A Newton–Krylov method for coupling transport with chemistry in porous media

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Outline

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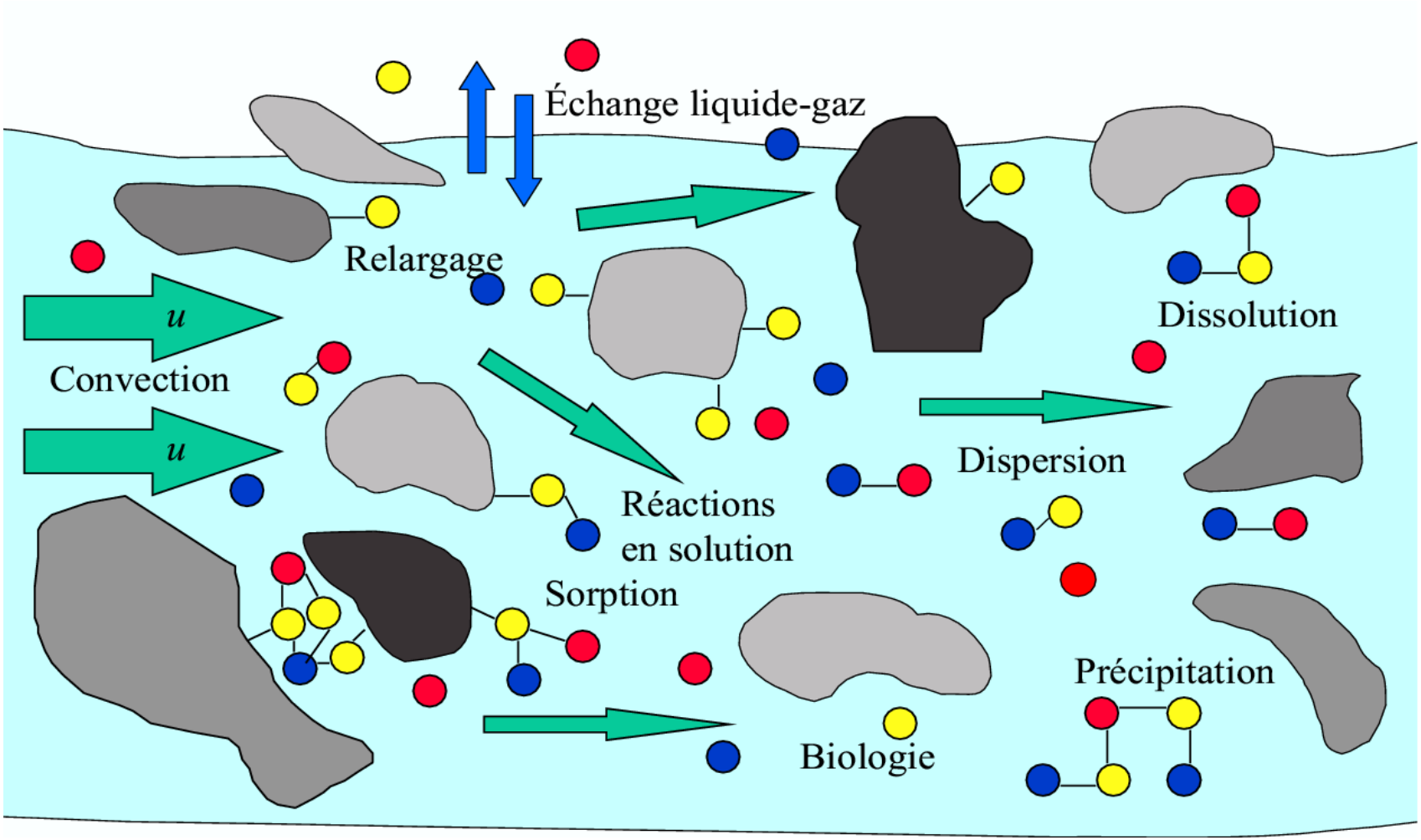
Reactive transport in a porous medium



Classification of chemical reactions

According to nature of reaction

Homogeneous In the same phase (aqueous, gaseous, ...)
Examples: Acid base, oxydo–reduction

According to speed of reaction

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Depends on relative speed of reactions and transport.

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In this talk: Equilibrium reactions, with sorption.

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Aqueous reactions: chemical equilibrium

Chemical reaction:

$$\alpha_1 C_1 + \alpha_2 C_2 \leftrightarrows S, \quad \text{in general } \sum_i \alpha_i C_i \leftrightarrows 0$$

Thermodynamic equilibrium: minimize (change in) Gibb's free energy

$$\Delta G = \Delta G_0 + RT \sum_i \alpha_i \ln(c_i), \quad R = 8.31 \text{ J/K/mol}$$

Leads to mass action law

$$\prod_i c_i^{\alpha_i} = K, \quad K = \exp\left(-\frac{\Delta G_0}{RT}\right)$$

Modeling general equilibrium

General chemical reactions : N_s species, N_r reactions

$$\sum_{j=1}^{N_s} \nu_{ij} Y_j \leftrightarrows 0, \quad i = 1, \ldots, N_r$$

ν_{ij} stoichiometric coefficients. Matrix equation $\nu Y = 0$

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ν has full rank : Rank $\nu = N_r$.

Basis for null-space of ν has dimensions $N_c = N_s - N_r$.

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Partition $\nu = \begin{pmatrix} B & N \end{pmatrix}$, $B \in \mathbf{R}^{N_r \times N_r}$ invertible, $N \in \mathbf{R}^{N_c \times N_r}$, $R = -B^{-1}N$

General solution of $\nu Y = 0$: $Y = \begin{pmatrix} X \\ C \end{pmatrix}$, $X = RC$. $C \in \mathbf{R}^{N_c}$, $X \in \mathbf{R}^{Nr}$.

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Example: carbonic acid dissociation

Species

$$H_2O,\ H_3O^+,\ OH^-,\ H_2CO_3,\ HCO_3^-,\ CO_3^{2-}$$

Reactions

$$H_3O^+ + OH^- \leftrightarrows 2H_2O,$$
$$H_2O + H_2CO_3 \leftrightarrows H_3O^+ + HCO_3^-,$$
$$HCO_3^- + H_2O \leftrightarrows CO_3^{2-} + H_3O^+.$$

Possible components

- $H_2O,\ H_3O^+, H_2CO_3,$
- $H_2O,\ H_3O^+, HCO_3^-,$
- $H_2O,\ H_3O^+, CO_3^{2-},$
- $H_2O,\ OH^-, H_2CO_3,$
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- $H_2O,\ OH^-, CO_3^{2-}.$

Components: the Morel tableau

Species in c: components, in x: secondary species.
Rewrite chemical system as (TDB give components, then species)

$$\sum_{j=1}^{N_c} r_{ij} C_j \leftrightarrows X_i$$

	Components					Equ. constants
	C_1	$\cdots$	C_j	$\cdots$	C_{N_c}	
X_1	R_{11}				R_{1N_c}	K_1
$\vdots$	$\vdots$					
X_i	R_{i1}		R_{ij}		R_{iN_c}	K_i
$\vdots$	$\vdots$					
X_{Ns}	R_{1N_s}				$R_{N_sN_c}$	K_{N_s}
Total conc.	T_1		T_i		T_{N_c}	

From chemistry to mathematics

- Each reaction, mass action law ($\{X_i\}$ = activity of X_i)

$$\{X_i\} = K_i \prod_{j=1}^{N_c} \{C_j\}^{r_{ij}}, \quad i = 1, \ldots, N_r$$

- Each component, mass conservation ($[X_i]$ = concentration of X_i)

$$T_j = [C_j] + \sum_{i=1}^{N_r} r_{ij}[X_i], \quad j = 1, \ldots, N_c$$

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Assume ideal solution $[X_i] = \{X_i\} := x$ (for dissolved species).

System of nonlinear algebraic equations

$$\log x = R \log c + \log K$$

$$T = c + R^T x$$

Sorption processes

Definition

Sorption is the accumulation of a fluid on a solid at the fluid–solid interface.

Main mechanism for exchanges between dissolved species and solid surfaces.

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Can be modeled as mass action law

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Sorptions isotherms

Definition

An adsorption isotherm relates F $(\mathrm{mol/g})$ quantity of adsorbed component to its concentration C $(\mathrm{mol/l})$ in the fluid

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Transport of one solute in saturated porous medium, interaction with solid phase :

$$\frac{\partial C}{\partial t} + \rho \frac{\partial F}{\partial t} + \mathrm{div}\left(\vec{u}C - D\nabla C\right) = 0$$

with

Non-equilibrium $\quad \dfrac{dF}{dt} = k(\Psi(C) - F)$

Equilibrium $\quad F = \Psi(C)$

Common equilibrium isotherms

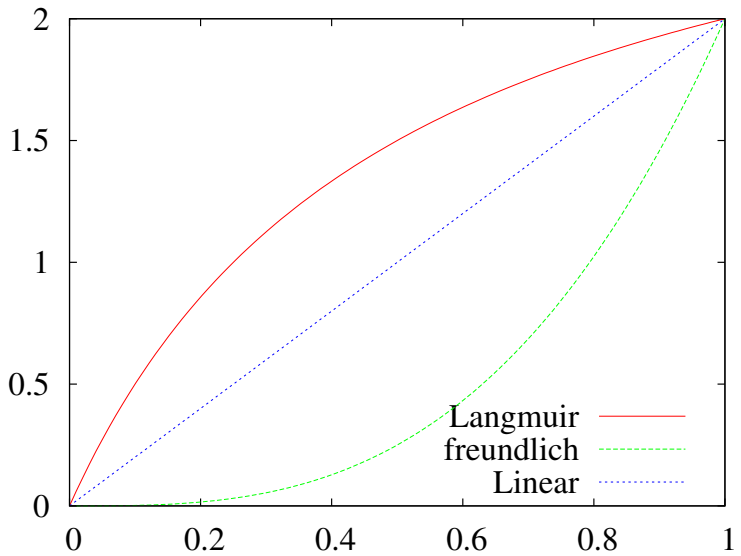
Linear $\Psi(C) = K_d C$

Langmuir $\Psi(C) = \dfrac{\kappa_1 C}{1 + \kappa_2 C}$

Concave near $C = 0$

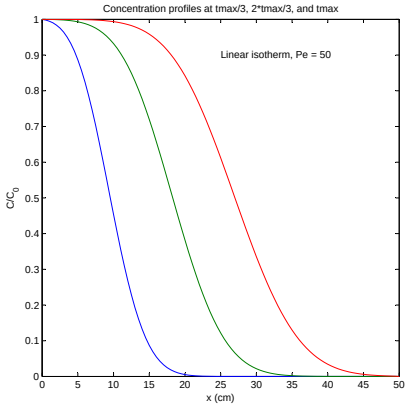
Freundlich $\Psi(C) = \kappa C^p$

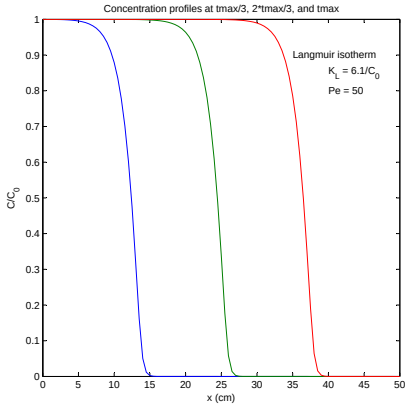
Concave near $C = 0$,
$\Psi'(0+) = \infty$ for $0 < p < 1$,
convex near $C = 0$ for
$1 < p$,.

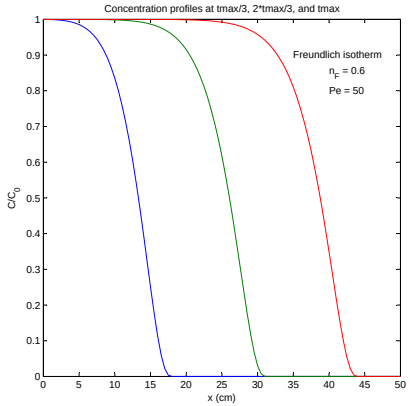


Analysis for “general” function Ψ : Knabner, van Duijn

Examples for linear, Langmuir and Freundlich isotherm







J. A. Cunningham (Texas A&M)

Outline

Reactions for aqueous/solid system

c_j aqueous components, s_j sorbant components, x_i aqueous secondary species, fixed y_i secondary species.

$$x_i \leftrightarrows \sum_{j=1}^{N_c} S_{ij} c_j, \qquad i = 1, \ldots, N_x$$

$$y_j \leftrightarrows \sum_{j=1}^{N_c} A_{ij} c_j + \sum_{j=1}^{N_s} B_{ij} s_j, \qquad i = 1, \ldots, N_y,$$

Mass action law

$$x_i = K_{x\,i} \prod_{j=1}^{N_c} c_j^{S_{ij}}, \qquad i = 1, \ldots, N_x$$

$$y_i = K_{y\,i} \prod_{j=1}^{N_c} c_j^{A_{ij}} \prod_{j=1}^{N_s} s_j^{B_{ij}}, \quad i = 1, \ldots, N_y,$$

Use logarithm: linear algebra

Mass conservation

$$c + S^t x + A^T y = T$$

$$s + B^T y = W,$$

T, W: total concentration in components

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The chemical problem

System of non-linear equations

$$
\begin{aligned}
c + S^T x + A^T y &= T, \\
s + B^T y &= W, \\
\log x &= S \log c + \log K_x, \\
\log y &= A \log c + B \log s + \log K_y.
\end{aligned}
$$

Dissolved total: $C = c + S^T x$, Fixed total: $F = A^T y$.

Role of chemical model

Given totals T (and W, known), split into mobile and immobile total concentrations.

$$C = \Phi(T), \qquad F = \Psi(T)$$

The chemical problem (2)

Take concentration logarithms as main unknowns

Nonlinear system

$$H(z) = \begin{pmatrix} T \\ W \end{pmatrix}$$

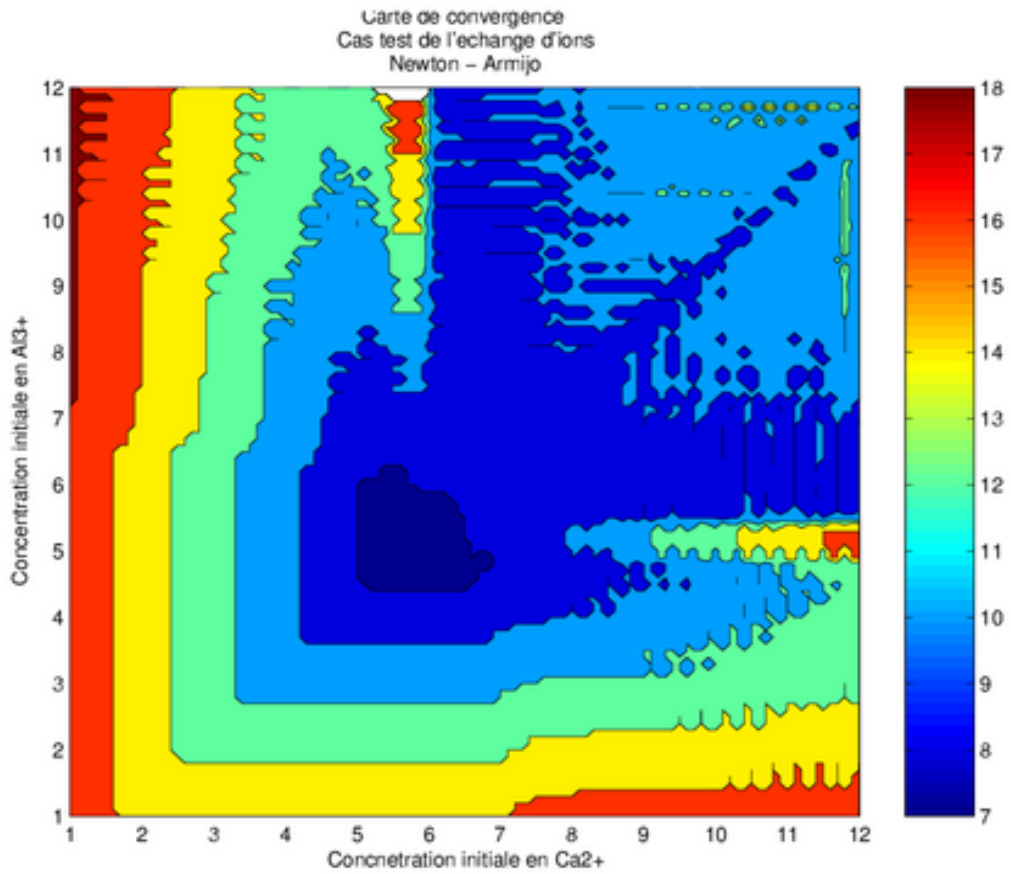
- $z = (\log c, \log s)$, $K = (\log K_x, \log K_y)$
- $H(z) = \exp(z + \bar{S}^T \exp(K + \bar{S}z)$

Jacobian matrix

$$H'(z) = \operatorname{diag} \exp(z) + \bar{S}^T \operatorname{diag}(\exp(K + \bar{S}z))\bar{S}$$

Numerical solution of nonlinear problem

Use globalized Newton's method (line search, trust region).



Ion exchange: 6 species, 4 components (vary initial guess)

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Transport in a porous medium

Diffusion–convection equation

$$\omega \frac{\partial c}{\partial t} - \mathbf{D}\frac{\partial^2 c}{\partial^2 x} + u\frac{\partial c}{\partial x} = f \quad \text{for } 0 < x < L$$

$$c = c_d \text{ at } x = 0 \quad -\mathbf{D}\frac{\partial c}{\partial x} = x_0 \text{ at } x = L$$

$$c(x, 0) = c_0(x), \quad 0 < x < L.$$

- ω : porosity
- $\mathbf{D}$: dispersion coefficient
- u : Darcy velocity

$$\text{Let } L(c) = -\mathbf{D}\frac{\partial^2 c}{\partial^2 x} + u\frac{\partial c}{\partial x}.$$

Assumption

Dispersion tensor independent of species

Numerical method for transport

Space-time finite difference method

$$\omega \frac{c_j^{n+1} - c_j^n}{\Delta t} - \mathbf{D} \frac{c_{j+1}^{n+\theta} - 2c_j^{n+\theta} + c_{j-1}^{n+\theta}}{\Delta x^2} + u \frac{c_j^{n+\theta} - c_{j-1}^{n+\theta}}{\Delta x} = f_j^{n+\theta}$$

$$c^{n+\theta} = \theta c^{n+1} + (1-\theta) c^n.$$

- Implicit scheme
- Unconditionally stable
- Upwind scheme (first order in space)
- $\theta = 1/2$: Crank Nicolson scheme (2nd order in time)

The coupled system

Transport for each species and component

$$\begin{aligned} \frac{\partial x_i}{\partial t} + L(x_i) &= r_i^x, & \frac{\partial c_j}{\partial t} + L(c_j) &= r_j^c, \\ \frac{\partial y_i}{\partial t} &= r_i^y, & \frac{\partial s_j}{\partial t} &= r_j^s, \end{aligned}$$

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Eliminate (unknown) reaction rates by using conservation laws: CD equations for totals ($T = C + F$)

$$\begin{aligned} &\frac{\partial T^{ic}}{\partial t} + L(C^{ic}) = 0, && ic = 1, \ldots, N_c \\ &T_{ix}^{ic} = C_{ix}^{ic} + F_{ix}^{ic} && ic = 1, .., N_c \text{ and } ix = 1, .., N_x \\ &F_{ix} = \Psi(T_{ix}) && ix = 1, \ldots, N_x. \end{aligned}$$

Number of transport equations reduced from $N_x + N_y$ to $N_c + N_s$

Different formulations (1)

CC formulation, explicit chemistry (J. Erhel)

$$\begin{cases} \dfrac{dC}{dt} + \dfrac{dF}{dt} + LC = 0 \\ H(z) - \begin{pmatrix} C + F \\ W \end{pmatrix} = 0 \\ F - F(z) = 0. \end{cases}$$

- $+$ Explicit Jacobian
- $+$ Chemistry function, no chemical solve
- $-$ Intrusive approach (chemistry not a black box)
- $-$ Precipitation not easy to include

Different formulations (2)

TC formulation, implicit chemistry

$$\begin{cases} \dfrac{dT}{dt} + LC = 0 \\ T - C - F = 0 \\ F - \Psi(T) = 0 \end{cases}$$

- $+$ Non-intrusive approach (chemistry as black box)
- $+$ Precipitation can (probably) be included
- $-$ No explicitJacobian (finite differences)
- $-$ One chemical solve for each function evaluation

Standard iterative algorithm

Block Gauss–Seidel method

Transport

$$\begin{cases} \dfrac{C^{n+1,k+1} + F^{n+1,k} - T^n}{\Delta t} + L(C^{n+1,k+1}) = 0, \\ T^{n+1,k+1} = C^{n+1,k+1} + F^{n+1,k}, \end{cases}$$

Chemistry

$$F^{n+1,k+1} = \Psi(T^{n+1,k+1})$$

Yeh–Tripathi (1989), Saaltink et al. (2001), Carrayrou (2001), Dimier, Montarnal et al. (2004).

DAE approach for CC

Coupled system is index 1 DAE (J. Erhel, C. de Dieuleveult)

$$M\frac{dy}{dt} + f(y) = 0$$

$$y = \begin{pmatrix} C \\ z \\ F \end{pmatrix}, \quad M = \begin{pmatrix} I & 0 & I \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad f(y) = \begin{pmatrix} L \otimes C \\ H(z) - \begin{pmatrix} C + F \\ W \end{pmatrix} \\ F - F(z) \end{pmatrix}$$

Use standard DAE software

Global method for TC

$$\begin{cases} \dfrac{C^{n+1} - C^n}{\Delta t} + \dfrac{F^{n+1} - F^n}{\Delta t} + L(C^{n+1}) = 0 \\ T^{n+1} = C^{n+1} + F^{n+1} \\ F^{n+1} = \Psi(T^{n+1}) \end{cases}$$

$$\Updownarrow$$

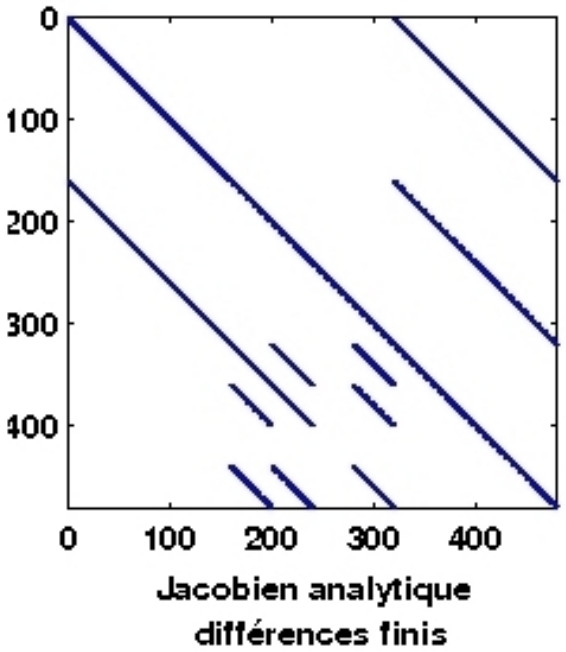
$$f\begin{pmatrix} C^{n+1} \\ T^{n+1} \\ F^{n+1} \end{pmatrix} = \begin{pmatrix} F^{n+1} + (I + \Delta t L)C^{n+1} - C^n - F^n \\ T^{n+1} - C^{n+1} - F^{n+1} \\ F^{n+1} - \Psi(T^{n+1}) \end{pmatrix} = 0.$$

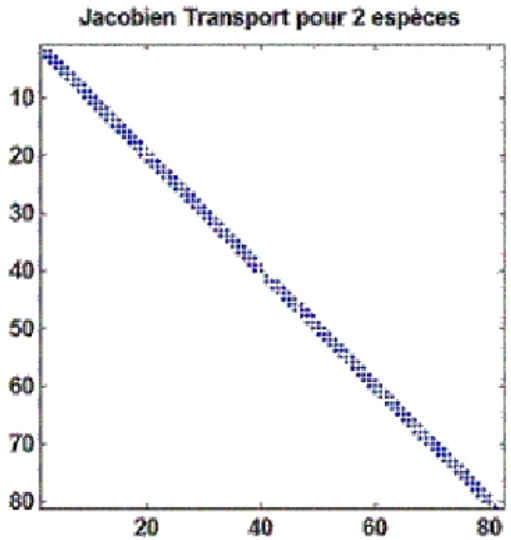
Solve by Newton's method

Structure of Jacobian matrix

Jacobian : $f'(C,T,F) = \begin{pmatrix} (I + \Delta t L) & 0 & I \\ -I & I & -I \\ 0 & -\Psi'(T) & I \end{pmatrix}$

$\Psi'(T)$ jacobian of chemistry





- Storage of jacobian matrix is expensive, size of matrix is $3N_xN_c \times 3N_xN_c$

Newton Krylov method

- Solve the linear system by an iterative method
- GMRES, TFQMR and BiCGStab require only jacobian matrix by vector products.
  Can be approximated by finite differences or computed analytically.

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Inexact Newton

- Approximation of the Newton's direction:

  $\|f'(x_k)d + f(x_k)\| \leq \eta \|f(x_k)\| \quad (0<\eta<1)$

- Choice of the forcing term η?
  - Keep quadratic convergence (locally)
  - Avoid oversolving the linear system

- $\eta = \gamma \|f(x_k)\|^2 / \|f(x_{k-1})\|^2$ (Kelley, Eisenstat and Walker)

Newton Krylov method (2)

Computing the jacobian-vector product

$$f'(y)w \approx \frac{f(y+hw) - f(y)}{h}$$

Choice of h ? $h = 10^{-7}\frac{\|x\|}{\|w\|}$ (Kelley).

Outstanding issue: preconditioning

References

- Hammond, Valocchi, Lichtner (CMWR, 2002)
- Knoll, Keyes (JCP, 2004)
- Mousseau, Knoll (JCP, 2004)

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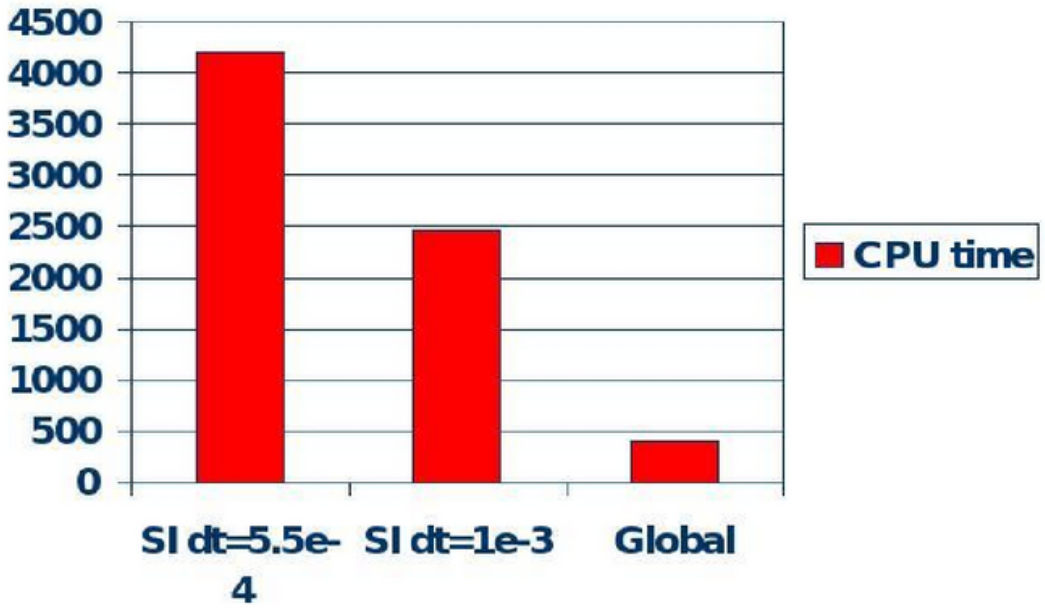
Pyrite test case

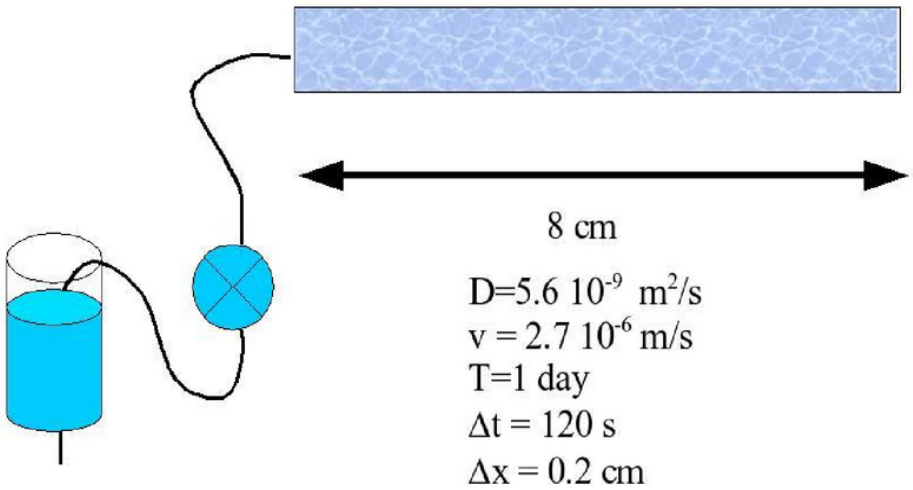
- 4 components, 39 aqueuous and 13 fixed species
- Somewhat artificial without precipitation
- Use DAE software (Variable time step and order. In Matlab, function ode15s modified to use UMFPACK).



C. de Dieuleveult's thesis (INRIA/Andra)

Example: ion exchange

Column experiment (Phreeqc ex. 11, Alliances ex. 3)

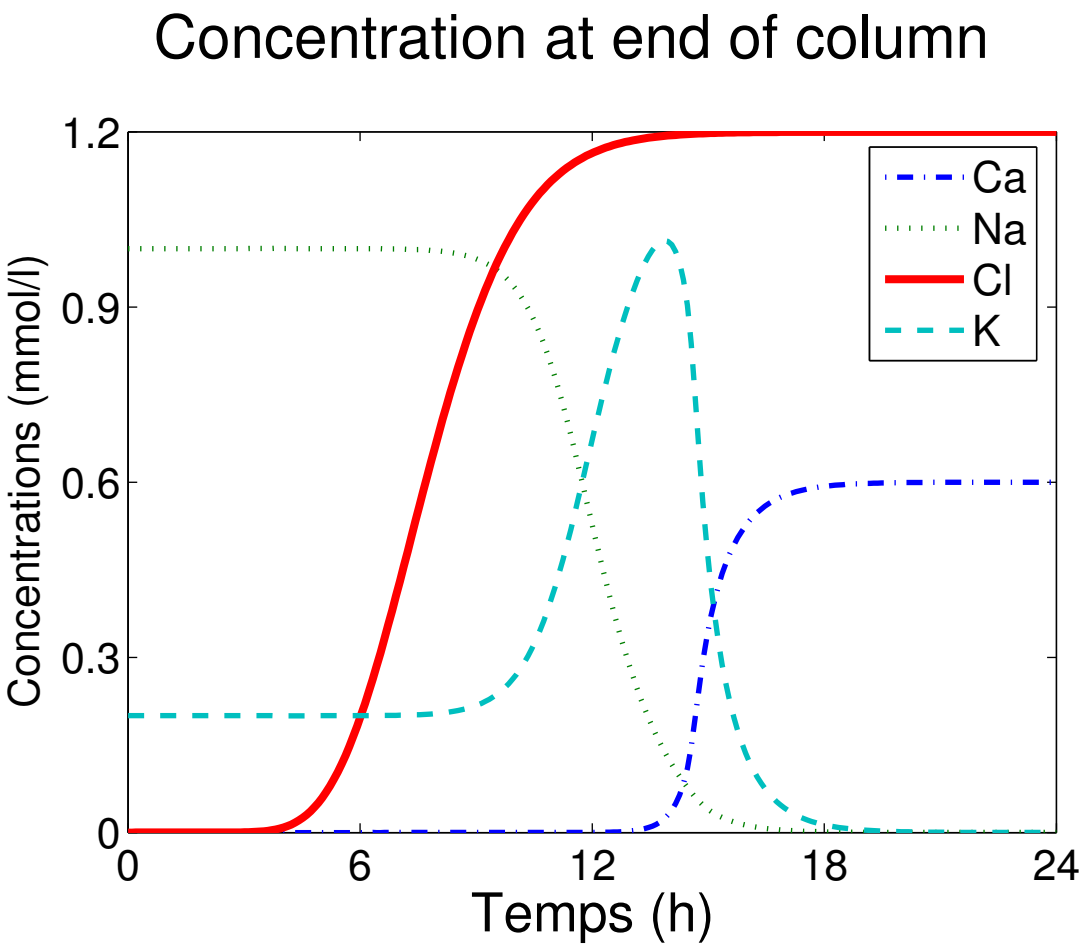


Column contains a solution with $1\,\mathrm{mmol\,Na}$, $0.2\,\mathrm{mmol\,K}$ and $1.2\,\mathrm{mmol\,NO_3}$. Inject solution with $1.2\,\mathrm{mmol\,CaCl_2}$. $CEC = 1.1\,10^{-3}$.

Chemical system:

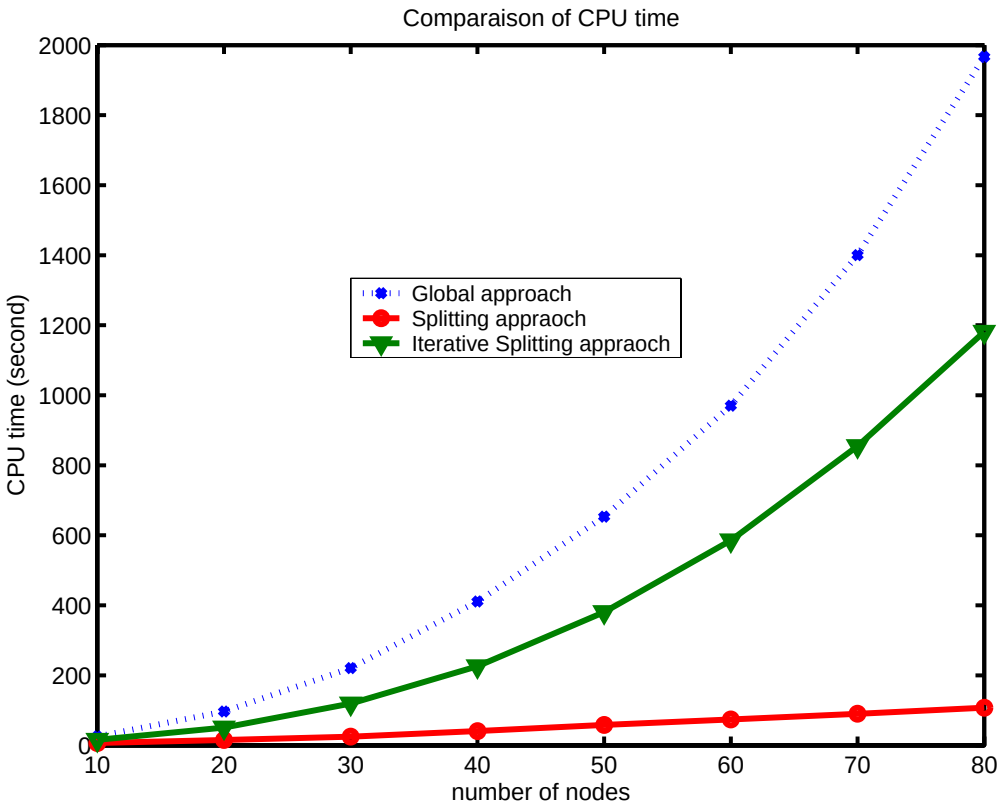
$$\mathrm{Ca^{2+}} + 2\mathrm{X^-} \leftrightarrows \mathrm{CaX_2}, \qquad \log K_1 = 0.8,$$
$$\mathrm{Na^+} + \mathrm{X^-} \leftrightarrows \mathrm{NaX}, \qquad \log K_2 = 0,$$
$$\mathrm{K^+} + \mathrm{X^-} \leftrightarrows \mathrm{KX}, \qquad \log K_3 = 0.7$$

Chromatography: result



Without diffusion, can be solved semi-analytically (Appelo et al.).
Extension to diffusive case ?

Algorithm performance



As mesh is refined

- Number of Newton iterations remains stable
- Number of GMRES iterations grows

For each time step:

Block Gauss-Seidel 20 - 27 iterations,

Newton–Krylov 4 - 7 Newton steps, 13-20 GMRES steps

Simplified MoMaS benchmark

One dimension, diffusive regime, shorter time period
Easy chemistry, Morel tableau

	X_1	X_2	X_3	X_4	S	K
C_1	0	-1	0	0	0	10^{-12}
C_2	0	1	1	0	0	1
C_3	0	-1	0	1	0	1
C_4	0	-4	1	3	0	10^{-1}
C_5	0	4	3	1	0	10^{35}
CS_1	0	3	1	0	1	10^{6}
CS_2	0	-3	0	1	2	10^{-1}

Initial: X_2, X_4, inject X_1, X_2, X_3, flush with X_2, X_4.

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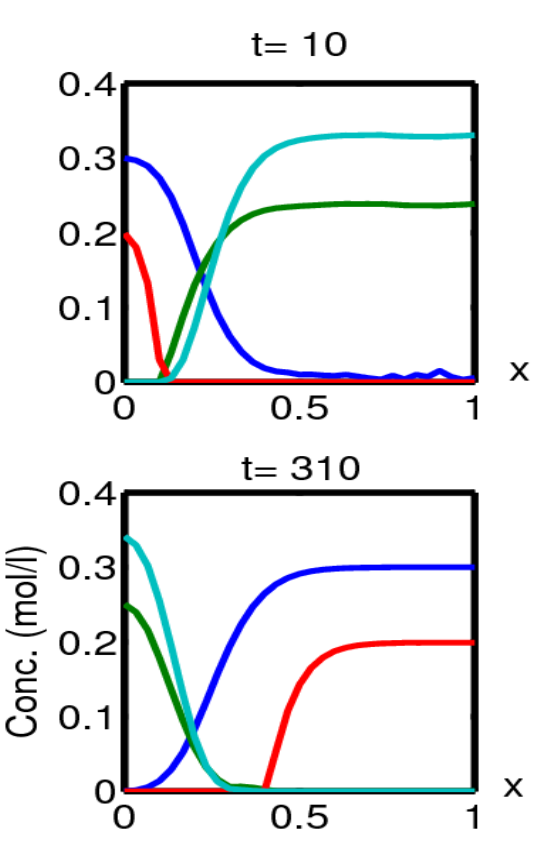
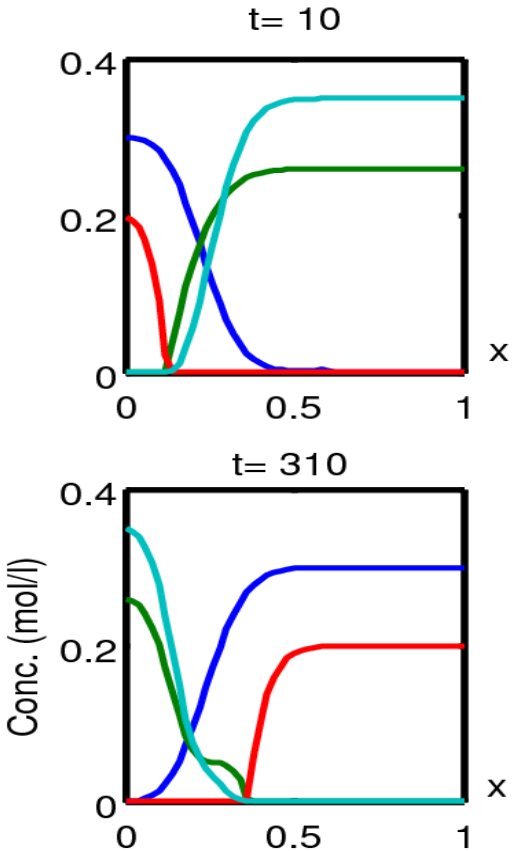
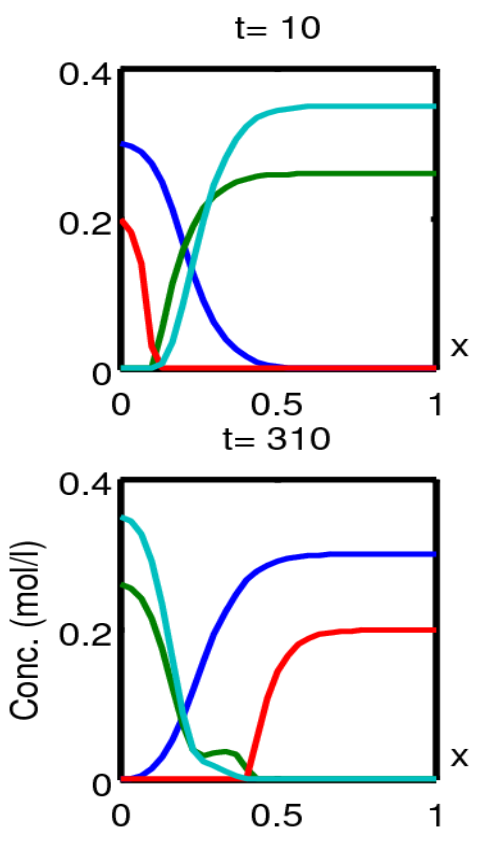
Simplified benchmark : results



Split
$\Delta x = 1/30$, $\Delta t = 2$.

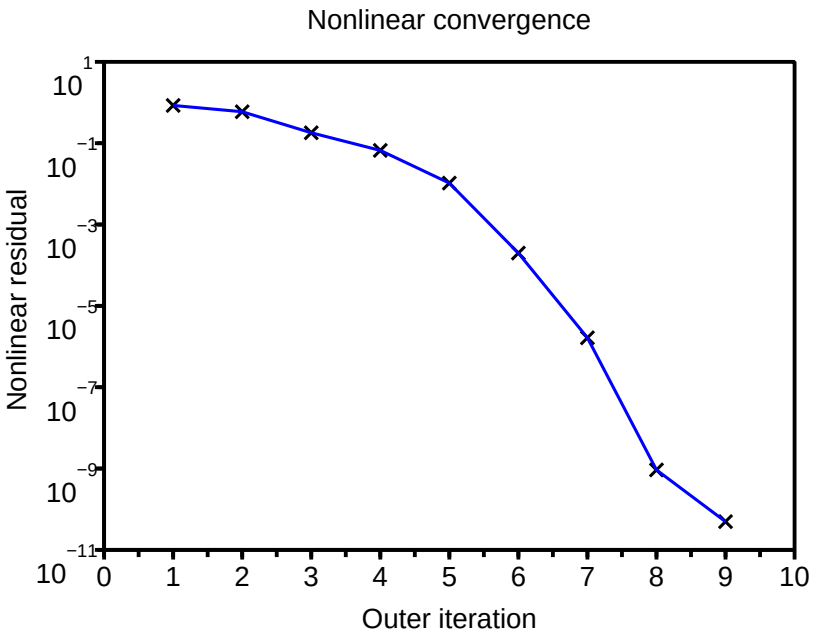


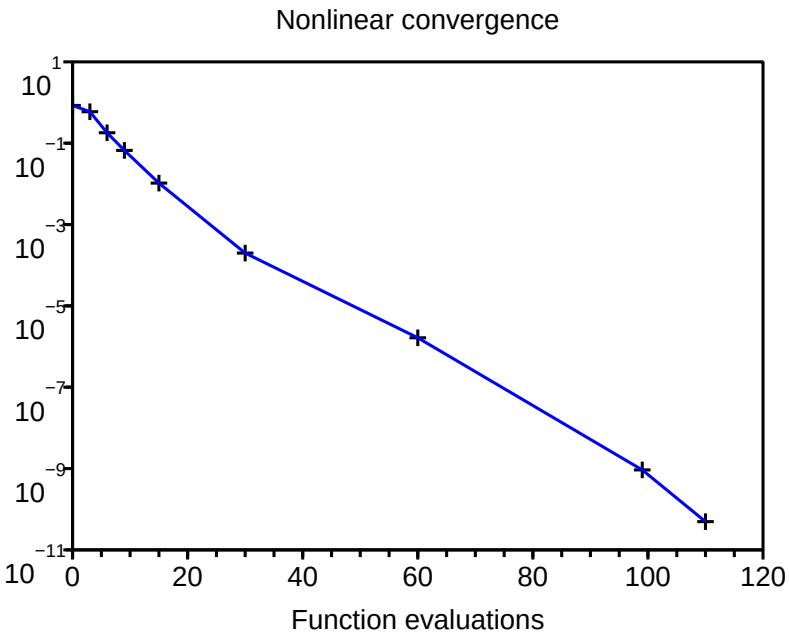
Split
$\Delta x = 1/50$, $\Delta t = 0.5$.



Global
$\Delta x = 1/30$, $\Delta t = 2$.

Benchmark: performance





For each time step:

- 8-9 Newton iterations
- Number of inner iterations increases for each further Newton iteration
- 80-120 function evaluations

MoMaS benchmark proposal

http://www.gdrmomas.org/ex_qualifications

Written by J. Carrayrou (IMFS).
International Scientific Committee
1D and 2D geometries

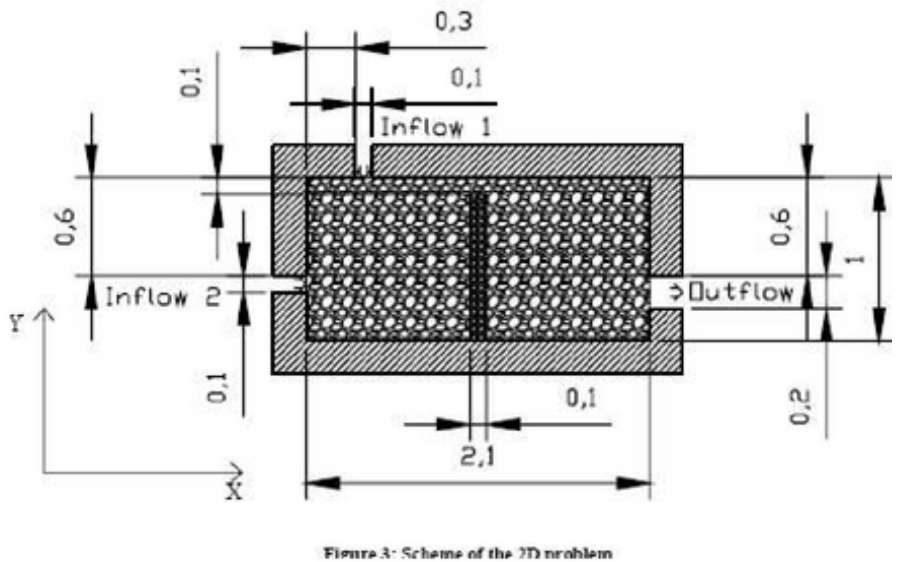


Figure 3: Scheme of the 2D problem

3 levels of chemical difficulty

- **Easy** Equilibrium, ion exchange
- **Medium** More species, kinetics
- **Hard** Precipitation–dissolution

Conclusions – Perspectives

- Formulation of reactive transport within mathematical framework
- Implementation of Newton – Krylov algorithm
- Preliminary performance tests

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Areas for further work

- Numerical analysis of algorithms ?
- Comparison of different formulations, and algorithms
- Handling of precipitation reactions
- Handling of per species diffusion coefficient
- Extension to multi-phase flows