molar volume (Molar mass / density), i.e. (grams/mol) / (grams/liter)
$I_r(\phi_r)$: reaction rate in function of mineral volume fraction (mol/Volume*time)
Δt: timestep length (time)

Mineral volume fraction is:

$$\phi_r = \frac{V_i}{\sum_j V_j}$$

Eq 7

In eq. 7, V_i is the volume of a single mineral species and the sum in the denominator is the sum of all volumes of each mineral species that compose a representative element of porous media.

Once mineral fraction change $\phi_r(t + \Delta t)$ is known, porosity change can be estimated by adding the sum of all volume fraction changes for each mineral species, see eq. 8

$$\phi(t + \Delta t) = \phi(t) - \sum_{r=1}^{M}(\phi_r(t + \Delta t) - \phi_r(t))$$

Eq 8.

To clarify the interaction of equations 6 and 8, assume a dissolution reaction in a single mineral species porous media with initial porosity of 0.3 and initial mineral volume fraction of 0.7, see **table 1**. The change of mineral volume fraction is -0.1 between times t and t + $(t + \Delta t)$.

	time (t)	time $(t + \Delta t)$
ϕ	0.3	0.4
ϕ_r	0.7	0.6

Since it's only 1 mineral species, the sum on the right side of eq. 8 is equivalent to -0.1. Then, the negative value of mineral volume fraction changes into a positive increment in porosity reflected on the increase in porosity from 0.3 to 0.4.

If porous media is composed only by a single mineral species, eq. 6 and 8 can be merged into a single equation, see eq 9.

$$\phi(t + \Delta t) = \phi(t) - \overline{V}_r \cdot I_r \cdot \phi(t = 0) \cdot \Delta t$$

Eq 9.

The typical units in eq 9. are:

$$\phi(t + \Delta t) = \phi(t) - \left(\frac{volume}{amount\ of\ substance}\right) \cdot \left(\frac{amount\ of\ substance}{volume * time}\right) \cdot \phi(t = 0) \cdot (\text{time})$$

$$\phi(t + \Delta t) = \phi(t) - \left(\frac{liters}{mol}\right) \cdot \left(\frac{mol}{liters * second}\right) \cdot \phi(t = 0) \cdot (\text{seconds})$$

If the chemistry calculations are done with other units such as milligrams per liter (mg/L), molar volume $(\overline{V}_r)$ can be substituted by density in eq. 9. Molar volume $(\overline{V}_r)$ definition is the following (sew eq. 10), where M is equal to molar mass (mass/mol) and ρ is density in (mass/volume) :

$$\overline{V}_r = \frac{M}{\rho}$$

Eq. 10

Substituting the molar volume $(\overline{V}_r)$ in **eq 9** with eq. 10 yields the following where reaction rate is in mol/volume*time.

$$\phi(t + \Delta t) = \phi(t) - \frac{M}{\rho} \cdot I_r \cdot \phi(t = 0) \cdot \Delta t$$

However, if reaction rate (I_r) is already in mg/L, molar mass (M) is no longer necessary, see **eq. 11**

$$\phi(t + \Delta t) = \phi(t) - \frac{I_r \cdot \phi(t = 0) \cdot \Delta t}{\rho}$$

Eq. 11

Typical units for eq. 11 are the following:

$$\phi(t + \Delta t) = \phi(t) - \frac{\left(\frac{milligrams}{liters * second}\right) \cdot \phi(t = 0) \cdot (seconds)}{(milligrams/liter)}$$

Eq. 9 was used by Ayora et. al **(1998)** to estimate porosity change in a simulation of the genesis of dedolomites, the replacement of dolomite by calcite. Eq. 11 was used by **Sanford & Konikow (1989)** to estimate porosity change in coastal aquifer due to the mixing of fresh and saline water intrusion.

1.2 Porosity evolution by the derivation of porosity definition

The linear model that describes porosity evolution can be obtained too by manipulating the definition of porosity, **eq 12**.

$$\phi = \frac{Volume\ voids}{Total\ volume} = \frac{V_v}{V_T}$$

Eq 12

Total Volume is assumed as constant over time. If there is precipitation or dissolution of minerals the volume of voids will change. Thus, the change of porosity is shown in **eq 13**:

$$\Delta\phi = \frac{\Delta V_v}{V_T}$$

Eq 13

The change in the volume of voids (V_v) can be estimated as the change in mass of minerals divided by density. The change in mineral mass is given by reaction rate(r), timestep length(Δt), porosity (ϕ) and total volume (V_T) , see **eq 14**. The results of models of homogeneous reactions, between liquids and solids, are given usually as solutions (mol/liter). Thus, to estimate the amount of mineral mass the product of rate (r) and time step (Δt) must be multiplied by porosity (ϕ) and total volume (V_T) to estimate the effective solution volume per volume of solid.

$$V_v = \frac{\Delta\ Mineral\ Mass}{\rho} = \frac{r \cdot \Delta t \cdot solution\ volume}{\rho} = \frac{r \cdot \Delta t \cdot \phi \cdot V_T}{\rho}$$

Eq. 14

Merging eq. 14 with eq. 13 yields:

$$\Delta\phi = \frac{\Delta V_v}{V_T} = \frac{\frac{r \cdot \Delta t \cdot \phi \cdot V_T}{\rho}}{V_T}$$

The variable total volume (V_T) cancels out and the result, eq 15, is equal to eq. 11.

$$\Delta\phi = \phi(t + \Delta t) - \phi(t) = \frac{r \cdot \Delta t \cdot \phi}{\rho}$$

Eq. 15

One lesson from this derivation is that eq 11 is invariant to the magnitude of the volume represented by an element in a finite element model. The element can be 2D or 3D and the element can represent either 1 liter or 100 liters and eq. 11 will apply.

1.3 Porosity evolution equation to use in the plug-in

Eq. 9 describes permeability increase when dealing with reactions rates in mol units. However, for the porosity evolution plug-in the input is not the reaction rate but the products of reactions. Thus, the units are mols when using PiChem and mg/L when using FeFlow Reaction Kinetics Editor. Then the equation included in the plug-in is the following:

$$\phi(t + \Delta t) = \phi(t) - a \cdot \overline{V}_r \cdot c_i \cdot \phi(t = 0)$$

Eq 16

$\phi(t = 0)$: initial porosity
$\phi_r(t + \Delta t)$: mineral volume fraction in time $t + \Delta t$
$\phi_r(t)$: mineral volume fraction in previous timestep
a = units conversion, 1 for mol/L input, it has to be calculated for mg/L input
$\overline{V}_r$: molar volume (calcite = 0.0369 Liters/mol)
c_i: amount of mineral precipitated/dissolved during time set (mol/L)

Eq. 16 is ready to work with the output of PiChem plug-in since it is mol/Liter. However, to use FeFlow Reaction Kinetics Editor output (mg/L) as input for porosity evolution plugin variable **a** in eq. 16 has to be estimated with **eq 17** in function of mineral reaction being simulated:

$$a = \frac{1}{1000} \cdot \frac{c_i}{M}$$

Eq 17

1/1000: conversion from mg/L to g/L
c_i: reaction out as concentration in mol/L
M: molar mass in grams/mol

1.4   Permeability evolution

The author has conducted a literature review of porosity and permeability relationship models. Among the models found on literature, the model mentioned by **Bernabé et al. (2003)** is more flexible to simulate ongoing precipitation/dissolution processes in porous media. Kozeny-Carman models uses a fixed exponent of 3 while Bernabé model, **eq 18**, uses a variable exponent depending on the ongoing process, the rate and the stage of development of such process. More details on the review……

$$k(t + \Delta t) \ = \ k_0 \left(\frac{\phi(t + \Delta t)}{\phi_0} \right)^\alpha$$

eq 18

$k(t + \Delta t)$ = permeability/hydraulic conductivity after reaction

k_0: initial permeability/hydraulic conductivity

$\phi(t + \Delta t)$: porosity after reaction

ϕ_0: initial porosity

α: variable exponent depending on process type and rate of development

In, eq 18 , the term elevated to exponent α contains adimensional porosity. $k(t + \Delta t)$ is related to k_0 by an dimensionless variable, thus eq 18 can be used for permeability either in units of m^2, milliDarcys, or even meters/second the SI units for hydraulic conductivity.

If the simulation only considers the development of porosity but not permeability, just add a 0 as exponent alpha.

The conversion between permeability in milliDarcy to m^2 is given by **eq 19** while the conversion from permeability in m^2 to hydraulic conductivity in meters/sec is given by **eq. 20** where pure water density (ρ_w) is 1000 kg/m^3 and dynamic viscosity of water (μ_w) at 25°C is 1.002e-3 N*s/m^2

$$k \ (m^2) = \frac{k \ (mD) \cdot 9.869e - 13}{1000}$$

Eq 19

$$K(m/s) = \frac{k \ (m^2) \cdot \rho_w \cdot g}{\mu_w}$$

Eq 20

1.5   Phi/K evolution transient simulation Vs Quasy-stationary approach

 Figure 1 explains the most simple approach to simulate reactive transport and its effects on porosity and permeability. In a certain time step, the solution to flow and mass transport is calculated, then mass transport output is used to estimate reaction products. Finally, the amount of reaction products is used to estimate the change in porosity and permeability. In this workflow, all simulation stages share the time step length. The time step length used for mass transport is applied to reaction and then to phi/K change. This is a transient simulation of phi/K evolution.

The practical implication of a transient simulation approach is that obtaining a numerically stable mass transport solution requires a time step of in the order of 1-10 days. Calcite dissolution reaction kinetics is in the order of 1 day to 95% of reaction completion. In contrast, significant evolution of

porosity and permeability corresponding to the dissolution rates in natural conditions may take 1e4, 1e5or even 1e7 days.

The transient is not an efficient approach to the simulation of processes that occur over geologically significant time periods. Over these long periods, porosity, permeability and reactions conditions do change, but the change is relatively smooth, thus the evolution of a geochemical system can be represented by a sequence of stationary states. Every stationary state fully describes the fluid composition and rates of reacting minerals corresponding to a particular state of alteration of the host rock **(Litchner, 1988)**

Since the time period separating stationary states is not restricted by stability or accuracy requirements needed by mass transport or reaction simulation, the time steps can be large enough to simulate geochemical systems in in geological time spans. Lichtner **(1988)** demonstrated analytically and numerically that the Quasy-Stationary approximation is valid if porosity, permeability and mineral surface area change slowly compared to the time required by fluid composition and mineral reaction rates to adjust to changes in host rock and establish a stationary state.

An application of the Quasy-Stationary approach is shown by Sanford & Konikow **(1989)**. Rates of change in porosity and permeability are calculated from short term mass transport and reaction simulations and then extrapolated to longer time periods. In a subsequent time step mass transport and reaction are solved again to obtain a new stationary state of porosity and permeability. In Sanford & Konikow porosity and permeability evolution simulation of a coastal aquifer, 10 short-term stationary state simulations of mass transport and reaction were done and then each one was extrapolated to 10,000 years to simulate in total 100,000 year of evolution. The Quasy-Stationary approach avoids simulating continuously 100,000 years of flow and mass transport of stationary states that produce very similar outcomes of fluid composition and reaction rate.
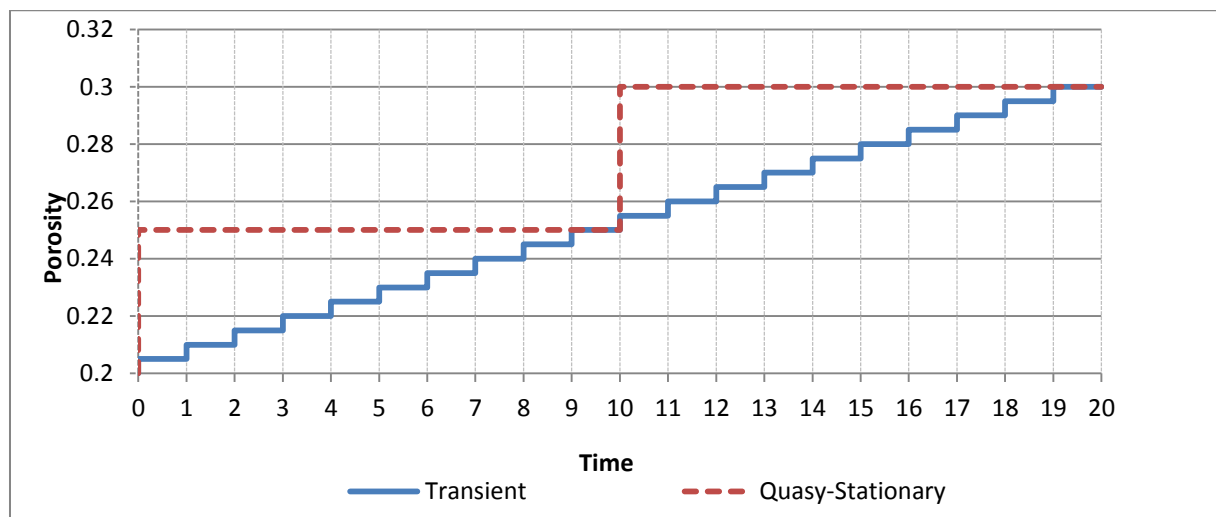

Figure 2, exaggerated representation of transient and quasy-stationary approaches to porosity evolution. The blue line is the transient approach that solves mass transport-reaction and porosity in every simulation time step. In this example, the quasy stationary approach extrapolates 10x the reaction rates from one mass transport timestep.
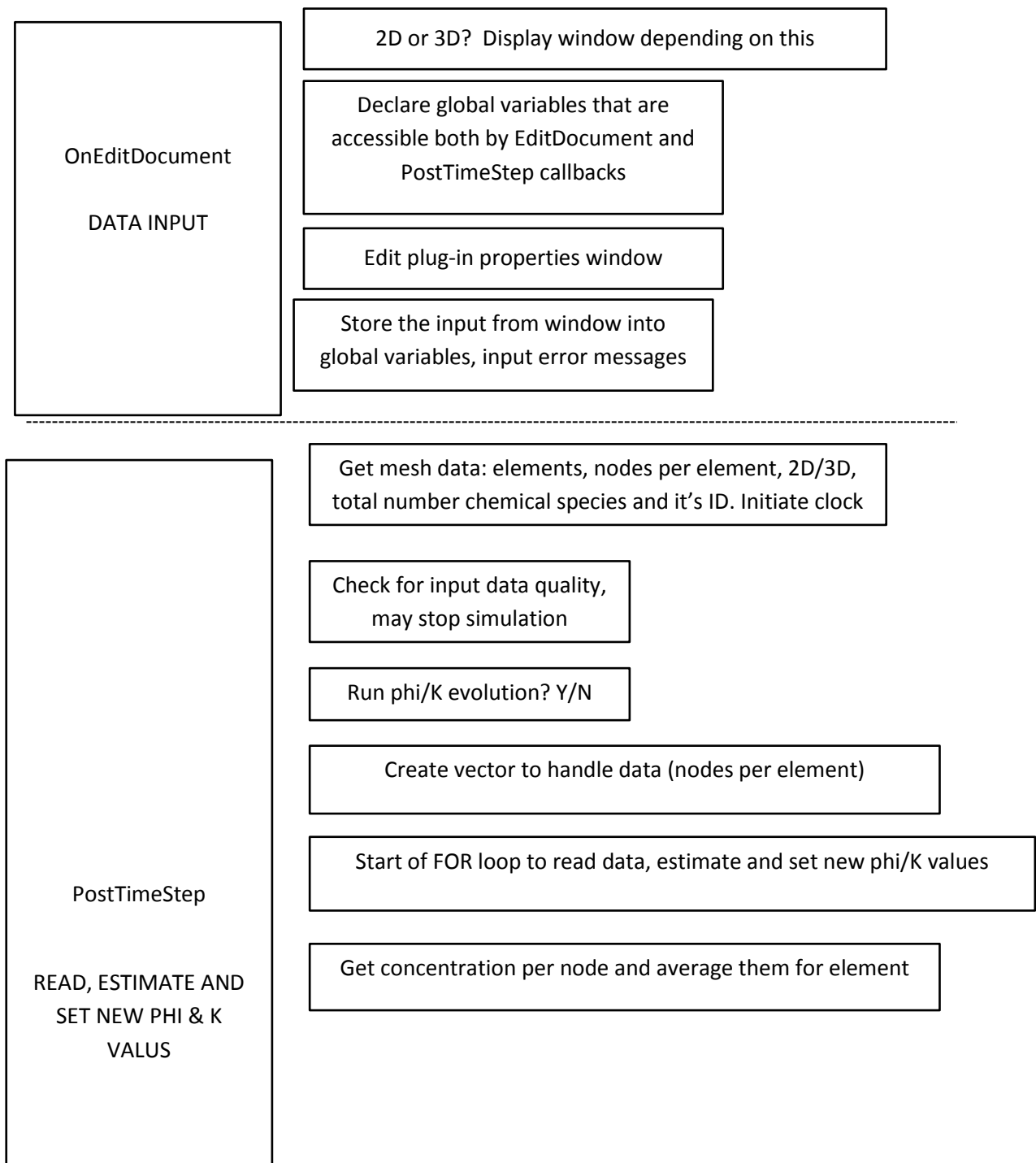
2 Plug-in Implementation

2.1 General implementation

Porosity and permeability plug-in needs the amount of reacted mineral to estimate changes in porosity and permeability. This input comes either from PiChem or FeFlow Reaction Kinetics Editor. The plug-in can handle both chemical reaction inputs, this process will be described in detail in following sections. Before, there is the general description of how the plug-in works. First, how to input the data and then how data is used. Data input is by using a OnEditDocument IFM Callback and Phi-K evolution estimation by a PostTimeStep Callback.

So far, the plug-in works only for the dissolution of mineral phases. Add and IF to handle following options: 0) only dissolution, 1) only precipitation, 2) both dissolution and precipitation.
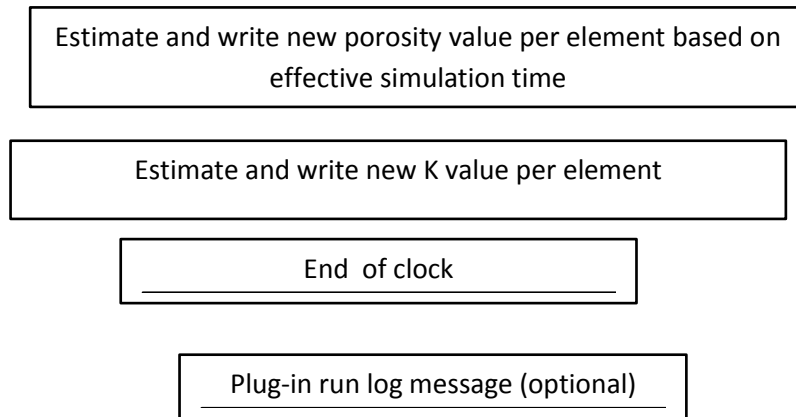
2.2 Detailed plug-in workflow

OnEditDocument

DATA INPUT

- 2D or 3D? Display window depending on this
- Declare global variables that are accessible both by EditDocument and PostTimeStep callbacks
- Edit plug-in properties window
- Store the input from window into global variables, input error messages

PostTimeStep

READ, ESTIMATE AND SET NEW PHI & K VALUS

- Get mesh data: elements, nodes per element, 2D/3D, total number chemical species and it's ID. Initiate clock
- Check for input data quality, may stop simulation
- Run phi/K evolution? Y/N
- Create vector to handle data (nodes per element)
- Start of FOR loop to read data, estimate and set new phi/K values
- Get concentration per node and average them for element

Estimate and write new porosity value per element based on effective simulation time

Estimate and write new K value per element

End of clock

Plug-in run log message (optional)

Figure 3, detailed plug in work flow.

2.3 2D-3D environment selection

The plug-in automatically checks if the flow and mass transport model is composed of 2D or 3D elements. The data input window appearance depends on this condition. The difference is in the amount of variables needed such as initial K for 2D and initial Kxx, Kyy and Kzz for 3D as seen in **figure 4.**

Porosity evolution plug-in works either in a 2D or 3D environment. To work on 2D it needs an initial porosity and permeability elemental distributions as input. These elemental distributions are created by the user in *FeFlow Data>User Data*. Heterogeneity of hydraulic conductivity or transmissivity depending on direction, is handled by an anisotropy variable found in *Data>Material Properties>Fluid Flow*. Porosity and permeability evolution plug-in increase both variables in an isotropic manner. A variable can be added to the code to increase hydraulic conductivity anisotropically in 2D, but it's not implemented yet on the plug-in.

To work on 3D, 3 hydraulic conductivity variables are required to describe initial hydraulic conductivities Kxx, Kyy and Kzz. If permeability development is anisotropic, it is also necessary to create 3 variables to handle anisotropy in hydraulic conductivity development. The variable that creates anisotropy in 3D hydraulic conductivity is the exponent of the phi/K relationship. For example, an exponent of 4 will yield greater increase than 3 for a unit increase in porosity.

2.4 Data input

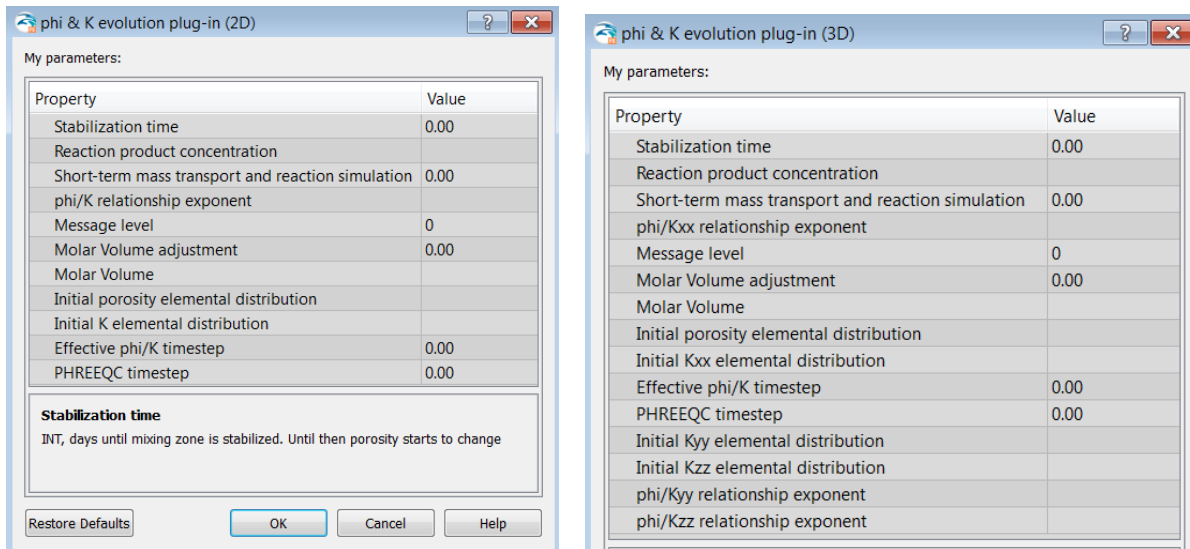Data input for the plug-in is by the *Edit Properties* option found in Plug-ins panel in FeFlow.

Figure 4, Input data window for 2D and 3D simulation

Reactive transport stabilization time (double)

Reactive transport simulations are diverse. Porosity evolution estimates can be done right at the start of simulation or when the desired reactive transport conditions are attained. The input variable created to handle this condition is named **Stabilization time.** An example of why this variable is needed is a saline intrusion simulation where the domain is initially full of freshwater. Porosity evolution calculation start until a stable mixing zone develops.

While the simulation arrives to Stabilization time, the following message is displayed in the Log window in FeFlow "Porosity unchanged, simulation time (float) days, time declared until mixing zone stabilizes (float) days".

Name of nodal reference distribution containing reaction output (string)

The **Reaction Product Concentration** value captures an STRING variable which corresponds to the name of the nodal distribution that contains PiChem output of the name of the nodal distribution that contains the FeFlow Reaction Kinetics Editor calculations output.

Short-term mass transport and reaction (double)

Phi/K evolution plug-in is written as PostTimeStep callback. This variable controls the frequency of porosity and permeability evolution estimates according to the Quasy-Stationary phi/K evolution approach. This variable controls the

phi/K relationship exponent (string)

Enter here the name of the elemental distribution that contains the value of the exponent that describes the porosity and permeability relationship as explained in **eq. 18.** This way every element can have a different value representing heterogeneous mineral composition. If the simulation only

accounts for the evolution of porosity but no permeability, the exponent of the relationship should be zero.

Message level (int)

On every phi/K update the plug-in displays on the FeFlow log window the following message "At simulation time of (float) days, the update of p and K values took (float) clicks of clock() or (float) seconds". On long simulations, the amount of messages in log affects the performance of FeFlow simulation, thus the level of feedback can be adjusted. A value of 0 means "All Messages" and it's useful for debugging, a value of 1 for "only phi & K update messages" and 2 for "No messages".

Molar volume adjustment (double)

The default input unit for the amount of substance is molar volume in L/mol units. However, if the reaction input value is in mg/L an adjustment factor needs to be calculated according to **eq 17.**

Molar volume (string)

Enter here the name of the elemental distribution that contains the Molar volume variable in L/mol units. It is used for **eq. 16** that describes porosity evolution along mineral dissolution. This way every element can have a different V_m value representing heterogeneous mineral composition.

Initial porosity elemental distribution (string)

The STRING value is the name of the initial porosity elemental distribution required for **eq. 18**

Initial K elemental distribution (string)

The STRING value is the name of the initial hydraulic conductivity elemental distribution required for **eq. 18**

Effective phi/K calculation timestep (double)

This variable controls the effective time-step to estimate the evolution of porosity and permeability corresponding to the Quasy-Stationary approach **(Lichtner, 1988)**. Values in days. The simulation time displayed in FeFlow is for the mass transport and reaction simulation. The accumulation of effective phi/K calculation timestep is shown in Feflow log window on every plug-in timestep.

PHREEQC timestep (double)

Timestep of geochemical calculations. This variable is used to convert the PHREEQC output in moles into a reaction rate used in the phi/K evolution extrapolation of the Quasy-Stationary approach.

Initial Kyy and Initial Kzz elemental distributions (String, 3D only)

Names of the elemental distributions containing the initial conductivity values Kyy and Kzz

phi/Kyy and phi/Kzz relationship exponent (string, 3D only)

Names of the elemental distributions that contain exponent values that describe the relationship between porosity and hydraulic conductivity values in Kyy and Kzz direction. Higher value exponents yield higher increase in conductivity for the same porosity change. For example, if a value of 3 is used for phi/Kxx, and a value of 5 is used for phi/Kyy, Kyy will grow faster than Kxx for the same porosity increase. See porosity and permeability relationship review.

2.5 Implementation with PiChem workflow

PiChem provides the input for porosity and permeability evolution plug-in, thus it needs to be run first. PiChem, needs the path to the database for chemical reaction constants (such as PHREEQC.dat), and paths to functioning PHREEQC models for each one of the chemical boundary conditions, and initial conditions in the model domain. PHREEQC has two approaches to geochemical modeling, equilibrium and kinetics.

2.5.1 Equilibrium approach

The equilibrium approach works under the assumption that all products in solution react until thermodynamical equilibrium in every reaction timestep in PiChem. PiChem plug-in demands the following:

a) Path to databases with thermodynamic data such as: PHREEQC.dat
b) Selected Output PHR file that establishes the reaction going on.
c) Boundary conditions
d) Initial conditions

Selected Output, Boundary and Initial conditions should be fully functional stand-alone PHREEQC models. The key to Thermodynamical Equilibrium approach is in Selected Output PHR file. For example, the following command lines indicates that during geochemical simulation timestep the solution must precipitate or dissolve Calcite until equilibrium.

"-equilibrium_phases Calcite"

The decision to use Equilibrium approach depends on the length of time selected for geochemical modelling. For example, if CO_2 is the acidity source, the time required for Calcite dissolution until equilibrium depends on the initial CO_2 concentration. The higher the concentration, the slower the process to equilibrium. **Figure 5** shows Calcite Solubility with different initial CO_2 concentrations in water. Log PCO_2 is the logarithm of CO_2 partial pressure of a gas phase that is in equilibrium with a water phase. -6.18 is the lowest CO2 concentration that corresponds to pure water, -3.4 is the atmospheric CO_2 concentration, while -1.223 is 150 times the atmospheric concentration of CO_2. Reaction kinetics is described by the PWP equation **(Appelo & Potsma, 2005)**. In conclusion, if

reaction time step is longer than 10 hours the reaction is almost in equilibrium and simulating it as equilibrium is a safe assumption. If the time step is smaller, reaction kinetics are necessary.
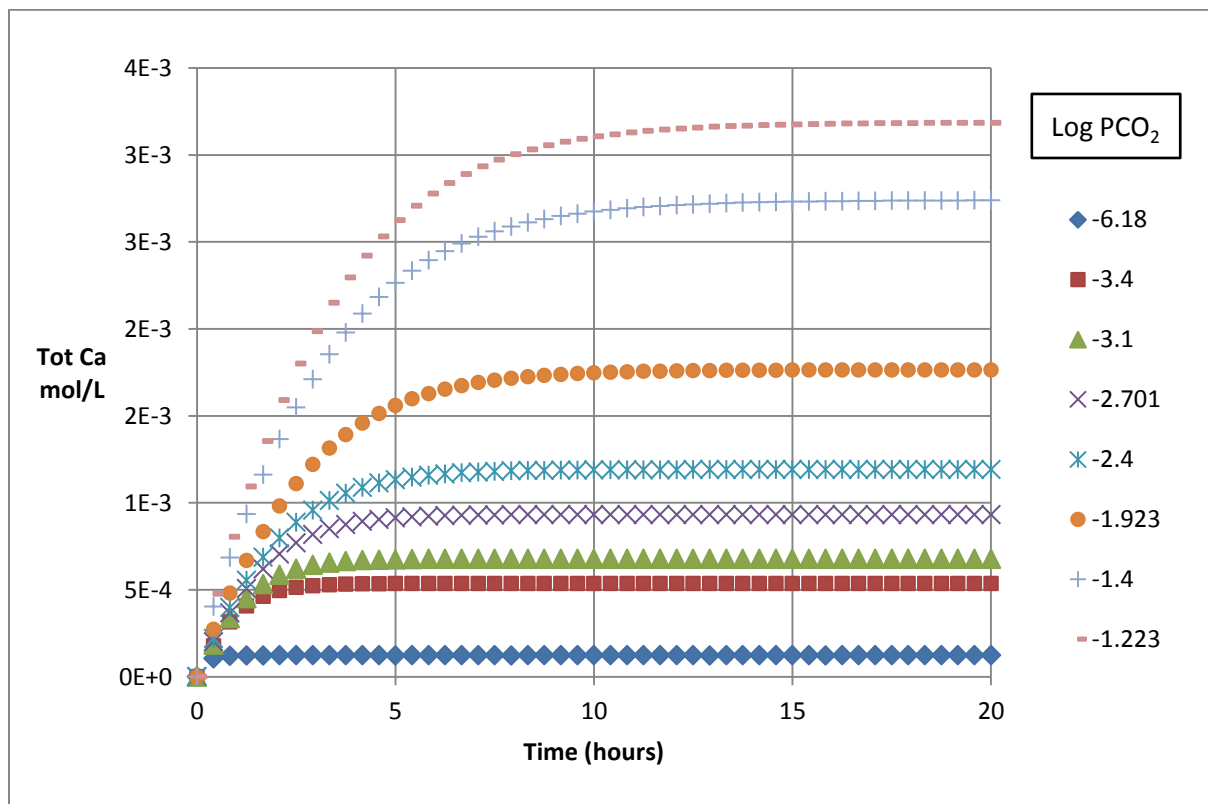

Figure 5, Calcite solubility at different CO2 partial pressures by the PWP equation **(Appelo & Potsma, 2005)**.

2.5.2 Kinetics approach

To model reaction assuming kinetic conditions only one line of code has to be changed in the Selected Output PHR file. PHREEQC offers two alternatives, use the kinetic models already contained in the PHREEQC.dat database or write custom equations into this database in BASIC language. The following lines of code instruct PHREEQC to simulate Calcite dissolution using the PWP equation **(Appelo & Potsma, 2005)**:

```
 KINETICS 1
Calcite;
-m0 1;
-parms 10 0.67;
```

Where the first line instructs kinetic reactions, *Calcite* indicates a reaction between the solution and $CaCO_3$, -m0 1 is the initial amount of reactant, -parms 10 0.67 are the surface to volume ratio (Area/Volume in 1/dm units) and the exponent for surface area change of porous media. As the porosity increases the surface area reduces making the reaction kinetics slower.

2.6 Implementation with FeFlow Reaction Kinetics Editor
Pending…..$

3 Benchmarks and examples of use

3.1 Henry Problem , test the Quasy-Stationary Approach in 2D

The first test of phi/k plug-in is in the Henry problem include in FeFlow benchmark FEM files. Dimensions, porosity, hydraulic conductivity, molecular diffusion and hydraulic boundary conditions are the same as demo FEM file. However, mass transport and chemical boundary conditions are changed to the Solutions 1 and 7 (table 2) coming Sanford & Konikow **(1989)**.

Solution 1
-units mmol/kgw
temp   25
pH   6.971
Ca   2.503
Alkalinity   5.0067 as HCO3
C 1 CO2(g)   -1.5
EQUILIBRIUM_PHASES
Calcite 0.0
END

Solution 7
-units mmol/Kgw
temp   25
pH   8.22
#pe   4.0
Ca   10.66
Mg   55.1
Na   485
K   10.6
Alkalinity   2.407 as HCO3
S(6)   29.3
Cl   566
EQUILIBRIUM_PHASES
CO2(g)   -3.4
Calcite   0.741
END

Freshwater (solution 1) is also used as the initial condition for water in the domain and equilibrium in every PHREEQC timestep is indicate as explained in section 2.5.1.

The purpose of the simulation is to compare the results between running a continuous simulation of mass transport, reaction and phi/k and a simulation using the Quasy-Stationary approach as explained in **section 1.5**

The input for the continuous simulation is the following **(figure 6a)**:

3) Short-term mass transport and reaction simulation: 1 day. This value means mass transport and reaction simulation will run for 1 day and then phi/K evolution plug-in will run
10) Effective phi/K timestep: 1day . This value means the porosity and conductivity values will be update with the same frequency as reaction estimates.
11) PHREEQC timestep: 1 day Since the output of PHREEQC is a concentration of reaction products in mol/L, it needs to be converted into a rate by dividing PHREEQC output by this value.

If the model runs for 120 days, mass transport, reaction and phi/K update will run 120 times. Results are in (**Figure 7a**)
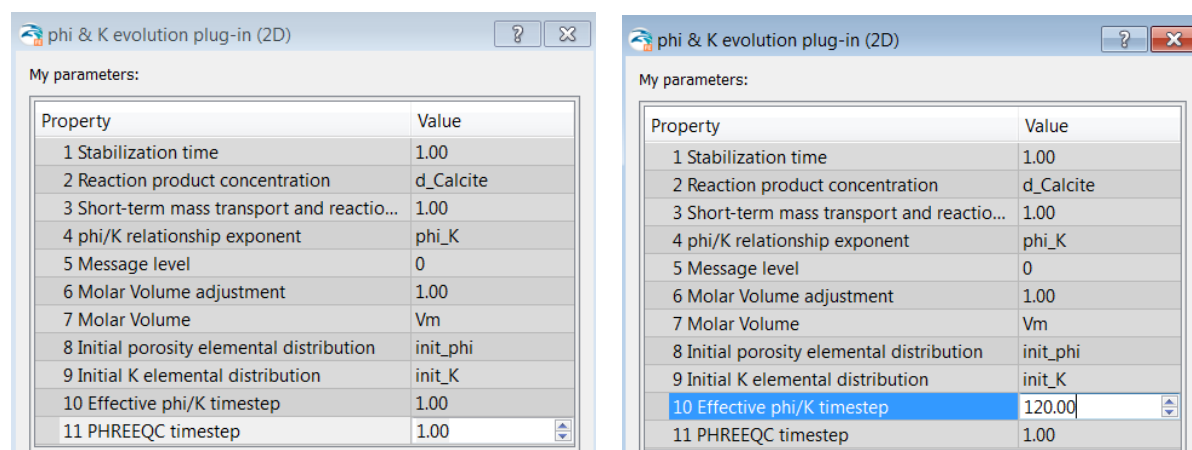

Figure 7, a) input data for continuous simulation, b) input data for quasy-stationary approach simulation

The only input change for the quasy-stationary approach simulation is the Effective phi/K timestep that changed from 1 to 120 days. With this adjustment the simulation will make 1 mass transport, reaction and phi/K update run to simulate 120 days of evolution. Results are in **Figure 7b**
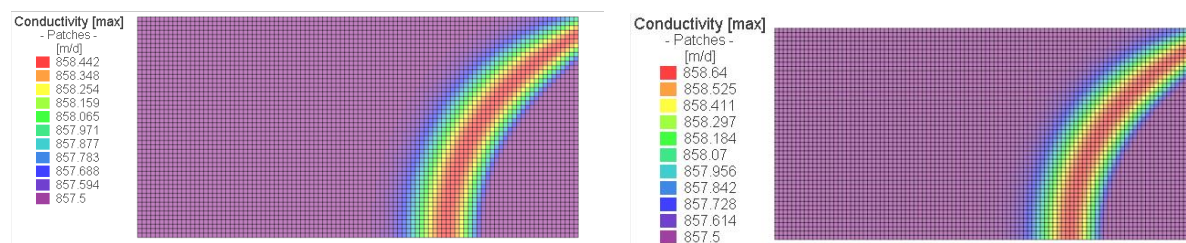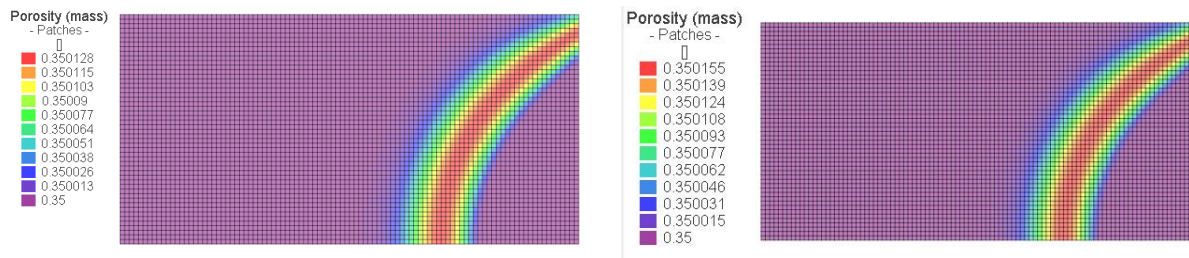
Figure 7, a) continuous simulation: 120 timesteps of mass transport, reaction and phi/K update, b) quasy-stationary simulation: 1 timestep of mass transport, reaction and phi/K update.

The difference in top porosity developed between continuous and quasy-stationary simulation is 0.01%, 0.350128 Vs 0.350155. Conductivity output is marginally higher in the quasy-stationary approach. The quasy-stationary approach produced an higher increase because all the reaction(thus K update) occurred in the same location, while the continuous simulation allowed the continuous update of permeability causing a modification of permeability field that caused a small displacement of the top reactivity zone (mixing zone) to the left. The gradual and minimal displacement of mixing zone causes a smaller top porosity development. Results the quasy-stationary approach require 100 times less computations and are comparable with continuous simulation under equilibrium chemistry conditions.

The full computational effort savings potential of the quasy-stationary approach needs to be tested for longer periods and under kinetic conditions.

3.2 Sanford & Konikow

3.3 I don't know a benchmark for 3D

The phi/K evolution plug-in has been tested for 3D environments but no know benchmark has been found.
Pending…..

4   Batch mode on Linux
Pending…..

5   Known bugs

a) Clicking on Cancel button on while on Edit Properties window of the plug-in will make FeFlow crash.

6   Bibliography

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