

Reactive flow and transport in the subsurface models, formulations and algorithms

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The INRIA logo is written in a stylized, red, cursive font.A small version of the red, cursive INRIA logo.

Acknowledgments

Joint work with

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ANR SHPCO2, GNR MoMaS, Andra, Itasca

Outline

- 1 Motivations: CO₂ storage
- 2 Models
 - Chemistry
 - Transport and coupled model
- 3 Numerical methods for solving chemistry and transport
 - Solving equilibrium chemistry
 - Flow and transport
- 4 Coupling transport and chemistry
 - Solving the coupled system
 - A Newton–Krylov method
 - Linear and non–linear preconditioning
- 5 Numerical results
 - MoMaS benchmark
 - Ion exchange, 2d “example 11 from PhreeqC
 - SHPCO₂

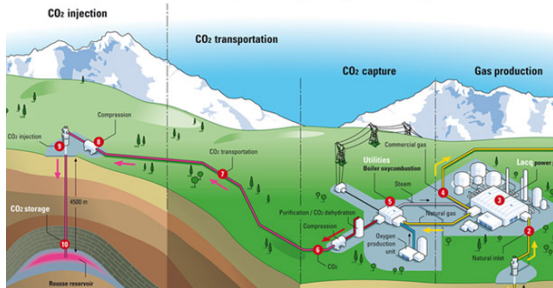
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CO₂ sequestration



Carbon capture & geological storage

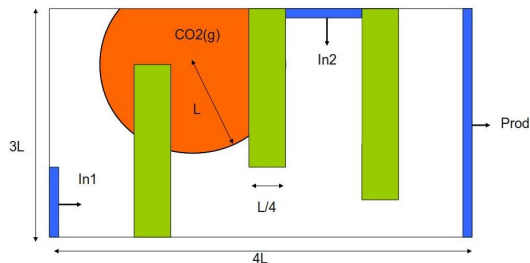


- Long term capture of CO₂ in saline aquifer
- Simulation to understand CO₂ migration through salt
- Coupling of liquid and gas phase, reactive transport

ANR SHPCO₂ project High Performance Simulation of CO₂ sequestration

CO₂ sequestration: a synthetic model (A. Michel, IFP)

Minimal chemical system that still "looks" realistic for CO₂ storage



Dissolution of CO₂ in water, dissolution of calcite. Gas assumed **immobile** (capillary trapping), decouples flow from reactive transport.

Chemical system

- $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$
- $\text{H}_2\text{O} + \text{CO}_{2(\text{aq})} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$
- $\text{CO}_{2(\text{g})} \rightleftharpoons \text{CO}_{2(\text{aq})}$
- $\text{CaCO}_3 + \text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-$

water dissociation

dissociation of liquid CO₂

gas dissolution

Dissolution of calcite

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Classification of chemical reactions

According to nature of reaction

Homogeneous In the same phase (liquid, gaseous, ...)
Examples: Acid base, redox reactions–reduction

Heterogeneous Involve different phases
Examples: Sorption, mineral precipitation / dissolution, gas 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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This talk: only **equilibrium** reactions

Modeling general equilibrium systems (1)

N_s species, N_r reactions, ν **stoichiometric matrix full rank**.

$$\sum_{j=1}^{N_s} \hat{S}_{ij} Y_j \rightleftharpoons 0, \quad i = 1, \dots, N_r \iff \hat{S} Y \rightleftharpoons 0$$

(Generally) more reactions than species, can assume **S has full rank**, null-space dimension $N_c = N_s - N_r$. [Morel (93)]: identify set of N_r **primary species** (more intrinsic view [Saaltink et al. (98)])

From chemistry to mathematics

- Each reaction \rightarrow **mass action law** (s_i, c_j denote concentrations)

$$s_i = K_i \prod_{j=1}^{N_c} c_j^{\hat{S}_{ij}}, \quad i = 1, \dots, N_r$$

- Each primary species \rightarrow mass conservation

$$T_j = c_j + \sum_{i=1}^{N_r} \hat{S}_{ij} s_i, \quad j = 1, \dots, N_c$$

Chemical equilibrium with liquid and solid species

Distinguish between **mobile** species (aqueous reactions), **immobile** species (sorption reactions) and **mineral** species (precipitation–dissolution reactions).

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$$\sum_{j=1}^{N_a} (S_{aa})_{ij} X_j^a \quad \Leftrightarrow 0 \quad i = 1, \dots, N_r,$$

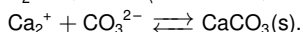
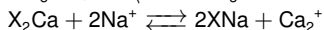
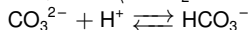
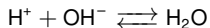
$$\sum_{j=1}^{N_a} (S_{sa})_{ij} X_j^a + \sum_{j=1}^{N_s} (S_{ss})_{ij} X_j^s \quad \Leftrightarrow 0 \quad i = 1, \dots, \bar{N}_r,$$

$$\sum_{j=1}^{N_a} (S_{pa})_{ij} X_j^a \quad - X_i^p \Leftrightarrow 0 \quad i = 1, \dots, N_p.$$

Special form for stoichiometric matrix : $\hat{S} = \begin{pmatrix} S_{aa} & 0 & 0 \\ S_{sa} & S_{ss} & 0 \\ S_{pa} & 0 & -I \end{pmatrix}.$

An example

Chemical system (from Saaltink et al. (1998))



Aqueous species:

$$X^a = (\text{H}^+, \text{OH}^-, \text{CO}_3^{2-}, \text{Na}^+, \text{Ca}_2^+, \text{H}_2\text{O}, \text{HCO}_3^-)^T,$$

sorbed species $X^s = (\text{X}_2\text{Ca}, \text{XNa})^T$

mineral species $X^p = (\text{CaCO}_3)^T$

Matrices

$$S_{aa} = \begin{pmatrix} 1 & 1 & 0 & 0 & 0 & -1 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & -1 \end{pmatrix}, \quad S_{sa} = (0 \quad 0 \quad 0 \quad 2 \quad -1 \quad 0 \quad 0),$$

$$S_{ss} = (1 \quad -2), \quad S_{pa} = (0 \quad 0 \quad 1 \quad 0 \quad 1 \quad 0 \quad 0).$$

Mass action law and solubility product

Aqueous and sorption reactions: mass action law

Take **log concentrations**, use linear algebra (vector, matrix notations)

$$\begin{pmatrix} S_{aa} & 0 \\ S_{sa} & S_{ss} \end{pmatrix} \begin{pmatrix} \log c \\ \log s \end{pmatrix} = \begin{pmatrix} \log K_a \\ \log K_s \end{pmatrix}$$

Reactions with minerals

Solubility product (logarithmic form)

$$\Pi = \log K_p - S_{pa} \log c.$$

Reaction occurs only if mineral is present

$$(\Pi = 0 \text{ and } p \geq 0) \text{ or } (\Pi \geq 0 \text{ and } p = 0)$$

Kernel matrix and total concentrations

Kernel matrix U st $US^T = 0$ (Saaltink et al. 1998), U^T basis of **null space** of S . Can be chosen to match S

$$U = \begin{pmatrix} U_{aa} & U_{as} & U_{ap} \\ 0 & U_{ss} & 0 \end{pmatrix}$$

Total concentrations

Total analytic concentrations (Yeh, Tripathi (1989))

$$\begin{pmatrix} T \\ \bar{T} \end{pmatrix} = \begin{pmatrix} U_{aa} & U_{as} & U_{ap} \\ 0 & U_{ss} & 0 \end{pmatrix} \begin{pmatrix} c \\ s \\ p \end{pmatrix}.$$

Total mobile and immobile concentrations

$$C = U_{aa} c, \quad \bar{C} = U_{as} s + U_{ap} p$$

$$T = C + \bar{C} = U_{aa} c + U_{as} s + U_{ap} p$$

Transport: advection, diffusion, dispersion

Convection–diffusion equation

$$\phi \partial_t \mathbf{c} - \underbrace{\operatorname{div}(\mathbf{D} \operatorname{grad} \mathbf{c})}_{\text{dispersion}} + \underbrace{\operatorname{div}(\mathbf{q} \mathbf{c})}_{\text{advection}} = f$$

- \mathbf{c} : concentration [mol/l]
- ϕ : porosity [–]
- \mathbf{D} diffusion – dispersion tensor [m/s]² (can be anisotropic)
- \mathbf{q} Darcy velocity [m/s]

Numerical method must handle advective flux (upwind to preserve monotonicity), usually implicit because of diffusion.

Must often choose between keeping **monotonicity** (essential for reactive transport) and controlling **numerical diffusion**. No perfect scheme

Notation $\operatorname{div}(\mathbf{q} \mathbf{c} - D \operatorname{grad} \mathbf{c}) \stackrel{\text{def}}{=} \mathcal{L} \mathbf{c}$

Coupled reactive transport model

Mas conservation for each species. Only **mobile** species are subject to transport

$$\begin{aligned}\phi \partial_t \mathbf{c} + \mathcal{L} \mathbf{c} &= \mathbf{S}_{aa}^T r_a + \mathbf{S}_{sa}^T r_s + \mathbf{S}_{pa}^T r_p, \\ \rho_s (1 - \phi) \partial_t \mathbf{s} &= \mathbf{S}_{ss}^T r_s, \\ \rho_s (1 - \phi) \partial_t \mathbf{p} &= - r_p.\end{aligned}$$

Elimination of reaction rates

Multiply conservation law by kernel matrix

$$\begin{aligned}\phi \partial_t \mathbf{C} + \rho_s (1 - \phi) \partial_t \bar{\mathbf{C}} + \mathcal{L} \mathbf{C} &= 0, \\ \rho_s (1 - \phi) \partial_t \bar{\mathbf{T}} &= 0.\end{aligned}$$

The coupled reactive transport problem

Transport for the total concentrations

$$\begin{aligned}\phi \partial_t \mathbf{C} + \rho_s (1 - \phi) \partial_t \bar{\mathbf{C}} + \mathcal{L} \mathbf{C} &= 0, \\ \rho_s (1 - \phi) \partial_t \bar{\mathbf{T}} &= 0.\end{aligned}$$

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Chemical equilibrium

$$\begin{pmatrix} S_{aa} & 0 & 0 \\ S_{sa} & S_{ss} & 0 \\ S_{pa} & 0 & 0 \end{pmatrix} \begin{pmatrix} \log c \\ \log s \\ \log p \end{pmatrix} = \begin{pmatrix} \log K_a \\ \log K_s \\ \log K_p - \Pi \end{pmatrix}$$

$(\Pi = 0 \text{ and } p \geq 0) \text{ or } (\Pi \geq 0 \text{ and } p = 0)$

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Total concentrations

$$\begin{pmatrix} T \\ \bar{T} \end{pmatrix} = \begin{pmatrix} U_{aa} & U_{as} & U_{ap} \\ 0 & U_{ss} & 0 \end{pmatrix} \begin{pmatrix} c \\ s \\ p \end{pmatrix}, \quad \mathbf{C} = U_{aa} \mathbf{c}, \quad \bar{\mathbf{C}} = U_{as} \mathbf{s} + U_{ap} \mathbf{p}$$

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Equilibrium problem with mineral reactions

For simplicity, lump together aqueous and sorption species, stoichiometric matrix S_{aa} , reduce to “Morel” form: $S_{aa} = (I, -\tilde{S}_{aa})$. Split species between **primary** $c^p =$ and **secondary** c^s . Use **logarithmic** form, $\xi^{p,s} = \log c^{p,s}$.

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Local chemical equilibrium problem:

$$\exp \xi^p + \tilde{S}_{aa}^T \exp(\xi^s) + S_{pa}^T p - T = 0, \quad \text{with } \xi^s = \tilde{S}_{aa} \xi^p - \log K_a,$$

$$(\log K_p - S_{pa} \xi = 0 \text{ and } p \geq 0) \text{ or } (\log K_p - S_{pa} \xi \geq 0 \text{ and } p = 0).$$

Challenges

- Difficult to solve non-linear system (Carrayrou, Jonval, Rozier-Awada);
- Determine which minerals are present, and which are not

Possible solution methods

- **Combinatorial search** Make an educated guess, (usually works, but **why?**)
- **Complementarity formulation** Solve with semi-smooth Newton's method (Kraütle et al (2011))
- **Non-linear equations with constraints** Use **Interior point methods** El Bakry, Tapia et al. (1996), Saaf (1997), Ben Gharbia et al. (2021)

The interior points method

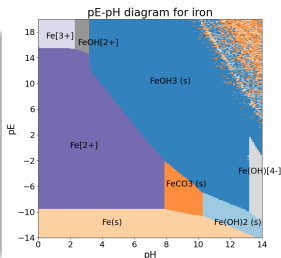
Introduce additional variable $z = -(S_{pa}\xi^p + \log K_p)$, $P = \text{diag } p$, $Z = \text{diag } z$, $e = (1, 1, \dots, 1)^T$. Solve relaxed problem $F_\mu(X) = 0$ by Newton's method, with

$$X = \begin{pmatrix} \xi \\ p \\ z \end{pmatrix}, \quad F_\mu(X) = \begin{pmatrix} F_e(\xi^p, p) \\ S_{pa}\xi^p + \log K_p + z \\ PZe - \mu e \end{pmatrix}$$

$$\text{Jacobian } J_\mu = \begin{pmatrix} I + \tilde{S}_{aa}^T Y \tilde{S}_{aa} & S_{pa}^T & 0 \\ S_{pa} & 0 & I \\ 0 & Z & P \end{pmatrix}, \quad Y = \text{diag exp}(\xi^s)$$

Algorithmic details

- Let $\mu \rightarrow 0$ during the Newton iterations:
if $|p \cdot z - \mu| < \mu$, then $\mu \leftarrow \rho \mu$ ($\rho = 10^{-2}$).
- Line search (reduce Newton step) to make sure p and z , remain positive, also reduce residual



Equilibrium chemistry without Morel

Chemical system $S \log \mathbf{c} = \log K$, $U\mathbf{c} = T$

Using QR factorization of $S^T = (Q_1 \quad Q_2) \begin{pmatrix} R_1 \\ 0 \end{pmatrix}$ gives $U = Q_2$.

Write $\mathbf{z} = \log \mathbf{c} = Q_1 \mathbf{z}_1 + Q_2 \mathbf{z}_2$, mass action law gives $R_1^T \mathbf{z}_1 = \log K$.

Non linear system becomes

$$Q_2^T \exp(Q_1 \mathbf{z}_1 + Q_2 \mathbf{z}_2) = T$$

Only unknown is \mathbf{z}_2 (size $N_s - N_r$). Recover **primary** and **secondary** species !

Jacobian is

$$J_c = Q_2^T C Q_2, \text{ with } C = \text{diag}(\mathbf{c}) = \text{diag}(\exp(\mathbf{z})).$$

Source of ill-conditioning is C (cf. J. Carrayrou).

The chemical equilibrium problem as a mapping

Role of chemical model

Give total \mathbf{T} , split into

$$\text{Liquid } \mathbf{C} = \mathbf{c} + \mathbf{S}_{cc}^T \mathbf{s},$$

$$\text{Solid } \bar{\mathbf{C}} = \mathbf{S}_{c\bar{c}}^T \bar{\mathbf{s}}$$

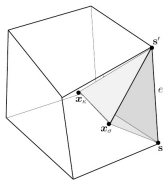
total concentrations

The chemical sub-problem defines a mapping

$$\Psi_{\mathbf{C}} : \mathbf{T} \mapsto \Psi_{\mathbf{C}}(\mathbf{T}) = \bar{\mathbf{C}} = U_{c\bar{c}} \bar{\mathbf{C}}, \quad \text{Jacobian } J_{\mathbf{C}} = \Psi_{\mathbf{C}}'(\mathbf{T}; j)_{j=1, \dots, N_h}$$

Evaluation of $\Psi_{\mathbf{C}}$ requires **solution** of chemical equilibrium for each grid point

Discrete advection–diffusion model; VAG scheme (1)



Vertex **A**pproximate **G**radient scheme (Eymard et al., 2012)

Mesh of domain Ω : $\mathcal{T} = \{\text{cells}\}$, $\mathcal{V} = \{\text{vertices}\}$

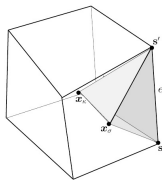
Discrete unknowns $W_{\mathcal{T}} = \{(c_v)_{v \in \mathcal{V}}, (c_K)_{K \in \mathcal{T}}\}$

Diffusion fluxes $F_{K,v}^d = \sum_{v' \in \mathcal{V}_K} T_K^{v,v'} (c_K^{n+1} - c_{v'}^{n+1})$, transmissivities $T_K^{v,v'}$ computed from local **finite element** submesh,

Advection fluxes defined through upwinding,

$$c_{K,v} = \begin{cases} c_K & \text{if } F_{K,v}^{\text{flow}} \geq 0, \\ c_v & \text{if } F_{K,v}^{\text{flow}} < 0. \end{cases}$$

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Discrete scheme

$$\begin{cases} \phi_K |K| \frac{c_K^{n+1} c_K^n}{\Delta t} + \sum_{v, v' \in \mathcal{V}_K} T_K^{v,v'} (c_K^{n+1} - c_{v'}^{n+1}) + \sum_{v \in \mathcal{V}_K} F_{K,v}^{\text{fl}} c_{K,v}^{n+1} = f_K, & \forall K \in \mathcal{T} \\ \phi_K |K| \frac{c_v^{n+1} c_v^n}{\Delta t} - \sum_{K \in \mathcal{V}_v, v' \in \mathcal{V}_K} T_K^{v,v'} (c_K^{n+1} - c_{v'}^{n+1}) - \sum_{K \in \mathcal{T}_v} F_{K,v}^{\text{flow}} c_{K,v}^{n+1} = f_v, & \forall v \in \mathcal{V} \end{cases}$$

Discrete advection-diffusion model: the VAG scheme (2)

Cell unknowns can be eliminated locally (static condensation), result linear system

$$\Phi \frac{c_{\mathcal{T}}^{n+1} - c_{\mathcal{T}}^n}{\Delta t} + A c_{\mathcal{T}}^{n+1} = f_{\mathcal{T}}^{n+1}.$$

ComPASS code (Lopez et al., 2018)

- Multiphase **compositional** thermal Darcy flow model (Coats formation)
- 2D discrete **fracture** or fault network coupled with the surrounding 3D matrix
- 3D conforming **polyhedral** meshes
- Newton Raphson algorithm with **phase appearance and disappearance**
- **CPR-AMG** preconditioner [Lacroix, Vassilevski, Wheeler, 2001], [Scheichl, Masson, Wendeburg, 2003]

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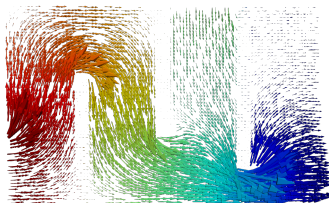
Condense transport solver, one time step

$$C^{n+1} = \Psi_{\mathcal{T}}(f^n, C^n)$$

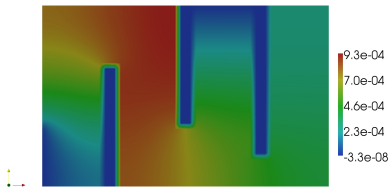
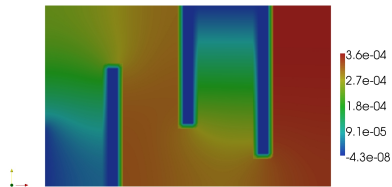
Flow and transport for synthetic CO₂ example



Pressure



velocity

Concentration, left $T = 12$ day, right $T = 37$ days

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Discrete coupled system

$$C^{n+1} = \Psi_T \left((1 - \phi) \rho_s \frac{\bar{C}^{n+1} - \bar{C}^n}{\Delta t}, C^n \right), \quad \text{for each species}$$

$$T^{n+1} = \bar{C}^{n+1} + C^{n+1}$$

$$\bar{C}^{n+1} = \Psi_C(T^{n+1}), \quad \text{for each grid cell.}$$

Useful notation: Kronecker product Erhel et al. (2013), Amir, K. (2019)00

$$\text{For } C \in \mathbf{R}^{N_c \times N_T}, \quad (A \otimes I)(\text{vec } C) = \text{vec}(CA^T)$$

Discrete non-linear system

$$\begin{pmatrix} C \\ T \\ \bar{C} \end{pmatrix} = \begin{pmatrix} (A \otimes I)C + (\Phi \otimes I)\bar{C} - \mathbf{b}^n \\ T - C - \bar{C} \\ \bar{C} - \Psi_C(T) \end{pmatrix} = 0$$

Overview of solution strategies

Fixed point (aka SI) Yeh–Tripathi, Carrayrou et al., Carrera et al.

- + easy to program, code reuse
- – not robust, small time steps

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Other approaches Erhel and de Dieuleveult, Knabner et al., Amir and K.
DAE formulation, reduction scheme, Newton–Krylov

Sequential Iterative Approach (SIA)

Based on “Total formulation”, alternate between solving transport (for all species), and chemistry (for all grid cells),

- Block Gauss–Seidel method, advocated by Yeh–Tripathi (1989). Enables reuse of existing transport and chemistry codes.
- Need to iterate to control conservation of mass, may need to reduce time step. If properly implemented, can be very accurate (Carrayrou et al, Lagneau et al., lots of others)

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Algorithm: Given $\bar{C}^{n+1,0}$, do for $k = 1, \dots$ until convergence

$$C^{n+1,k+1} = \Psi_T \left((1 - \phi) \rho_s \frac{\bar{C}^{n+1,k} - \bar{C}^n}{\Delta t}, C^n \right), \quad \text{transport for each species}$$

$$T^{n+1,k+1} = \bar{C}^{n+1,k} + C^{n+1,k+1}$$

$$\bar{C}^{n+1,k+1} = \Psi_C(T^{n+1,k+1}), \quad \text{chemistry for each grid cell.}$$

- Transport parallel over species
- Chemistry parallel over grid cells, may need to control **load balancing**

A global method from the fixed–point formulation (1)

Discrete non-linear system

$$\begin{cases} c^{n+1} = \psi_T \left(\frac{\bar{c}^n - \bar{c}^{n+1}}{\Delta t}, c^n \right) \\ \bar{c}^{n+1} = \psi_C(c^{n+1} + c^{n+1}) \end{cases}$$

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Discrete non-linear system

$$\begin{cases} C^{n+1} = \Psi_T \left(\frac{\bar{C}^n - \bar{C}^{n+1}}{\Delta t}, C^n \right) & \text{uncoupled} \\ \bar{C}^{n+1} = \Psi_C(C^{n+1} + C^{n+1}) \end{cases}$$

Can also eliminate C

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

Can be solved by block Gauss Seidel or by **Newton's** method

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Can be solved by block Gauss Seidel or by **Newton's** method

Residual computation

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

A global method from the fixed–point formulation (2)

Solution by Newton–Krylov method

- Solve the linear system by an **iterative** method (GMRES)
- Requires only jacobian matrix by vector products, Jacobian not stored
- Keep transport and chemistry as black–boxes
- Used for CFD, shallow water, radiative transfer(Keyes, Knoll, JCP 04), and for reactive transport (Hammond et al., Adv. Wat. Res. 05)

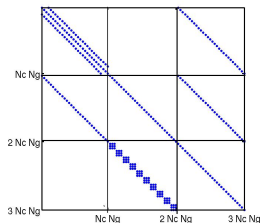
A global method from the fixed–point formulation (2)


Solution by Newton–Krylov method

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- + **Non-intrusive** approach
- + **Precipitation** can be included
- – One chemical equilibrium **solve** for each function evaluation

L. Amir, MK (Comp. Geosci. 09, IJNAM 19)



Jacobian with block structure 

Newton–Krylov method

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)

Computing the Jacobian - vector product

Numerical approximation [Keyes and Knoll, 2004]

$$Jv = f'(x)v \approx \frac{f(x + \epsilon v) - f(x)}{\epsilon}$$

Expensive, requires solving chemistry

Analytical calculation

$$J_f \begin{pmatrix} v_C \\ v_T \\ v_{\bar{C}} \end{pmatrix} = \begin{pmatrix} (A \otimes I)v_C + (\Phi \otimes I)v_{\bar{C}} \\ -v_C + v_T - v_{\bar{C}} \\ v_{\bar{C}} - J_C v_T \end{pmatrix}.$$

Linear preconditioning

Jacobian matrix **not explicitly computed**, but **\mathbf{J}_f has a known block structure**, use only **block preconditioners**

Block Jacobi

$$\mathbf{P}_{\text{BJ}}^{-1} \mathbf{J}_f \mathbf{v} = \begin{pmatrix} v_C & + ((A^{-1}M) \otimes I) v_{\bar{C}} \\ v_C + & v_T - & v_{\bar{C}} \\ - J_C v_T & & \end{pmatrix}$$

Block Gauss Seidel

$$\mathbf{P}_{\text{BGS}}^{-1} \mathbf{J}_f \mathbf{v} = \begin{pmatrix} v_C + & ((A^{-1}M) \otimes I) v_{\bar{C}} \\ v_T - & v_{\bar{C}} + & ((A^{-1}M) \otimes I) v_{\bar{C}} \\ v_{\bar{C}} - J_C v_{\bar{C}} + J_C & ((A^{-1}M) \otimes I) v_{\bar{C}} \end{pmatrix}$$

Remark

Neither A^{-1} nor the Kronecker product are computed.

$w = ((A^{-1}M) \otimes I) v_{\bar{C}}$ is computed by solving $AW = MV_{\bar{C}}^T$ with $v_{\bar{C}} = \text{vec}(V_{\bar{C}})$, and $w = \text{vec}(W)$.

Could use *approximate* solves

Non-linear preconditioning and elimination

Elimination of the unknowns T and C

Reduced system $h(\bar{\mathbf{C}}) = \bar{\mathbf{C}} - \Psi_C \left((A^{-1} \otimes I) (\mathbf{b}^n - (M \otimes I)\bar{\mathbf{C}}) + \bar{\mathbf{C}} \right) = 0$.

Jacobian by vector product $J_h \mathbf{v} = \mathbf{v} - J_C J_T \mathbf{v} = \mathbf{v} - J_C \mathbf{v} + J_C ((A^{-1}M) \otimes I) \mathbf{v}$.

Elimination is a **linear change of variables** leads to a **block factorization** of original Jacobian

$$J_f = J_f B = \begin{pmatrix} A \otimes I & 0 & 0 \\ -I & I & 0 \\ 0 & -J_C & \mathbf{J}_h \end{pmatrix} \begin{pmatrix} I & 0 & (A^{-1}M) \otimes I \\ 0 & I & -(I - A^{-1}M) \otimes I \\ 0 & 0 & I \end{pmatrix}.$$

Links between elimination and block preconditioning

\mathbf{J}_h is Schur complement of J_f , both BJ and BGS
replace \mathbf{J}_h by I

Details: [Amir, M.K., IJNAM, 2019]

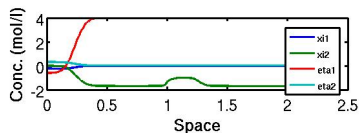
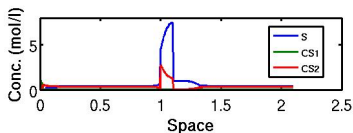
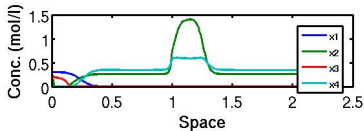
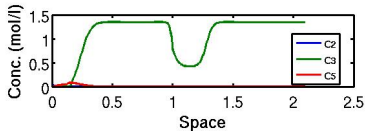
Outline

- 1 Motivations: CO₂ storage
- 2 Models
 - Chemistry
 - Transport and coupled model
- 3 Numerical methods for solving chemistry and transport
 - Solving equilibrium chemistry
 - Flow and transport
- 4 Coupling transport and chemistry
 - Solving the coupled system
 - A Newton–Krylov method
 - Linear and non–linear preconditioning
- 5 Numerical results
 - MoMaS benchmark
 - Ion exchange, 2d “example 11 from PhreeqC
 - SHPCO₂

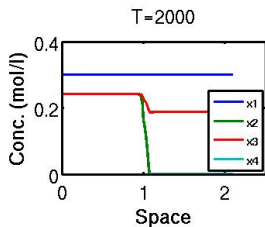
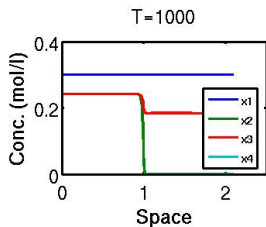
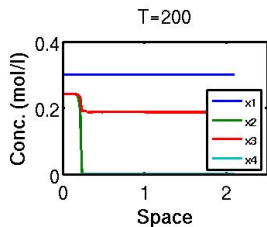
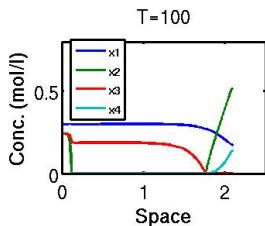
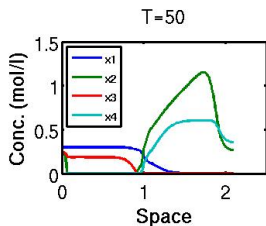
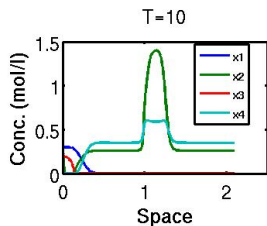
MoMaS benchmark (easy, 1D)

- 9 liquid, 3 sorbed primary species.
- Huge variation in equilibrium constants, large stoichiometric coeffs.
- Long simulation time
- Set-up by J. Carrayrou, MK, P. Knabner (Comp. Geo. 2009)

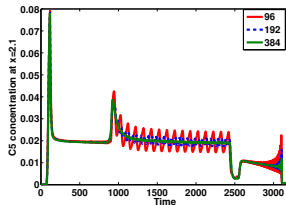
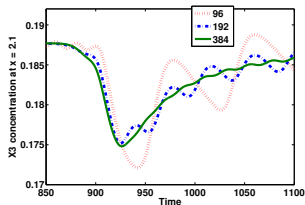
Species concentrations, $t = 10$



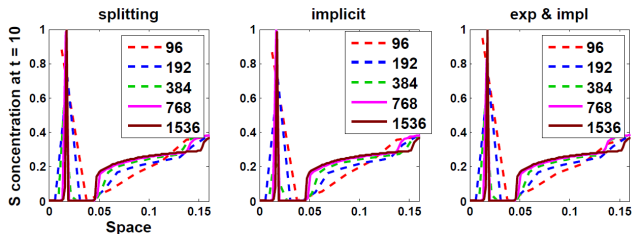
Evolution of the concentrations



Accuracy, spatial discretization



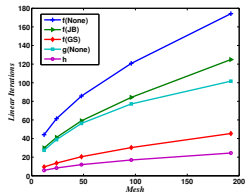
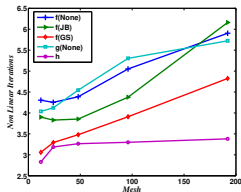
Elution curves: left X_3 , right C_5



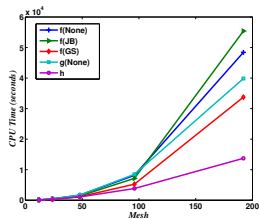
Concentration of species S at $t=10$, different schemes

Preconditioning efficiency

- Non-linear elimination **has the smallest number both for NL. and L. iterations**
- independence of the mesh size.**



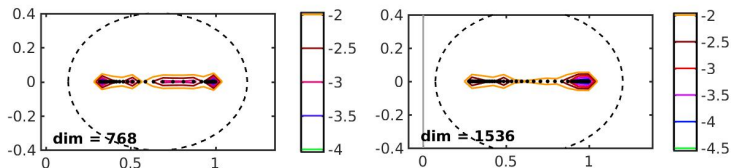
- Non-linear elimination requires less CPU time than other methods (1D model !)
- Good efficiency, with **BGS precondition. as a distant second.**
- BJ precondition. or elimination of T do not bring an improvement



Mesh independance convergence of GMRES: field of value explanation

Convergence of GMRES depends of Field of Values [Eigtool (Embree, Trefethen)]

$$W(J_h) = \left\{ \frac{x^* J_h x}{x^* x}, x \in \mathbf{C}, x \neq 0 \right\}.$$

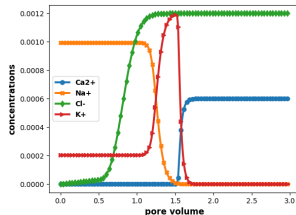
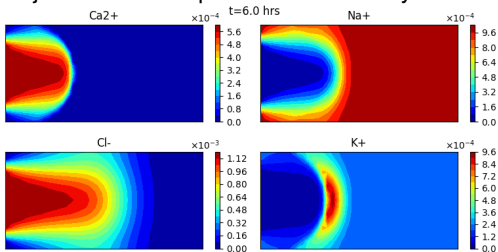


Field of values and pseudo-spectra of J_h for $N_x = 768$ and $N_x = 1536$.

The field of values is inside of the dashed curves, it is bounded away from zero, independly of mesh size.

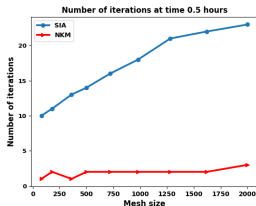
Ion exchange: 2D PhreeqC, Example 11

Inject calcium on part of left boundary into a K-Na solution

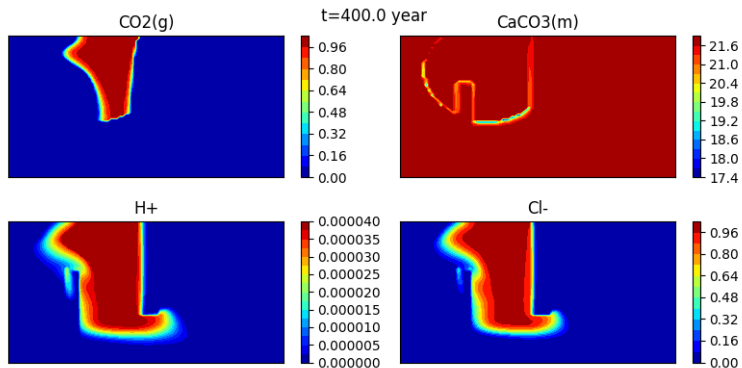


Fixed-point – precondition. Newton-Krylov comparison

- Nb. of iterations \nearrow with the mesh resolution for SIA while it remains stable, small for NKM.
- NKM gives **convergence independent of the mesh size**.



SHPCO2 Benchmark (precipitation) - IFPEN



Conclusion and perspectives

- Extension of the capabilities of the equilibrium chemical solver to handle **mineral precipitation and dissolution**;
- **Heterogenous, 2D configurations** : Ex11, SHPCO2
- Number of iterations is **independent of the mesh size**

- Improve the robustness of the NKM method in the presence of minerals.
- Improve the computation of the Jacobian matrix by vector product, by exploiting the known block structure of the matrix

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