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Reactive transport in porous media

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MOX, Politecnico di Milano

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1. Motivations

2. Basic models and methods
   - Flow model
   - Transport model
   - Chemistry

3. Reactive transport
   - Single species with sorption
   - Multi-species equilibrium chemistry

4. Preconditioning (joint work with A. Taakili)

Outline

Nuclear waste storage (1)

- Assess safety of deep geological nuclear waste storage (clay layer)
- Long term simulation of radionuclide transport (one million years)
- Wide variation of scales : from package (meter) to regional (kilometers)
- Geochemistry: large number of species
- Strong government regulation
- Main actors : ANDRA, cea, EDF
- Research in mathematical and numerical modeling is conducted in the CNRS MOMAS group (Director A. Ern).

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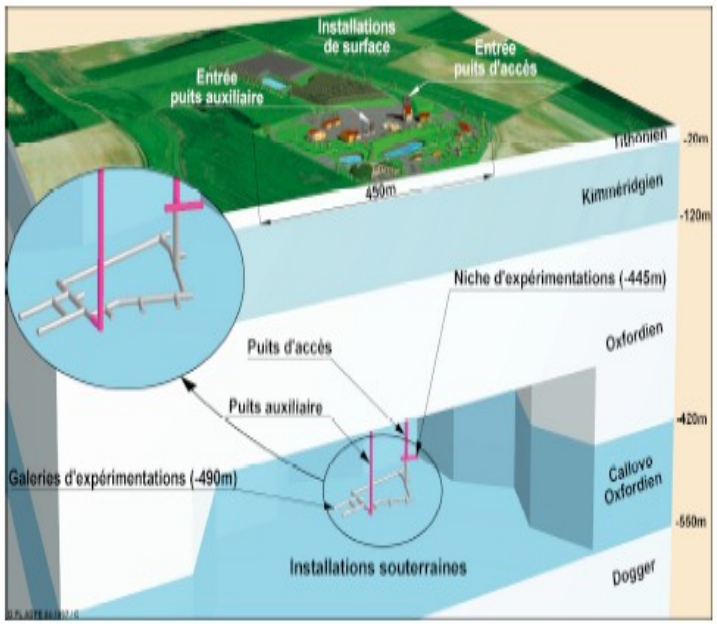
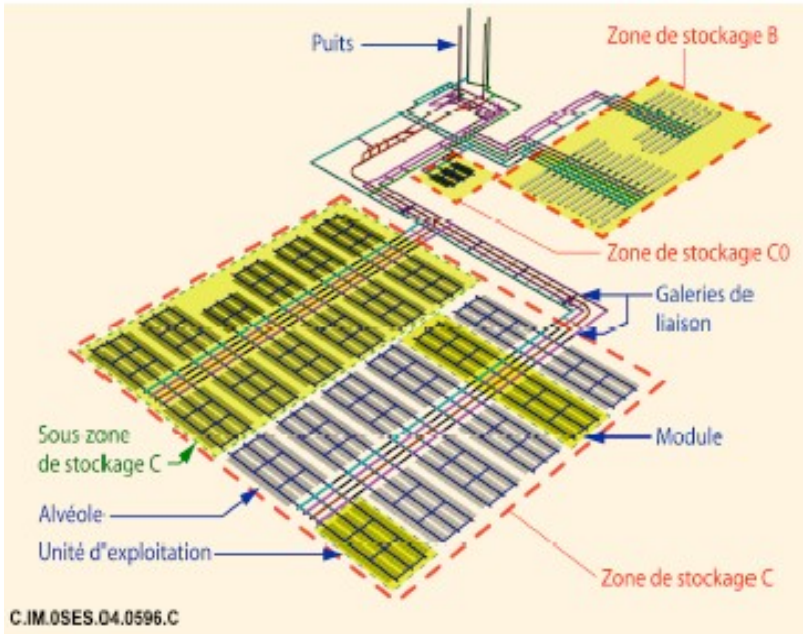
Nuclear waste storage (2)

Present choice in France: a sedimentary geological formation (in the Meuse region)



ANDRA



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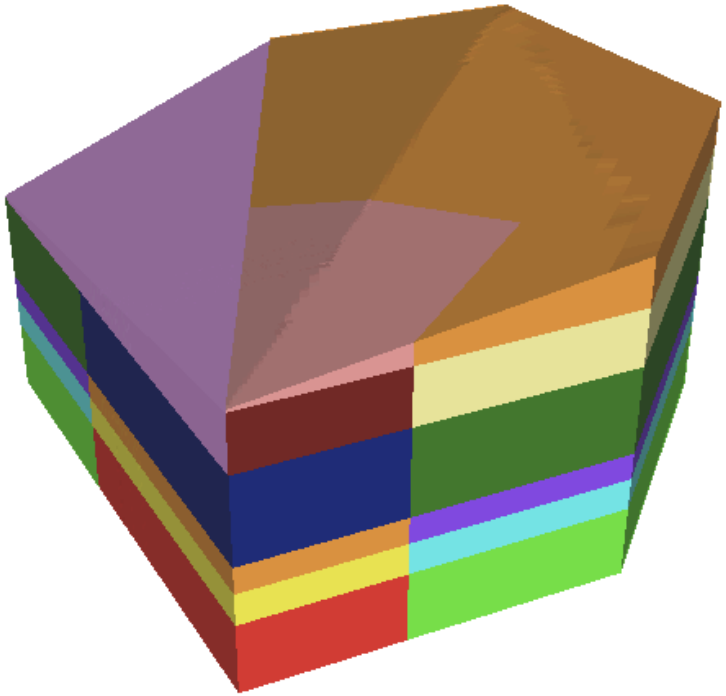
A 3D far field model

Used as a benchmark, similar to Andra safety model

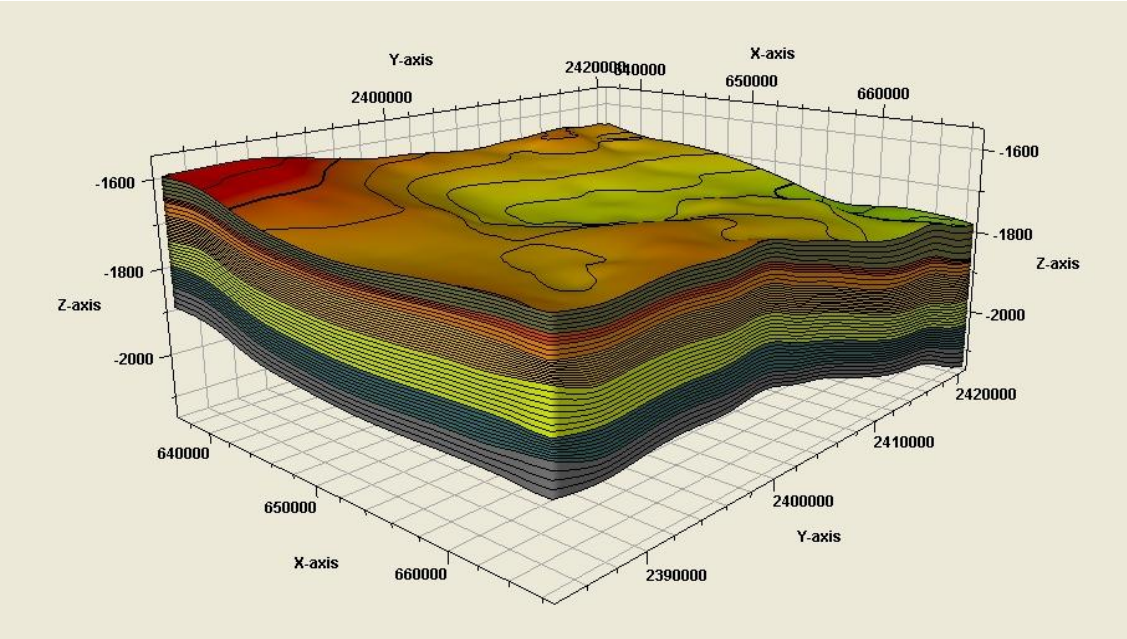


Blown-up 30 times vertically

Difficulties

- Distorted geometry (horizontal $\approx$ 40 km, vertical 700 m)
- Strong heterogenities (permeability varies by 8 orders of magnitude)
- General hexahedral mesh
- Simulation over 500 000 years

CO_2 sequestration



Geological model, BRGM (21 million grid points)

- Long term capture of CO_2 in saline aquifer
- Simulation to understand CO_2 migration through salt
- Coupling of liquid and gas phase, reactive transport

SHPCO2 project (funded by ANR) High Performance Simulation of CO_2 sequestration

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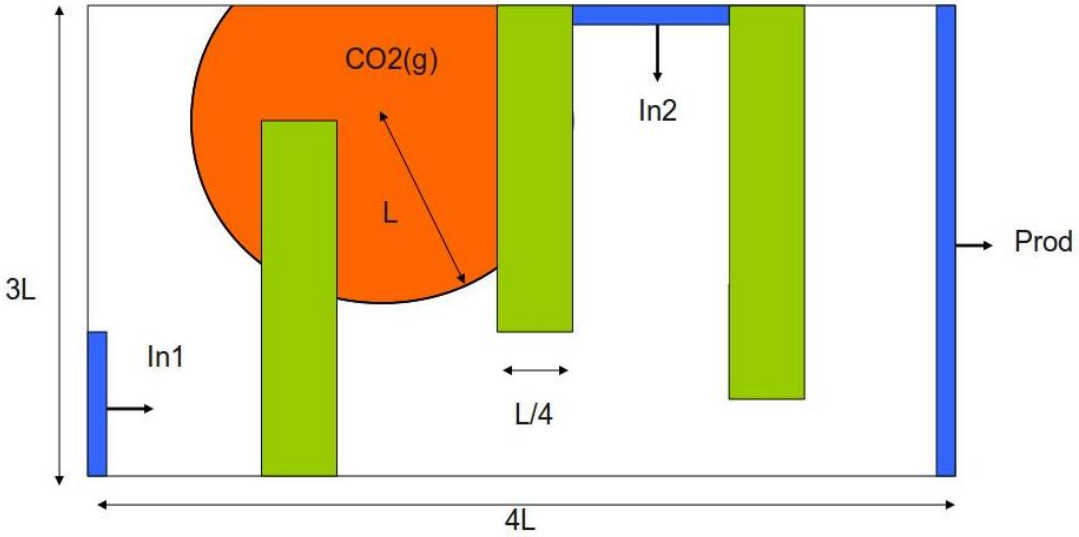
CO_2 sequestration: a synthetic model

Minimal chemical system that still ”looks like” realistic for CO_2 storage



Dissolution of CO_2 in water, dissolution of calcite. Gas assumed immobile (capillary trapping), decouples two phase flow from reacftive transport.

Chemical system

- $H_2O \rightleftharpoons H^+ + OH^-$ water dissociation
- $CO_{2\,(g)} \rightleftharpoons CO_{2\,(aq)}$ gas dissolution
- $H_2O + CO_{2\,(aq)} \rightleftharpoons HCO_3^- + H^+$ dissociation of aqueous CO_2
- $CaCO_3 + H^+ \rightleftharpoons Ca_2^+ + HCO_3^-$ Dissolution of calcite

Outline

Flow model

Flow equations

$q = -K\nabla h$ Darcy's law h piezometric head

$\nabla \cdot q = 0$ incompressibility q Darcy velocity

K permeability tensor (heterogeneous, anisotropic)

Mixed finite elements

- Approximate both head and velocity
- Continuous flux across element faces
- Locally mass conservative
- Allows full diffusion tensor

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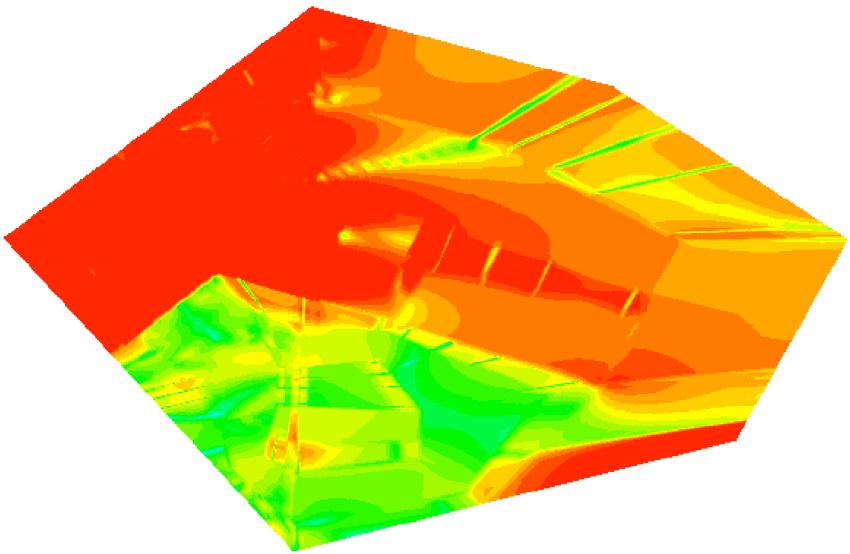
Extension: a composite mixed finite element for hexahedra

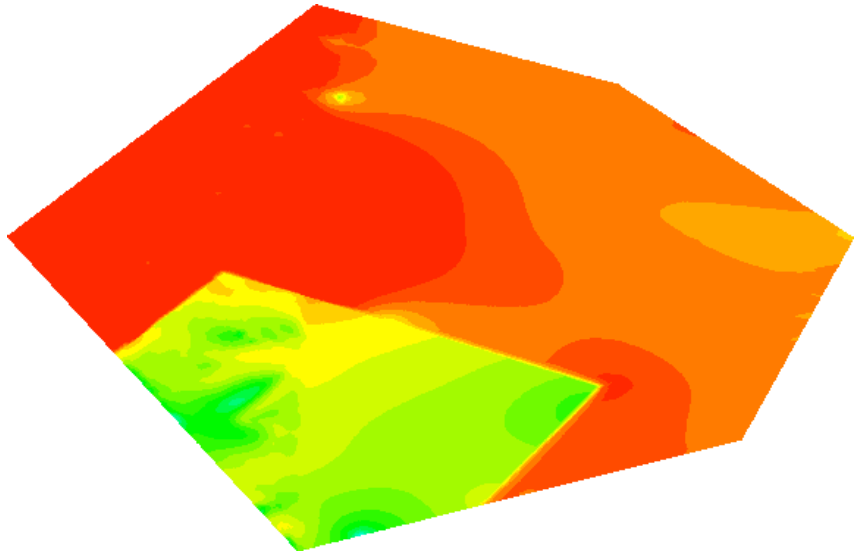
- Convergence theory not valid for RTN space over general (deformed) hexahedra,
- Kuznetsov, Repin (2003): construct macroelement on a hexahedron by subdividing it into 5 tetrahedra. Same DOFs as before, optimal order error

Mixed finite elements

Simulation for 3D far field benchmark model, horizontal cros section of modulus of velocity



RTN FE



New FE

A. Sboui's PhD thesis, Sboui, Jaffré , Roberts SIAM J. SCi. Comp. (2009).

Transport model

Convection–diffusion equation

$$\phi \frac{\partial c}{\partial t} - \underbrace{\operatorname{div}(\mathbf{D} \operatorname{grad} c)}_{\text{dispersion}} + \underbrace{\operatorname{div}(\mathbf{u} c)}_{\text{advection}} + \phi \lambda c = f$$

- c: concentration $[\mathrm{mol/l}]$
- ϕ: porosity [–]
- λ radioactive decay $[\mathrm{s}^{-1}]$
- $\mathbf{u}$ Darcy velocity $[\mathrm{m/s}]$

Dispersion tensor

$$\mathbf{D} = d_e \mathbf{I} + |\mathbf{u}|[\alpha_l \mathbf{E}(\mathbf{u}) + \alpha_t (I - \mathbf{E}(\mathbf{u}))], \quad E_{ij}(\mathbf{u}) = \frac{u_i u_j}{|\mathbf{u}|}$$

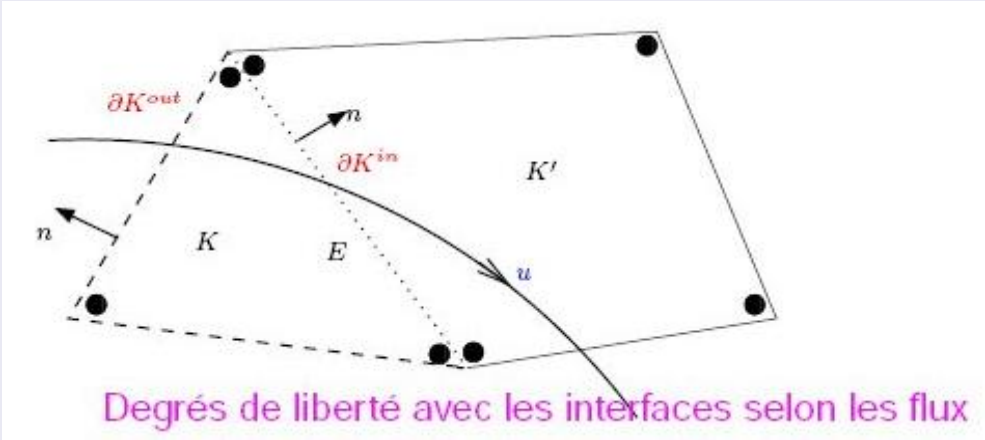
α_l, α_t dispersicity coeff. $[\mathrm{m}]$, d_e molecular diffusion $[\mathrm{m/s^2}]$

Solution by operator splitting

Advection step

Explicit, finite volumes / discontinuous Galerkine

- Locally mass conservative
- Allows unstructured meshes
- CFL condition: use sub–time–steps



Dispersion step

Like flow equation (time dependent): mixed finite elements (implicit)

See Ackerer et al., Putti et al., Arbogast et al., ...

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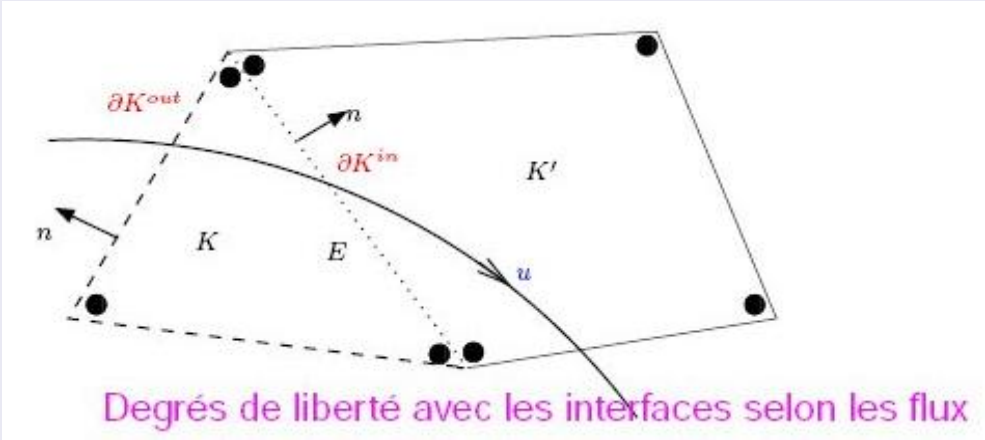


Degrés de liberté avec les interfaces selon les flux

Dispersion step

Like flow equation (time dependent): mixed finite elements (implicit)

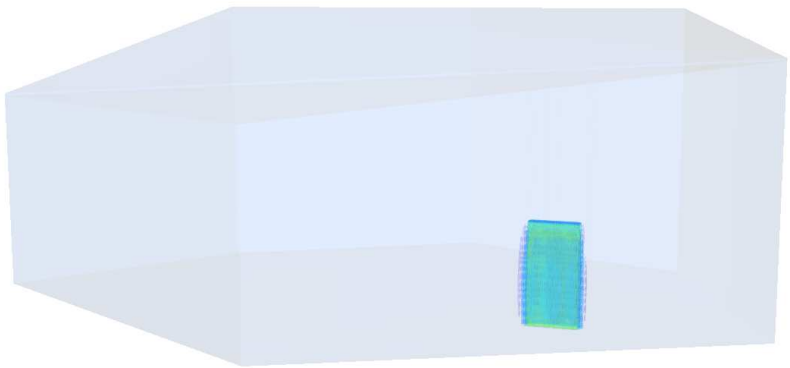
See Ackerer et al., Putti et al., Arbogast et al., ...

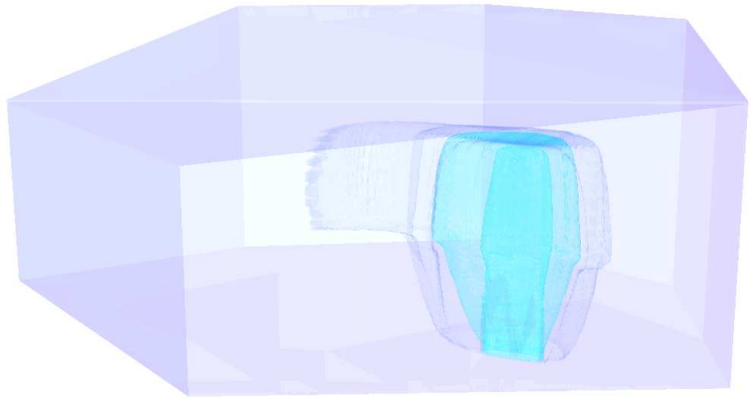
Condense transport solver, one time step

$$C^{n+1} = \Psi_T(f^n, C^n)$$

Transport around a nuclear waste storage site

GdR MoMaS benchmark, Andra model



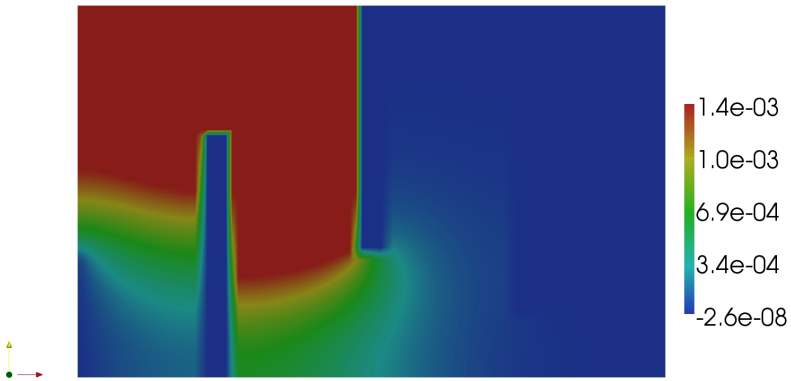


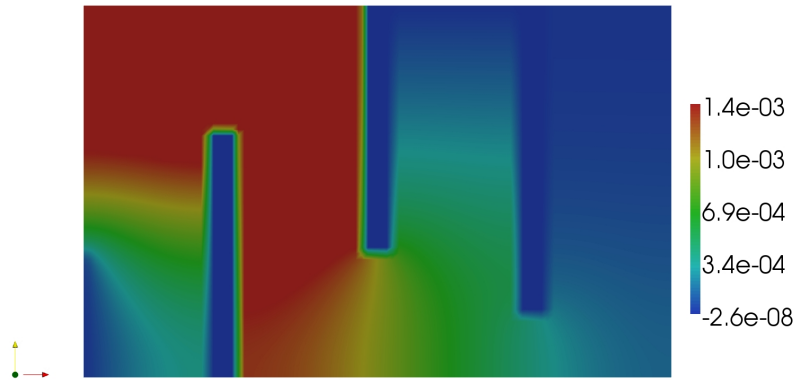
Concentration at 130 000 years

Concentration at 460 000 years

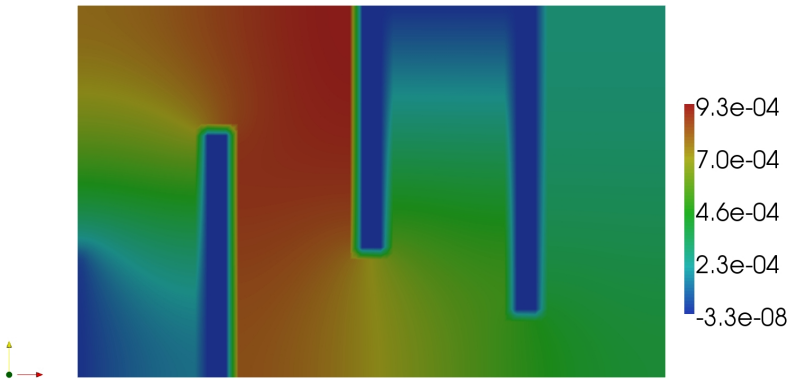
A. Sboui, E. Marchand (INRIA, Estime)

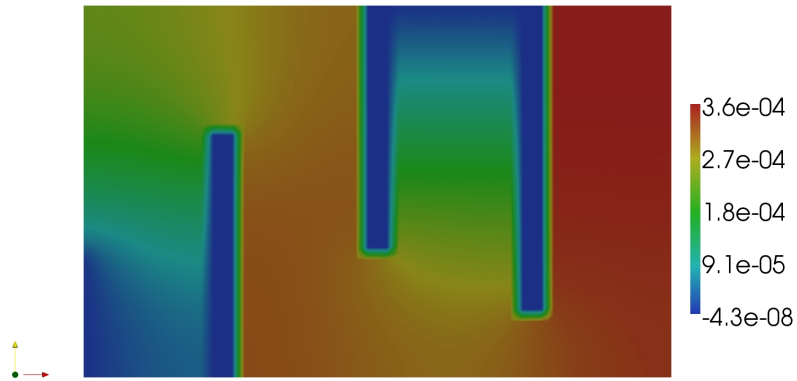
Transport for synthetic CO_2 example (M. Franco)





Left $T = 1$ day, right $T = 6$ days





Left $T = 12$ day, right $T = 37$ days

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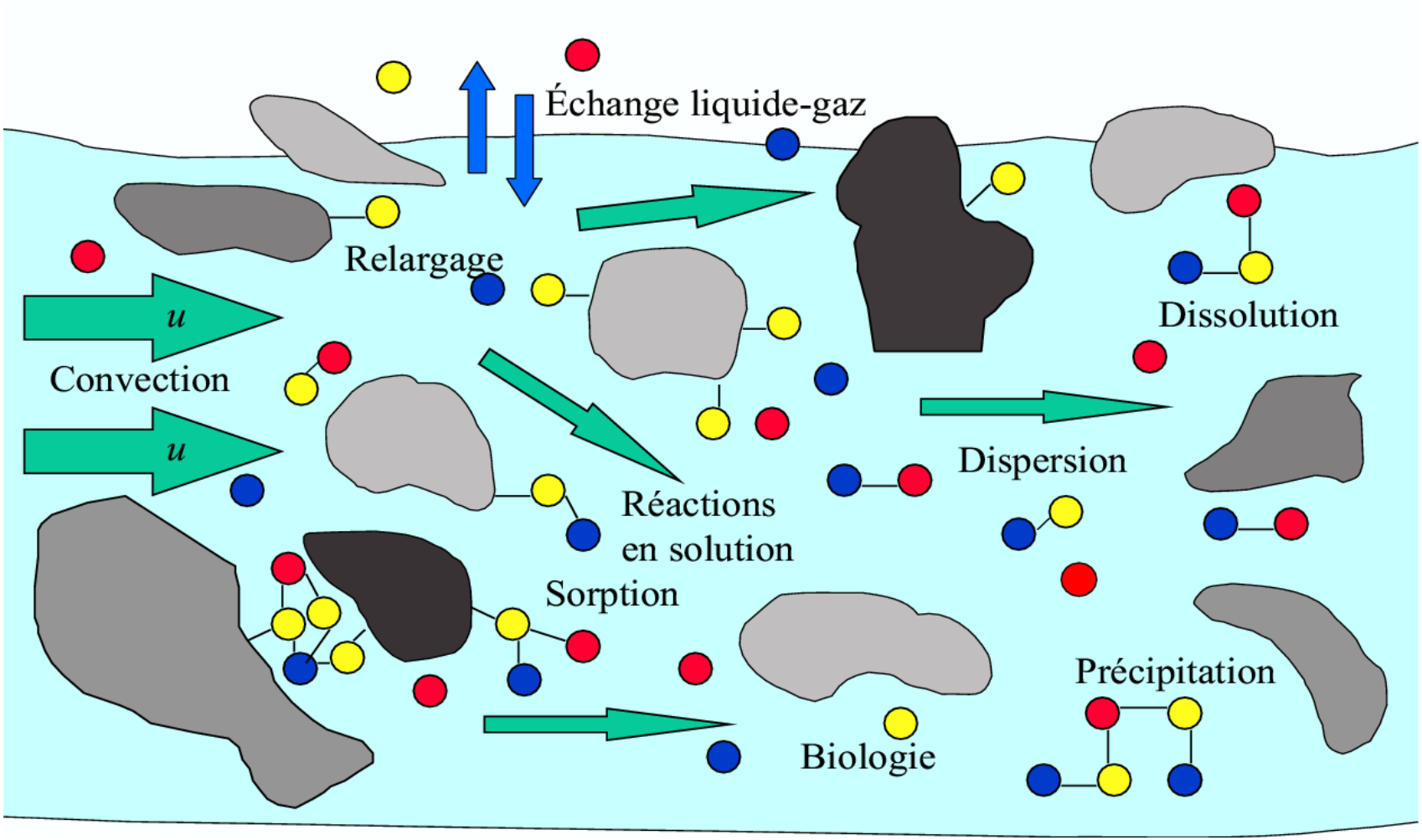
Chemical phenomena



Classification of chemical reactions

According to nature of reaction

Homogeneous	In the same phase (aqueous, gaseous, ...) Examples: Acid base, oxydo–reduction
Heterogeneous	Involve different phases Examples: Sorption, precipitation / dissolution, ...

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Slow reactions	Irreversible, modeled using kinetic law
Fast reactions	Reversible, modeled using equilibrium

Depends on relative speed of reactions and transport.

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In this talk: Equilibrium reactions, with sorption.

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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Several possible mechanisms

Surface complexation Formation of bond between surface and aqueous species, due to electrostatic interactions. Depends on surface potential.

Ion exchange Ions are exchanged between sorption sites on the surface. Depends on Cationic Exchange Capacity.

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Can be modeled as mass action law

Modeling general equilibrium models

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

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

General solution of $\nu Y = 0$: $Y = \begin{pmatrix} x \\ c \end{pmatrix}$, $x = Hc$. $c \in \mathbf{R}^{N_c}$, $x \in \mathbf{R}^{Nr}$.

Chemical equilibrium

Only take into account equilibrium, with aqueous and sorption reactions

Chemical reactions, mass action laws

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

$$\bar{x}_i \leftrightarrows \sum_{j=1}^{N_c} A_{ij} c_j + \sum_{j=1}^{N_s} B_{ij} \bar{c}_j, \qquad i = 1, \ldots, N_y,$$

c_j aqueous (mobile) components, $\bar{c}_j$ sorbed (immobile) components,
x_i aqueous secondary species, $\bar{x}_i$ fixed secondary species.

Numerical solution of nonlinear problem

System of non-linear equations

Mass action law

$$\log x = S \log c + \log K,$$
$$\log \bar{x} = A \log c + B \log \bar{c} + \log \bar{K}.$$

Mass conservation

$$c + S^T x + A^T \bar{x} = T, \qquad T \text{ known from transport}$$
$$\bar{c} + B^T \bar{x} = W, \qquad W \text{ imposed}$$

Take concentration logarithms as main unknowns

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

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Role of chemical model

Given totals T (and W, known), split into

Mobile $C = c + S^T x$,

Fixed $F = A^T \bar{x}$.

total concentrations

Result of chemical problem

$$F = \Psi_C(T)$$

Outline

Sorption models

Definition

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

Common isotherms

Linear $\psi(C) = K_d C$

Langmuir $\psi(C) = \dfrac{k_f \sigma_0 C}{k_f C + k_b}$

Freundlich $\psi(C) = \gamma C^{1/p}$ $(p > 1$ possible$)$

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Coupled model

$$\phi \frac{\partial C}{\partial t} + \phi \frac{\partial F}{\partial t} + LC = 0, \quad L \text{ adv. diff operator}$$
$$F = \Psi(C).$$

Mathematical, numerical analysis: van Duijn, Knabner, Frolkovic

Formulations of coupled system

After space and time discretization,

Coupled formulation

$$F\begin{pmatrix} C \\ F \end{pmatrix} = \begin{pmatrix} (\mathbf{M}+\Delta t\mathbf{L})C + \mathbf{M}F + b \\ F - \Psi(C) \end{pmatrix} = 0$$

Eliminate F $F_1(C) = (M+\Delta tL)C + M\Psi(C) - b^n$

Eliminate C $F_2(F) = F - \Psi\left(\mathbf{M}+\Delta t\mathbf{L})^{-1}(b-\mathbf{M}F)\right)$

Jacobian for coupled formulation,with $D = \mathrm{diag}(\Psi'(C_1),\ldots,\Psi'(C_N))$

$$J = \begin{pmatrix} \mathbf{M}+\Delta t\mathbf{L} & \mathbf{M} \\ -\mathbf{D} & I \end{pmatrix}$$

$J_2 = I + \mathbf{D}(\mathbf{M}+\Delta t\mathbf{L})^{-1}\mathbf{M}$ is Schur complement of J

Multicomponent models: the coupled system

Transport for each species (same dispersion tensor for all species)
Eliminate (unknown) reaction rates by using conservation laws ($T = C + F$)

$$\phi \frac{\partial T^{ic}}{\partial t} + L(C^{ic}) = 0, \quad ic = 1, \ldots, N_c$$

$$T_{ix}^{ic} = C_{ix}^{ic} + F_{ix}^{ic} \qquad ic = 1, .., N_c \text{ and } ix = 1, .., N_x$$

$$F_{ix} = \Psi(T_{ix}) \qquad ix = 1, \ldots, N_x.$$

Coupling methods

Iterative, based on fixed point (Yeh Tripathi '89, Carrayrou et al. '04)

Substitution, global (Saaltink '98, Hammond et al. '05)

Reduction method (Knabner, Kraütle, '06)

Coupling formulations and algorithms(1)

CC formulation, explicit chemistry

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

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

Coupled system is index 1 DAE

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

Use standard DAE software

C. de Dieuleveult (Andra thesis), J. Erhel, MK (JCP '09)

Coupling formulations and algorithms(2)

TC formulation, implicit chemistry

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

- + Non-intrusive approach (chemistry as black box)
- + Precipitation can (probably) be included
- − One chemical solve for each function evaluation

$$\begin{cases} C^{n+1} = \Psi_T \left(\dfrac{F^n - F^{n+1}}{\Delta t}, C^n \right) \\ T^{n+1} = C^{n+1} + F^{n+1} \\ F^{n+1} = \Psi_C(T^{n+1}) \end{cases}$$

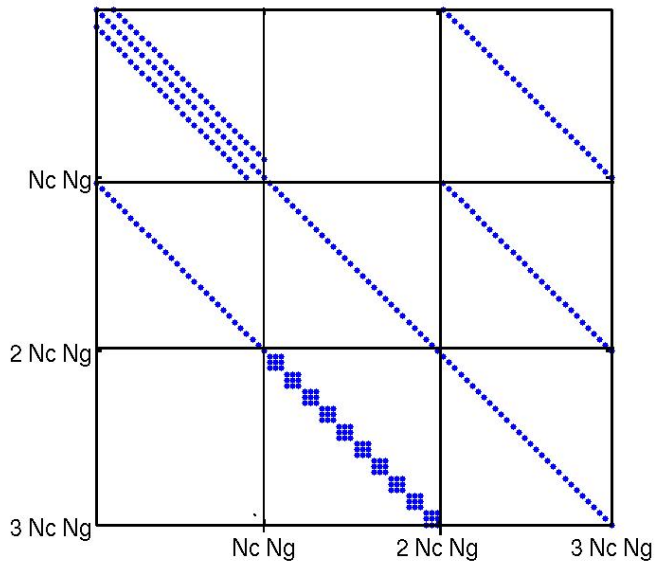
Fixed point problem, can be solved by block Gauss Seidel or by Newton's method

Coupled problem (2)

Solution by block Gauss–Seidel (fixed point) or by Newton–Krylov : keep transport and chemistry as black–boxes (up to Jacobian computation)
Residual computation:

1. Apply Ψ_T : solve transport for each species,
2. Apply Ψ_C: solve chemistry for each grid cell.

Jacobian structure



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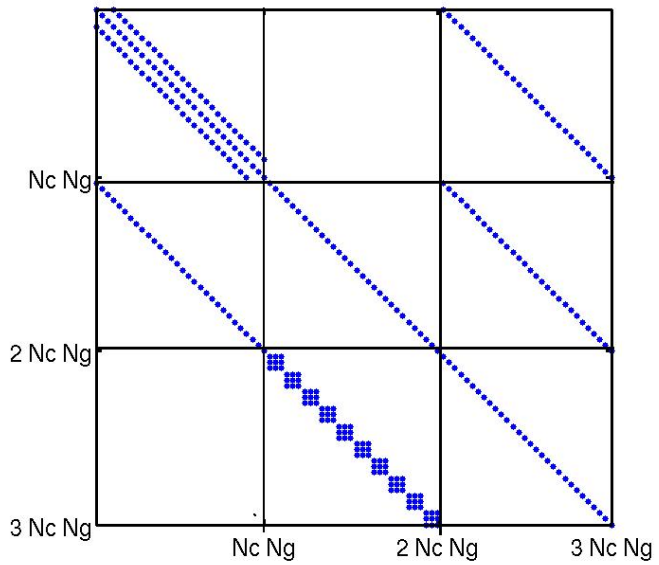

Alternative formulation

Eliminate T, C

$$F^{n+1} = \Psi_C \left(F^{n+1} + \Psi_T \left(\frac{F^{n+1} - F^n}{\Delta t}, C^n \right) \right)$$

Solution by Newton–Krylov

- Solve the linear system by an iterative method (GMRES)
- Requires only jacobian matrix by vector products.

Used for CFD, shallow water, radiative transfer(Keyes, Knoll, JCP 04), and for reactive transport (Hammond et al., Adv. Wat. Res. 05)

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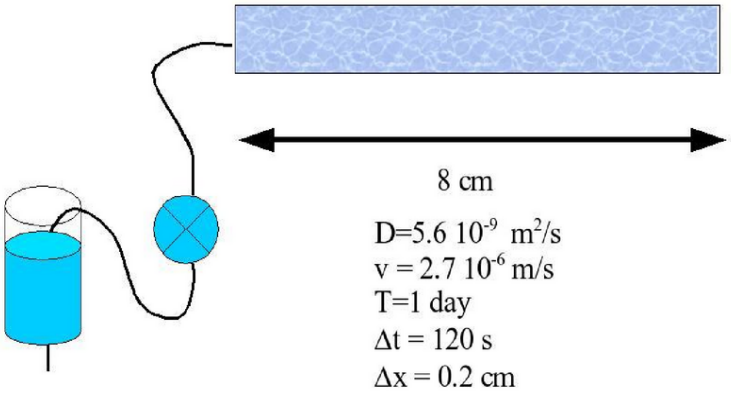
Inexact Newton

- Approximation of the Newton's direction $\|f'(x_k)d + f(x_k)\| \leq \eta \|f(x_k)\|$
- 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)

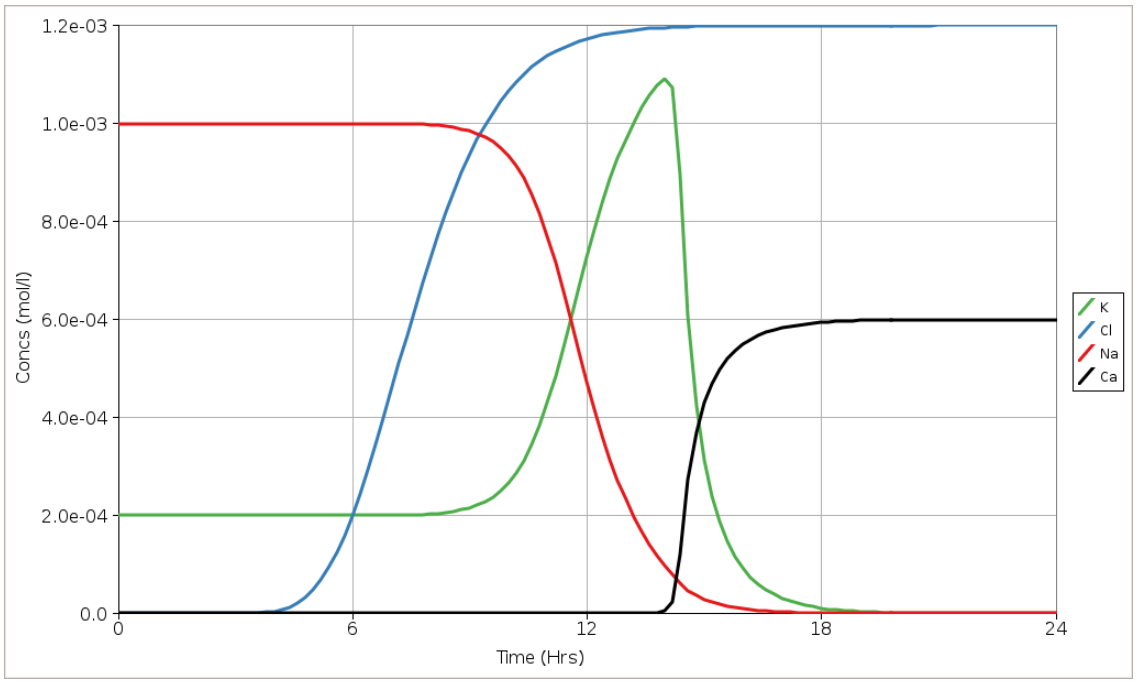
L. Amir's thesis, Amir, MK (Comp. Geosci. 09)

Example: ion exchange

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

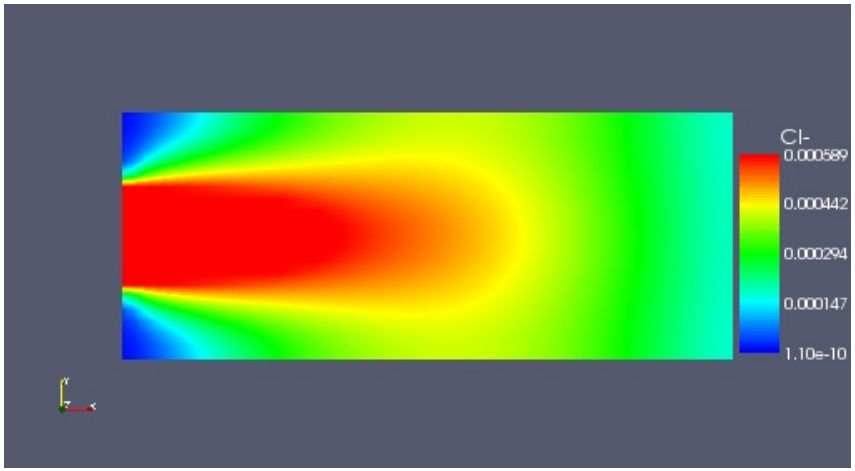


Column contains a solution with 1mmol, Na, 0.2mmol, K and 1.2mmol, NO_3. Inject solution with 1.2mmol $CaCl_2$. $CEC = 1.1\,10^{-3}$.

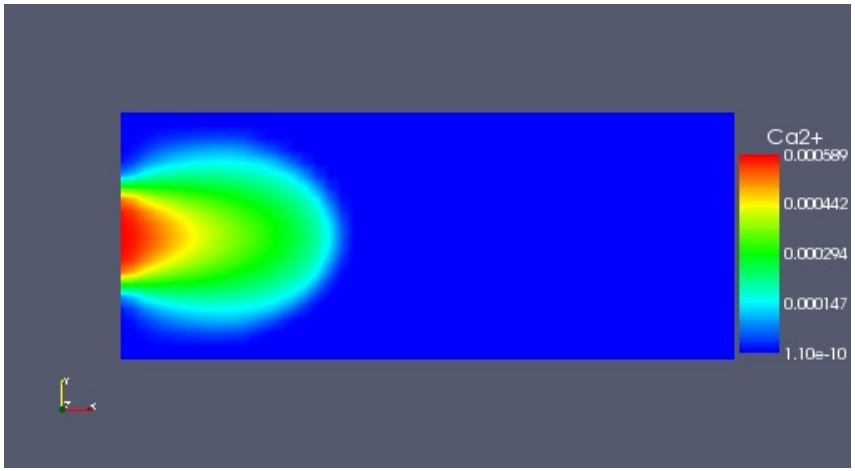


Ion exchange example (ctd)

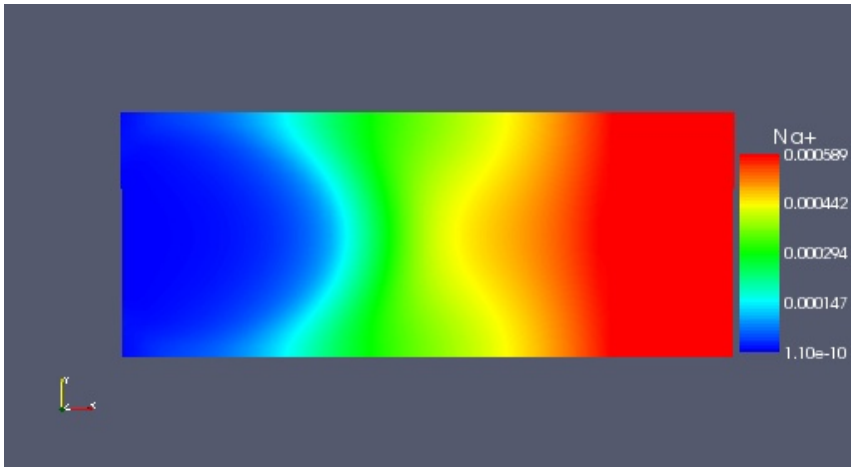
Snapshots at $t = 35$



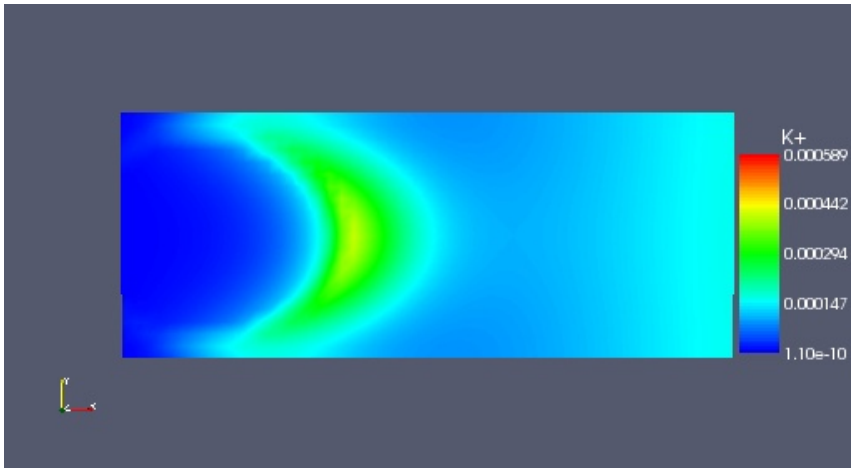
Cl



Ca



Na



K

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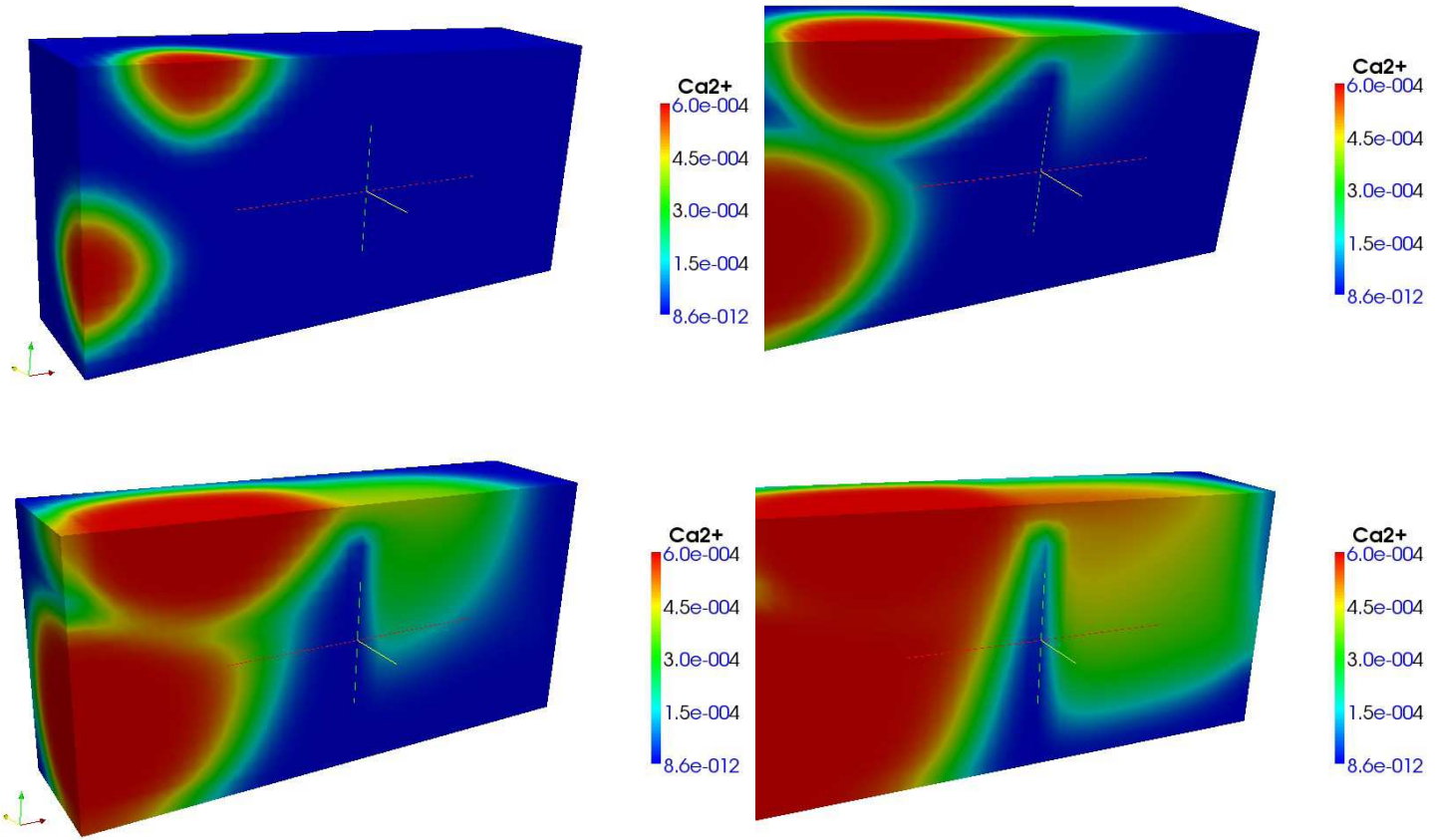
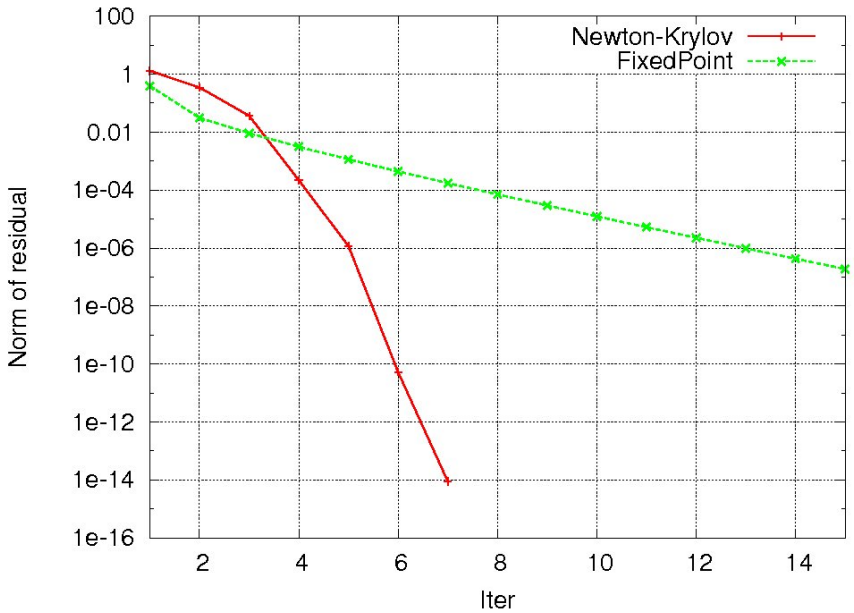
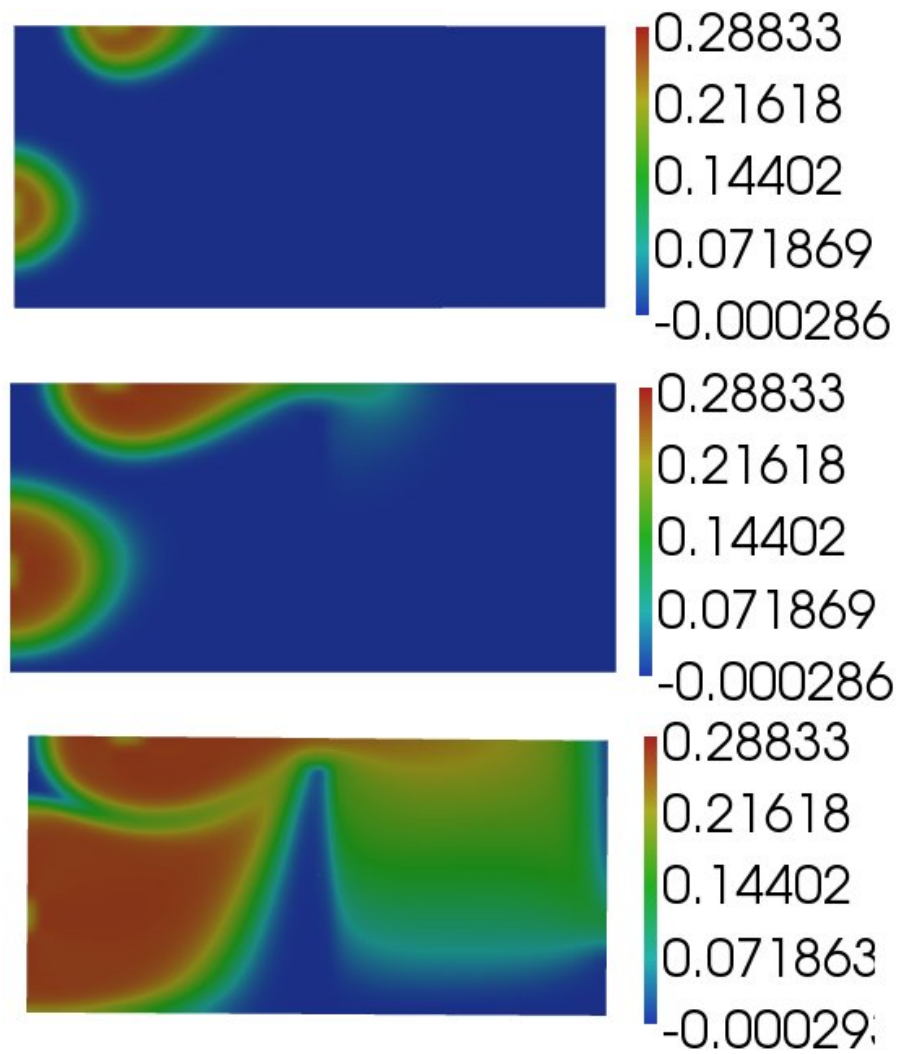
3D example (O. Saouli)



Performance of Newton's method



Convergence of Newton and fixed point



Outline

Preconditioning

- Essential for good linear performance
- Difficult for matrix free formulation

Block Jacobi

$$\mathbf{P} = \begin{pmatrix} \mathbf{M} + \Delta t \mathbf{L} & 0 \\ 0 & \mathbf{I} \end{pmatrix}$$

Solve transport at each step

Preconditioning

- Essential for good linear performance
- Difficult for matrix free formulation

Block Jacobi

$$\mathbf{P} = \begin{pmatrix} \mathbf{M} + \Delta t \mathbf{L} & 0 \\ 0 & \mathbf{I} \end{pmatrix}$$

Solve transport at each step

Block Gauss–Seidel preconditioner

$$\mathbf{P} = \begin{pmatrix} \mathbf{M} + \Delta t \mathbf{L} & 0 \\ -\mathbf{D} & \mathbf{I} \end{pmatrix}$$

Solve transport at each step, some coupling

Formulation with elimination of C equivalent to Schur complement of Gauss–Seidel.

Gmres convergence: field of values analysis

Convergence of GMRES not determined by eigenvalues (Greenbaum, Strakos).

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Nevertheless ...

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Nevertheless ...

Eigenvalues of preconditioned operators

Assume spectrum$(\mathbf{M} + \delta t \mathbf{L}) \approx O(1/h^2)$.

Jacobi $\Lambda(P^{-1}J) \subset [1 - iCh, 1 + iCh]$

Gauss-Seidel $\Lambda(P^{-1}J) \subset [1, 1 + Ch^2]$, 1 is multiple ev

Schur $\Lambda(J_2) \subset [1, 1 + Ch^2]$

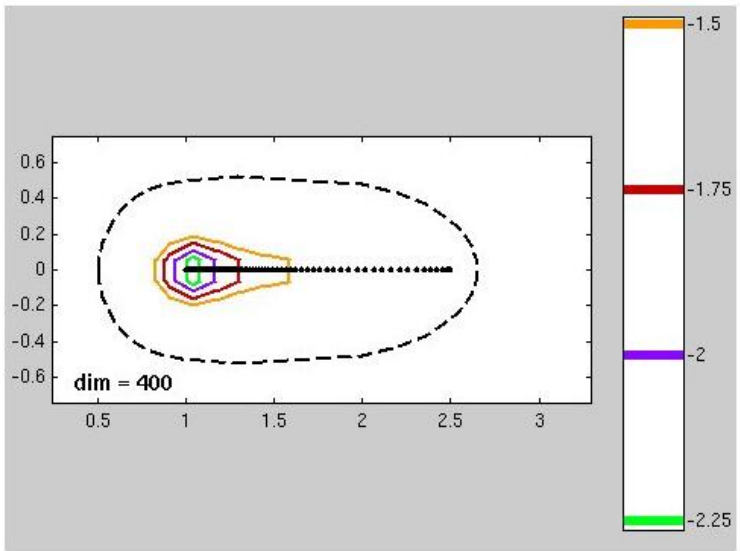
Bounded independent of h.

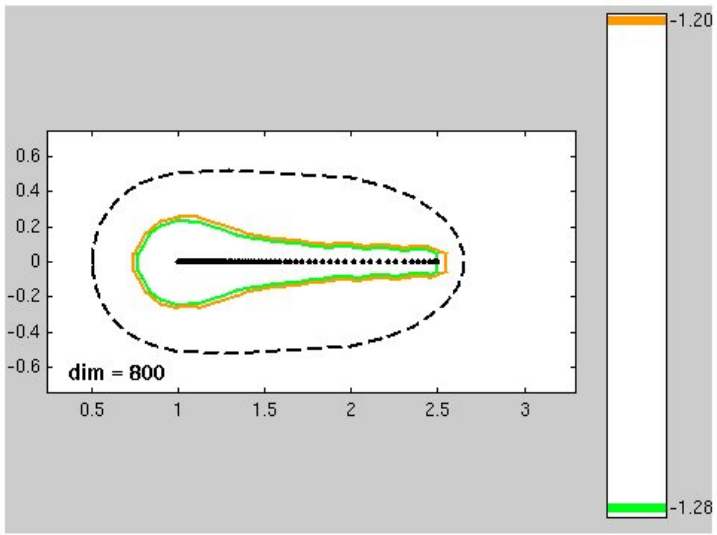
Field of value analysis

GMRES convergence

$$W(A) \equiv \left\{ \frac{x^* A x}{x^* x} | x \in \mathbb{C}^n, x \neq 0 \right\}, \text{ convex set, contains eigenvalues of } A$$

$$\frac{\|r_k\|_2}{\|r_0\|_2} \leq 2 \min_{p \in \mathcal{P}_k^*} \max_{z \in W(A)} \|p(z)\|_2.$$





Eingenvalues, field of values and pseudospectrum for GS preconditioning

Preconditioner performance

	h		$h/2$		$h/4$		$h/8$	
	NI	LI	NI	LI	NI	LI	NI	LI
None	8	54	10	100	17	238	33	658

Preconditioner performance

	h		$h/2$		$h/4$		$h/8$	
	Nl	Ll	Nl	Ll	Nl	Ll	Nl	Ll
None	8	54	10	100	17	238	33	658
BGS	8	11	10	15	14	22	21	36

Preconditioner performance

	h		$h/2$		$h/4$		$h/8$	
	NI	LI	NI	LI	NI	LI	NI	LI
None	8	54	10	100	17	238	33	658
BGS	8	11	10	15	14	22	21	36
Elimination	6	25	6	25	6	25	6	25

Inverting transport gives mesh independent convergence for both linear (LI) and nonlinear (NI) iterations.

In practice: approximate inverse should give spectral equivalence

Conclusions – perspectives

- Robust methods for solving flow and transport in porous media
- Preliminary results for reactive transport
- Newton–Krylov promising framework, implementation in progress

- Move to two-phase (multiphase) flows (water and gas)
- Transport in fractured media
- For chemistry, take into account “real” phenomena (minerals, kinetics,...)