Upscaling of Transport Properties; Reacting Porous Media

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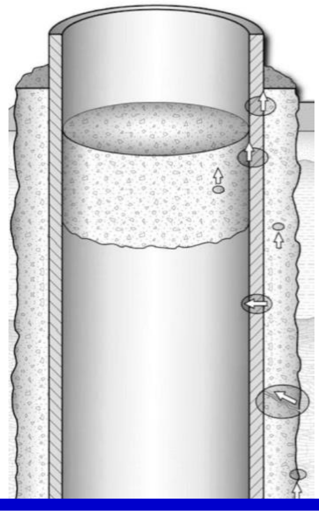
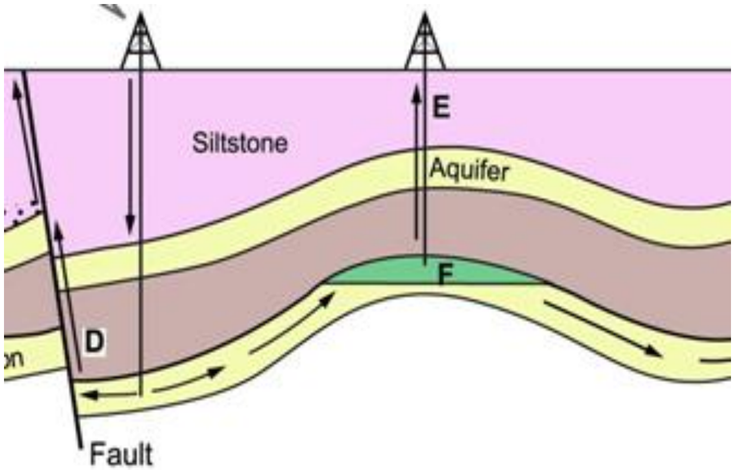
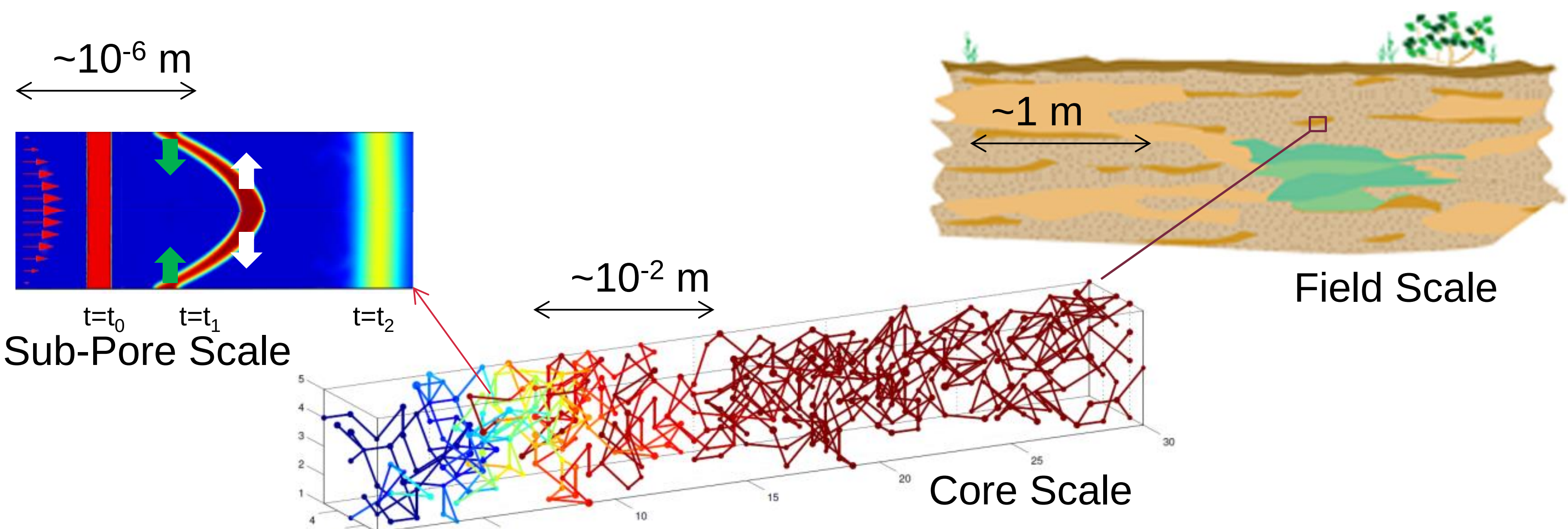
Problem Examples

Cement Degradation Process



CO_2 Storage in Geological Formations



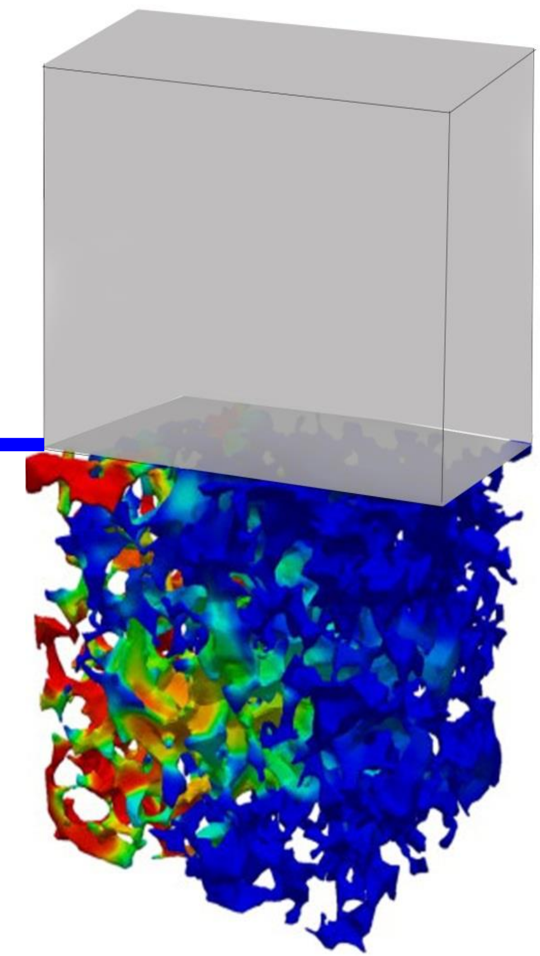


Pore Scale vs. Filed (Continuum) Scale

Θ porosity
c species concentration
D is the dispersion coefficient
v is the average velocity that solute is moving
R describes reactions, and λ adsorption retardation

$$\underbrace{\lambda \frac{\partial\left(\theta \bar{c}^{k}\right)}{\partial t} = \nabla\cdot\left(\theta D \nabla \bar{c}^{k}\right) - \nabla\cdot\left(\theta v \bar{c}^{k}\right) + \sum \bar{R}_{k}}_{Macro\ Scale\ Parameters}$$

Field (continuum) scale



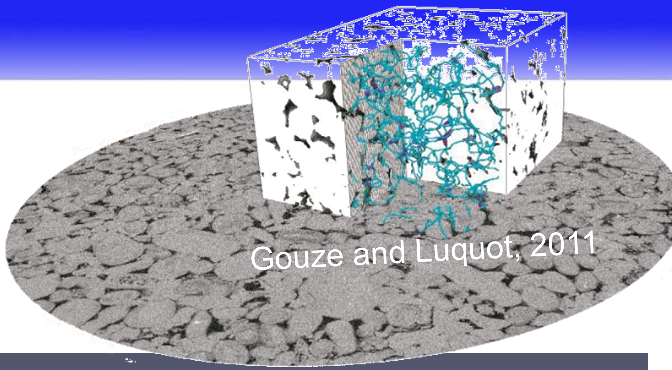
$$\frac{\partial\left(c^{k}\right)}{\partial t} = \nabla\cdot\left(D_{mol} \nabla c^{k}\right) - \nabla\cdot\left(v c^{k}\right) + \sum R_{k}$$

No porosity!! No Dispersion!!

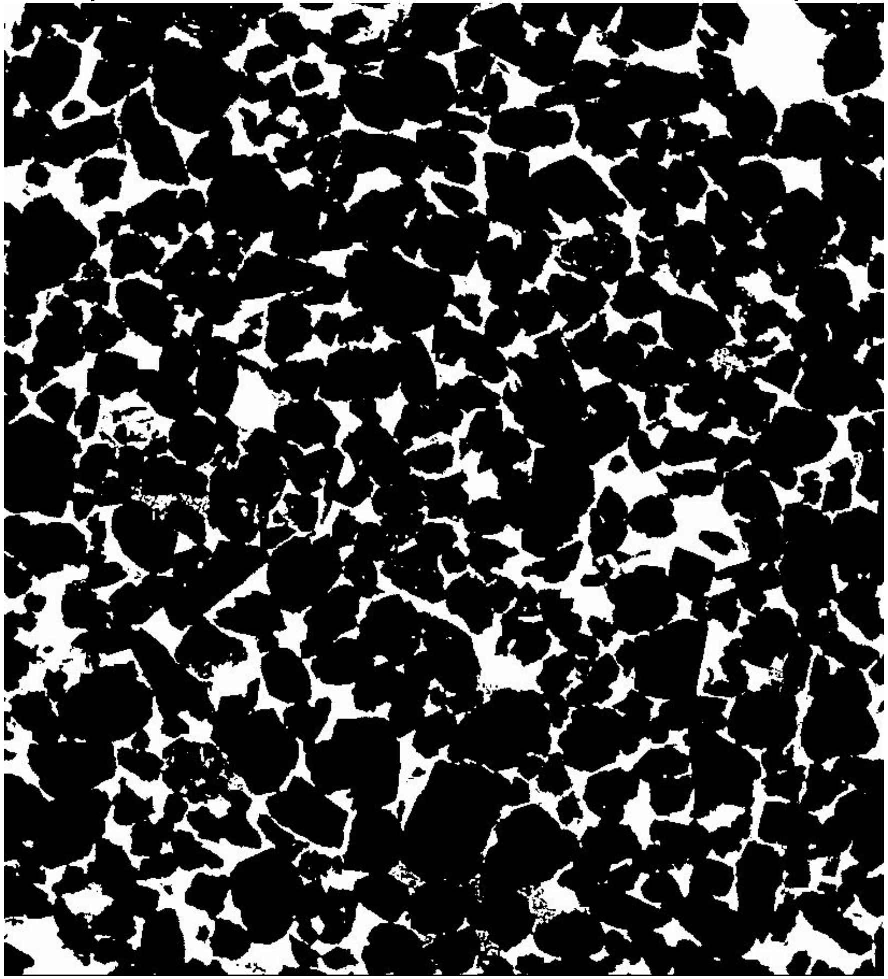
c species concentration
D Diffusion coefficient
v pore velocity that solute is moving
R describes reactions

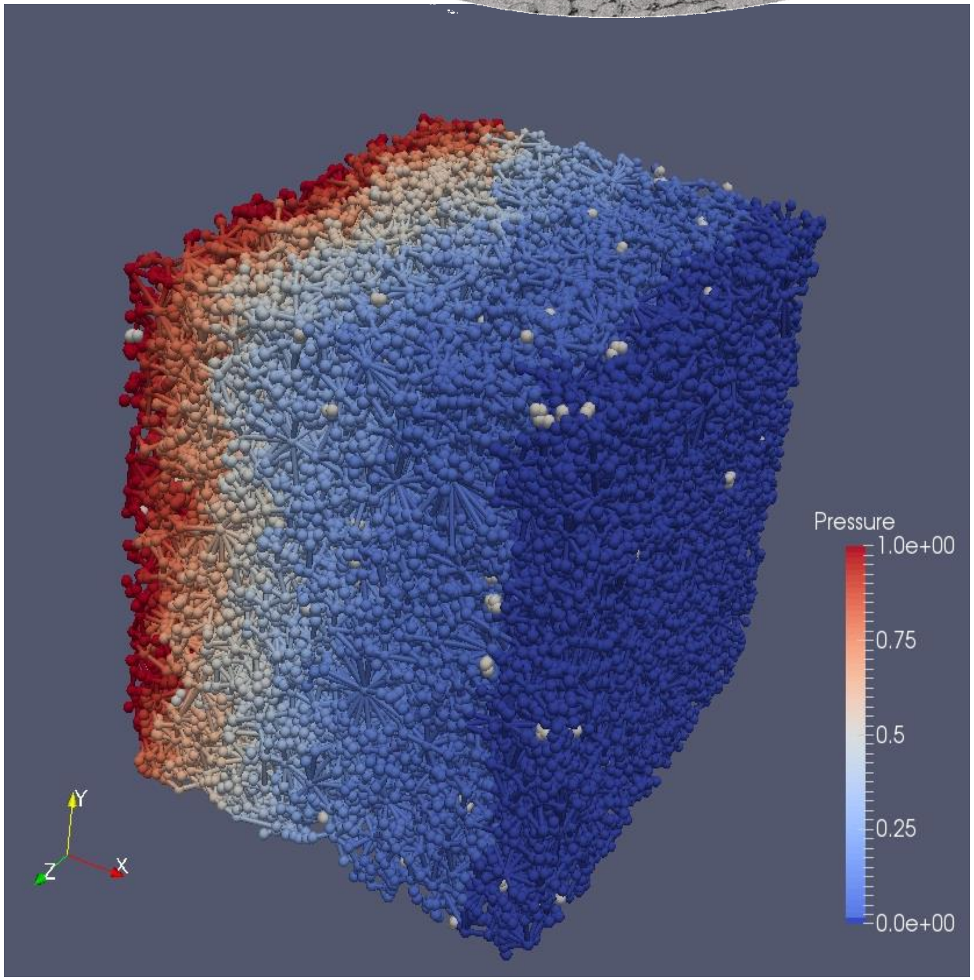
Pore scale

Pore Space Representation



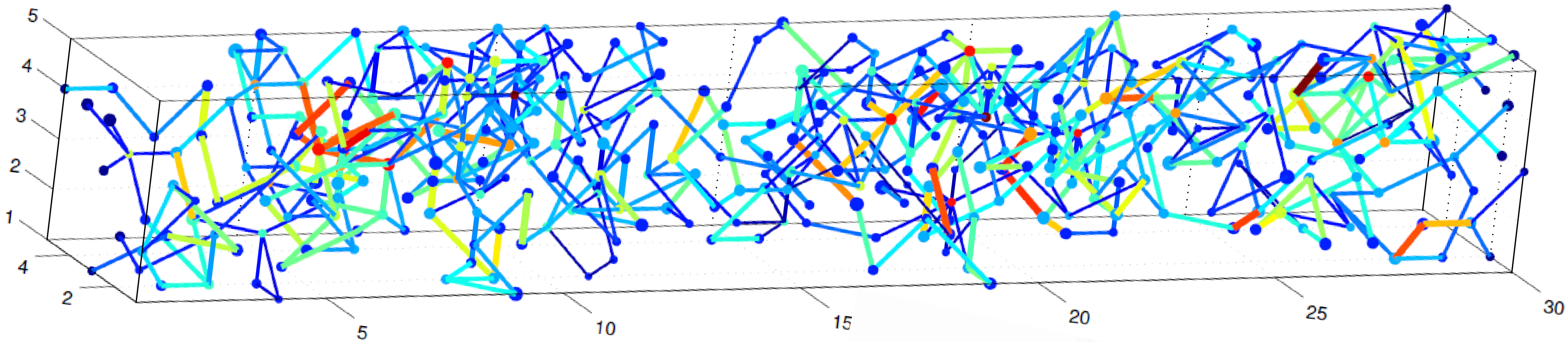
Bentheimer Sandstone – Data from Gent University
Sample size 3*mm* each side, voxel size is 4.28 µm



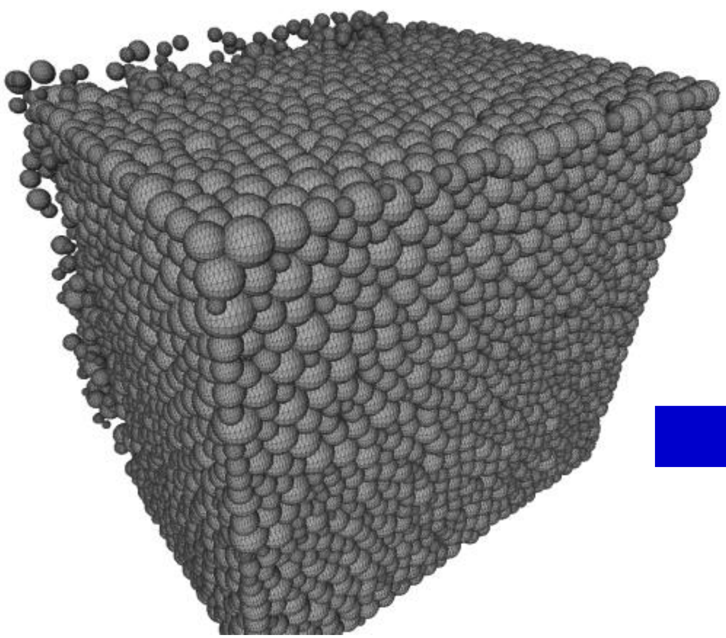


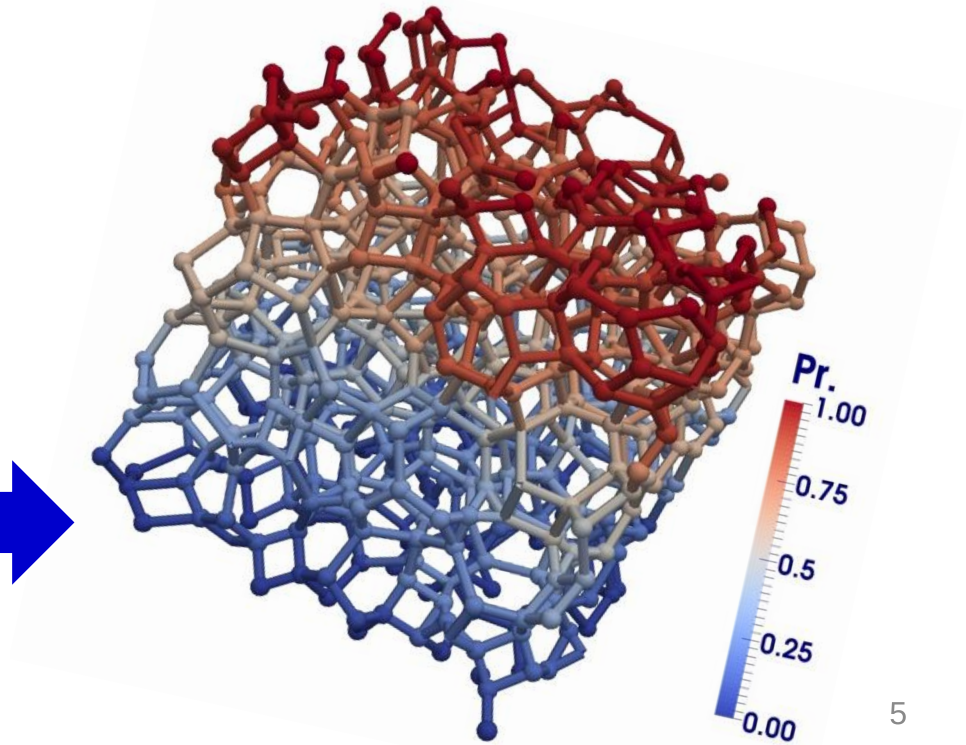
Capturing the Soil/Rock Topology

Multi-Directional Random Structure



Grain Packing





Raoof, Amir, and S. Majid Hassanizadeh. "A new method for generating pore-network models of porous media." Transport in porous media 81.3 (2010)

Governing Equations

Advection

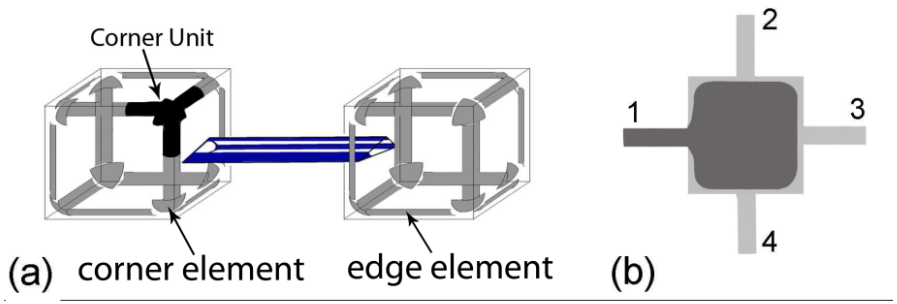
$$V_{CU,i}\frac{d}{dt}(c_{CU,i}) = \sum_{j=1}^{N_{in}^{throat}}\sum_{k=1}^{N_{edge}^{ij}} q_{ij,k}c_{ij,k} + \sum_{n=1}^{N_{in,edge}^{CU,i}} q_{i,n}c_{CU,n} - Q_{CU,i}c_{CU,i} +$$

$$\sum_{j=1}^{z_i}\sum_{k=1}^{N_{edge}^{ij}} DA_{ij,k}\frac{(c_{ij,k}-c_{CU,i})}{l_{ij}} + \sum_{n=1}^{N_{edge}^{CU,i}} DA_{i,n}\frac{(c_{CU,n}-c_{CU,i})}{l_{i,n}} - R_{CU,i}.$$

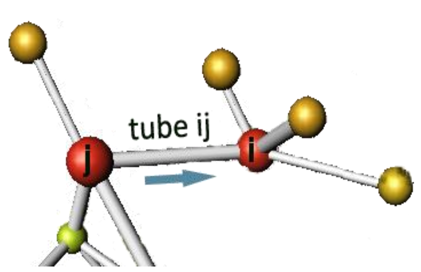
Diffusion **Reaction**

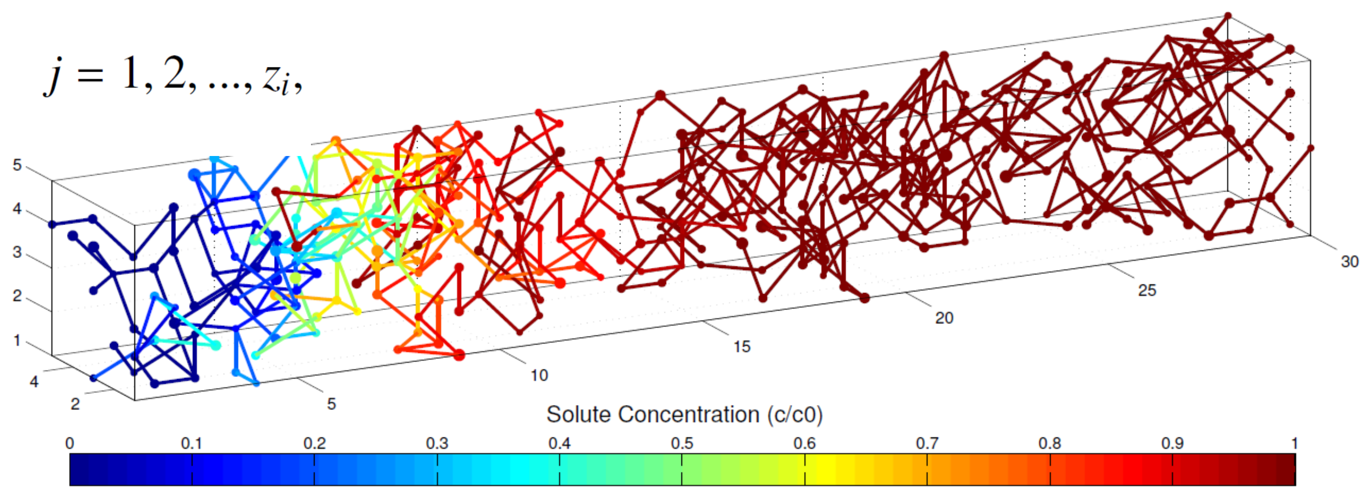
$$R^l = \sum_{m=1}^{N_{reaction}} a^{l,m}r^l,$$

$$V_{ij,k}\frac{d}{dt}\left(c_{ij,k}\right) = |q_{ij,k}|c_{CU,j} - |q_{ij,k}|c_{ij,k} + DA_{ij,k}\frac{\left(c_{CU,j} - c_{ij,k}\right)}{l_{ij}} + DA_{ij,k}\frac{\left(c_{CU,i} - c_{ij,k}\right)}{l_{ij}} - R_{ij,k},$$

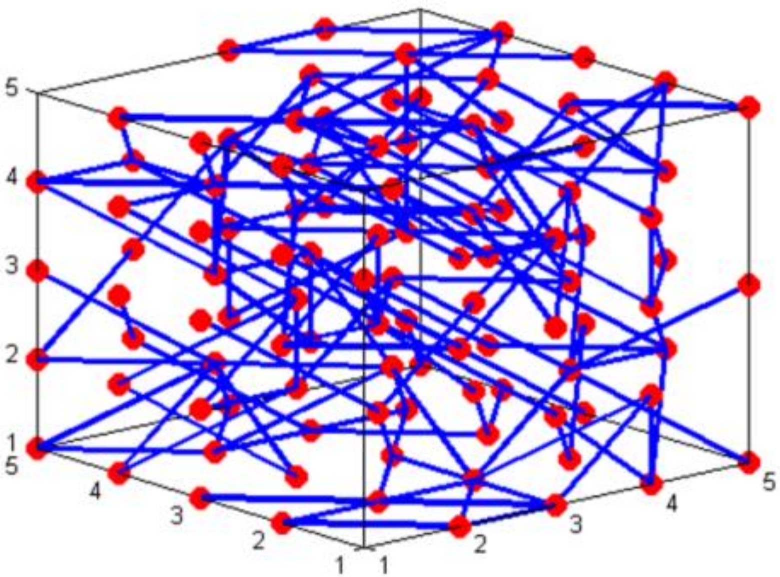


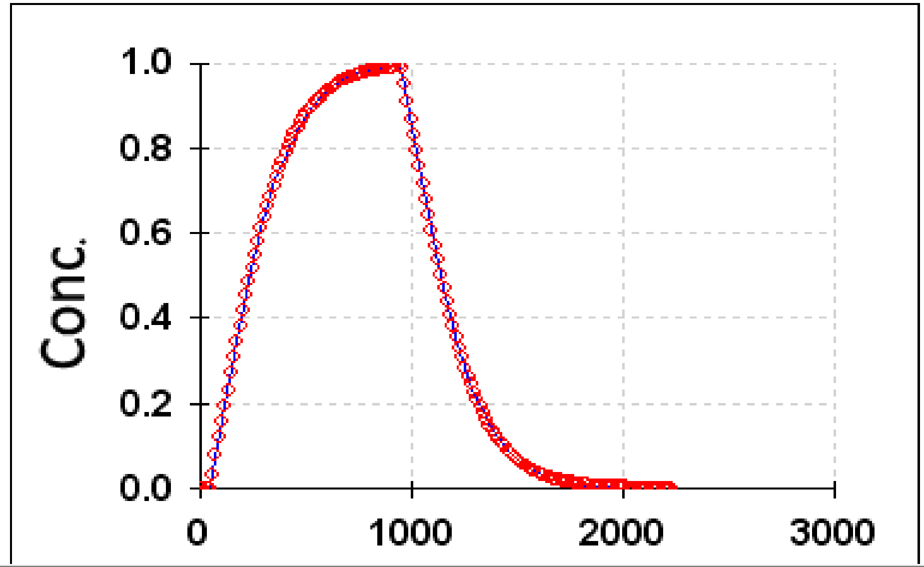
$$\sum_{n=1}^{N_{edge}^{CU,i}} q_{i,n} + \sum_{j=1}^{z_i} q_{ij,tot} = 0; \qquad j = 1, 2, ..., z_i,$$

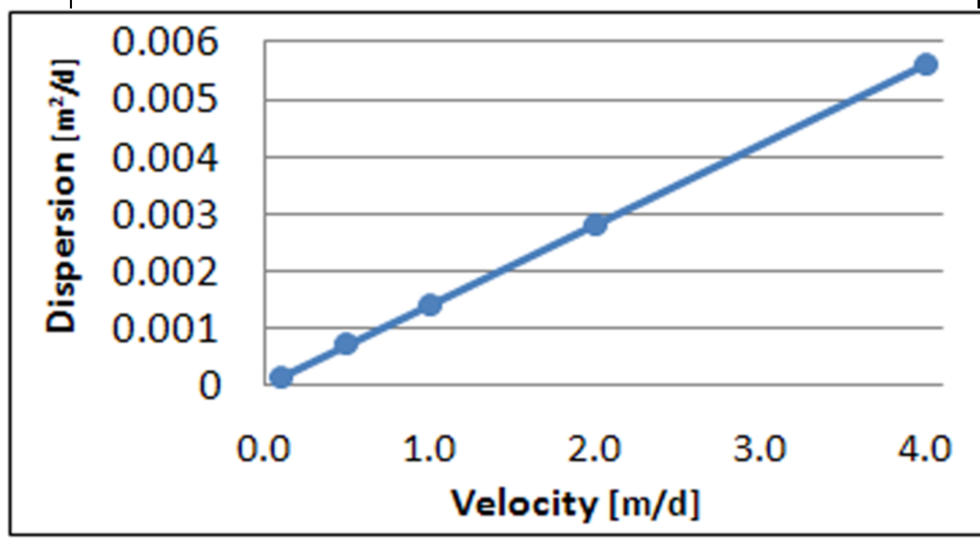




Modeling Flow and (Adsorptive) Transport





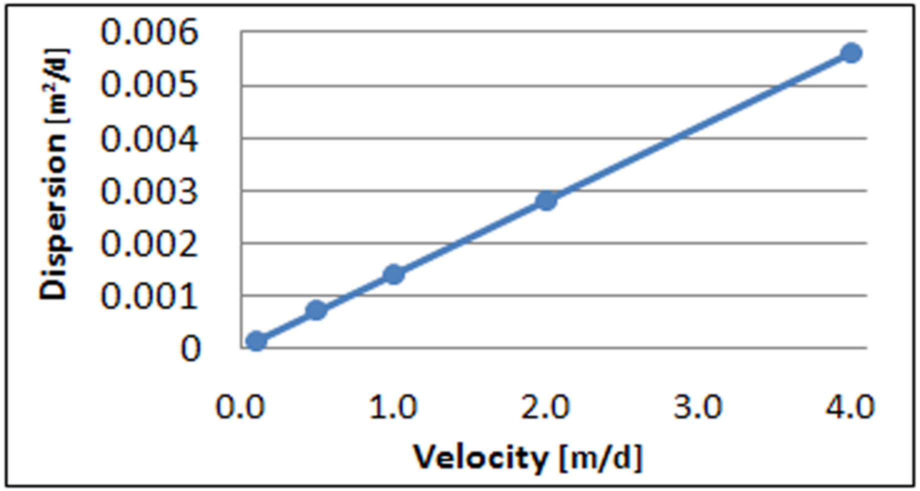


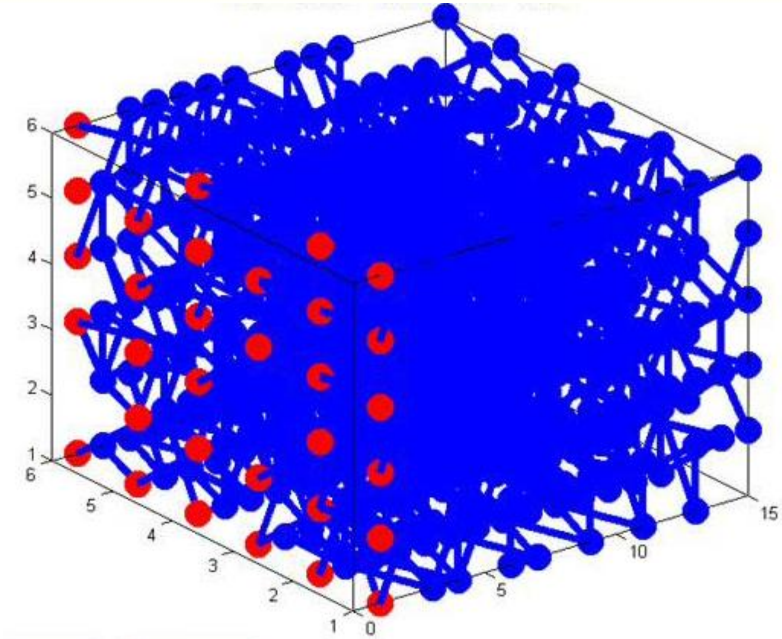
Macro scale solute transport

$$\frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z}\right) - \frac{\partial q C}{\partial z}$$

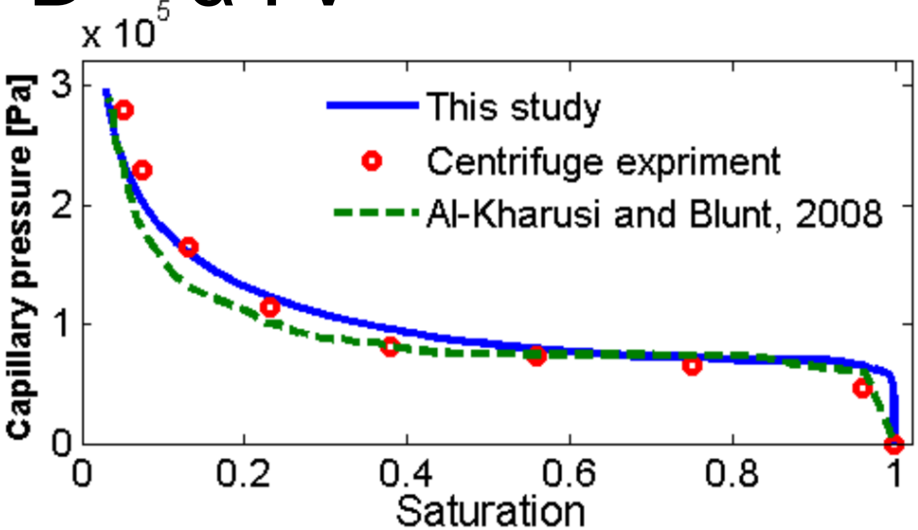
- *Raoof, Amir, S. Majid Hassanizadeh, and Anton Leijnse. "Upscaling transport of adsorbing solutes in porous media: Pore-network modeling."* Vadose Zone Journal *9.3 (2010): 624-636.*
- *Raoof, Amir, and Seyed Majid Hassanizadeh. "UPSCALING TRANSPORTOF ADSORBING SOLUTES IN POROUS MEDIA." Journal of Porous Media 13.5 (2010).*

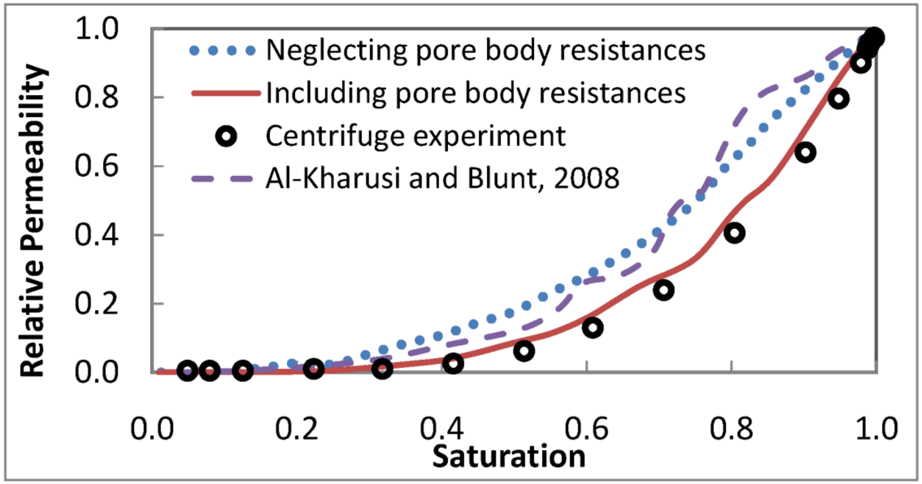
From Saturated to Partially-Saturated





$$D = \alpha \cdot v$$





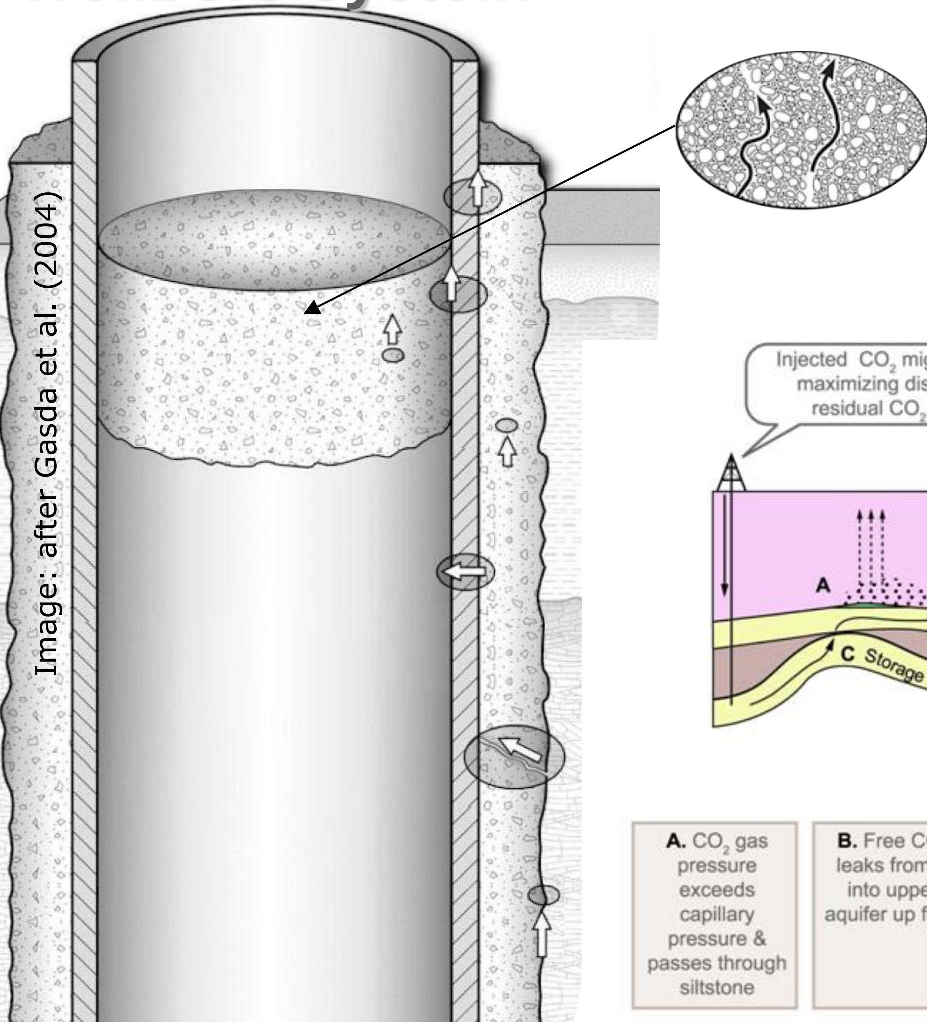
Raoof, A., and S. M. Hassanizadeh. "A new formulation for pore-network modeling of two-phase flow." Water Resources Research 48.1 (2012).

Raoof, A., and S. M. Hassanizadeh. "Saturation-dependent solute dispersivity in porous media: Pore-scale processes." *Water Resources Research* (2013).

CO_2 Leakage Through Wellbore Cement

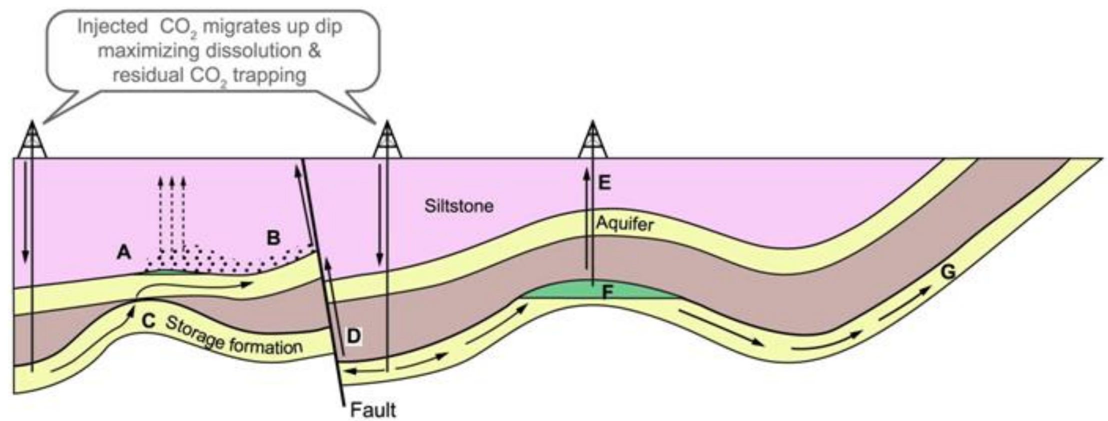
One of the primary concerns is that chemical degradation of the cement used to seal wellbores may provide or enhance preferential pathways for CO_2 escape.

Wellbore System



Through pore space: *degradation*

Image: after Gasda et al. (2004)

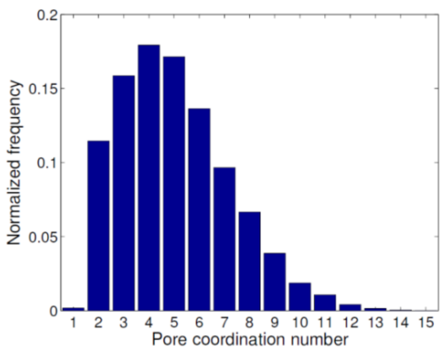


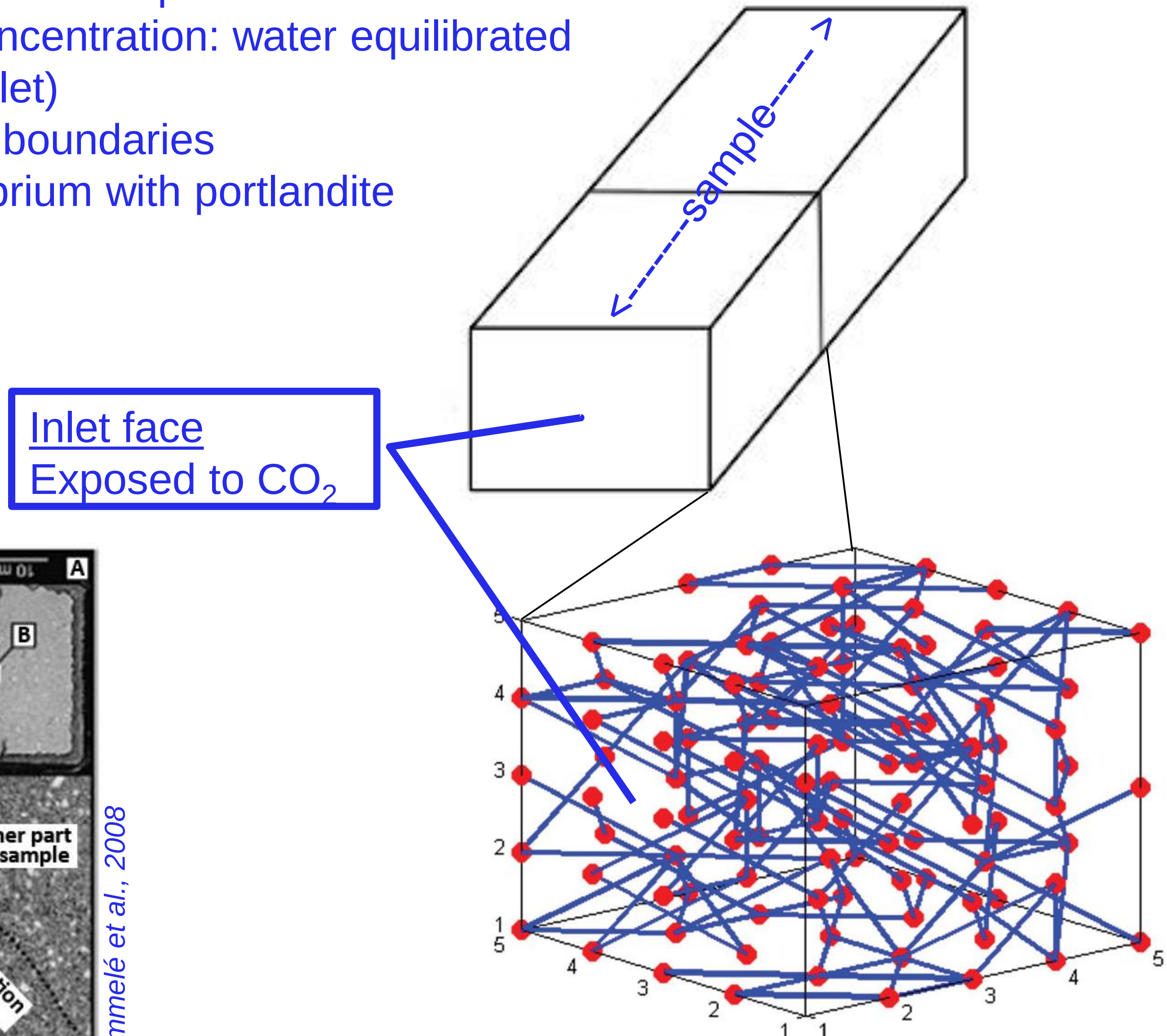
Potential Escape Mechanisms

A. CO_2 gas pressure exceeds capillary pressure & passes through siltstone	**B.** Free CO_2 leaks from A into upper aquifer up fault	**C.** CO_2 escapes through 'gap' in cap rock into higher aquifer	**D.** Injected CO_2 migrates up dip, increases reservoir pressure & permeability of fault	**E.** CO_2 escapes via poorly plugged old abandoned well	**F.** Natural flow dissolves CO_2 at CO_2 / water interface & transports it out of closure	**G.** Dissolved CO_2 escapes to atmosphere or ocean

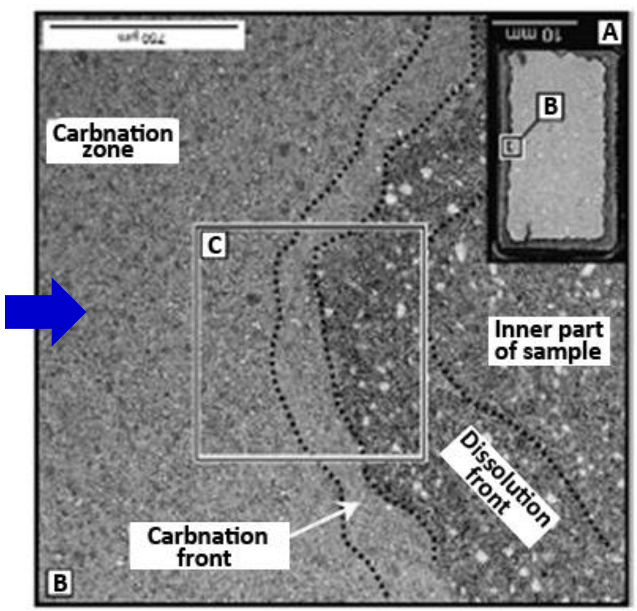
Pore Network Modeling Setup for Cement

-Only diffusive transport of components
-B.C.: constant inlet concentration: water equilibrated with CO_2 (Dirichlet)
-B.C.: no-flux at lateral boundaries
-I.C.: solution in equilibrium with portlandite





Face Exposed to CO_2



Rimmelé et al., 2008

Equilibrium constants and enthalpies of reaction

No.	equilbrium	$K_{25°C}$	ΔH^0(kJ/mol)
1	$H_2O \rightleftharpoons H^+ + OH^-$	$1.007 \times 10^{-14\ a}$	
2	$CO_2(aq) \rightleftharpoons H_2CO_3^*$	$3.390 \times 10^{-2\ b}$	-20.37^c
3	$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$	$4.446 \times 10^{-7\ b}$	7.7^c
4	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$4.688 \times 10^{-11\ b}$	14.9^c
5	$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	$3.360 \times 10^{-9\ a}$	-10.63^a
6	$Ca_2^+ + HCO_3^- \rightleftharpoons CaHCO_3^+$	$10.0^{\ b}$	25.82^d
7	$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$	$5.020 \times 10^{-6\ a}$	-16.94^a
8	$Ca_2^+ + OH^- \rightleftharpoons CaOH^+$	$19.95^{\ b}$	7.23^e

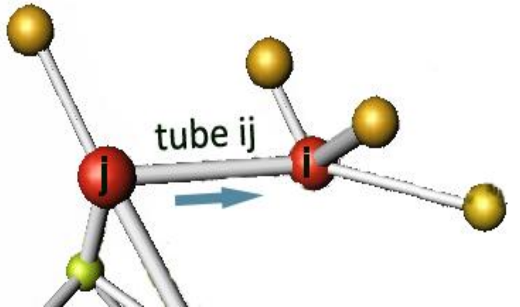
Rate equation for calcite dissolution/precipitation

$$Rate = A_c(k_1 a_{H^+} + k_2 a_{H_2CO_3^*} + k_3)\left(1 - \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{eq}}\right)$$

Li et al., 2008

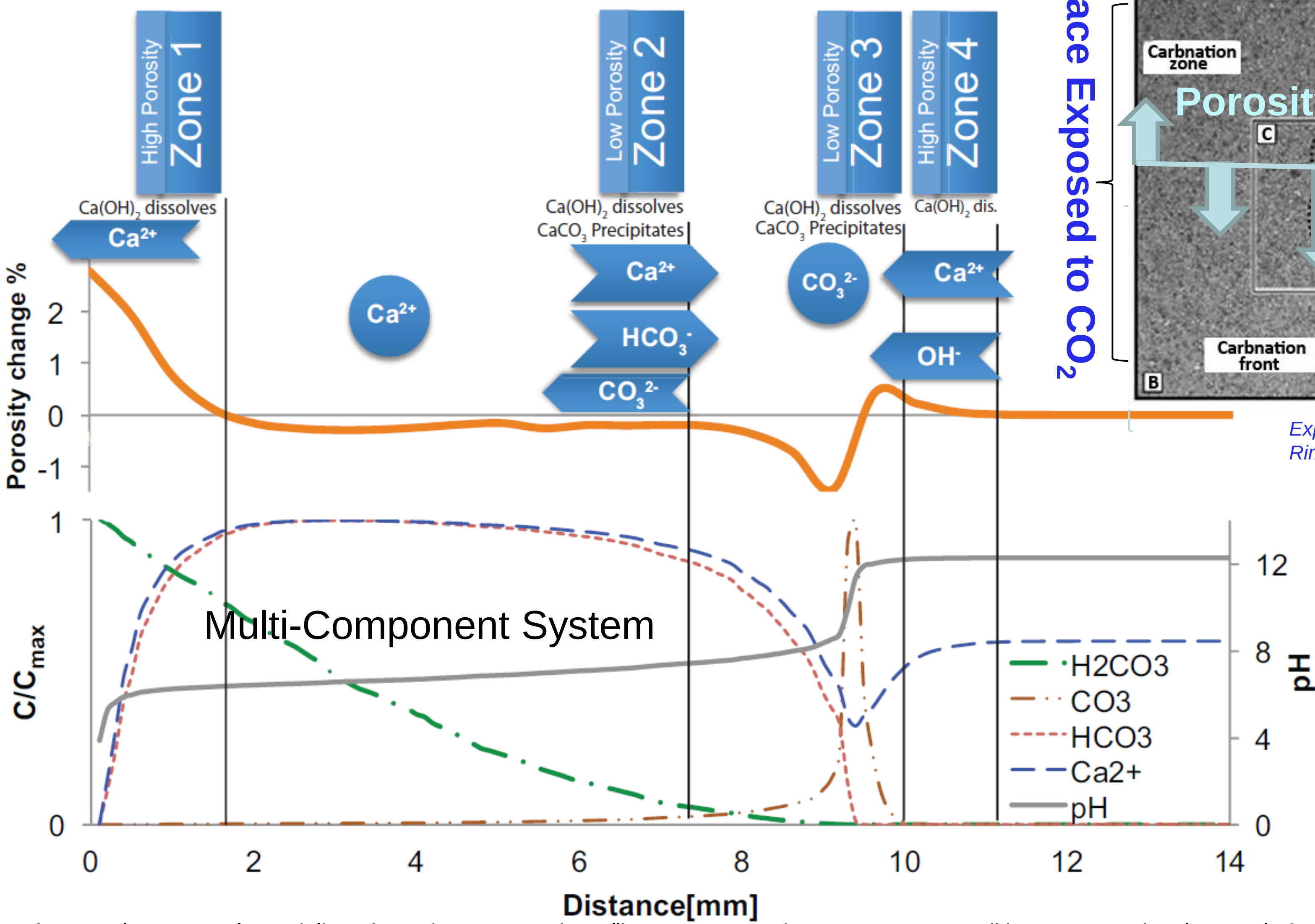
Rate equation for portlandite dissolution/precipitation:

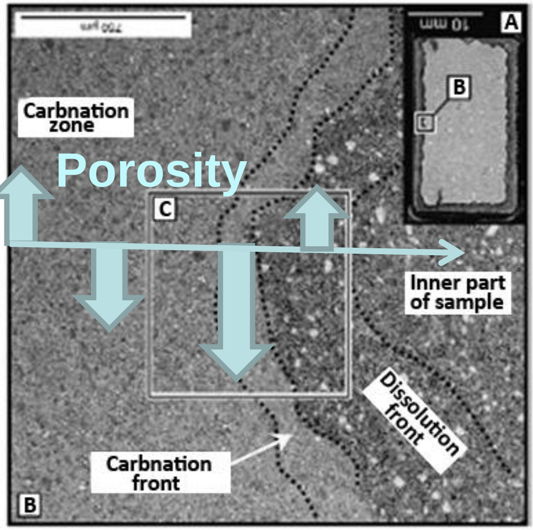
$$Rate = A_p k_p \left(1 - \frac{a_{Ca^{2+}} (a_{OH^-})^2}{K_{eq}}\right)$$



Wellbore cement degradation

Creation of different distinct zones with different porosities.

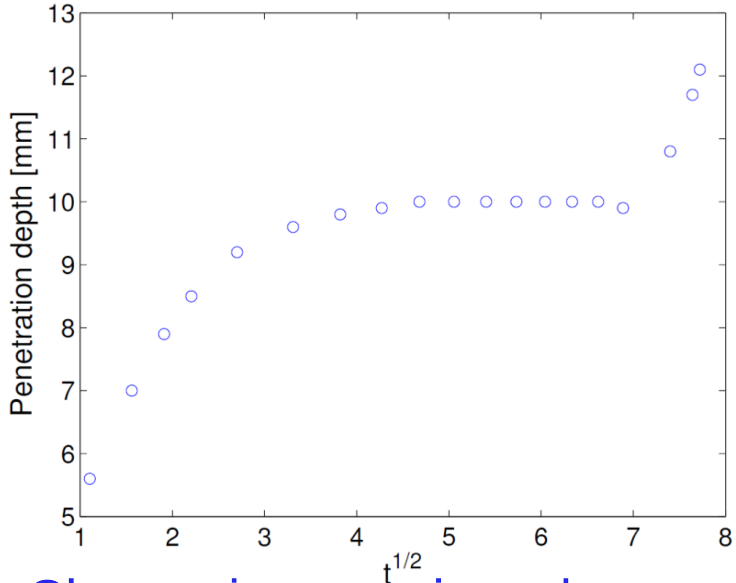




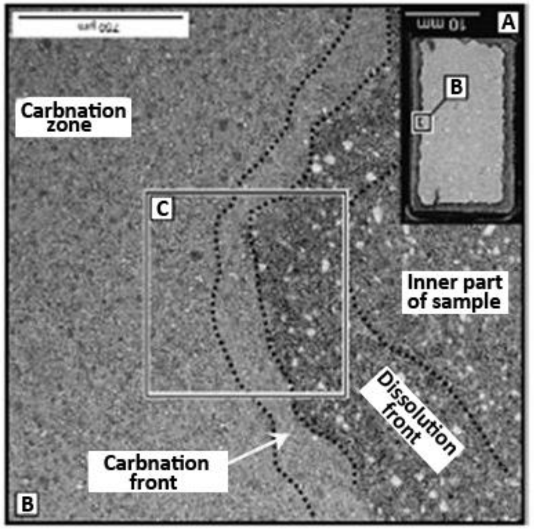
Experimental observation. Rimmelé et al., 2008

Raoof, A., et al. "Pore-scale modeling of reactive transport in wellbore cement under CO2 storage conditions." International Journal of Greenhouse Gas Control (2012).

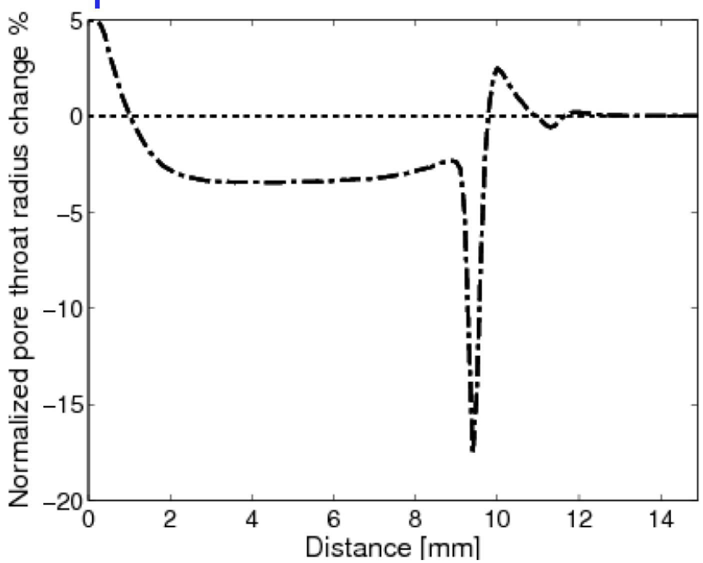
CO_2 Penetration Depth

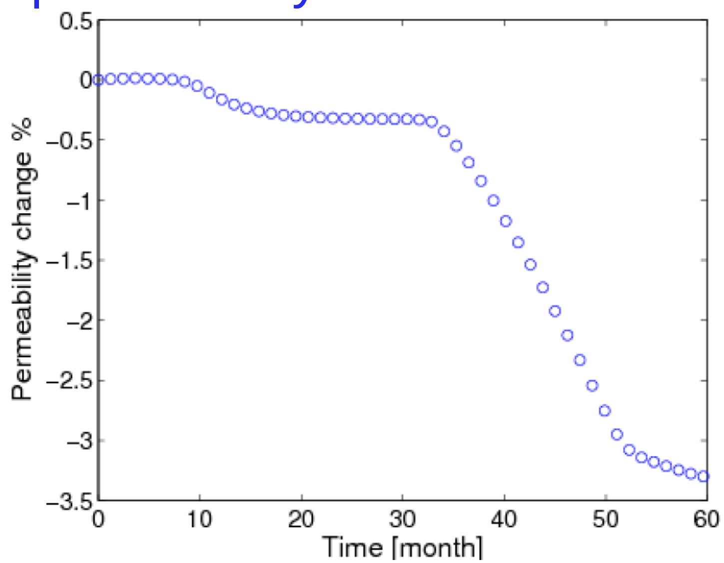


Plot of penetration depth versus square root of time during CO_2 attack, revealing different reactive transport regimes.



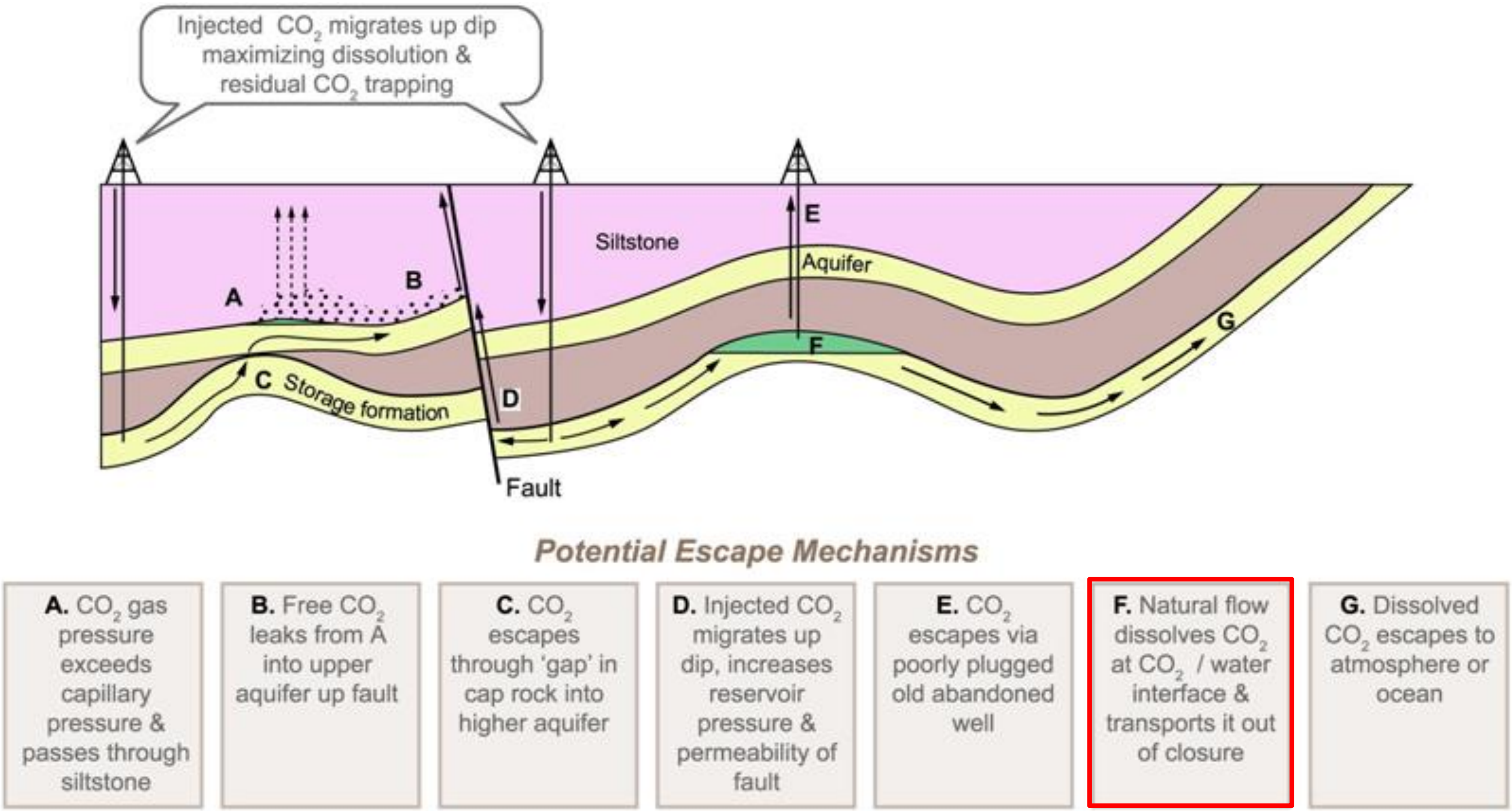
Change in pore sizes decreases average permeability due to the carbonation.





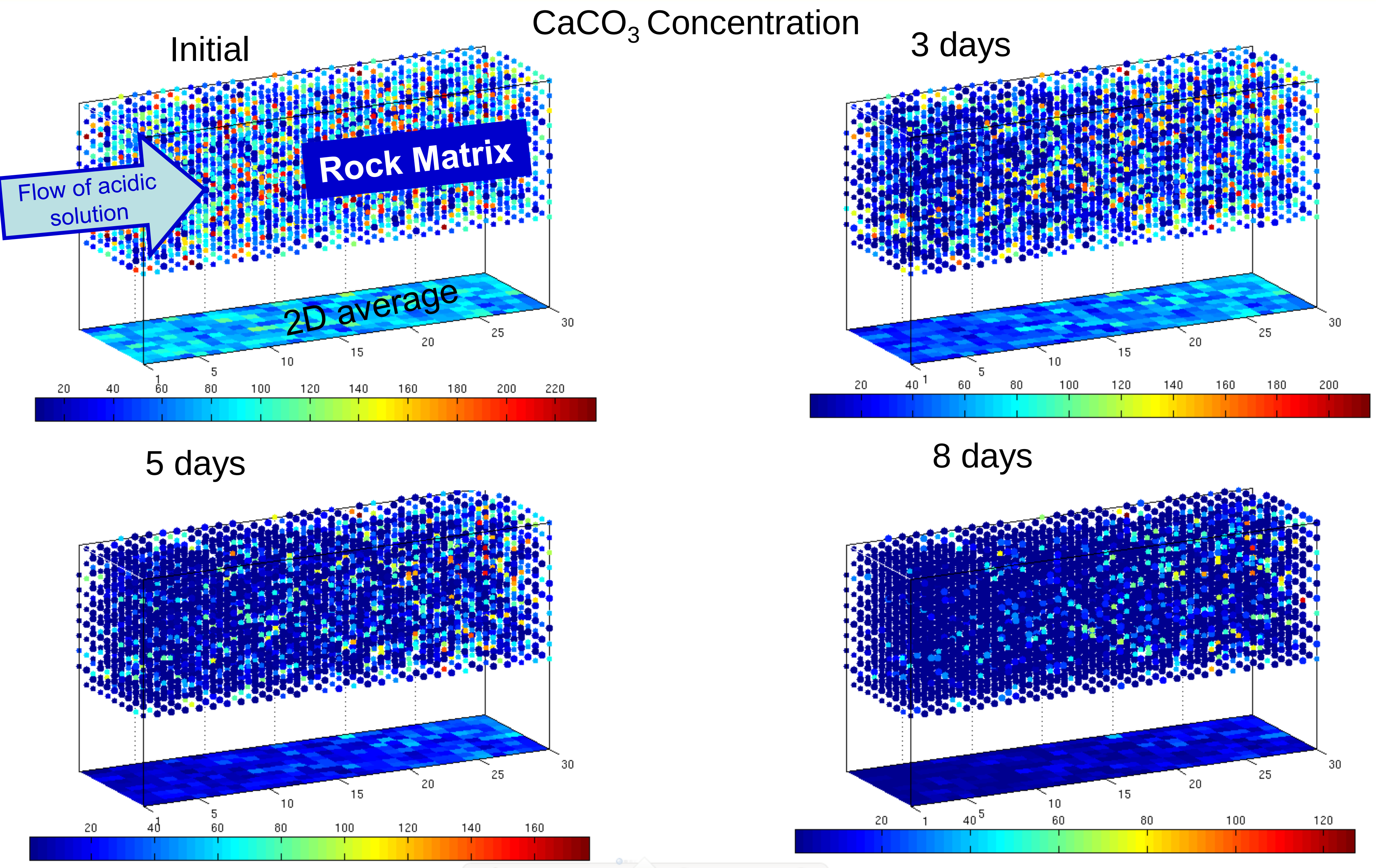
Raoof, A., et al. "Pore-scale modeling of reactive transport in wellbore cement under CO2 storage conditions." International Journal of Greenhouse Gas Control (2012).

Reactive Transport in CO_2 Storage Rock Reservoirs

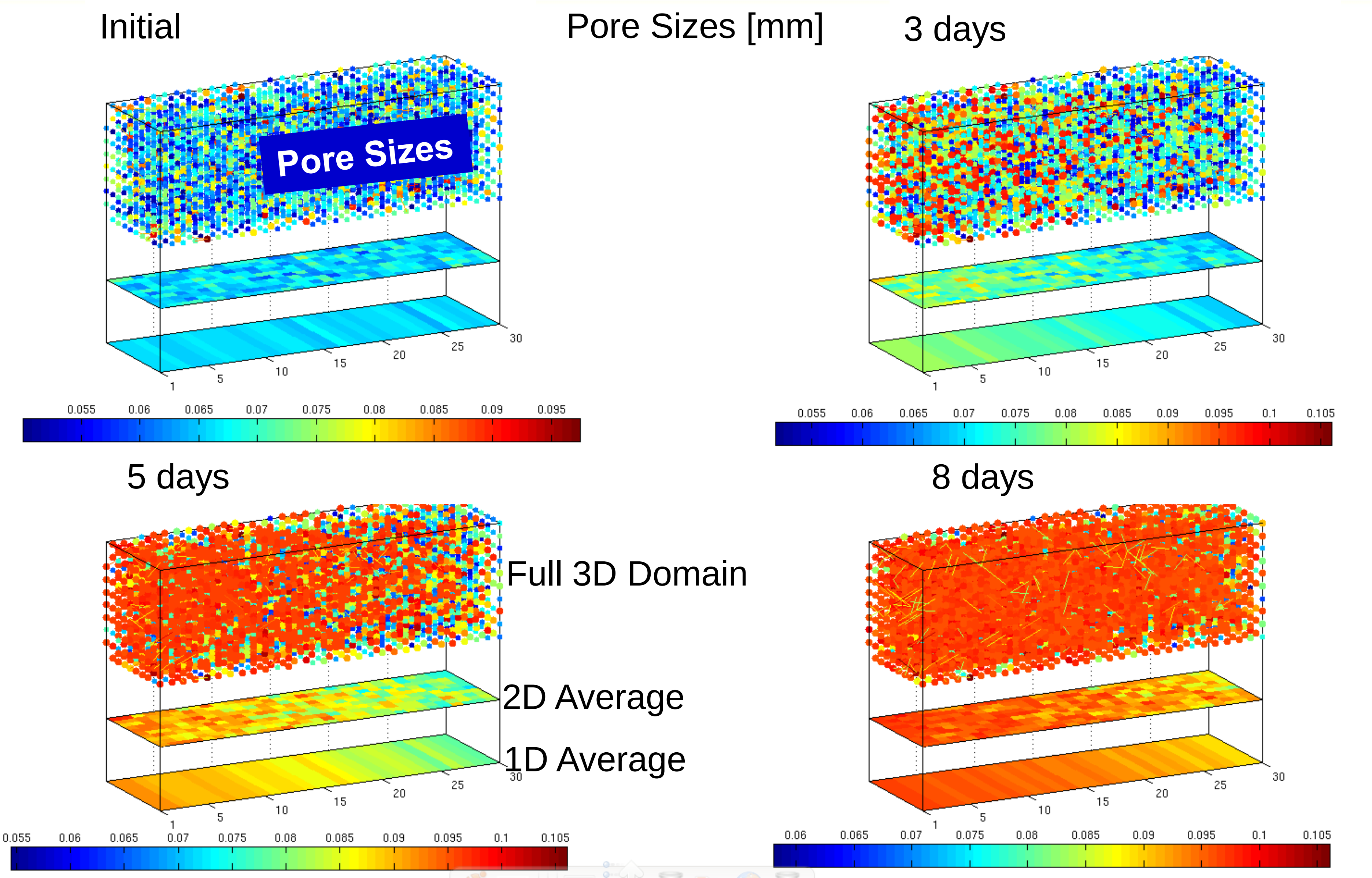


IPCCC website: publications and data

Uniform Dissolution, High Flow Rate (High Pe)



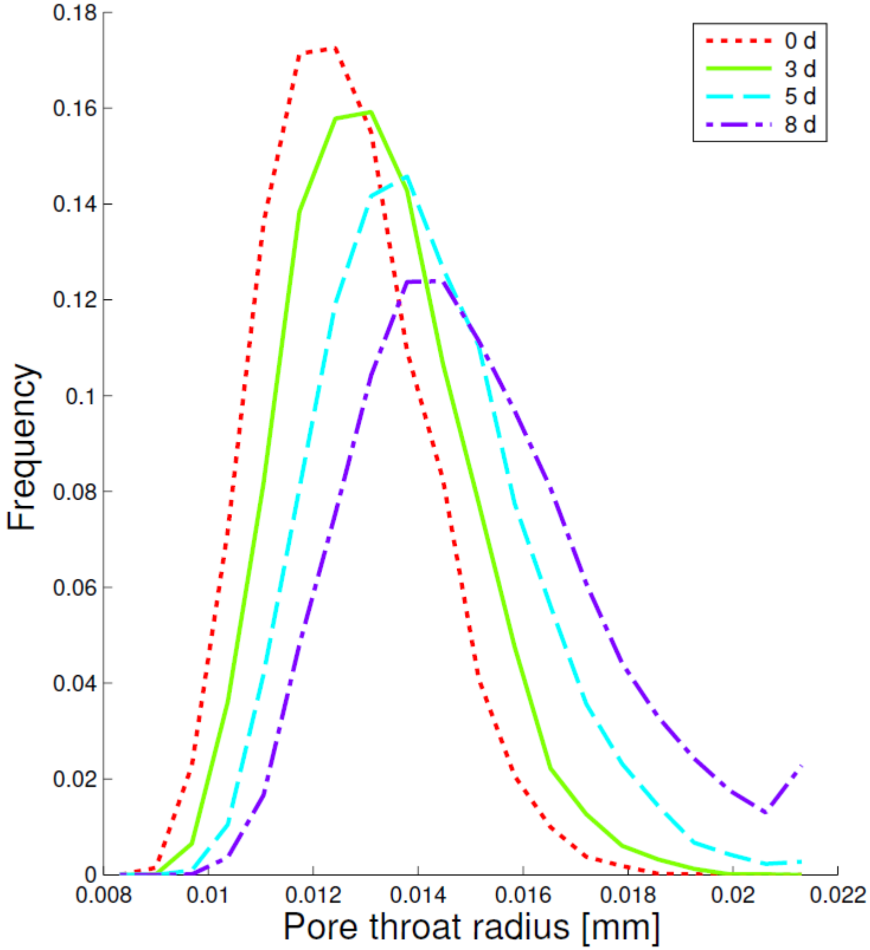
Uniform Pore Space Evolution, High Flow Rate (High Pe)

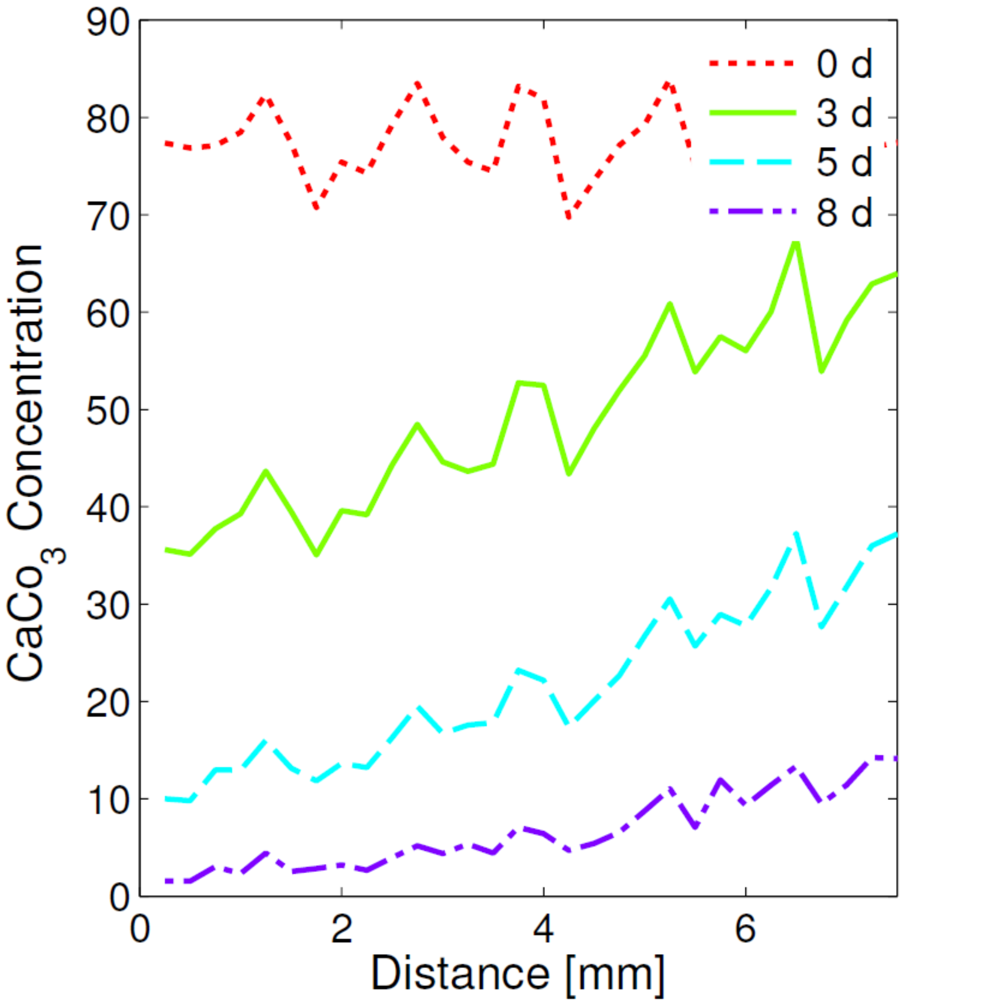


Evolution in Pore Size Distribution, High Flow Rate (High Pe)

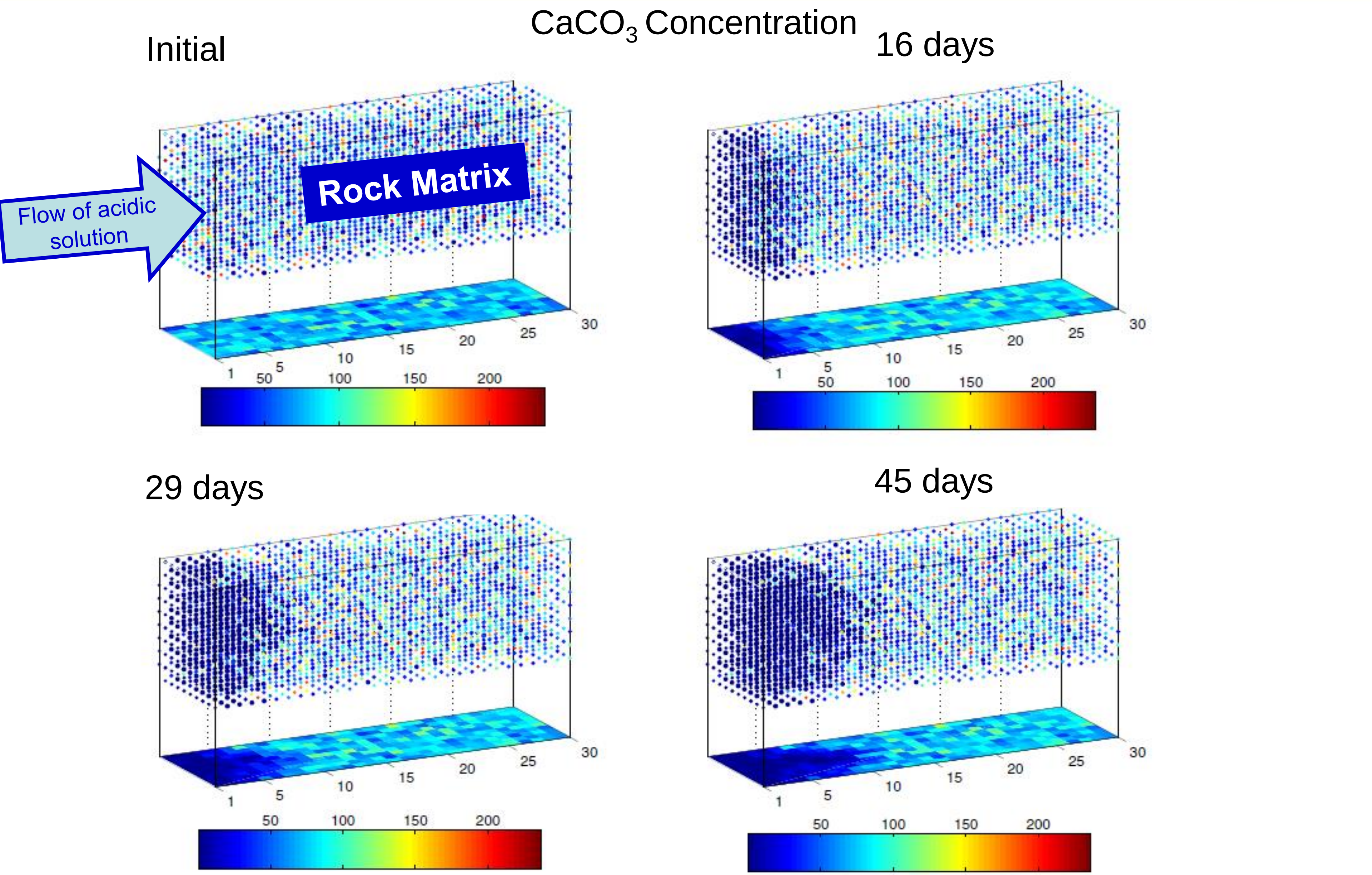
We can observe the evolution in pore size distribution `during the dissolution process.

Initial Pore Size Distribution

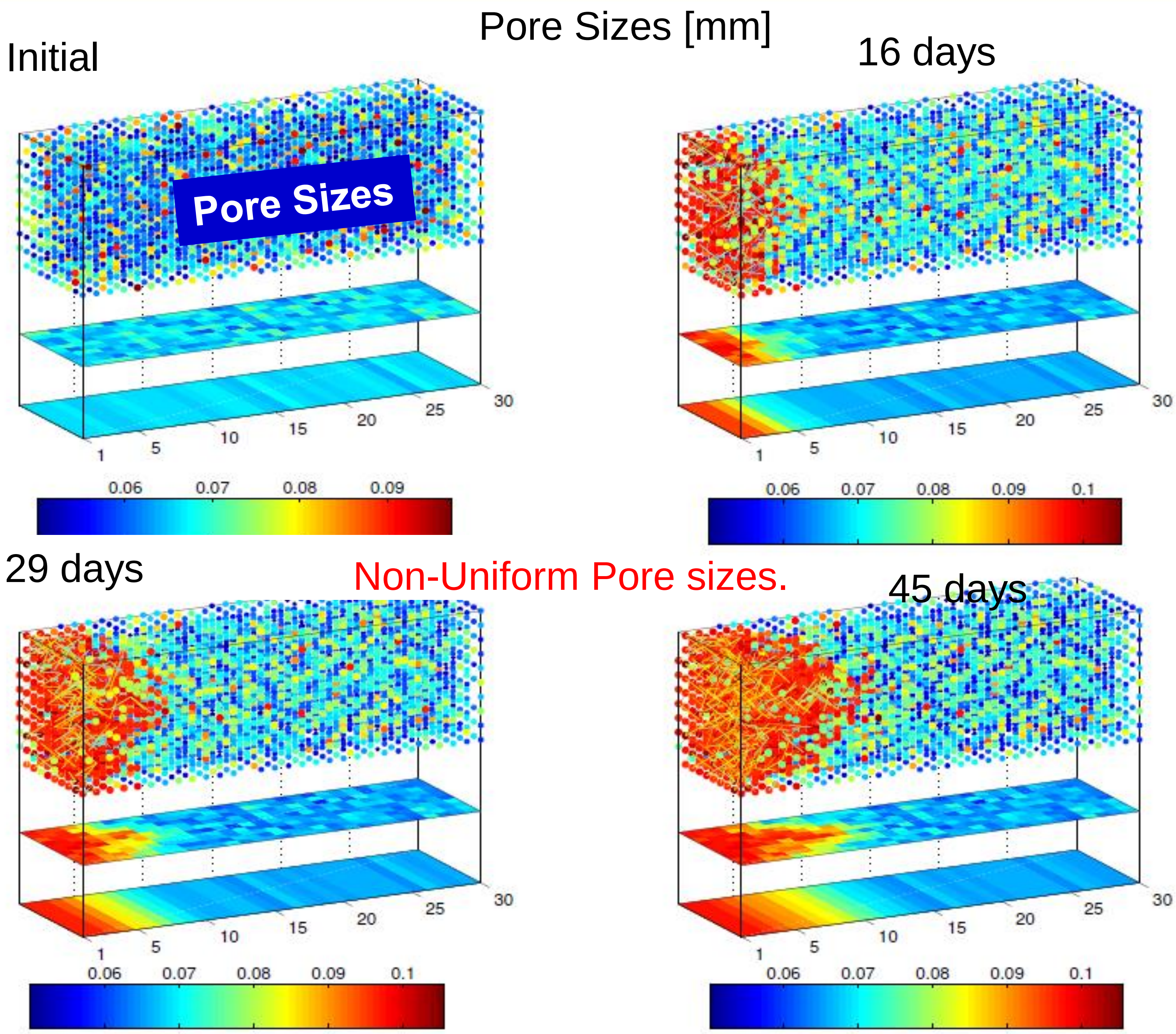




Non-Uniform Dissolution, Low Flow Rate (Low Pe)

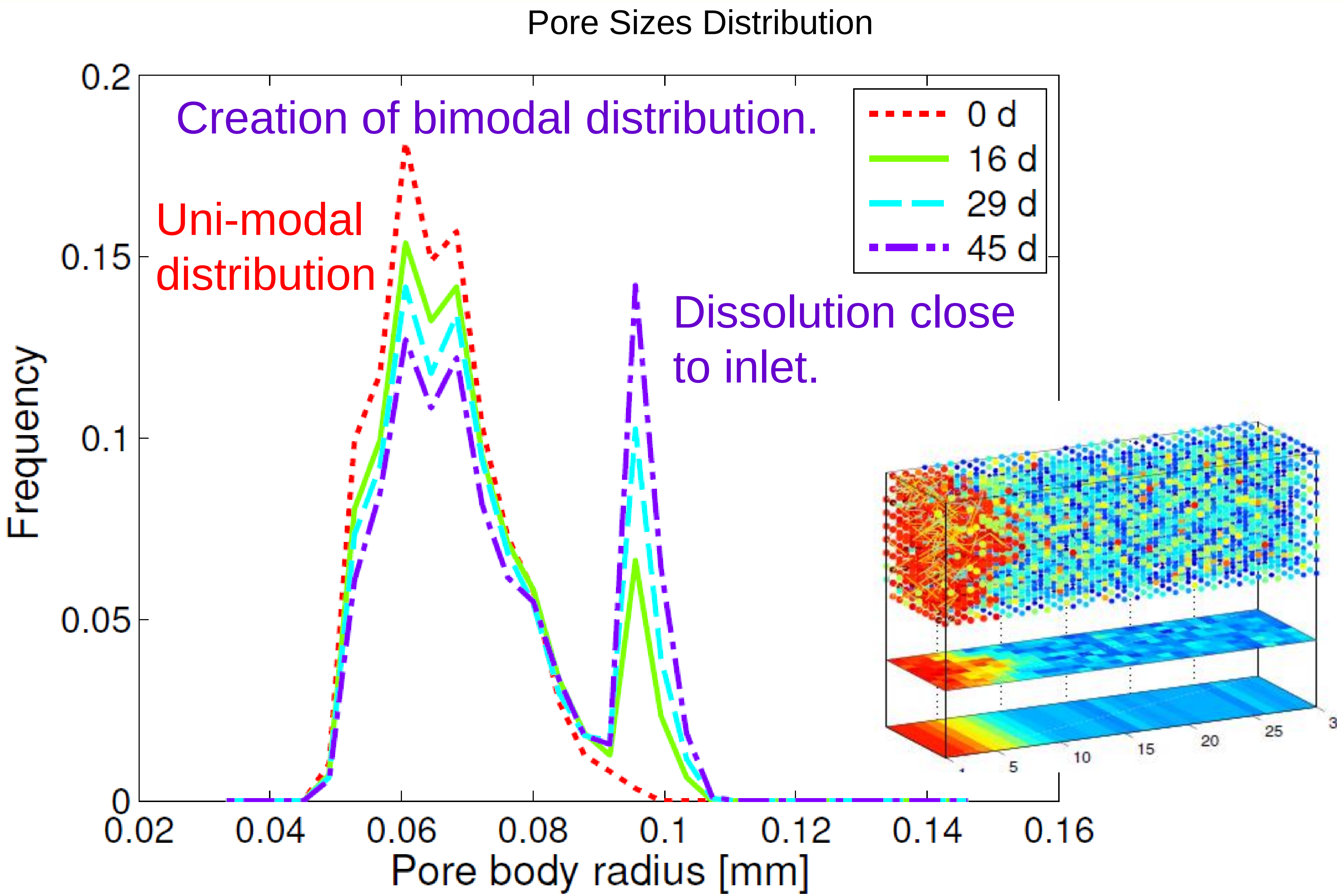


Non-Uniform Pore Space Evolution, Low Flow Rate (Low Pe)

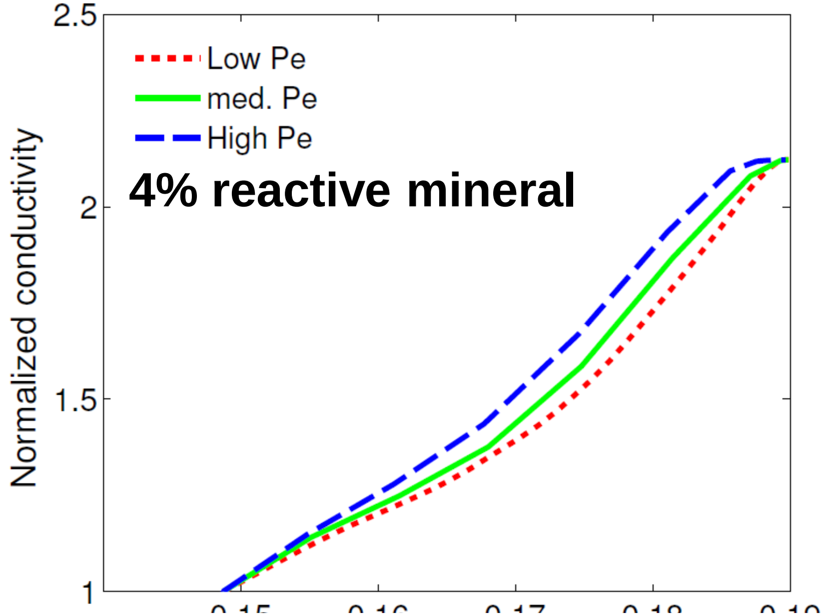


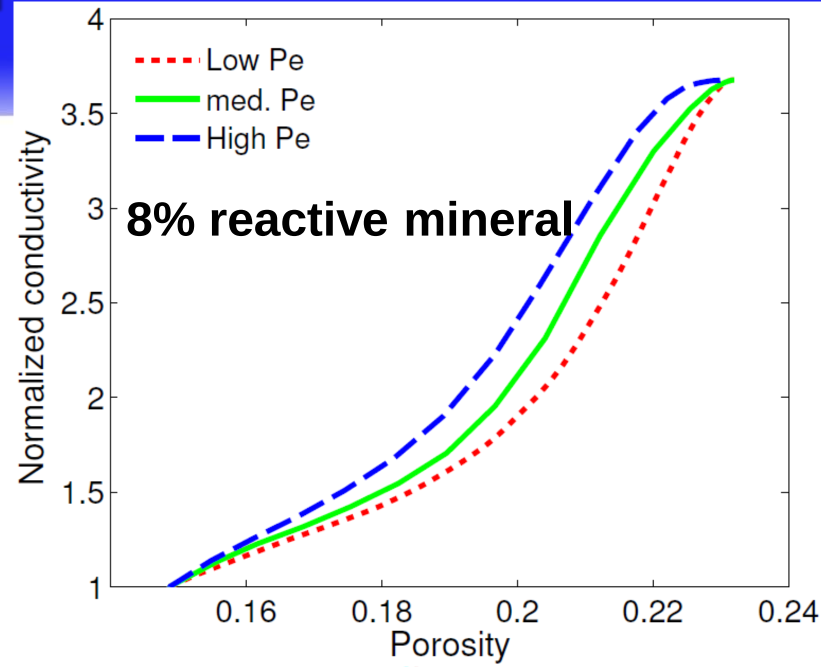
Non-Uniform Pore sizes.

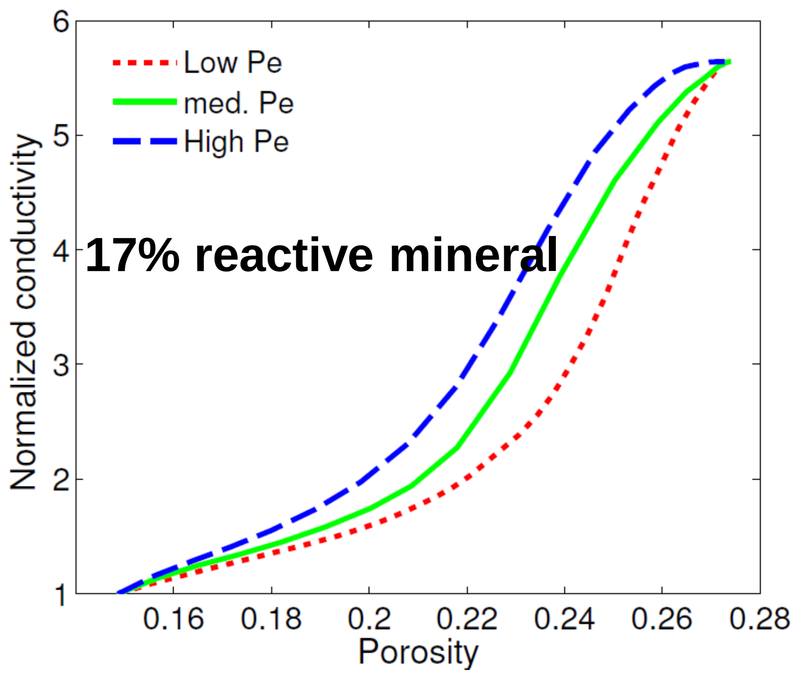
Evolution in Pore Size Distribution, Low Flow Rate (Low Pe)

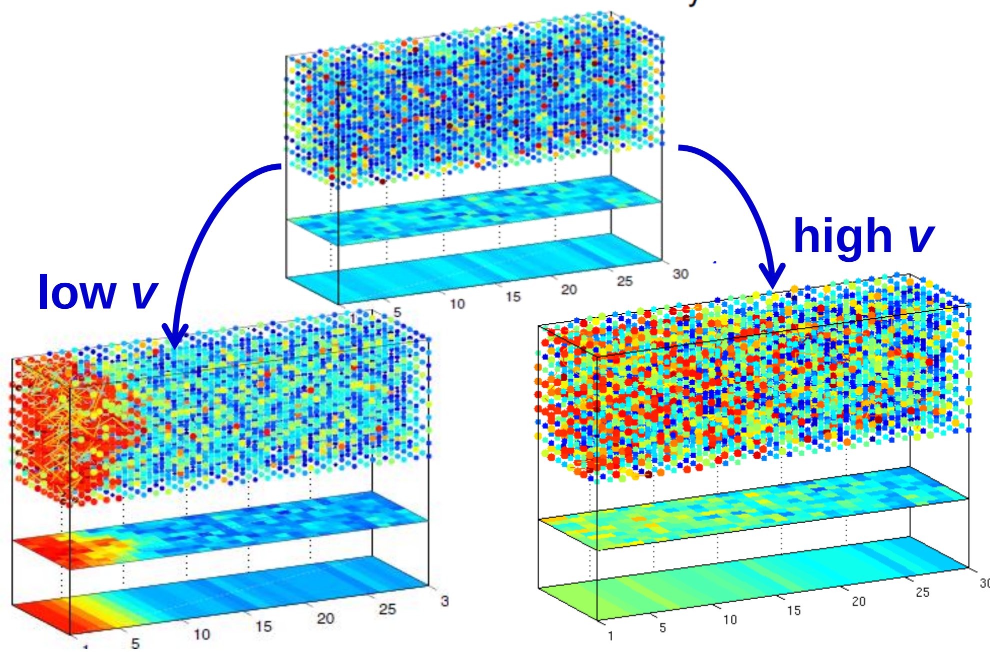


Porosity-Permeability Relation









Raoof, A., et al. "PoreFlow: A complex pore-network model for simulation of reactive transport in variably saturated porous media." Computers & Geosciences 61 (2013): 160-174.

Dissolution in Carbonates; Wormholing