Reactive Transport Upscaling: Mixing, Spreading and Multirate Mass Transfer

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Reactive Transport

A simple example for mixing-driven reactive transport is the precipitation of gypsum

$$Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4. \quad (1)$$

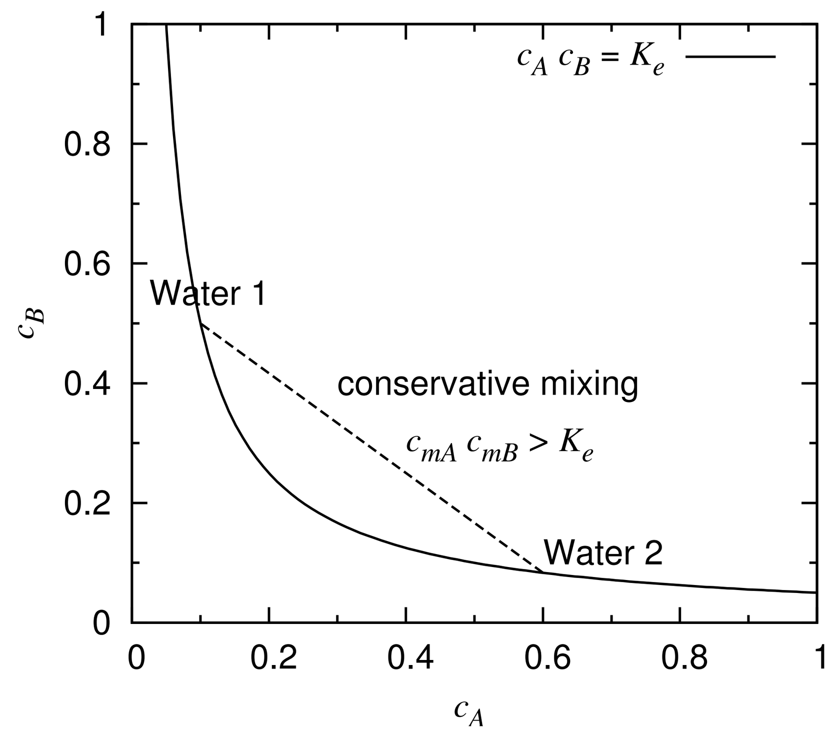

Fig. 1: Mixing of different waters leads to oversaturation $\Omega = \frac{c_{mA} c_{mB}}{K_e} \geq 1$.

Different waters are transport by advection **q** and mix due to hydrodynamic dispersion **D**. Mass balance gives

$$\phi \frac{\partial c_i}{\partial t} + [\nabla \cdot \mathbf{q} - \nabla \cdot \mathbf{D} \nabla]\, c_i = -r \quad (2)$$

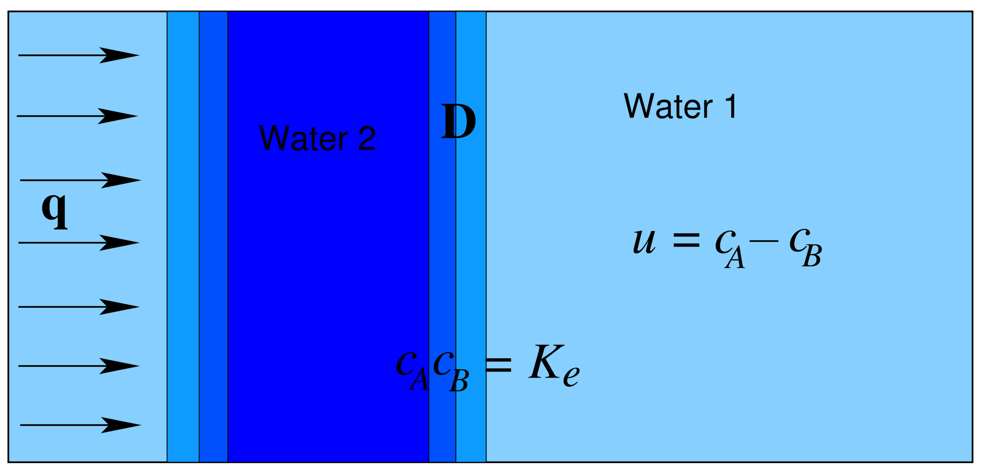

Fig. 1: Mixing-driven reaction, $c_A = [Ca^{2+}]$ and $c_B = [SO_4^{2-}]$.

The component $u = c_A - c_B$ satifies

$$\phi \frac{\partial u}{\partial t} + [\nabla \cdot \mathbf{q} - \nabla \cdot \mathbf{D} \nabla]\, u = 0 \quad (3)$$

and the reaction rate can be expressed by

$$r = \phi \underbrace{\frac{d^2 c_A}{du^2}}_{\text{reaction factor}} \underbrace{\nabla u \cdot \mathbf{D} \nabla u}_{\text{mixing factor}}$$

De Simoni et al. (2005)

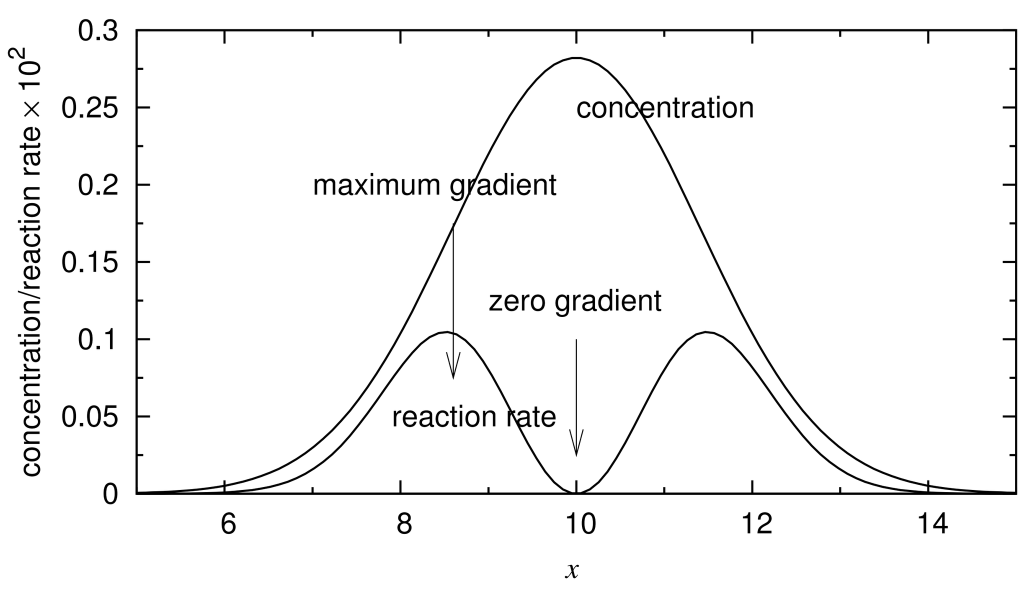

Fig. 2: Mixing by dispersion is driven by the gradient of the conservative component.

Heterogeneity

- Enhanced mixing and spreading

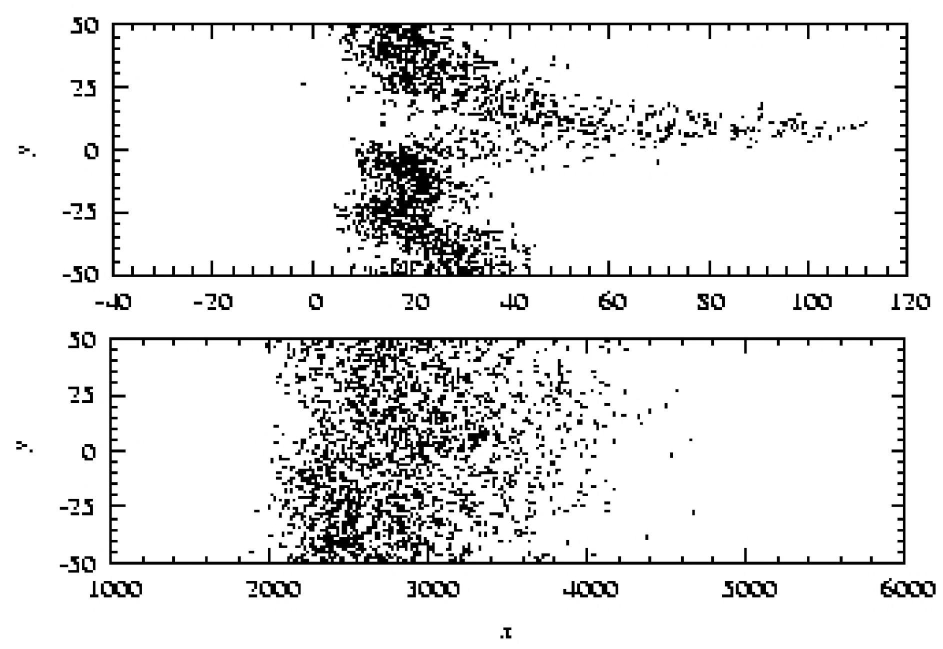

Fig. 3: Simulated particle plumes in a heterogeneous medium (*Zavala et al.*, 2008).

- Enhanced reaction rates

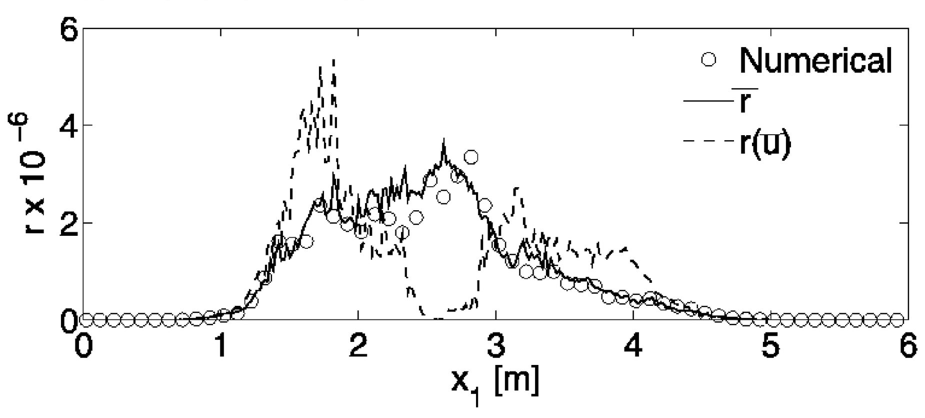

Fig. 4: Simulated reaction rates in a strongly heterogeneous medium (*Luo et al.*, 2008).

- Transport is non-Fickian

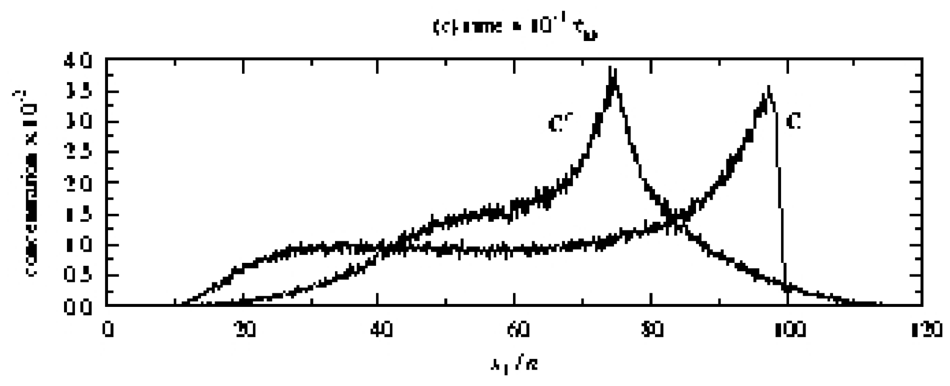

Fig. 5: Simulated effective and apparent concentration profiles for flow in a fracture (*Dentz and Carrera*, 2007).

Multirate Mass Transfer

Volume averaging

$$\bar{c}_i(\mathbf{x}, t) = \frac{1}{V_m} \int_{V_m} d^d y\, c_i(\mathbf{x} + \mathbf{y}) + \frac{1}{V_{im}} \int_{V_{im}} d^d y\, c_i(\mathbf{x} + \mathbf{y}). \quad (4)$$

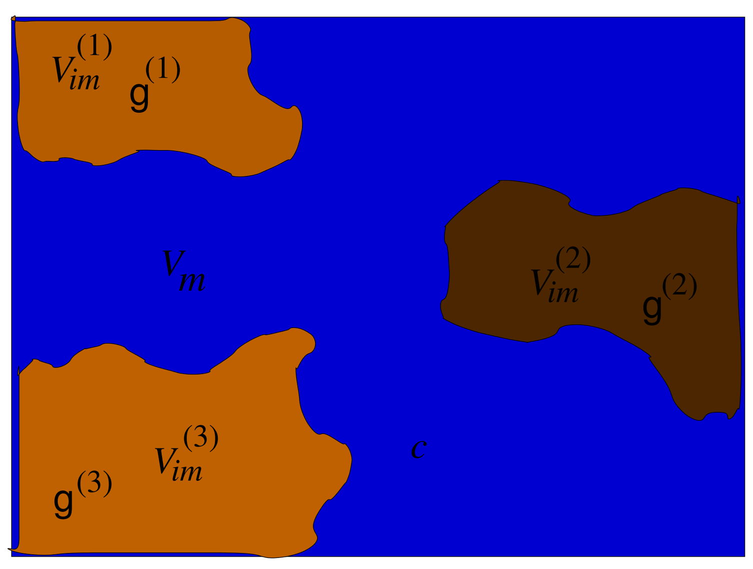

Fig. 6: Mass transfer processes between stagnant and mobile zones within the averaging volume.

Averaging over the processes below the scale L of the averaging volume V gives

$$\bar{\phi}_m \frac{\partial \bar{c}_i}{\partial t} + \bar{\phi}_{im} \frac{\partial \bar{g}_i}{\partial t} + \left[\nabla \cdot \bar{\mathbf{q}}(\mathbf{x}) - \nabla \cdot \overline{\mathbf{D}}(\mathbf{x}) \nabla\right] \bar{c}_i = -\bar{r}_m \quad (5)$$

Mass transfer

$$\frac{\partial \bar{g}^{(n)}}{\partial t} = \alpha \left[\bar{c}_i - \bar{g}_i^{(n)}\right] - \bar{r}_{im}^{(n)}. \quad (6)$$

The total immobile concentration is given by the weighted sum over all immobile concentrations

$$g_i(\mathbf{x}, t) = \sum_n p_n g_i^{(n)}(\mathbf{x}, t) \quad (7)$$

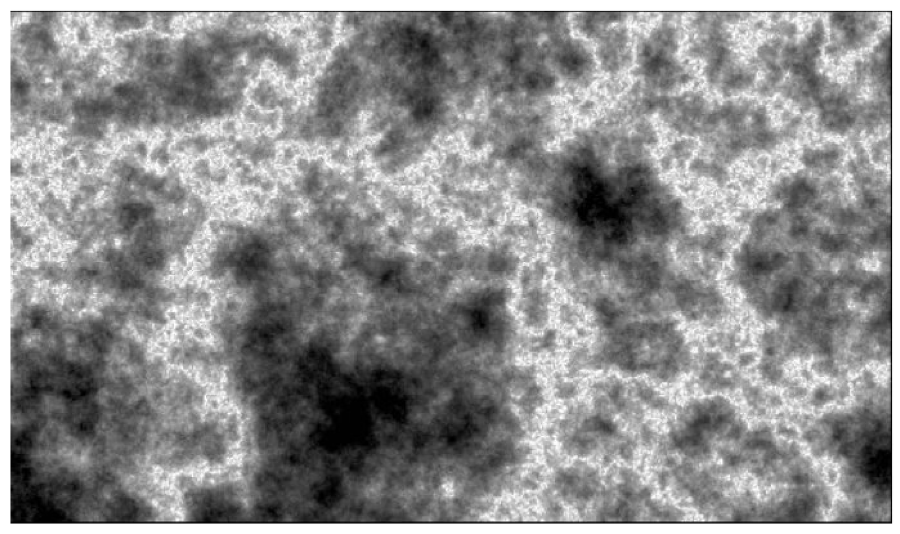

Fig. 7: Realization of a connected conductivity field.

The reaction rate is given by

$$\bar{r} = \bar{r}_m + \sum_n p_n \bar{r}_{im}^{(n)}. \quad (8)$$

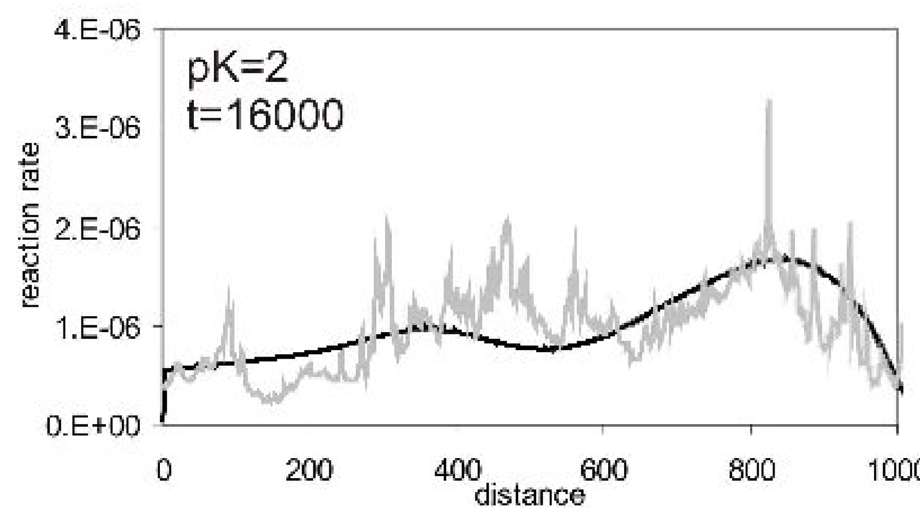

Fig. 8: Reaction rate for transport in the above conductivity field and obtained from the effective reactive trasport model (*Willmann et al.*, 2008).

Numerical Implementation for PA Exercises

- Reactive transport: module CHEPROO (*Bea et al.*, 2008).
- Multirate mass transfer: module mod-MRMT (*Silva et al.*, 2008)
- Reactive multirate mass transfer:
  module RMRMT = CHEPROO + mod-MRMT

References

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