Flow, transport and chemistry in porous media: numerical methods for coupled problems

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Motivations

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

Reactive transport
- Single species with sorption (joint work with A. Taakili)
- Multi-species equilibrium chemistry
Outline

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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, EDF

Research in mathematical and numerical modeling is conducted in the CNRS MOMAS group (Director A. Ern).
Present choice in France: a **sedimentary** geological formation (in the Meuse region)
A 3D far field model

Used as a benchmark, similar to Andra safety model

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

Blown-up 30 times vertically
CO₂ sequestration

- Long term capture of CO₂ in saline aquifer
- Simulation to understand CO₂ migration through salt
- Coupling of liquid and gas phase, reactive transport

SHPCO project (funded by ANR) High Performance Simulation of CO₂ sequestration

Sleipner project, Norway
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Darcy’s law and mixed finite element

**Flow equations**

\[ q = -K \nabla h \quad \text{Darcy’s law} \]
\[ \nabla \cdot q = 0 \quad \text{incompressibility} \]

\( h \) piezometric head

\( q \) Darcy velocity

**Mixed finite elements**

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

\[ (0,1) \quad E_3 \quad q_3 \]
\[ (0,0) \quad W_4 \quad W_3 \quad q_4 \]
\[ (1,0) \quad E_1 \quad q_1 \]

\[ (0,0) \quad E_2 \quad W_1 \quad W_2 \]

\[ (1,0) \quad E_4 \quad q_2 \]

\[ \text{valeur de la charge} \]
\[ \text{valeur de la charge et son gradient} \]
A composite mixed finite element for hexahedra (1)

The problem

Standard convergence theory not valid for RTN space over general (deformed) hexahedra, pressure space does not contain constant functions (T. Russell)

Kuznetsov, Repin (2003): construct macroelement on a hexahedron by subdividing it into 5 tetrahedra
A composite mixed finite element for hexahedra (2)

Features

- Same DOFs as before (average pressure in each element, flux across each face)
- Standard error estimates shown to apply: optimal order error (under regularity assumption).

Construction

\[ \mathcal{W}_h = \{ \mathbf{v}_h \in H(\text{div}, \Omega); \mathbf{v}_h|_{T_i} \in RTN_0(T_i), i = 1, \ldots, 5, \]
\[ \text{div} \mathbf{v}_h \text{ const. on } H, \mathbf{v}_h \cdot \mathbf{n} \text{ constant on faces of } H \} . \]

\(\mathbf{v}_h\) is uniquely defined by its normal components across the 6 faces, so \(\mathcal{W}_h\) contains constants.

A composite mixed finite element for hexahedra (3)

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

RTN FE

New FE
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Transport model

### Convection–diffusion equation

\[ \omega \frac{\partial c}{\partial t} - \text{div}(D \text{ grad } c) + \text{div}(uc) + \omega \lambda c = f \]

- \( c \): concentration [mol/l]
- \( \omega \): porosity [-]
- \( \lambda \): radioactive decay [s\(^{-1}\)]
- \( u \): Darcy velocity [m/s]

### Dispersion tensor

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

- \( \alpha_I, \alpha_t \): dispersivity coeff. [m], \( d_e \): molecular diffusion [m/s\(^2\)]
Solution by operator splitting

Advection step
Explicit, finite volumes / discontinuous Galerkin
- Locally mass conservative
- Keeps sharp fronts
- Small numerical diffusion
- Allows unstructured meshes
- CFL condition: use sub–time–steps

Dispersion step
Like flow equation (time dependant): mixed finite elements (implicit)
First order method
Example: transport around an obstacle

MoMaS benchmark for reactive transport. Here transport only

Concentration at $t = 25$

J. B. Apoung, P. Hav, J. Houot, MK, A. Semin, O. Saouli
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)
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Chemical phenomena

- Convection
- Relargage
- Échange liquide-gaz
- Dissolution
- Dispersion
- Réactions en solution
- Sorption
- Biologie
- Précipitation
- Biologie
# Classification of chemical reactions

### According to nature of reaction

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### According to speed of reaction

- **Slow reactions**: Irreversible, modeled using kinetic law
- **Fast reactions**: Reversible, modeled using equilibrium

In this talk: Equilibrium reactions, with sorption.
## Classification of chemical reactions

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Depends on relative speed of reactions and transport.
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, ...

According to speed of reaction

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

Depends on relative speed of reactions and transport.

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

Can be modeled as mass action law
General chemical reactions: \( N_s \) species, \( N_r \) reactions

\[
\sum_{j=1}^{N_s} \nu_{ij} Y_j \leftrightarrow 0, \quad i = 1, \ldots, N_r
\]

\( \nu_{ij} \) stoichiometric coefficients. Matrix equation \( \nu Y = 0 \)

Assumption \( \nu \) has full rank: \( \text{Rank} \nu = N_r \). Basis for null-space of \( \nu \) has dimensions \( N_c = N_s - N_r \).

Partition \( \nu = (G \ N) \), \( B \in \mathbb{R}^{N_r \times N_r} \) invertible, \( N \in \mathbb{R}^{N_c \times N_r} \). Let \( H = -G^{-1}N \).

General solution of \( \nu Y = 0 \): \( Y = (x_c)Hc, \quad x = Hc \in \mathbb{R}^{N_r} \).
Modeling general equilibrium models

General chemical reactions: \( N_s \) species, \( N_r \) reactions

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General chemical reactions: $N_s$ species, $N_r$ reactions

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

M. Kern (INRIA)
The chemical problem

$c$ (resp. $\bar{c}$) mobile (resp. fixed) primary species
$x$ (resp. $\bar{x}$) mobile (resp. fixed) secondary species

System of non-linear equations

\[
\begin{align*}
  c + S^T x + A^T \bar{x} & = T, \\
  \bar{c} + B^T \bar{x} & = W,
\end{align*}
\]

Mass conservation

\[
\begin{align*}
  \log x & = S \log c + \log K, \\
  \log \bar{x} & = A \log c + B \log \bar{c} + \log \bar{K}.
\end{align*}
\]

Mass action law

Role of chemical model

Given $T$ (and $W$, known), split into mobile $C$ and fixed $F$ concentrations.

\[
C = c + S^T x = \Phi(T), \quad F = A^T \bar{x} = \Psi(T)
\]
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Sorption models

One species reacts with rock matrix, description by a sorption isotherm:
\[ v = \Psi(u). \]

*u* aqueous concentration, *v* fixed “concentration”

### Common isotherms

- **Linear**
  \[ v = K_d u \]

- **Langmuir**
  \[ v = \frac{k_f \sigma_0 u}{k_f u + k_b} \]

- **Freundlich**
  \[ v = \gamma u^{1/p} \quad (p > 1 \text{ possible}) \]

### Coupled model

\[
\omega \frac{\partial u}{\partial t} + \omega \frac{\partial v}{\partial t} + Lu = 0, \quad L \text{ adv. diff operator}
\]

\[ v = \Psi(u). \]

Mathematical, numerical analysis: van Duijn, Knabner, Barrett, Kacur, Frolkovic
Formulations of coupled system

After space and time discretization, the coupled formulation is given by:

\[ F(u, v) = 0 \]

with

\[
F\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} (M + \Delta L)u + Mv + b \\ v - \Psi(u) \end{pmatrix}
\]

Eliminate \( v \) to get:

\[ F_1(u) = (M + \Delta tL)u + M\Psi(u) - b^n \]

Eliminate \( u \) to get:

\[ F_2(u) = v - \Psi((M + \Delta L)^{-1}(b - Mv)) \]

Jacobian for the coupled formulation, with \( D = \text{diag}(\Psi'(u_1), \ldots, \Psi'(u_N)) \):

\[
J = \begin{pmatrix} M + \Delta L & M \\ -D & I \end{pmatrix}
\]

\[ J_2 = I + D(M + \Delta tL)^{-1}M \] is the Schur complement of \( J \).
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 $\eta$?
  - Keep quadratic convergence (locally)
  - Avoid oversolving the linear system

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

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

Possible choices

Block diagonal \( P = \text{diag}(M + \Delta tL, I) \),

Block Gauss Seidel “Physics based”, equivalent to (linear) sequential method

\[
P = \begin{pmatrix} M + \Delta tL & 0 \\ -D & I \end{pmatrix}
\]

Approximate block factorization ?
Numerical results

Geometry of MoMaS reactive transport benchmark (2D), LifeV + Kinsol (Sundials)

<table>
<thead>
<tr>
<th>$\sigma_0$</th>
<th>0.125</th>
<th>0.25</th>
<th>0.4</th>
<th>0.45</th>
<th>0.5</th>
</tr>
</thead>
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<tr>
<td>nb nonlin iter</td>
<td>5</td>
<td>6</td>
<td>6</td>
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The coupled system

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

\[
\begin{align*}
\omega \frac{\partial T^{ic}}{\partial t} + L(C^{ic}) &= 0, \quad ic = 1, \ldots, N_c \\
T^{ic}_{ix} &= C^{ic}_{ix} + F^{ic}_{ix} \quad \text{ic} = 1, \ldots, N_c \text{ and } ix = 1, \ldots, N_x \\
F_{ix} &= \Psi(T_{ix}) \quad \text{ix} = 1, \ldots, N_x.
\end{align*}
\]

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, Kratle, '06)
Coupling formulations and algorithms (1)

CC formulation, explicit chemistry

\[
\begin{align*}
\omega \frac{dC}{dt} + \frac{dF}{dt} + LC &= 0 \\
H(z) - \begin{pmatrix} C + F \\ W \end{pmatrix} &= 0 \\
F - F(z) &= 0.
\end{align*}
\]

- + 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)
TC formulation, implicit chemistry

\[
\begin{align*}
\omega \frac{dT}{dt} + LC &= 0 \\
T - C - F &= 0 \\
F - \Psi(T) &= 0
\end{align*}
\]

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

\[
\begin{align*}
C_{n+1} &= (M + \Delta t L)^{-1} (C^n + F^n - F^{n+1}) \\
T^{n+1} &= C^{n+1} + F^{n+1} \\
F^{n+1} &= \Psi(T^{n+1})
\end{align*}
\]

Fixed point problem, can be solved by block Gauss Seidel or by Newton’s method
Solution by Newton–Krylov

**Structure of Jacobian matrix**

\[
f'(C, T, F) = \begin{pmatrix}
I & 0 & (I + \Delta tL)^{-1} \\
-1 & I & -1 \\
0 & -\Psi'(T) & I
\end{pmatrix}
\]

- Transport independent for each species
- Chemistry independent for each grid cell

**Find a good preconditioner?**

- Is block diagonal good enough?
- Physics based (cf. Hammond et al.)?
Example: ion exchange

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

Column contains a solution with 1mmol Na, 0.2mmol K and 1.2mmol NO₃. Inject solution with 1.2mmol CaCl₂. \( CEC = 1.1 \times 10^{-3} \).
Ion exchange example (ctd)

Snapshots at $t = 35$

Cl

Ca

Na

K
Difficult test case, heterogeneous medium, with complex chemistry (even for “easy” level).
12 species, eq. constants vary by 45 orders of magnitude (1D, Matlab code, L.Amir’s thesis).
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,...)