# Upscaling "dissolution" mechanisms in porous media

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# Outline

- Background
- Pore-scale model and effective surface
- Darcy-scale models
- Stability
- Large-scale models?
- Conclusions



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# Introduction

- Dissolution: geochemistry, karsts, salt mines, NAPL, petrol.
   Engng, aerospace industry...
- Problems:
  - Multiple-scale analysis
  - History effects
  - Instabilities





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# **Example 1: acidizing treatment**



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# **Example 2: ablation of composite structures**



### **Upscaling Surface Heterogeneities: The concept of Effective Surface**



### Non-ablative case: various approaches



#### **Direct Simulation**

 $\langle c \rangle + \tilde{c} \rightarrow$  Effective surface, effective BC (jump conditions)

*Eg : Ochoa et al., Wood et al., Valdès-Parada et al.* 

Meso-scale modelling, GTE → Effective surface, effective BC Eg : Chandesris et al., Goyeau et al.

#### **Domain decomposition**

Achdou et al., Jäger and Mikelic, ...

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# Extension of Wood et al. (2000)



Flow: Blasius

**u**. $\nabla c = \nabla .D\nabla c$  in the fluid domain  $-\mathbf{n}_{\gamma\kappa}.D\nabla c = k(\mathbf{x})c$  at  $\Sigma$   $c(y = h) = C_0$  at top of B.L.  $c(x = x_0) = c(x = x_0 + l)$ 



# **Extension of Wood et al. (2000)** $c = \langle c \rangle + \tilde{c}$ with $\mathbf{u} \cdot \nabla \langle c \rangle = \nabla \cdot D \nabla \langle c \rangle$ in the fluid domain $-\mathbf{n}_{\gamma\kappa}.D\nabla\langle c\rangle = \langle k(\mathbf{x})c\rangle_{\Sigma}$ at $\Sigma$ and $\mathbf{u} \cdot \nabla \tilde{c} = \nabla \cdot D \nabla \tilde{c}$ in the fluid domain $-\mathbf{n}_{\gamma\kappa}.D\nabla\tilde{c} = k\,\tilde{c} + \tilde{k}\,c - \langle k\,\tilde{c} \rangle_{\Sigma}$ at $\Sigma$

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# Extension of Wood et al. (2000)

$$\tilde{c} = s(\mathbf{x}) \langle c \rangle + \dots$$
  
with

 $\mathbf{u}.\nabla s = \nabla.D\nabla s$  in the fluid domain

$$-\mathbf{n}_{\gamma\kappa}.D\nabla s = k\,s + \tilde{k} - \left\langle \tilde{k}\,s \right\rangle_{\Sigma} \quad \text{at} \quad \Sigma$$

$$k_{eff} = \left\langle k \right\rangle_{\Sigma} + \left\langle \tilde{k} s \right\rangle_{\Sigma}$$



# **Results for circular patches (far from entrance region)**





### **Results**

#### two limit cases

$$-Da <<1, C(x) = C_0 \rightarrow k_{eff} = \langle k \rangle$$

- Da >>1,  $k_{eff} = k^*$  (harmonic mean of the reactivities)

#### general case

influence of geometry
slight influence of Re
(for low Re...)





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## Ablative case: transient $\rightarrow$ DNS

- Ablation leads to non-differentiable surfaces
- Limits of ALE and phase field methods → adapted VOF method (Aspa, 2006)



### **Example 1: steady-state surface**



 $k_m = 0.4 \, m/s$  et  $k_i = 3.2 \, m/s$ 

(b) Observation

30 µm



# **Example 2: porous composites**





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- Projected Areas: A<sub>m,p</sub> and A<sub>f,p</sub>
- Steady-state ablation: uniform velocity implies

$$\xi k_f \cos(\theta_f) = \xi k_m \cos(\theta_m) \Rightarrow$$

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$$k_{f} \frac{A_{f}}{A_{f,p}} = k_{m} \frac{A_{m}}{A_{m,p}} \Rightarrow \frac{A_{f}}{A_{f,p}} = \tilde{k}$$
$$k_{eff} = \langle k \rangle \approx k_{m} \qquad \neq \langle k \rangle_{t=0}$$

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- Limit Cases: simple models
  - Da<<1, max(k)</pre>
  - Da>>1, k-harmonic mean
- Intermediate Da → complex simulations







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# Dissolution: Darcy-scale (core-scale) models?



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# Target 1: Dissolution Instabilities (Wormholing)



# Target 2: "Optimum flow rate"

Optimum injection rate: minimum injected acid volume to breakthrough

 $Q_{opt} = f$  (length core,  $C_{NaCl}$ ...)



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### **Simplified Pore-scale problem**

N.-S. +  $\frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{v}c) = \nabla \cdot (D\nabla c) \quad \text{in the fluid domain}$   $c = C_{eq} \text{ at } A_{\beta\sigma}$ 

Note (binary case):

$$-\mathbf{n}.D\nabla c = kc \iff c = C_{eq} \approx 0 \text{ at } A_{\beta\sigma} \text{ if } Da >> 1$$



# Darcy-scale: Local Non-Equilibrium Models

- Local equilibrium dissolution:  $C_{A\beta} = \langle c_{A\beta} \rangle^{\beta} = C_{eq}$  produces sharp fronts
- LNE: Heuristic model classically used in Chemical Engineering (discussion in Quintard & Whitaker, 1994, 1999)



# **Upscaling (framework)**

(Quintard and Whitaker, 1999; Golfier et al., 2001)

- **Deviations**  $\mathbf{v}_{\beta} = \varepsilon_{\beta}^{-1} \mathbf{V}_{\beta} + \tilde{\mathbf{v}}_{\beta}$   $c_{A\beta} = C_{A\beta} + \tilde{c}_{A\beta}$
- Coupled pore-scale and averaged equations

$$\frac{\partial \left(\varepsilon_{\beta}C_{A\beta}\right)}{\partial t} + \nabla \cdot \left(\mathbf{V}_{\beta}C_{A\beta}\right) + \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot c_{A\beta} \left(\mathbf{v}_{A\beta} - \mathbf{w}\right) dA = \nabla \cdot \left[D\left(\varepsilon_{\beta}\nabla C_{A\beta} + \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} dA\right)\right] - \nabla \cdot \left\langle \tilde{\mathbf{v}}_{\beta} \tilde{c}_{A\beta} \right\rangle$$

$$\frac{\partial \tilde{c}_{A\beta}}{\partial t} + \tilde{\mathbf{v}}_{\beta} \cdot \nabla C_{A\beta} + \mathbf{v}_{\beta} \cdot \nabla \tilde{c}_{A\beta} - \underbrace{\varepsilon_{\beta}^{-1} \nabla \cdot \left\langle \tilde{\mathbf{v}}_{\beta} \tilde{c}_{A\beta} \right\rangle}_{\ll \mathbf{v}_{\beta} \cdot \nabla \tilde{c}_{A\beta}} = \nabla \cdot \left(D \nabla \tilde{c}_{A\beta}\right) - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} dA\right]}_{\ll \nabla \cdot \left(D \nabla \tilde{c}_{A\beta}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} dA\right]}_{\ll \nabla \cdot \left(D \nabla \tilde{c}_{A\beta}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} dA\right]}_{\ll \nabla \cdot \left(D \nabla \tilde{c}_{A\beta}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} dA\right]}_{\ll \nabla \cdot \left(D \nabla \tilde{c}_{A\beta}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} dA\right]}_{\ll \nabla \cdot \left(D \nabla \tilde{c}_{A\beta}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} dA\right]}_{\ll \nabla \cdot \left(D \nabla \tilde{c}_{A\beta}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} dA\right]}_{\ll \nabla \cdot \left(D \nabla \tilde{c}_{A\beta}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} dA\right]}_{\ll \nabla \cdot \left(D \nabla \tilde{c}_{A\beta}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{A\beta} dA\right]}_{\ll \nabla \cdot \left(D \nabla \tilde{c}_{A\beta}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{\beta\sigma} dA\right]}_{\otimes \nabla \cdot \left(D \nabla \tilde{c}_{A\beta}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{\beta\sigma} dA\right]}_{\otimes \nabla \cdot \left(D \nabla \tilde{c}_{\beta\sigma}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{\beta\sigma} dA\right]}_{\otimes \nabla \cdot \left(D \nabla \tilde{c}_{\beta\sigma}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{\beta\sigma} dA\right]}_{\otimes \nabla \cdot \left(D \nabla \tilde{c}_{\beta\sigma}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{\beta\sigma} dA\right]}_{\otimes \nabla \cdot \left(D \nabla \tilde{c}_{\beta\sigma}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{\beta\sigma} dA\right]}_{\otimes \nabla \cdot \left(D \nabla \tilde{c}_{\beta\sigma}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{\beta\sigma} dA\right]}_{\otimes \nabla \cdot \left(D \nabla \tilde{c}_{\beta\sigma}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_{\beta\sigma} dA\right]}_{\otimes \nabla \cdot \left(D \nabla \tilde{c}_{\beta\sigma}\right)} - \underbrace{\varepsilon_{\beta}^{-1} D \nabla \cdot \left[\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde$$



# **Upscaling : problems**

- Quasi-steady dissolution: terms like
   n<sub>βσ</sub> · (v<sub>Aβ</sub> w) may be neglected in the
   problem for the deviations
- "Closure" = approximate solution of the coupled equations
  - Quasi-steady solution?
  - But...historical effect remains through
     the interface evolution

A simple example: the tube problem (Graetz's problem, Pe>>1)

Classical Problem



Dissolution



Non-local in space and time

...see Golfier et al. (2001), Pierre et al. (2005)



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# 2D and 3D cases (MQ & SW, 94, 99, FG et al., 2002)

• Representation of the deviations:

$$\tilde{c}_{A\beta} = c_{A\beta} - \left\langle c_{A\beta} \right\rangle^{\beta} = \mathbf{b}_{\beta} \cdot \nabla \left\langle c_{A\beta} \right\rangle^{\beta} - s_{\beta} \left\langle c_{A\beta} \right\rangle^{\beta} + \dots$$

• Darcy-Scale equation:  $\frac{\partial}{\partial t} (\varepsilon_{\beta} \langle c_{A\beta} \rangle^{\beta}) + \nabla \cdot (\langle \mathbf{v}_{\beta} \rangle \langle c_{A\beta} \rangle^{\beta}) - \nabla \cdot [\mathbf{d}_{\beta} \langle c_{A\beta} \rangle^{\beta}] - \mathbf{u}_{\beta} \cdot \nabla \langle c_{A\beta} \rangle^{\beta})$   $= \nabla \cdot (\mathbf{D}_{\beta}^{*} \cdot \nabla \langle c_{A\beta} \rangle^{\beta}) - \alpha \langle c_{A\beta} \rangle^{\beta}$ • + cell problems — "effective" properties

# **Comparison with numerical experiments** Pe=185





# **Problem with evolving geometry :** Effective Coefficients ( $\alpha$ , D<sub> $\beta$ </sub>, K)

• Effective coefficients as a function of the time evolution of the interface (example of direct simul.: Bekri et al.)?

- $-\alpha$ (t, Pe, ...)  $\rightarrow \alpha$ ( $\epsilon$ , Pe)
- $-D_{\beta}(t, Pe, ...) \rightarrow D_{\beta}(\varepsilon, Pe)$
- $-K(t) \rightarrow K(\varepsilon)$

Correlations obtained using: numerical simulation, closure pbs, experiments, ...



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# Transport and Dissolution: numerical model Dimensionless equations



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### **3D example**

#### I.C.: random permeability field



# **Stability Analysis**

2D Reference Simulations



# Stability of the linearised problem (Cohen, 2006)



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### **Dissolution Diagram (Golfier et al., 2001)**



#### **Peclet Number**

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# "Optimum flow rate"

### $\bullet$ Need "mainly" to calibrate $\alpha$

 $\alpha = A \alpha_0$ 

where  $\alpha_0$  is the correlation obtained from the closure problem + simple unit cell





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# **Confinement Effect:** « wormhole competition », Cohen et al. (2007)



# **Confinement (cont.)**



Dominant wormhole growth rate increases with domain height



### **Effect of geometry: ex. radial**



# Effect of geometry on optimum flowrate



# Extension of LNE models to complex phase diagrams, and multicomponent systems

# • Equilibrium conditions at $A_{\beta\sigma}$ $\begin{bmatrix} & & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & & \\$



# Expression for the mass exchange terms

$$\begin{bmatrix} \cdot \\ \mu_{\beta} |_{\langle c_{\beta} \rangle^{\beta}} \\ \cdot \end{bmatrix} + J_{\beta} \begin{bmatrix} \tilde{c}_{\beta} \\ \tilde{c}_{\beta} \end{bmatrix} = \begin{bmatrix} \cdot \\ \mu_{\sigma} |_{\langle c_{\sigma} \rangle^{\sigma}} \\ \cdot \end{bmatrix} + J_{\sigma} \begin{bmatrix} \tilde{c}_{\sigma} \\ \tilde{c}_{\sigma} \end{bmatrix}$$

# • Case 1: diagonal $J_{\beta}$ and $J_{\sigma}$

exchange term for species 
$$i \div \mu_{\beta i} \Big|_{\langle c_{\beta} \rangle^{\beta}} - \frac{J_{\sigma i}}{J_{\beta i}} \mu_{\sigma i} \Big|_{\langle c_{\sigma} \rangle^{\sigma}}$$

### General case?



## Example: ZrO<sub>2</sub> / Zr (Belloni, 2008)

TMI-2 (28 mars 1979) Upper grid damade Coating of Loose core debris previously molten material Crust on bypass region interior surfaces Previously molter material Lower plenum debris Ablated incore instrument guide



Time (s):

574.

0.9848

0.9696

0.9545

0.9393

0.9241

0.9089

0.8938

0.8786

0.8634

0.8482

0.0135

C

# Example: ZrO<sub>2</sub> / Zr (Belloni, 2008)

$$\frac{\partial}{\partial t} \left( \varepsilon_{l} \rho_{l} \langle C_{l} \rangle^{l} \right) + \nabla \left( \varepsilon_{l} \rho_{l} \langle C_{l} \rangle^{l} \langle \mathbf{v}_{l} \rangle^{l} \right)$$

$$+ C_{l}^{*} \frac{\partial}{\partial t} \left( \varepsilon_{s} \rho_{s} \right) =$$

$$\nabla \left( \varepsilon_{l} \rho_{l} \mathbf{D}_{l} \cdot \nabla \langle C_{l} \rangle^{l} \right) + \rho_{l} h_{ml} \left( C_{l}^{*} - \langle C_{l} \rangle^{l} \right)$$

$$+ \text{ similar equation for } s$$

$$+ \text{ Averaging of the mass balance BC at } A_{ls}:$$

$$\frac{\partial}{\partial t} \left( \varepsilon_{s} \rho_{s} \right) = \frac{1}{C_{l}^{*} - C_{s}^{*}} \left( \rho_{s} h_{ms} \left( C_{s}^{*} - \langle C_{s} \rangle^{s} \right) \right)$$

$$+ \rho_{l} h_{ml} \left( C_{l}^{*} - \langle C_{l} \rangle^{l} \right)$$

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## **Flow in Heterogeneous Systems**



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# **Core-scale description**

- fluid zone/porous zone
   1D effective medium
- 1- equation model?
  - 1 single equation
  - easy to implement
  - loss of information



- 1 equation for each zone
- Darcy-scale problem is similar to the pore-scale problem in the case of equilibrium dissolution



pb. with non-locality and history effects

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# **Core-Scale Volume Fractions: Definitions**

Wormhole volume fraction: φ<sub>ω</sub>
 Core-scale porosity

$$\varepsilon^* = \frac{1}{V_{\infty}} \int_{V_{\infty}} \varepsilon \, dV$$

if Local Equilibrium dissolution:

$$\boldsymbol{\varepsilon}^* = \boldsymbol{\varphi}_{\boldsymbol{\omega}} + (1 - \boldsymbol{\varphi}_{\boldsymbol{\omega}}) \,\boldsymbol{\varepsilon}$$



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# **Ex.: 2-equation model (Golfier et al., 2004**, **2006**) $\nabla . \mathbf{V}_{\beta}^{\boldsymbol{\sigma}} = 0$ $\nabla \mathbf{P}_{\beta}^{\boldsymbol{\sigma}} = -\mu_{\beta} (\mathbf{K}^{\boldsymbol{\sigma}})^{-1} \cdot \mathbf{V}_{\beta}^{\boldsymbol{\sigma}}$

$$\nabla . \mathbf{V}_{A\beta}^{\eta} = 0$$
$$\nabla \mathsf{P}_{\beta}^{\eta} = -\mu_{\beta} (\mathbf{K}^{\eta})^{-1} \cdot \mathbf{V}_{A\beta}^{\eta}$$

pb. with regional velocities?

Transport and Dissolution :  $\varphi_{\sigma} \frac{\partial C^{\sigma}{}_{A\beta}}{\partial t} + \mathbf{V}^{\sigma}{}_{\beta} \cdot \nabla C^{\sigma}{}_{A\beta} = \frac{1}{P_{\rho}} \nabla \cdot \left( \mathbf{D}^{**} \cdot \nabla C^{\sigma}{}_{A\beta} \right) - \alpha^{*} C^{\sigma}{}_{A\beta}$  $\frac{\partial \varphi_{\sigma}}{\partial t} = \frac{\beta}{\rho_{\sigma}} \alpha^* \quad C^{\sigma}{}_{A\beta}$  $C^{\eta}{}_{A\beta} = 0$  in  $\eta$ -region need Darcy-scale local equilibrium!

0.9

#### **Obtained Correlations: permeability**



# New Model (Cohen et al., 2006)



# Validation: example from dominant wormhole regime





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# Example (Cohen, 2006)

#### • 3D radial simulation



# Conclusions

- Effective Surface:
  - If not limit cases, or if no steady-state:  $\rightarrow$  DNS?
  - Coupling with instabilities?
- Darcy-scale models:
  - LNE model has potential for representing instabilities with a minimum of parameters
  - Coupling with strong heterogeneities?
- Reservoir-scale models?

