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Computation of the Longitudinal Dispersion Coeffcient in an adsorbing porous medium using homogenization

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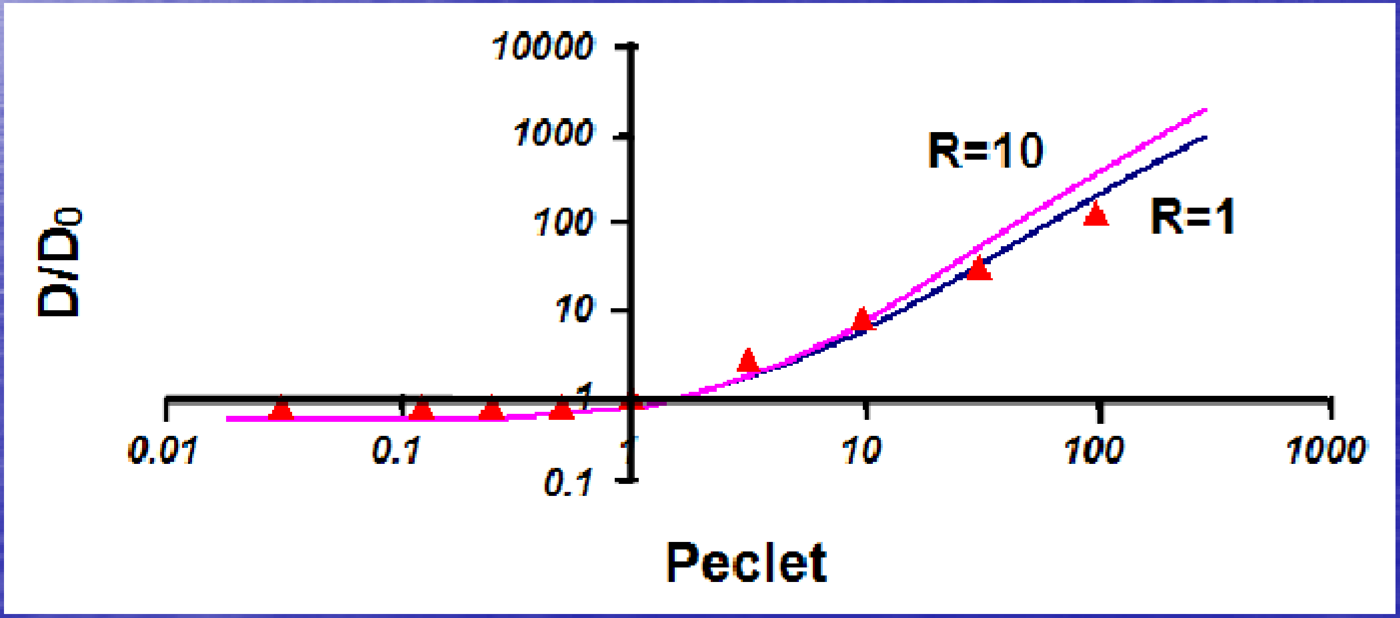
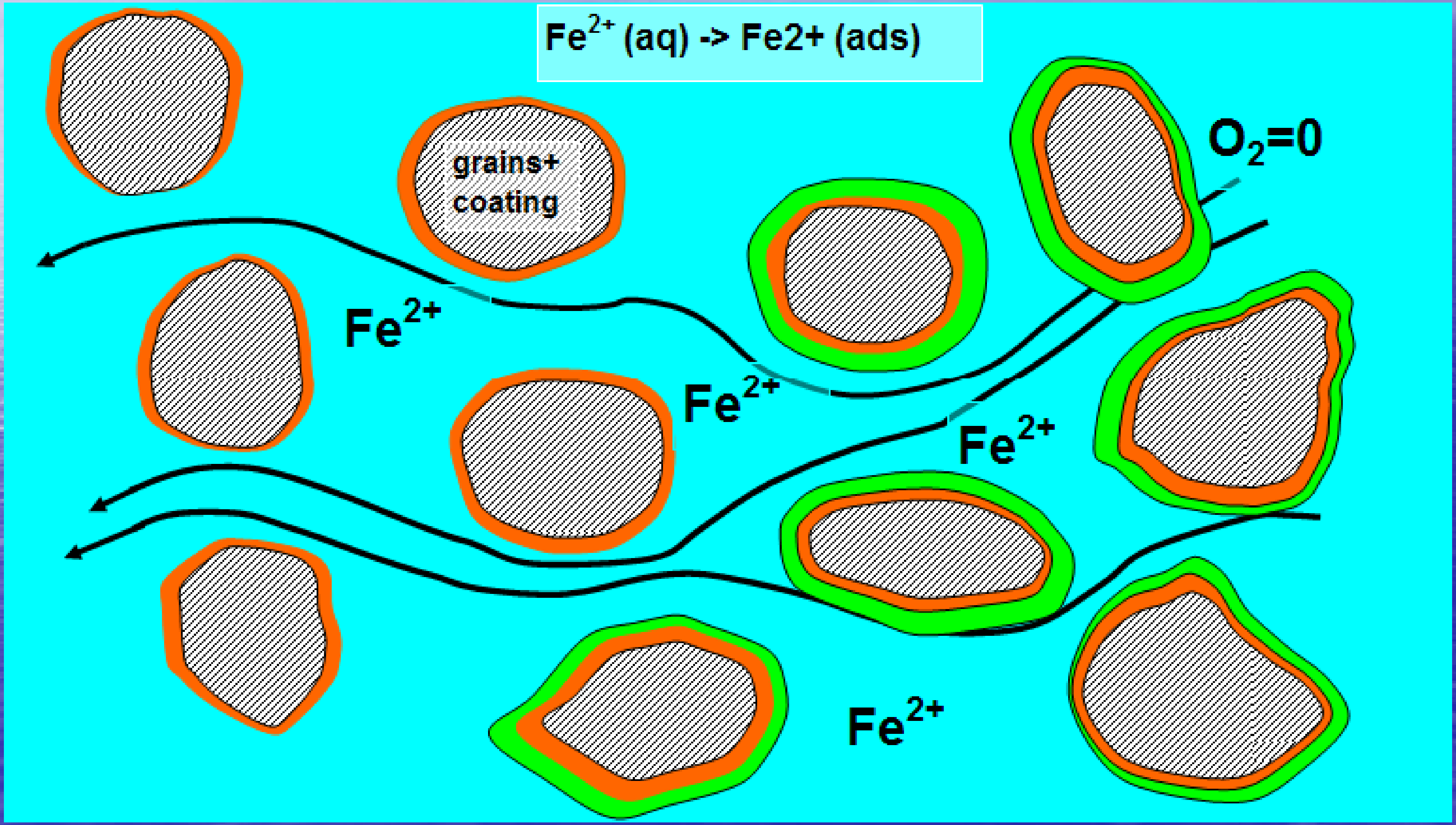


Use of Tube Wells For Safe Drinking Water

Risk of > 50 μg/l As

- Skin lesions evident on hands and feet of many villagers, problems with teeth
- After two decades of As poisoning increased risk (1:10)(report of WHO) of fatal cancer in the lungs, liver, bladder and kidneys
- One of 150 people in Holland die in traffic accidents; one of 60 in fatal accidents near and around the house

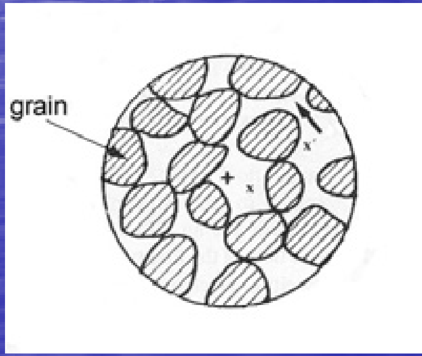
Simplified convection diffusion-reaction model during production; high perm downstream



Homogenization from pore to core

Microscale (l)

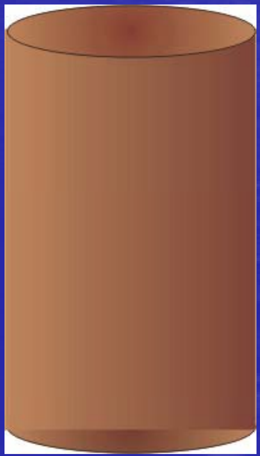
~ 10^{-4} m



Macroscale (L)

laboratory

~ 10^{-2} m



Model

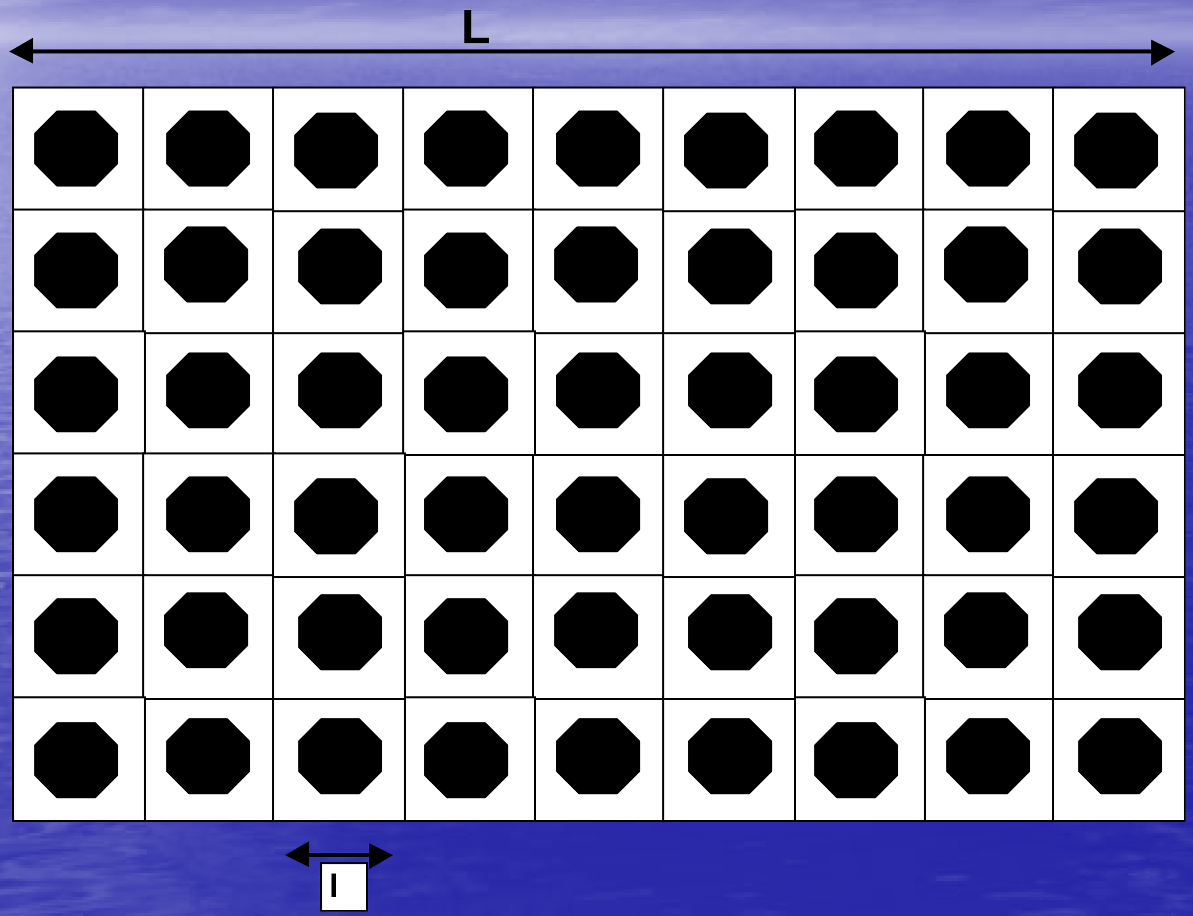
- Iron^{2+} ions behave like the transport of tracer like species, i.e., solutes with no influence on the water flow.
- The transport mechanisms are convection and diffusion.
- There is equilibrium between the adsorbed concentration on the grain and the fluid adjacent to it.
- The adsorption isotherm can be linear or follow non linear behavior (Langmuir, Freundlich etc.).

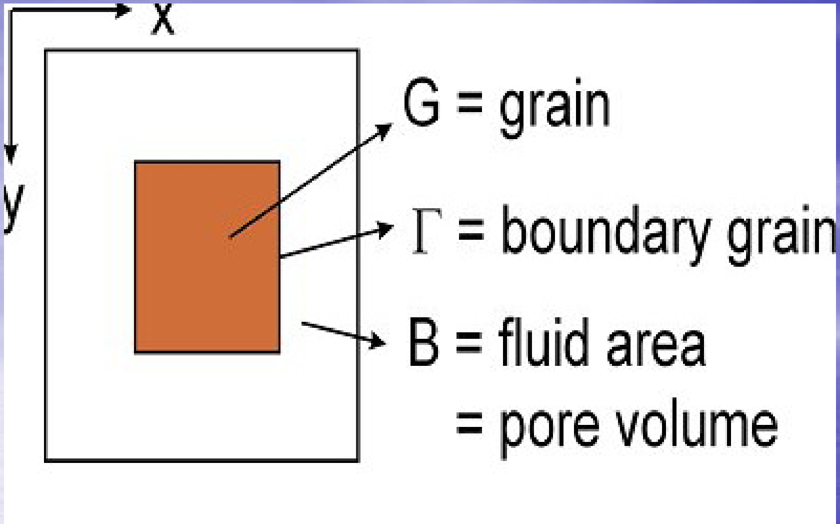
$$\frac{\partial c}{\partial t}\left(1+\frac{dc_s}{dc}\right)+\mathbf{div}\left(\mathbf{v}c\right)=\mathbf{div}\left(D\left(\mathbf{v}\right)\cdot\mathbf{grad}\,c\right)$$

Assumptions

- The fluid (water) is incompressible.
- Flow at the micro-scale follows Stokes law
  – **grad P = $\mu \Delta$ v, div v = 0,** solved for unit cell + periodic BC's outside the bracket of homogenization
- The fluid of interest is water containing dissolved Fe(II) ions flowing around the grains.
- At the grain boundary the dissolved Fe(II) precipitates according to the diffusive flux towrds the grain leading to an accumulation $(\partial c_s/\partial t)_\Gamma$
- Gravity effects can be disregarded.

Homogenization uses the PUC and and the scaling factor ε=l/L





Starting point are equations on the micro-scale

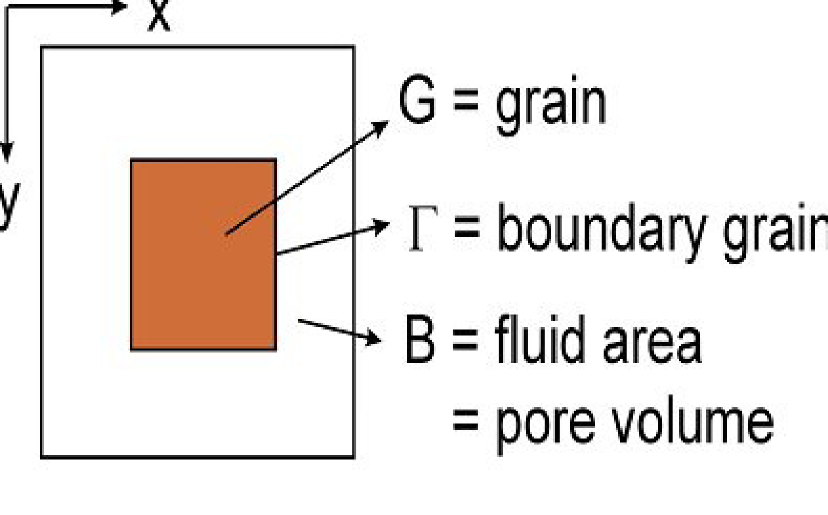
- Diffusion convection in fluid phase
- Rate of precipitation at boundary grain
- Definition adsorbed concentration based on flow domain

$$\frac{\partial c}{\partial t} = \nabla \bullet \left(D \nabla c - \mathbf{v} c \right)$$

$$\left(-D \, \mathbf{grad} \, c \right)_n = \delta \left(\frac{\partial c_a}{\partial t} \right)_\Gamma \quad \text{at } \Gamma$$

$$\mathbf{v} = 0 \quad \text{at } \Gamma,$$

$$c_s = \frac{\delta}{\varphi l^N} \oint c_a \, \mathrm{d}s.$$



$$c^{(1)} = \chi \cdot \mathbf{grad}_b c^{(0)}.$$

to solve for $c^{(1)}$

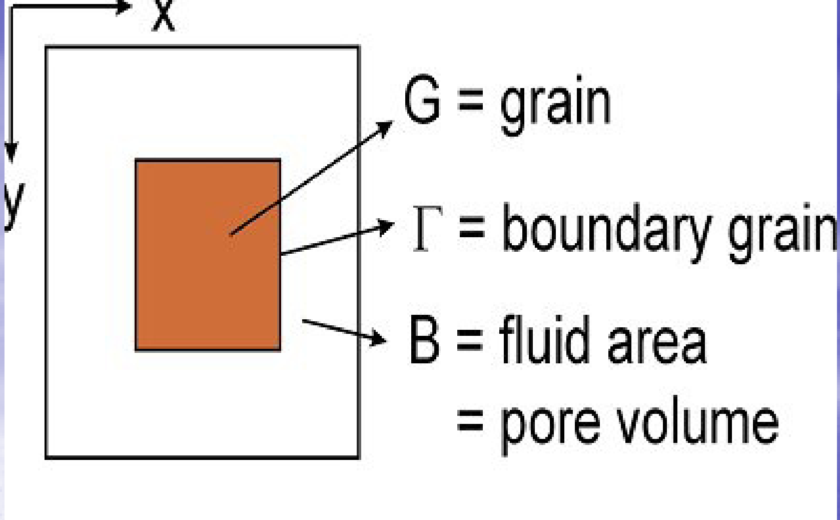
For the case that

$$\mathbf{grad}_b c^{(0)} = -\mathbf{e}_x$$

$$-\frac{\overline{\mathbf{v}_x}}{R} + \mathbf{div}_s \cdot \left(\mathbf{v} \left(\chi_1 + x_s \right) \right) = \frac{1}{Pe} \mathbf{div}_s \cdot \left(\mathbf{grad}_s \left(\chi_1 + x_s \right) \right),$$

We apply semi-periodic boundary conditions:

- periodic boundary conditions for the faces that are not perpendicular to the flow direction
- semi-periodic boundary conditions for the faces perpendicular to flow.
- Semi-periodic boundary conditions means that, e.g., the concentration at one face is equal to the corresponding concentration at the other face augmented with the global concentration difference.
- The same procedure is applied for the pressure, but here also the velocities are strictly periodic.

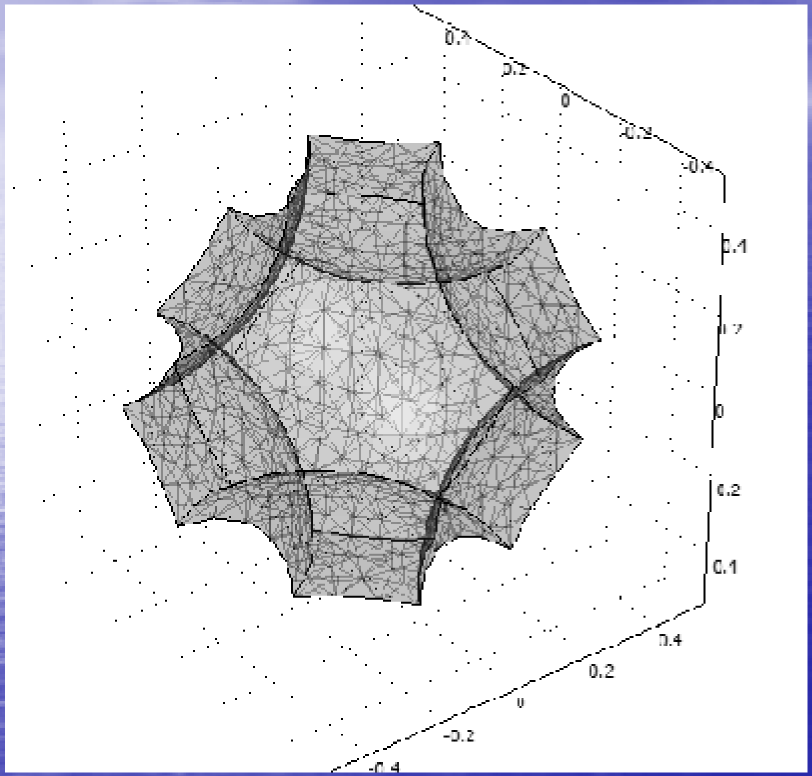


- The coefficients can be calculated from χ
- dispersion coefficient D_{xx}^{d}
- diffusion coefficient D_{xx}^{m}

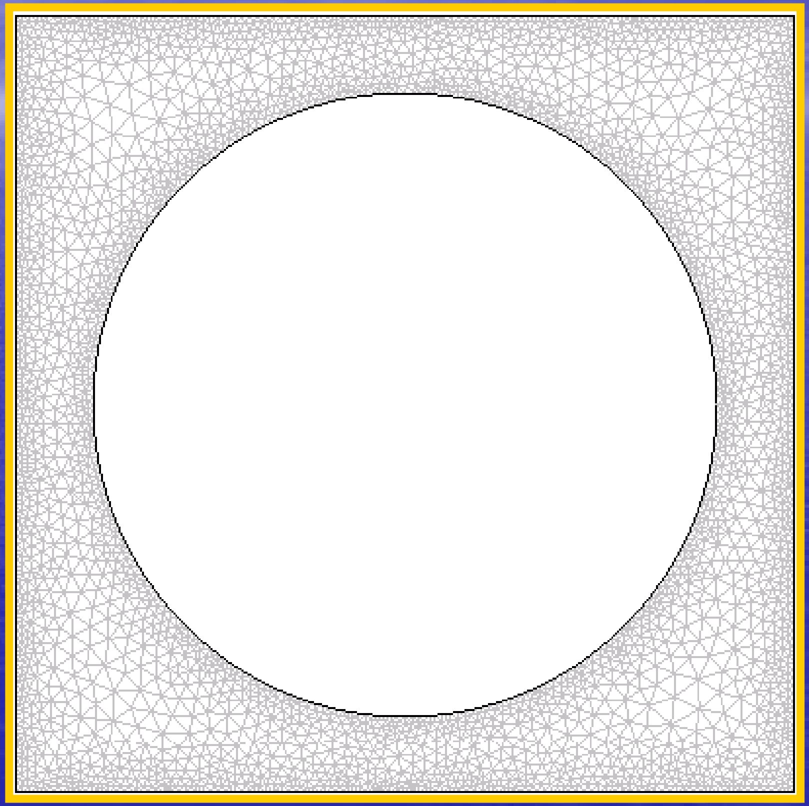
$$\mathbf{D}^{d} = -\frac{1}{|\Omega|}\frac{Pe}{\varphi}\int_{|\Omega_l|}\mathbf{V}\otimes\boldsymbol{\chi}\,dV$$

$$\mathbf{D}^{m} = \frac{1}{|\Omega|}\int_{|\Omega_l|}\left(\mathbf{I}+\nabla_s\otimes\boldsymbol{\chi}\right)dV,$$

Comsol Models

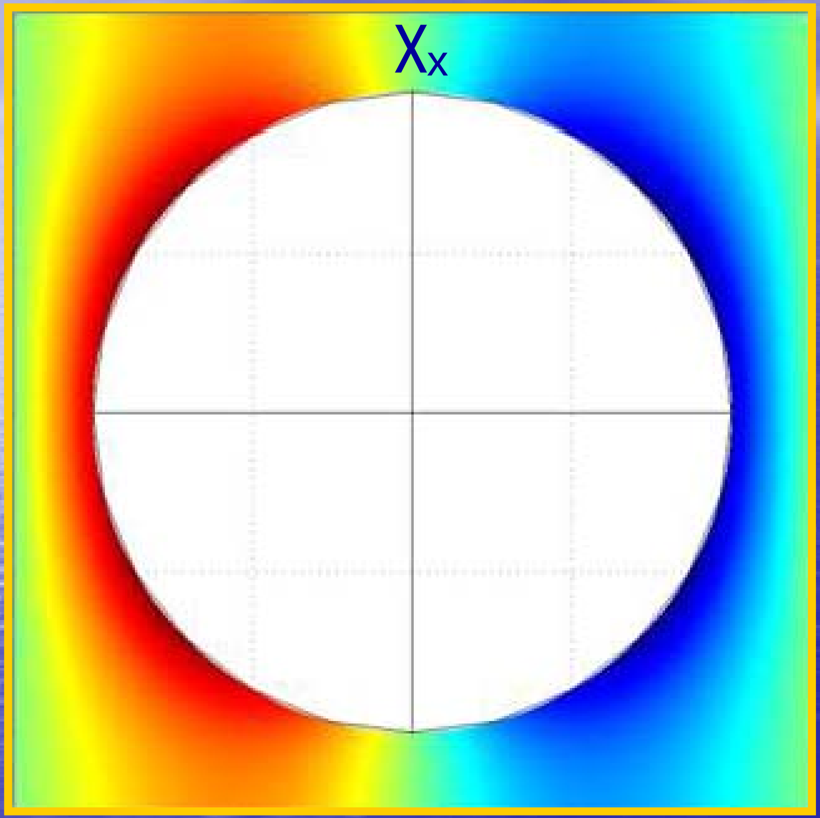


3-Dimensional

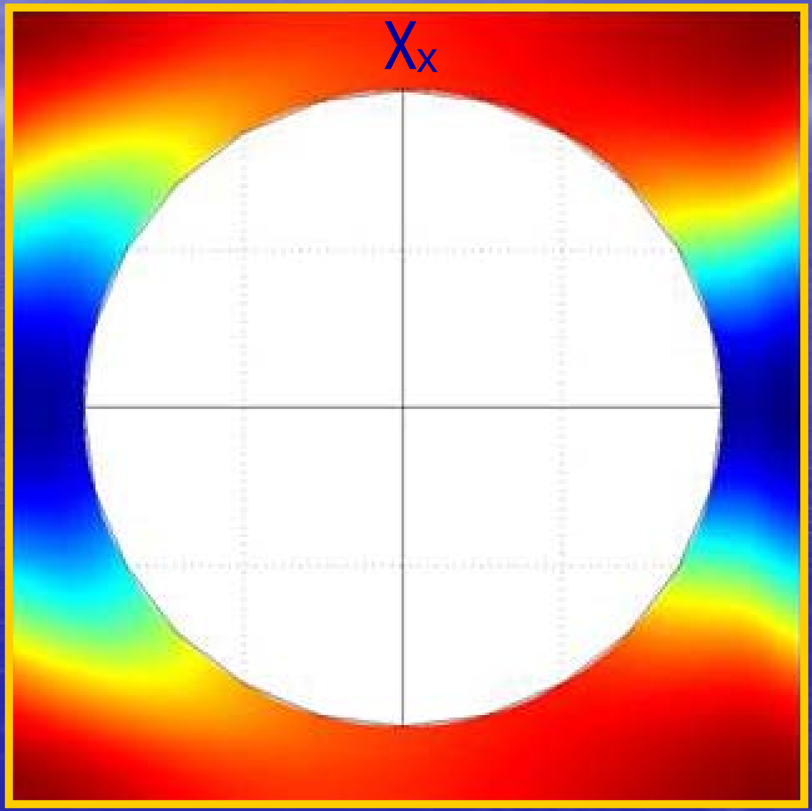


2-Dimensional

Concentration fluctuation profiles

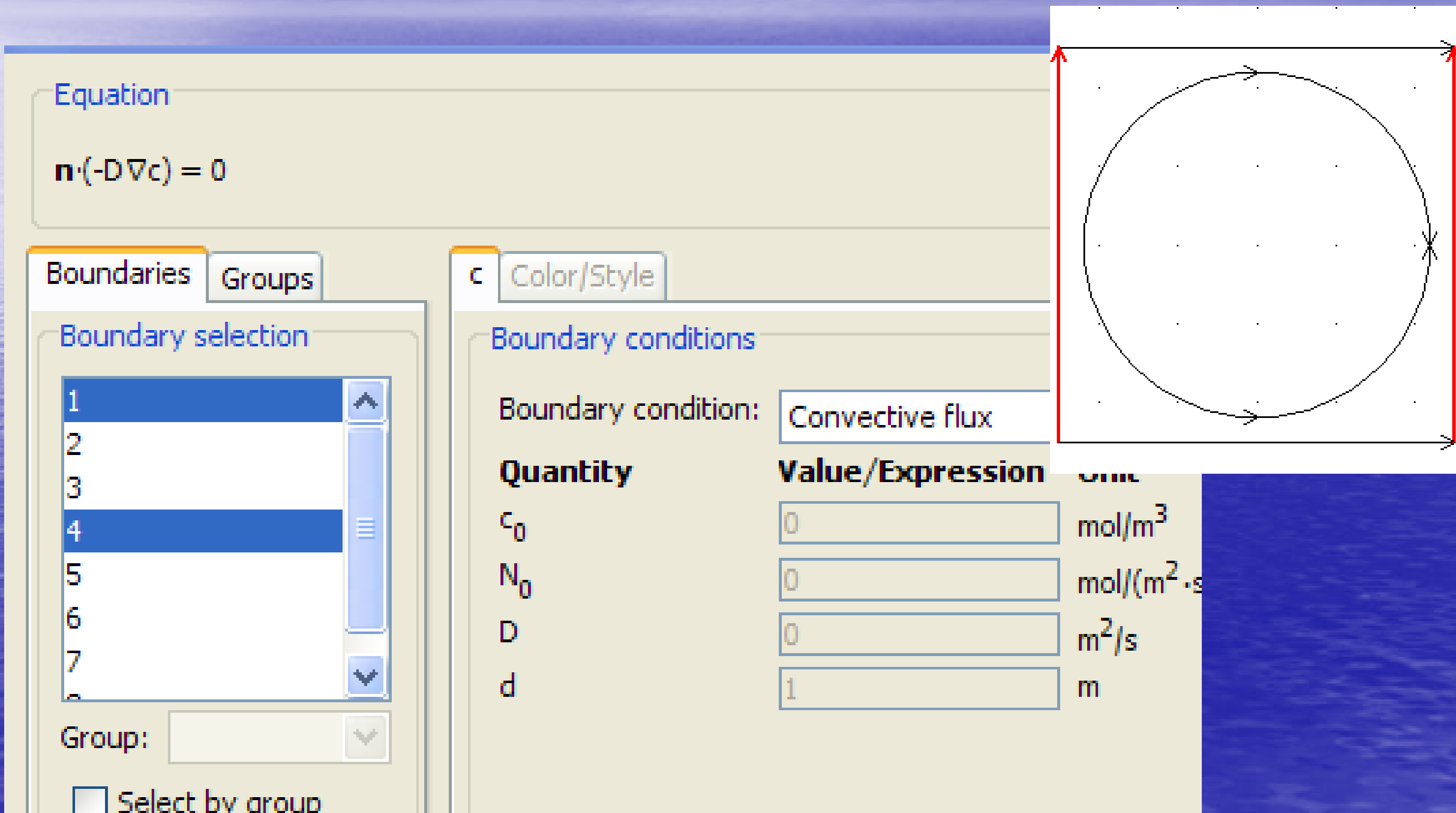


Diffusion dominated

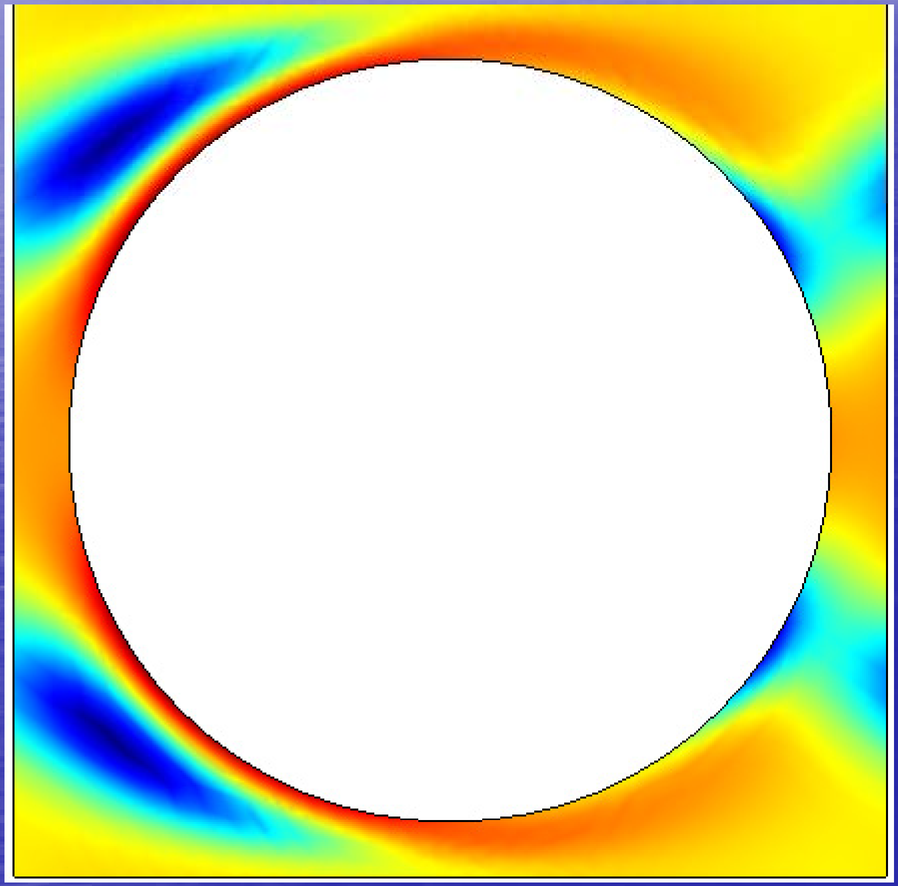


Dispersion dominated

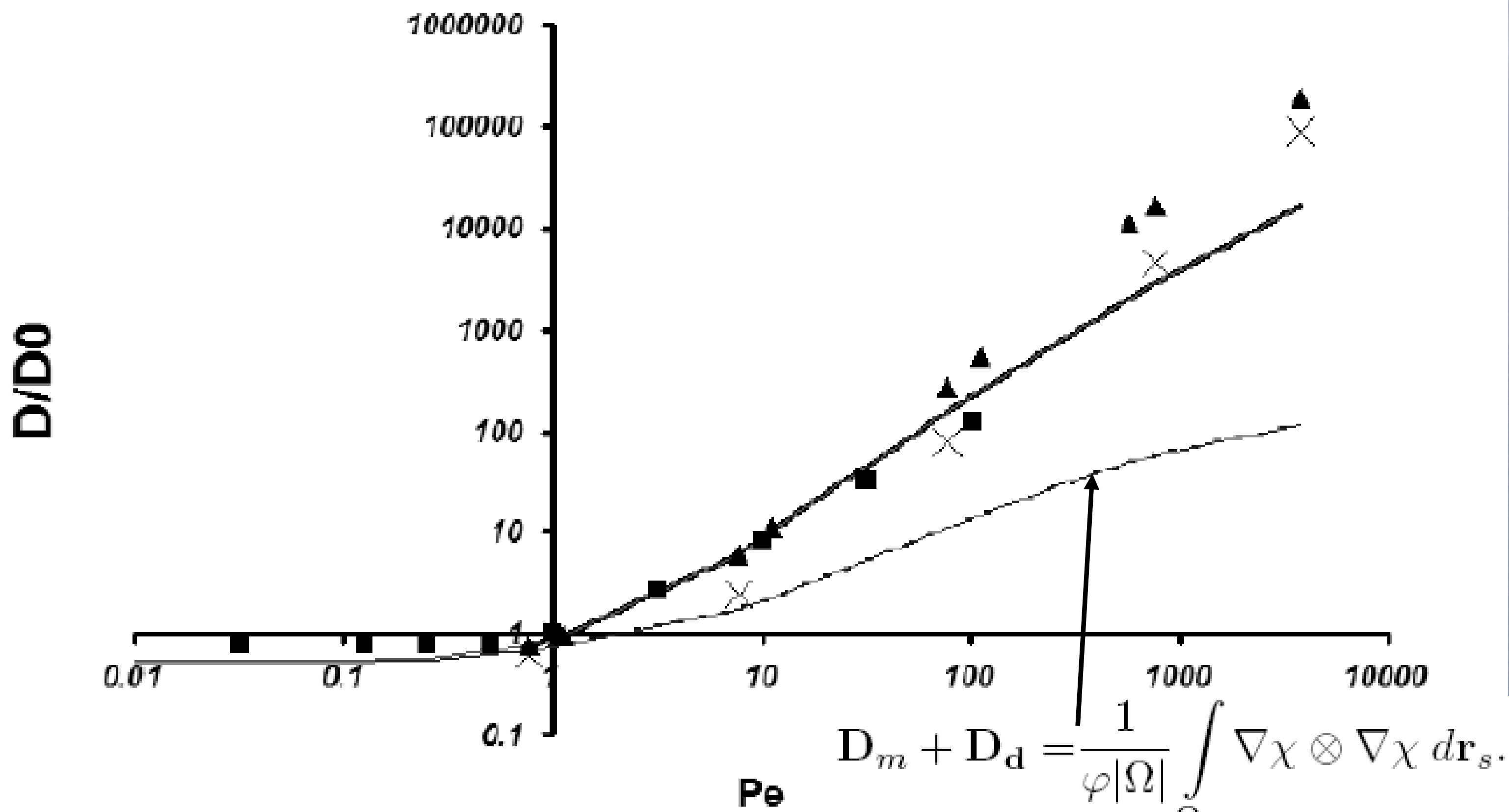
Convective flux for semi-periodic BC’s



Also ∂_x c must be continuous



Comparison 2-D



$$\mathbf{D}_m + \mathbf{D_d} = \frac{1}{\varphi|\Omega|} \int_{\Omega_f} \nabla\chi \otimes \nabla\chi \, d\mathbf{r}_s .$$

Figure 2: The squares are the experimental data [2], the

crosses are the data from [10] whereas the triangles are data from Edwards et al. [9]. The drawn curve is for a simple square arrays of cylinders with ' = 0:37:.

Comparison 3-D

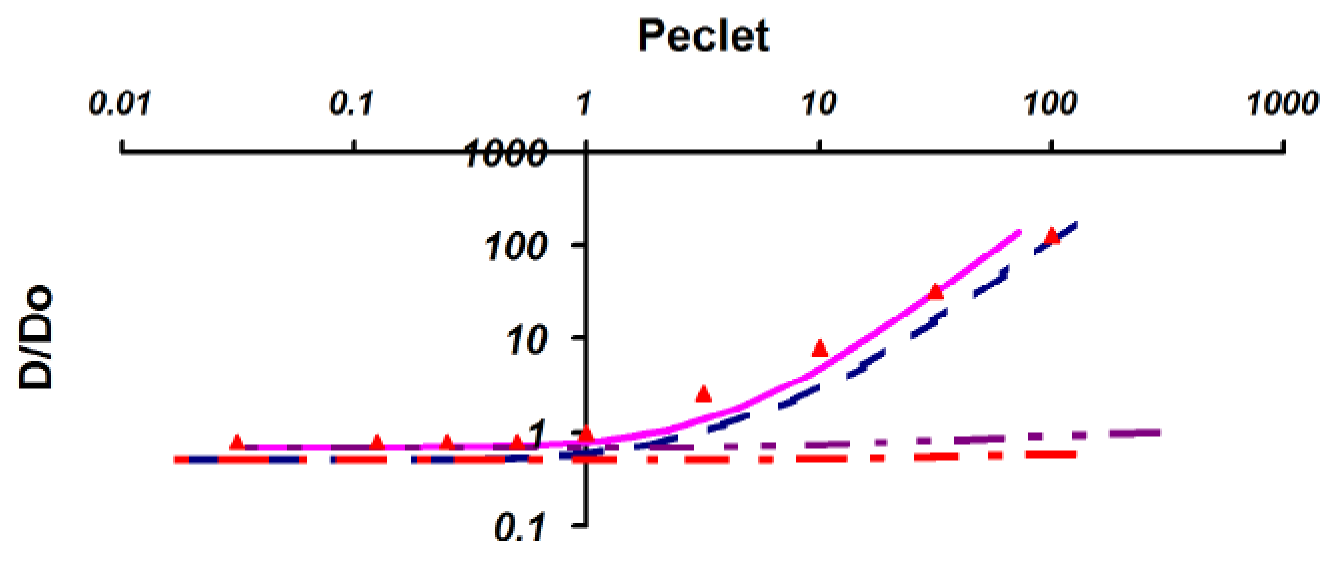


Figure 5: Longtudinal (upper curves) and transverse (lower curves) dispersion divided by molecular diffusion versus Peclet number. The Peclet number is based on the interstitial velocity $v = u/\varphi$. The characteristic dimension is the size of the unit cell. Dashed (dashed-dot-dot) line has unit cell **big spheres** (left) and the drawn (dashed-dot) line **small spheres** . The triangles denote experimental points [7]

Comparison 2-D

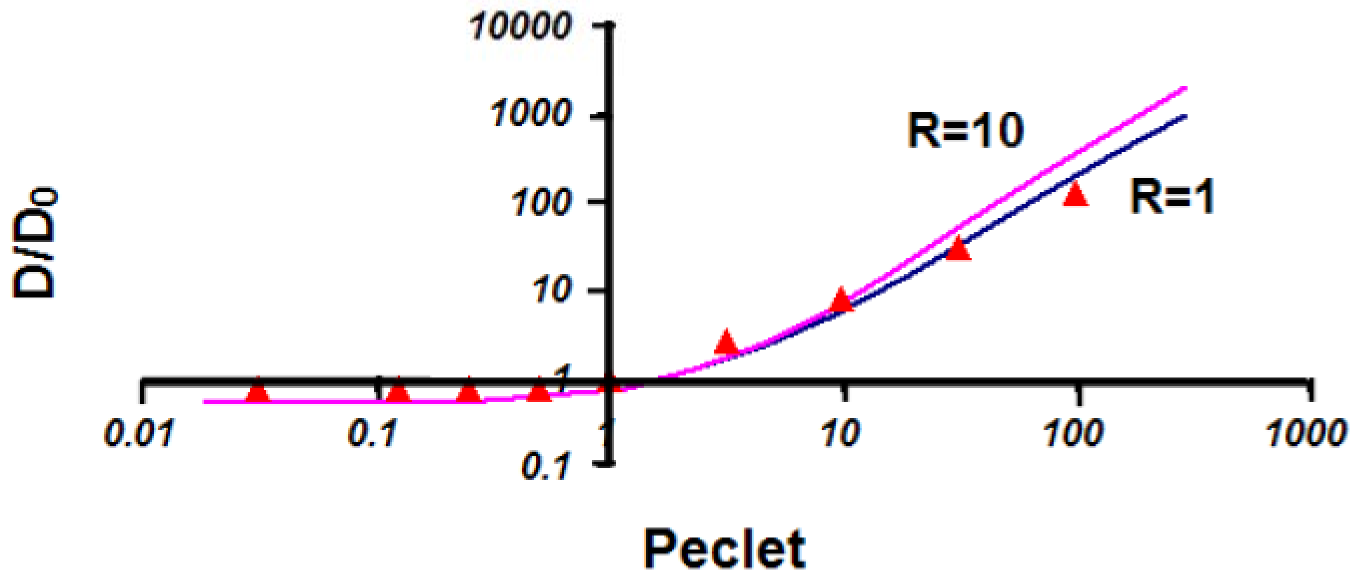


Figure 6: The effect of adsorption on the dispersion coefficient. With adsorption, i.e., the retardation factor $R = 10$, the longitudinal dispersion coefficient is higher.

Conclusions

- Homogenization is a useful method to obtain upscaled equations. The method leads to up-scaled equations for the laboratory scale that are less dependent on intuition than upscaled equations obtained with REV averaging.
- Explicit expressions for the dispersion tensor are obtained based on comparison of the convective diffusion equation used for contaminant transport.

Conclusions

- Commercial Finite Element Method software, e.g., COMSOL can be used to solve the unconventional equations, the solution of which is necessary to obtain quantitative results.
- The computed longitudinal dispersion coefficients as a function of the Peclet number show good agreement with experimental literature data.

Thank you for attention

Questions?

COMSOL

- The 3-D simulation with the corner spheres of radii a=0.510 (0.583) was carried out with 5832 (3128) mesh points, with 27420 (14495).
- Tetrahedal Lagrangian quadratic elements. COMSOL used shlag(2,′c′) shape functions with integration order 4 and constraint order 2.
- A simulation with 1731 (955) mesh points and 7746 (4068) elements gave results that deviated at most 0.133% (0.288%).

Remediation methods: Problem driven versus Technology driven

- Drill tube wells to deeper aquifers (one billion $)
- Better use of region's abundant rainfall
- Use filters inside the well
- Ex-situ treatment e.g. leave water settling for a while or use chemicals
- In-situ treatment

- Are deeper layers truly devoid of Arsenic?
- Only during monsoon
- Expensive and complex maintenance
- Unreliable and logistically difficult
- Clogging of wells?

Core-scale Transport equations (Boudour et al. TIPM 25:121-146 (1996))

- Darcy's equation for incompressible fluids

Modified Diffusion convection equation in porous medium

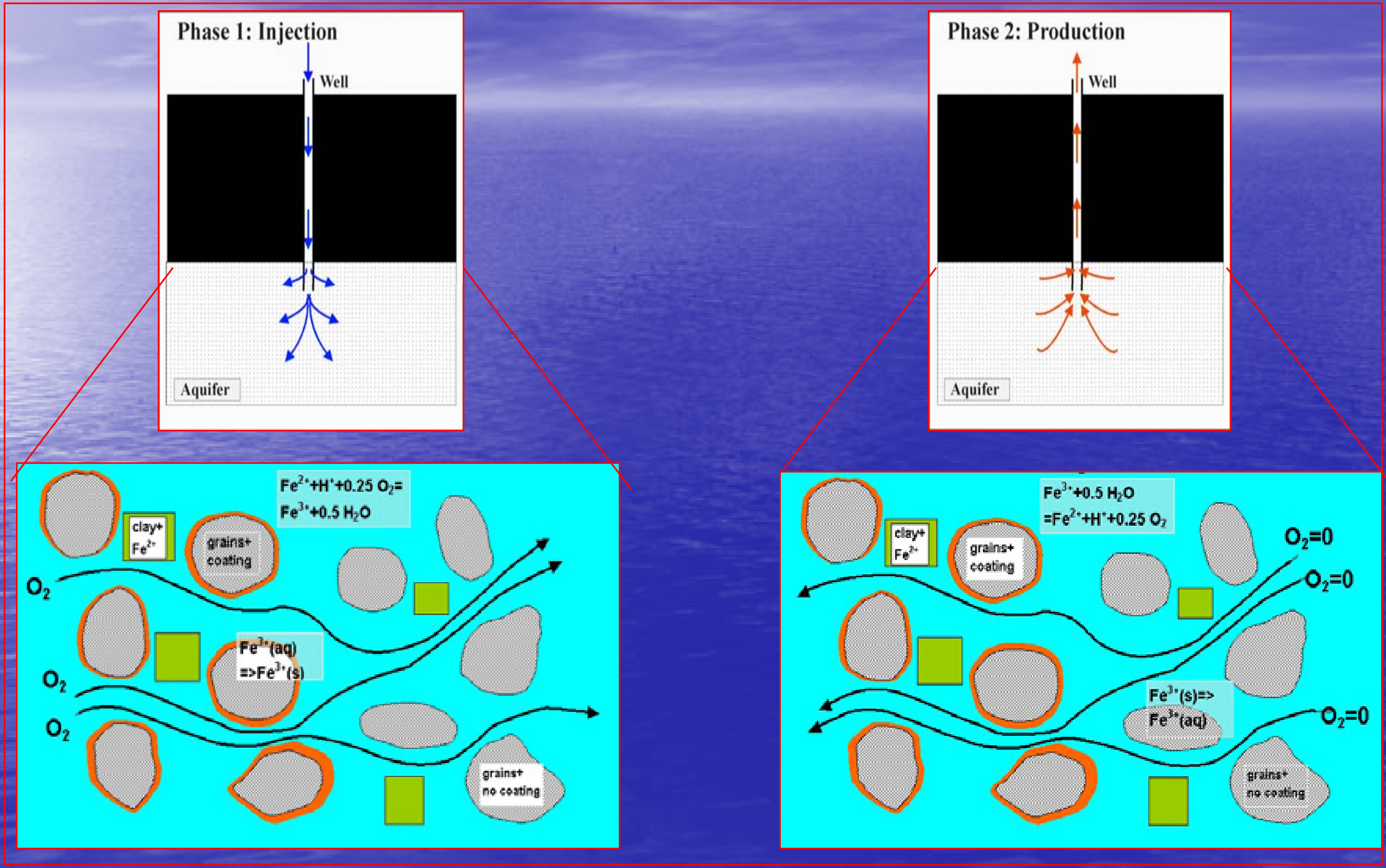
$$\mathbf{u} = -\frac{k}{\mu}(\nabla p - \rho \mathbf{g}) = \frac{Q}{A}$$

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

$$\varphi \frac{\partial c}{\partial t} = \nabla \bullet \left(\varphi \underline{\underline{D}}_{eff} \bullet \nabla c - \mathbf{u} c\right) + \varphi \bar{R}$$

$$+ \, \mathbf{div}\left(k_s(c - c^*)\mathbf{D}_k\right) + a_s k_s (c - c^*)$$

Principle



Phase 1: Injection
Well
Aquifer
Phase 2: Production
Well
Aquifer
$Fe^{2+}+H^{+}+0.25\ O_2=$
$Fe^{3+}+0.5\ H_2O$
clay+
Fe^{2+}
grains+
coating
O_2
O_2
O_2
$Fe^{3+}(aq)$
$=>Fe^{3+}(s)$
grains+
no coating
$Fe^{3+}+0.5\ H_2O$
$=Fe^{2+}+H^{+}+0.25\ O_2$
clay+
Fe^{2+}
grains+
coating
$O_2=0$
$O_2=0$
$Fe^{3+}(s)=>$
$Fe^{3+}(aq)$
$O_2=0$
grains+
no coating

Arsenicosis-The Patient

Current projects

CO_2 sequestration
EOR
In-situ remediation

Central role for upscaling and simulation

Micro-Scale Model

HOMOGENIZATION

Core-Scale Model

Core-scale model

HOM. / SIM

Macro-scale model

Macro-scale model

SIMULATION

Oil Field Model

Capil pressure
Contact angles
adsorption

Core flooding

Natural convection

Iron(III) complexes

$Fe^{3+} + H_20$	=	$FeOH^{2+} + H^+$	□	$\log {}^*K_1$	=	-3.05
$Fe^{3+} + 2H_20$	=	$Fe(OH)_2^+ + 2H^+$	□	$\log {}^*\beta_2$	=	-6.31
$2Fe^{3+} + 2H_20$	=	$Fe(OH)_2^{4+} + 2H^+$	□	$\log {}^*\beta_{22}$	=	-2.91
$Fe^{3+} + 3H_20$	=	$Fe(OH)_3(aq) + 3H^+$	□	$\log {}^*\beta_3$	=	-13.8
$Fe^{3+} + 4H_20$	=	$Fe(OH)_4^- + 4H^+$	□	$\log \beta_4$	=	-22.7
$3Fe^{3+} + 4H_20$	=	$Fe_3(OH)_4^{5+} + 4H^+$	□	$\log {}^*\beta_{43}$	=	-5.77
$Fe(OH)_3(s) + 3H^+$	=	$Fe^{3+} + 3H_20$	□	$\log {}^*K_{so}$	=	3.96

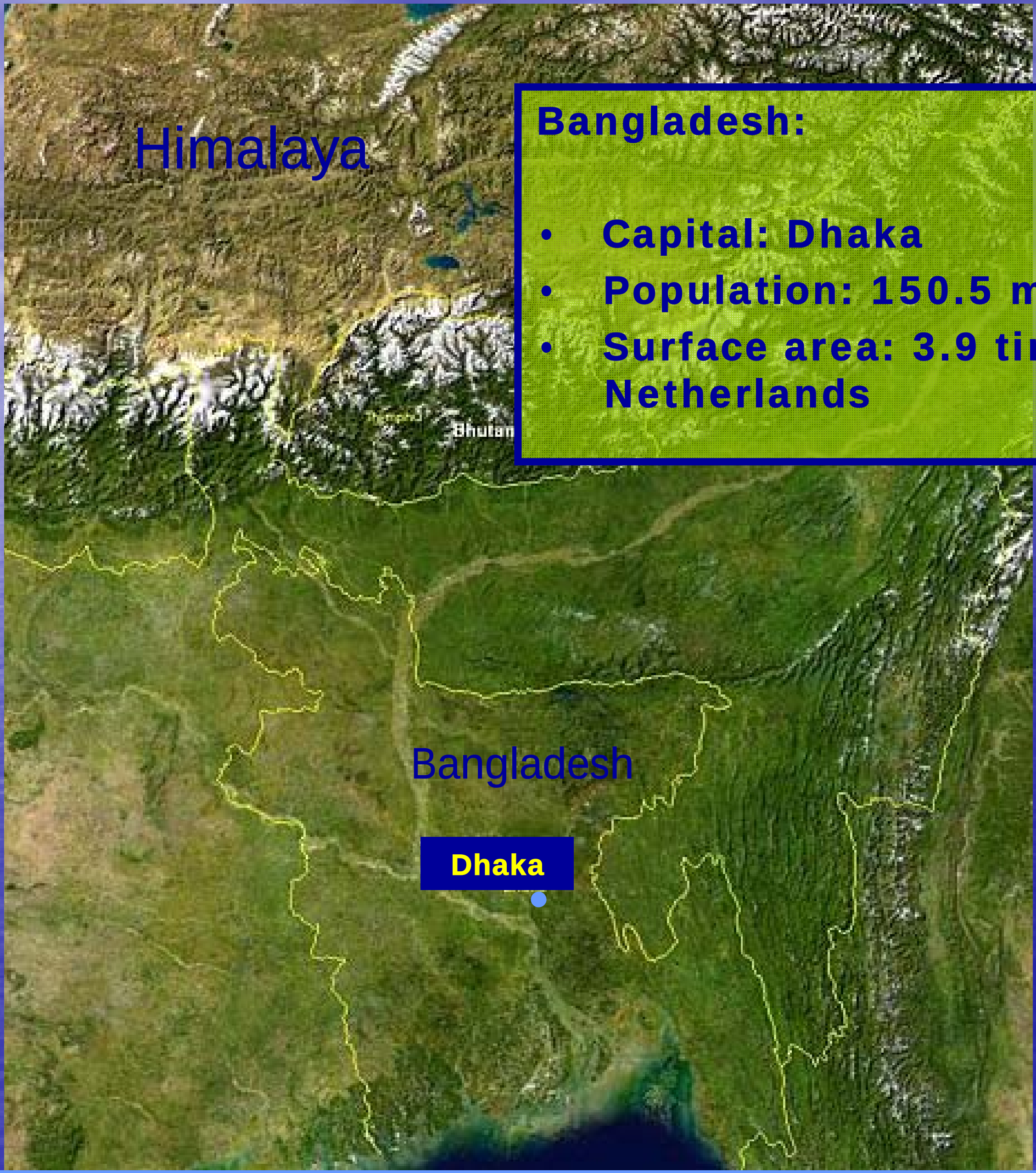
The total Fe^{3+} concentration, which is present in the complexes and free ions can be calculated with the following formula (Stumm and Morgan, 1996)

$$Fe_T = [Fe^{3+}]\left(1 + \frac{{}^*K_1}{[H^+]} + \frac{{}^*\beta_2}{[H^+]^2} + \frac{{}^*\beta_3}{[H^+]^3} + \frac{{}^*\beta_4}{[H^+]^4} + \frac{2[Fe^{3+}]{}^*\beta_{22}}{[H^+]^2} + \frac{3[Fe^{3+}]{}^*\beta_{43}}{[H^+]^3}\right)$$

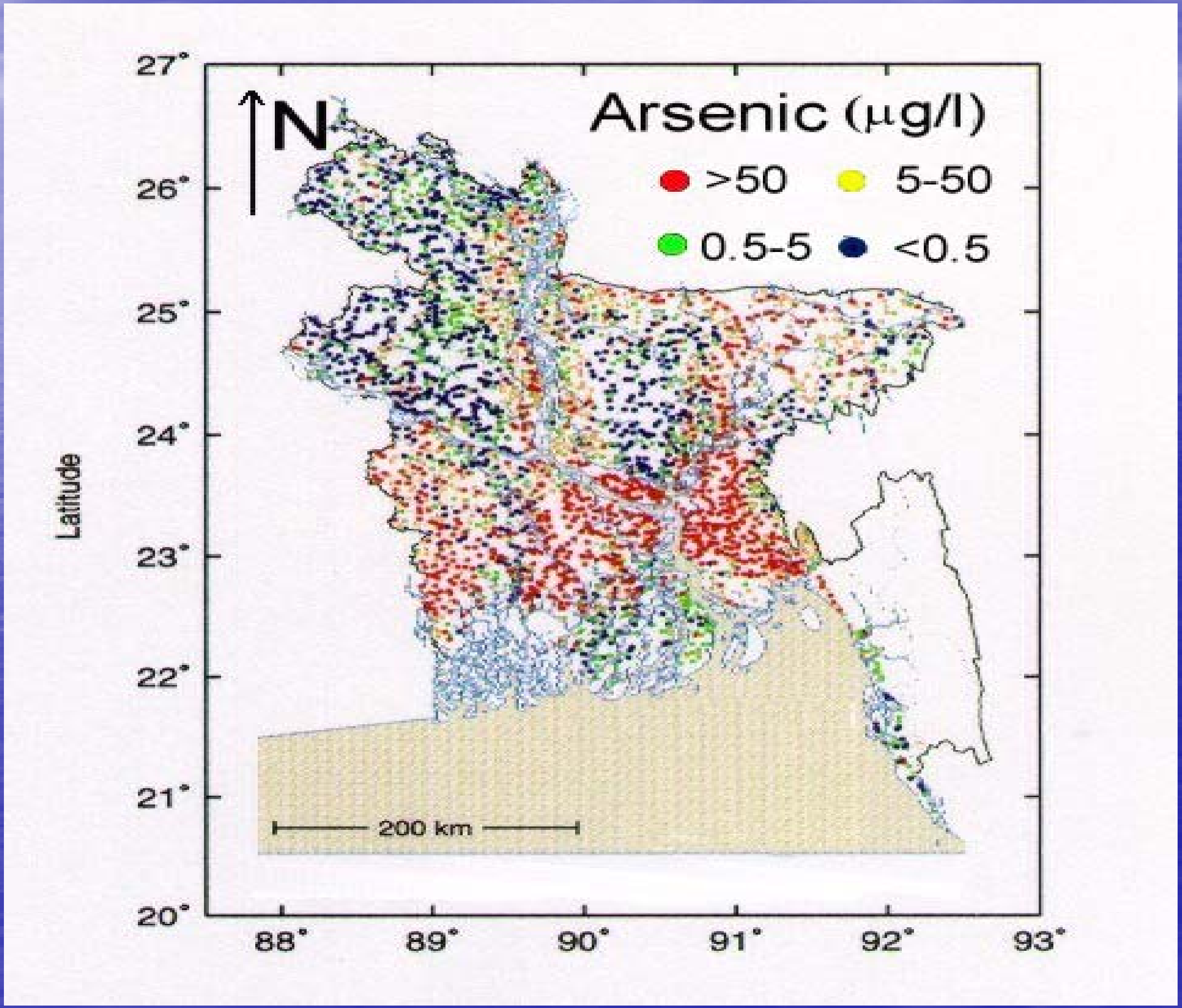
with Fe_T is the total $[Fe^{3+}]$ as free ion and as aquo-complex (Stumm and Morgan, 1996).

Bangladesh:

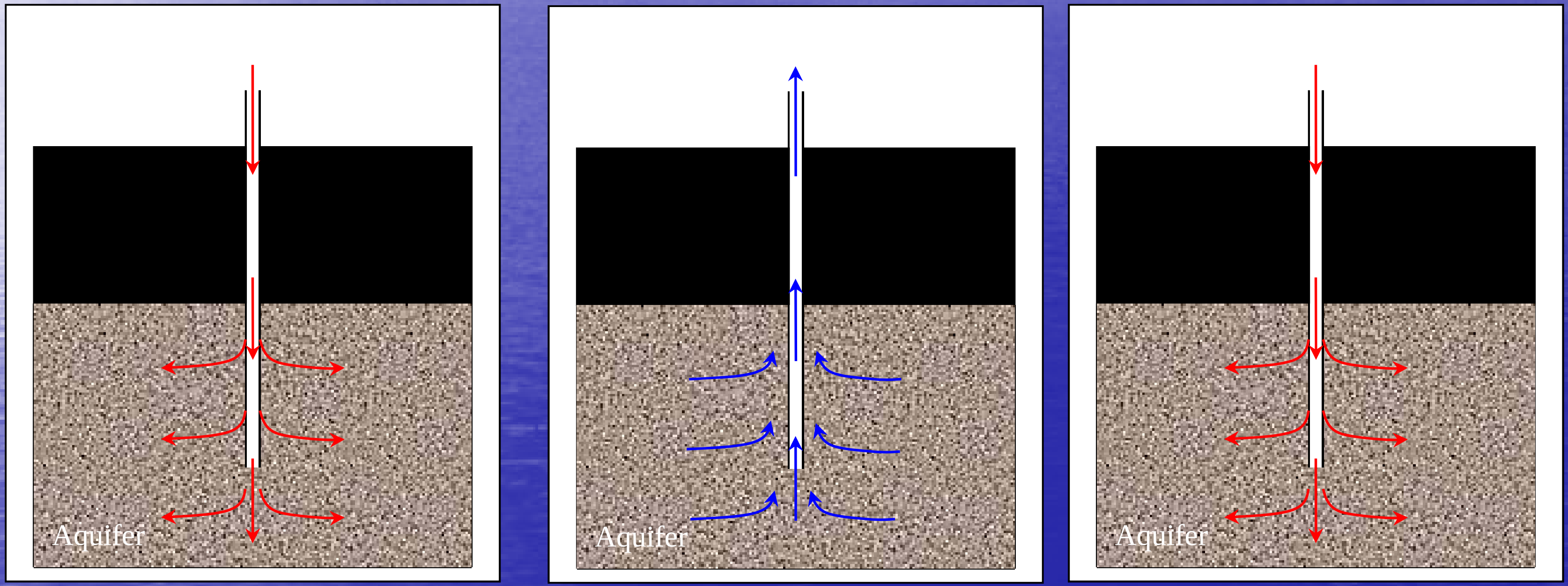
- **Capital: Dhaka**
- **Population: 150.5 million (2007)**
- **Surface area: 3.9 times the Netherlands**



MAC in Western world 10 $\mu g/l$



Mitigation method: Injection of aerated water to cover grains with Fe(III) filter by oxidizing abundant Fe(II)



Fe III scavenges the As and improves drinking water produced (middle panel)

As time proceeds Fe(II) precipitates on grains: $Fe(II)_{aq}$->$Fe(II)_{ads}$