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Pore-Scale Analysis of Mixing Efficiency in Porous Media with Chemical Reaction Dependent Viscosity

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Overview

- Mixing-induced reactive subsurface flows in porous media are important:
  - degradation of contaminants
  - viscous fingering in petroleum recovery
  - geochemistry of carbon sequestration
  - engineered fluids for enhanced recovery or remediation
- We examine the case of reaction products that change the viscosity of the fluid to evaluate the impact of viscosity variations on mixing efficiency and dispersion
- Experiments have demonstrated reactants that can alter solution viscosity
  - Polymer solutions
  - Solutions with metal ions
  - Syrup and sodium hydroxide
- Pore scale simulations on high performance computers suggest that mixing-induced chemical reactions can alter fluid properties (e.g., viscosity and density) and shear rate enabling engineered solutions for subsurface operations and for CO_2 sequestration

Pore scale model for reactive flow in model porous media

Mixing-induced chemical reactions can alter fluid properties (viscosity and density), mixing efficiency, and shear rate, to produce engineered fluid solutions

$$\mu = \mu_0\left(1 + \mu' C_C\right); \qquad \mu' = \frac{1}{\mu_0}\frac{d\mu}{dC_C}.$$

$$A + B \rightarrow C$$

Loosely packed array
Porosity = 0.556
Grain diameter = 0.07 cm

Closely packed array
Porosity = 0.434
Grain diameter = 0.03 cm

μ is the viscosity of the solvent. We consider **thickening** ($\mu' > 0$) and **thinning** ($\mu' < 0$) viscosity with product concentration (C_c) via a bimolecular reaction

Math formulation and numerics

Dimensionless Model Formulation

Fluid Flow:

$$\nabla \bullet \mathbf{u} = 0$$

$$Sc^{-1}\frac{\partial \mathbf{u}}{\partial t} + \mathrm{Re}\,\mathbf{u} \bullet \nabla \mathbf{u} = -\nabla p + \nabla \bullet \left[\bar{\mu}\left(\nabla \mathbf{u} + (\nabla \mathbf{u})^{T} \right) \right]$$

Reactive species transport (A+B → C):

$$\left(\frac{\partial}{\partial t} + Pe\,\mathbf{u} \bullet \nabla \right) c_A = \delta_A \nabla^2 c_A - Da\; c_A c_B$$

$$\left(\frac{\partial}{\partial t} + Pe\,\mathbf{u} \bullet \nabla \right) c_B = \delta_B \nabla^2 c_B - Da\; c_A c_B$$

$$\left(\frac{\partial}{\partial t} + Pe\,\mathbf{u} \bullet \nabla \right) c_C = \nabla^2 c_C + Da\; c_A c_B$$

Dimensionless parameters (Re→0):

$$Sc = \frac{\mu_0}{\rho D_C} \qquad \delta_A = \frac{D_A}{D_C} \qquad Pe = \frac{Ul}{D_C}$$

$$Da = \frac{k c_{A,0} l^2}{D_C} = \frac{\text{diffusion time scale}}{\text{reaction time scale}}$$

Reaction-dependent viscosity:

$$\bar{\mu} = \mu / \mu_0 = 1 + \bar{\mu}' c_C \qquad \bar{\mu}' = \frac{C_{A,0}}{\mu_0}\frac{d\mu}{dC_C}$$

Stabilized Finite Elements

Flow: Polynomial pressure projection stabilization
Dohrmann & Bochev (2004)

$$\int_{\Omega} \mathbf{w} \bullet \left(\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \bullet \nabla \mathbf{u} \right) d\Omega + \int_{\Omega} \nabla \mathbf{w} : \boldsymbol{\tau}\, d\Omega - \int_{\Gamma} \mathbf{w} \bullet \boldsymbol{\tau} \bullet \mathbf{n}\, d\Gamma$$

$$+ \int_{\Omega} q \nabla \bullet \mathbf{u}\, d\Omega - \int_{\Omega} \frac{1}{\mu} (p - \pi p)(q - \pi q)\, d\Omega = 0$$

Transport: Standard FEM

Numerical model verification

Flow fields, drag, permeability:

Closely-packed

Loosely-packed

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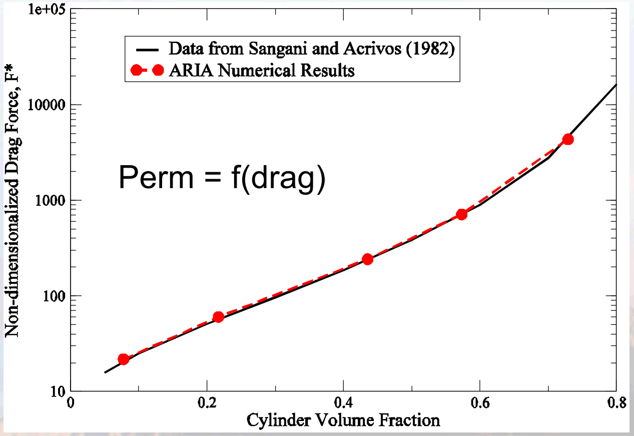
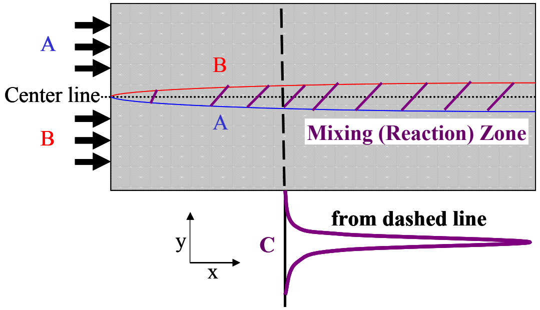
Drag on a typical cylinder



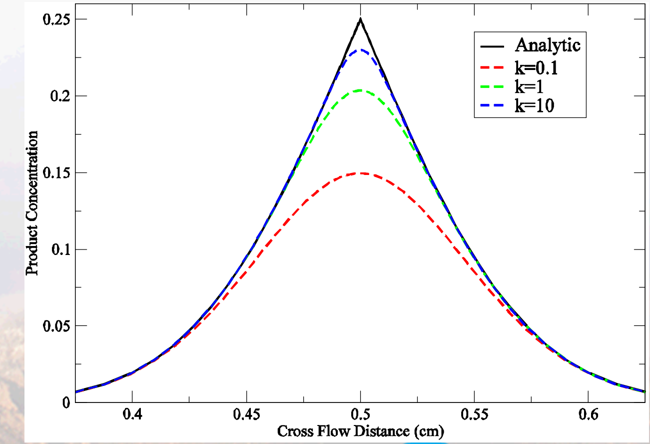
Perm = f(drag)

Darcy-scale reactive transport in a uniform flow field



Self-similar solution: $$D_T = \frac{1}{X^3}\frac{9\pi v}{16 C_0^2 \varphi^2}\left[\int_0^X m(x)\,dx\right]^2$$

Impact of reaction rate on outflow concentration



Product concentration and flow fields

Loosely packed array at *Pe*=200

Constant viscosity (*Da*=5000)

Viscous thickening (*Da*=5000)

conditionally stable?

Viscous thinning (*Da*=5000)

Viscous thickening (*Da*=50)

Viscous thinning (*Da*=50)

0.05 cm/s

0.05 cm/s

Constant viscosity

0.05

0.05

thickening

0.15

0.15

thinning

Closely packed array at *Pe*=70.7

Constant viscosity (*Da*=625)

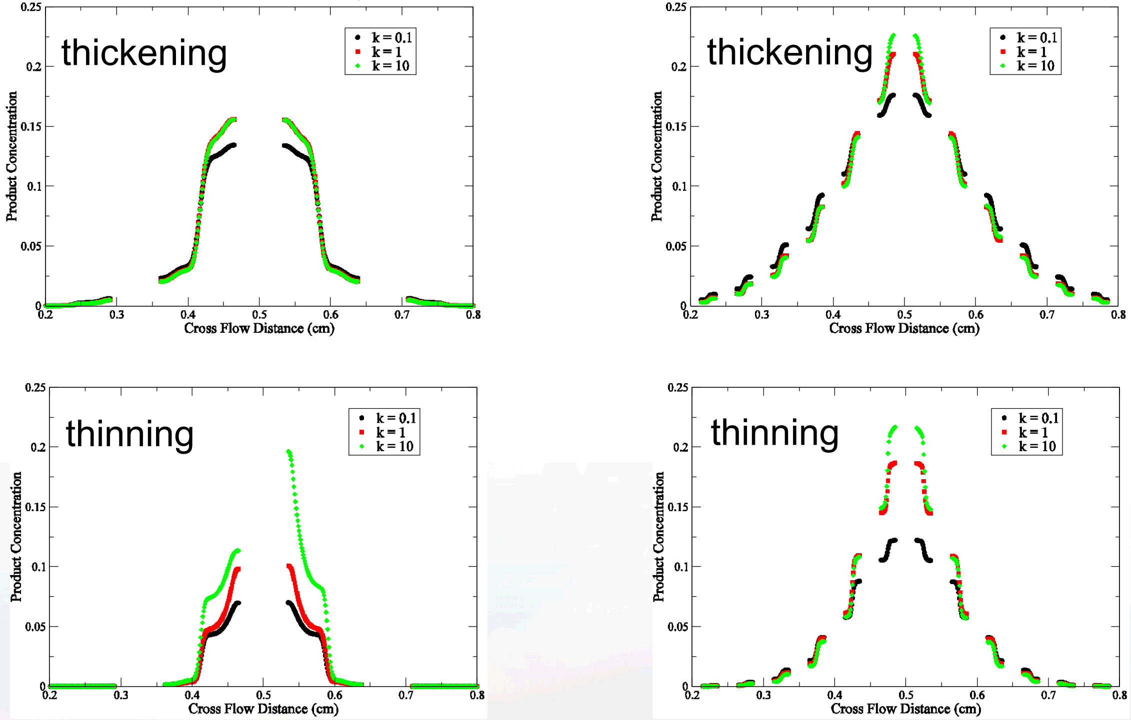
Viscous thickening (*Da*=625)

Viscous thinning (*Da*=625)

Viscous thickening (*Da*=6.25)

Viscous thinning (*Da*=6.25)

Product concentration at exit (2 cm)



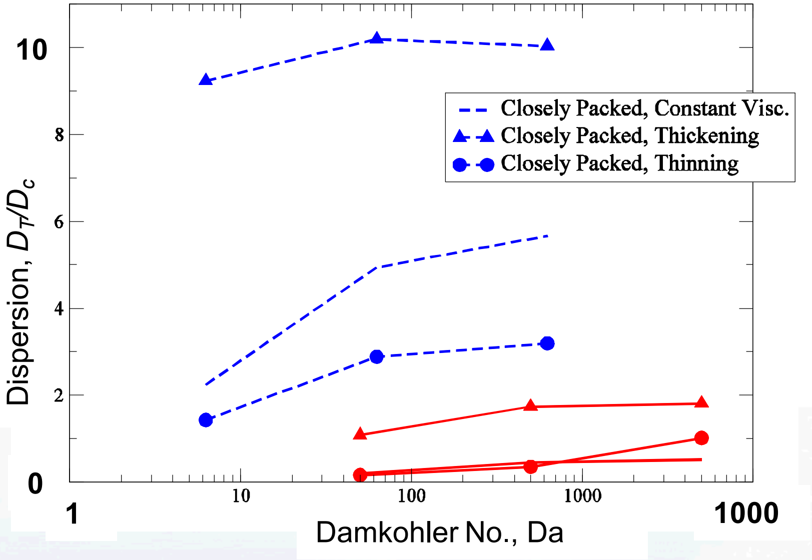
Loosely packed, ϕ = 0.56

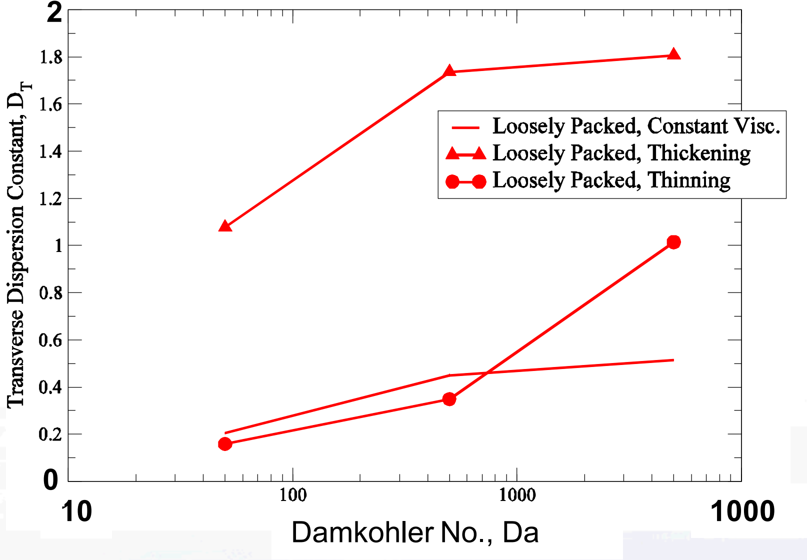
Closely packed, ϕ = 0.43

- Thickening viscosity increases transverse product formation and dispersion
- Lower porosity and high Pe enhance mixing and reaction due to higher interfacial area and smaller diffusion time scale
- Thinning viscosity promotes flow focusing along the mixing plane, resulting in streamline compression and less transverse dispersion
- Viscous thinning reactions can become unstable at high Da and Pe, leading to enhanced mixing

Upscaled dispersion

$$D_T = \frac{1}{X^3}\frac{9\pi\nu}{16C_0^{\,2}\varphi^2}\left[\int_0^X m\left(x\right)dx\right]^2$$





- Dispersion increases with viscous thickening reactions
- Dispersion decreases with viscous thinning reactions (less than constant viscosity)
- Dispersion increases with decreasing porosity (closely packed vs. loosely packed arrays)
    - Increased interfacial area with closely packed array
    - Smaller diffusion time-scale with closely packed array
- Dispersion can increase in viscous thinning reactions at high Da owing to flow instability and oscillation of reaction zone across centerline

Concluding Remarks

Scientific Achievement

Developed a computationally powerful & highly parallelized pore-scale model to examine flow in porous media with chemical reaction dependent viscosity

Significance and Impact

Pore scale simulations on high performance computers suggest that mixing-induced chemical reactions can alter fluid properties (e.g., viscosity and density) and shear rate enabling engineered solutions for CO_2 sequestration

Conclusions:

- More reaction product was formed when fluid viscosity increases with increasing product concentration (viscous thickening) than the opposite case (viscous thinning)
- Enhanced mixing at pore scale leads to enhanced reaction rates at high local ratio of reaction rate to flowrate (Da) and lower porosity
- Flows with viscous thinning reactions can become unstable at high Da, leading to enhanced mixing and reaction rates under high Peclet number and higher porosity

Product concentration & flow velocity

0.05 cm/s

A →
B →

(a) Constant viscosity

0.05 cm/s

A →
B →

(b) Viscous thickening

0.15 cm/s

A →
B →

(c) Viscous thinning

Comparison of reaction product (A+B -> C) concentration and flow velocity in the loosely packed array for different viscosity variations. Hot (or cool) color depicts high (or low) concentration and velocity. Onset of Instability is shown in (c).

S.M. Davison, H. Yoon, and M.J. Martinez, Advances in Water Resources, 38, 70-80 (2012)