Part of an Excellence Ph.D. Course

Politecnico di Torino – June 27th, 2012

DITAG

A talk on:

Transport of colloids and nanoparticles in saturated porous media for environmental remediation

Rajandrea SETHI, Tiziana TOSCO, Alberto TIRAFERRI and GROUNDWATER ENGINEERING GROUP

DIATI – Politecnico di Torino

Ingegneria degli Acquiferi
Groundwater Engineering

DITAG
POLITECNICO DI TORINO

Program

- Transport in porous media of:

  1. Ideal colloids: latex particles
  2. Non-ideal colloids: iron particles for the remediation of contaminated aquifer systems

What is a colloid?

- A **colloid** is a chemical mixture (not a solution) in which one phase (**dispersed phase**) is evenly dispersed into another phase (**dispersion medium**).
- The colloids has and homogeneous aspect.
- A colloidal system may be solid, liquid, or gaseous.

What is a colloid?

Medium / Phases		**Dispersed Phase**		
		Gas	Liquid	Solid
Dispersion Medium	Gas	**None** (All gases are mutually miscible)	**Liquid Aerosol** Examples: fog, mist, hair sprays	**Solid Aerosol** Examples: smoke, cloud, air particulates
	Liquid	**Foam** Example: whipped cream	**Emulsion** Examples: milk, mayonnaise, hand cream	**Sol** Examples: pigmented ink, blood
	Solid	**Solid Foam** Examples: aerogel, styrofoam, pumice	**Gel** Examples: cheese silicagel, opal	**Solid Sol** Example: glass

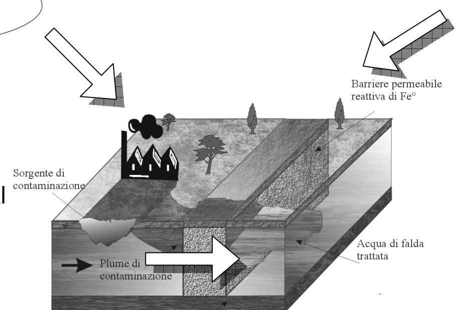
Colloids in aquifer systems (porous media)

DITAG
POLITECNICO DI TORINO

Contaminants

Anthropogenic or natural nano- and micro-particles:

- Chemical
- Farmaceutical
- Fly ashes
- Bacteria



Remediation technologies

Nanoscale zerovalent iron

Colloid facilitated transport

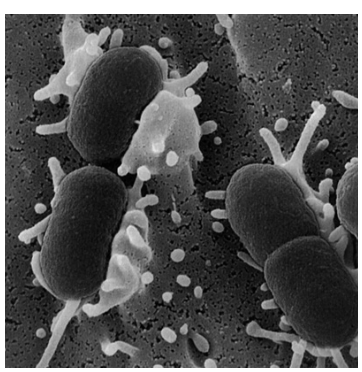
Natural colloids
+ sorbed contaminats

(adapted from Freyria, 2007)

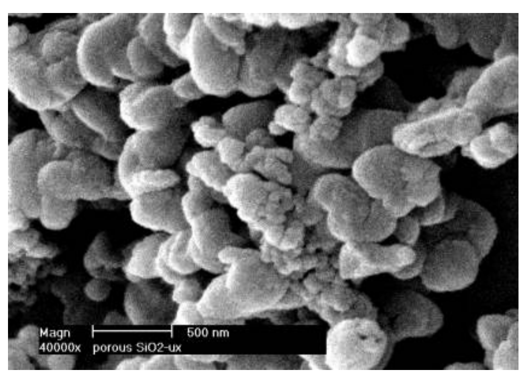
Natural colloids in aquifer systems

DITAG
POLITECNICO DI TORINO

Bacteria



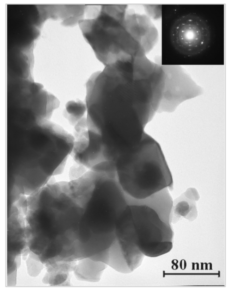
Clay particles



Engineered colloids

DITAG POLITECNICO DI TORINO

Nanoscale iron

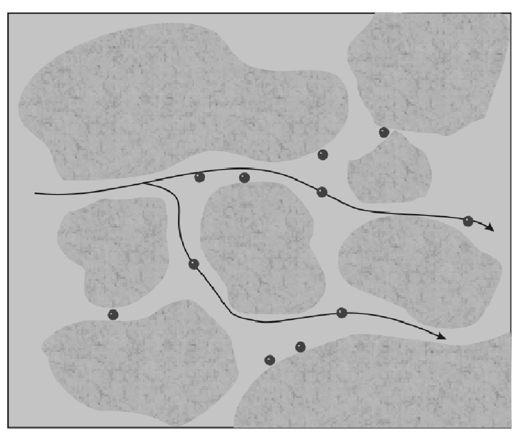


15 – 100 nm

Transport of colloids in porous media

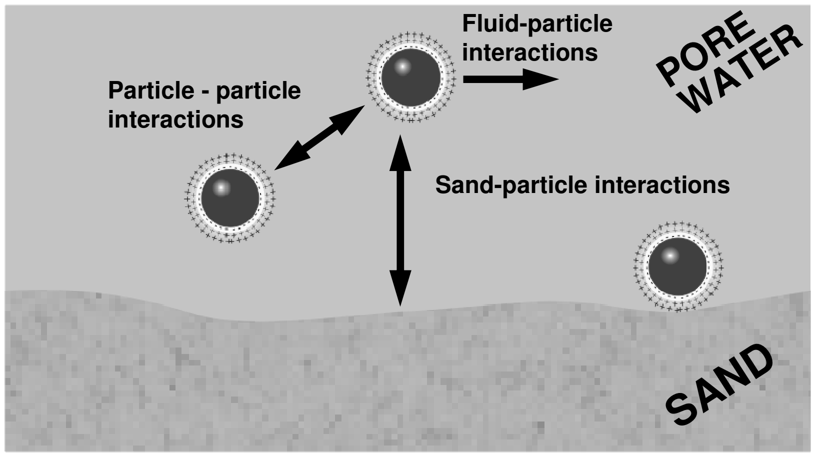
DITAG POLITECNICO DI TORINO

- Mechanisms:
  - Advection
  - Hydrodynamic dispersion
  - Interaction with solid phase
  - Particle-particle interaction



DITAG
POLITECNICO DI TORINO

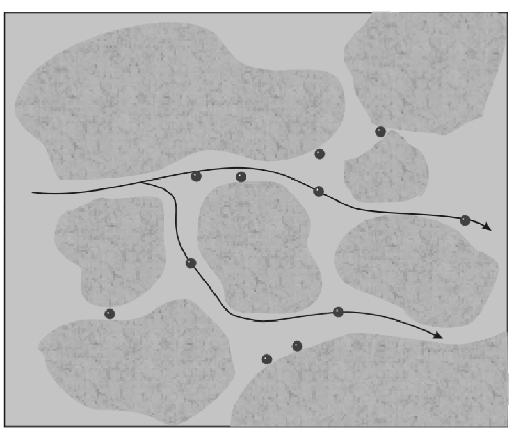
Colloids in porous media: interaction forces

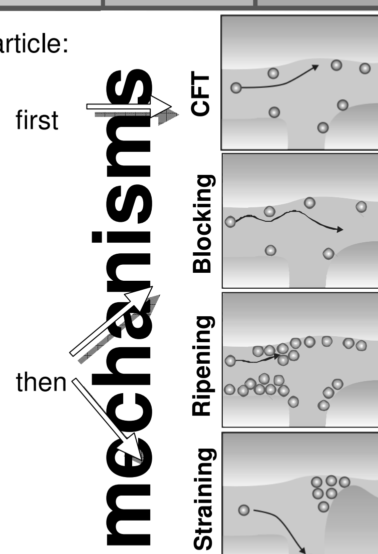


DITAG
POLITECNICO DI TORINO

Transport of colloids in porous media

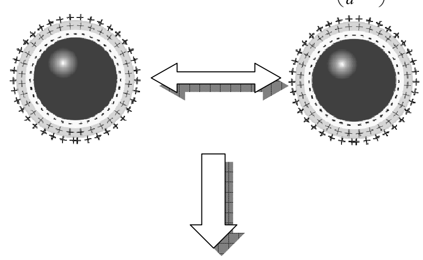
Interaction with porous media and particle-particle:





Particle-particle interaction

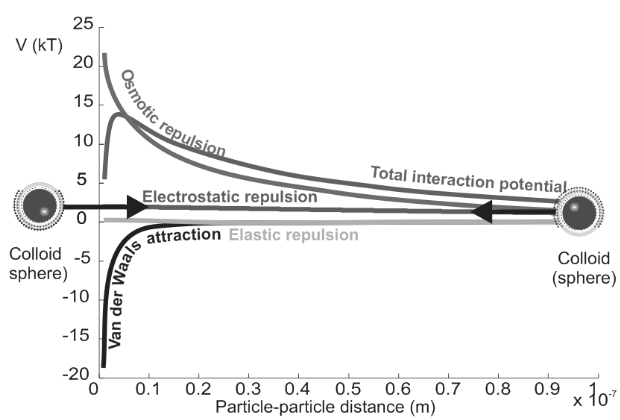
- Colloidal interactions have different origins:
  - Van der Vaals $V_{VdW} = -\frac{Aa}{12s(1+14s/\lambda)}$
  - Electrostatic $V_{ES} = 32\pi\varepsilon_r\varepsilon_0 a\zeta^2\gamma^2 e^{-\kappa\cdot s}$
  - Magnetic $V_M = -\frac{8\pi\mu_0(\sigma_s\rho)^2 a^3}{9\left(\frac{s}{a}+2\right)^3}$



DLVO & extended DLVO theory

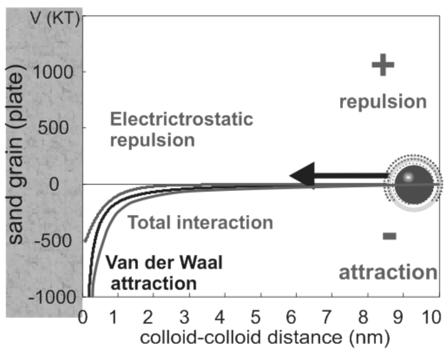
Particle – Particle interactions

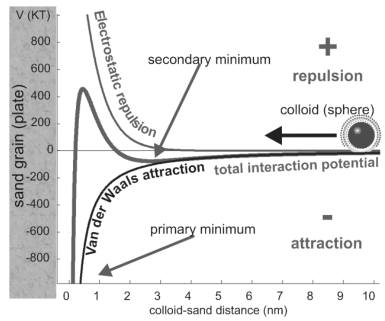
Particle-particle interaction:



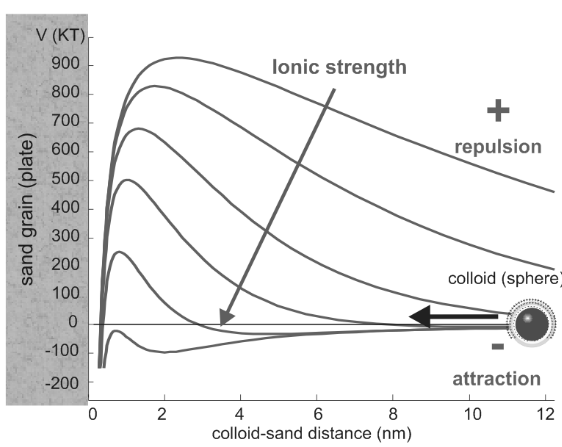
Sand – particles interaction

- Favorable deposition (different charge)
- Unfavorable deposition (same charge)



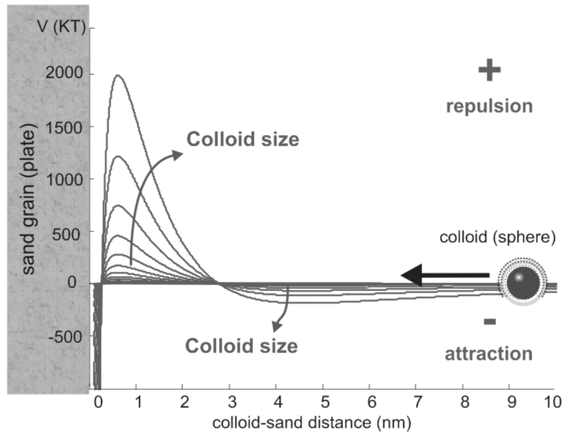


Unfavorable deposition Role of ionic strength



The presence of ions screens the surface charge of the colloids thus reducing electrostatic repulsion

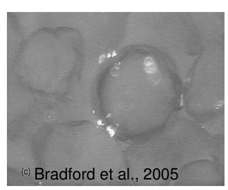
Role of particle size

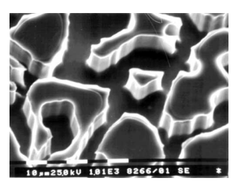


Colloids in porous media: different approaches

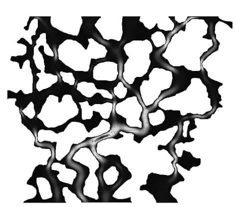
- **Microscale**

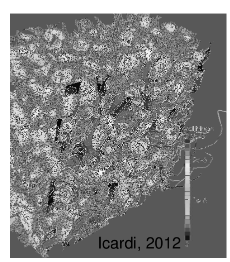
Laboratory tests



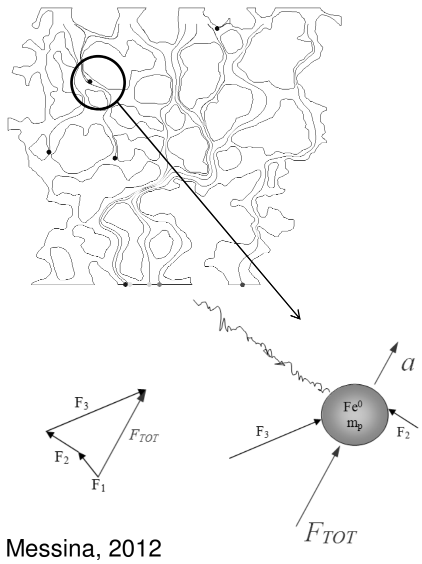


Mathematical models





Forces acting on a particle

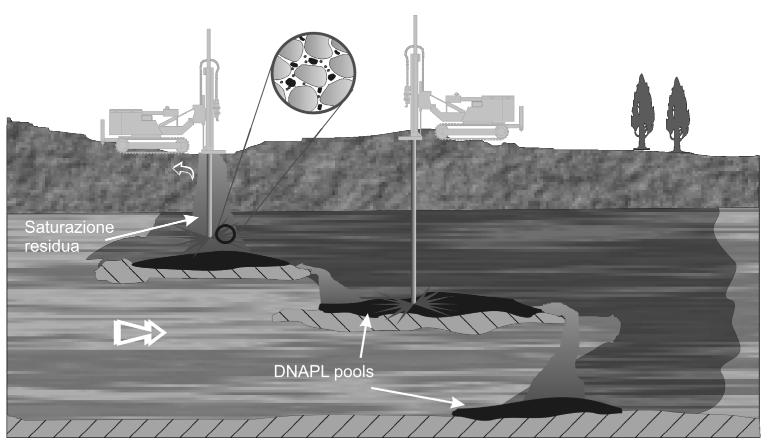


$$\bar{F} = m_p \bar{a} = \sum_i F_i = F_D + F_G + F_B + F_{EDL} + F_{VdW}$$

Drag force	$\vec{F}_D = \frac{4}{3}\pi a_p^3 \rho_p F(\vec{u} - \vec{v})$
Gravity force	$\vec{F}_G = \frac{4}{3}\pi a_p^3 (\rho_p - \rho_f)\vec{g}$
Brownian force	$F_B = R\sqrt{\frac{2\xi kT}{\Delta t}}$
Electric double layer	$\vec{F}_{EDL} = \varepsilon_0 \varepsilon_r a_p \frac{(\xi_p^2 + \xi_c^2)\kappa e^{-\kappa h}}{2(1 - e^{-2\kappa h})}\left[2\frac{\xi_p \xi_c}{(\xi_p^2 + \xi_c^2)} - e^{-\kappa h}\right]$
Van der Waals force	$\vec{F}_{VdW} = -\frac{H a_p}{6h^2}\frac{\lambda(\lambda + 28h)}{(\lambda + 14h)^2}$

Messina, 2012

Macroscale



Macroscopic approach

$$S(s)\frac{\partial h}{\partial t}+\frac{\partial q_i}{\partial x_i}=Q_\rho+Q_{EB}(c,s)$$ Flow equation

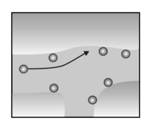
$$\varepsilon^m v_i^m=q_i^m=-\frac{\rho_0 g K_{ij}(s)}{\mu_0}\frac{\mu_0}{\mu}\left(\frac{\partial h}{\partial x_j}+\frac{\rho(c)-\rho_o}{\rho_0}e_j\right)$$ Momentum balance

$$\frac{\partial}{\partial t}\left(\varepsilon^m(s)c\right)+\frac{\partial}{\partial t}(\rho_b s)=-\frac{\partial}{\partial x_i}\left(\varepsilon^m v_i c\right)+\frac{\partial}{\partial x_i}\left[\varepsilon^m\left(D_{ij}^{mol}+D_{ij}^{disp}\right)\frac{\partial c^f}{\partial x_j}\right]$$ Mobile particles

$$\frac{\partial}{\partial t}(\rho_b s)=f(c,s)$$ Immobile particles

Colloidal transport

- 2 coupled equations:



- Mobile phase (water)
- Immobile phase (sand)

$$\begin{cases}\dfrac{\partial(\varepsilon_m c)}{\partial t}+\dfrac{\partial(\rho_b s)}{\partial t}=\dfrac{\partial}{\partial x}\left(\varepsilon_m D\dfrac{\partial c}{\partial x}\right)-\dfrac{\partial(q_m c)}{\partial x}\\[2ex] \rho_b\dfrac{\partial s}{\partial t}=f(c,s)\end{cases}$$

Exchange term

- Different formulations/mechanisms:

CFT (irreversible)

$$\rho_b \frac{\partial s}{\partial t} = \varepsilon_m k_a c$$

Linear

$$\rho_b \frac{\partial s}{\partial t} = \varepsilon_m k_a c - \rho_b k_d s$$

Langmuirian

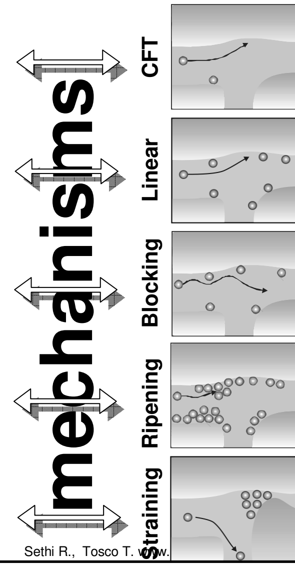
$$\rho_b \frac{\partial s}{\partial t} = \varepsilon_m \left(1 - \frac{s}{s_{\max}}\right) k_a c - \rho_b k_d s$$

Tosco, Sethi

$$\rho_b \frac{\partial s}{\partial t} = \varepsilon_m \left(1 + A_{rip} s^{\beta_{rip}}\right) k_a c - \rho_b k_d s$$

Bradford

$$\rho_b \frac{\partial s}{\partial t} = \varepsilon_m \left(\frac{d_{50} + x}{d_{50}}\right)^{-\beta_{str}} k_a c - \rho_b k_d s$$

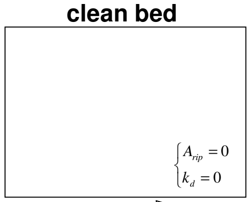


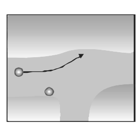
Sethi R., Tosco T. www.

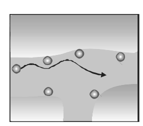
General use of ripening equation

- TSE can be used to simulate different mechanisms:

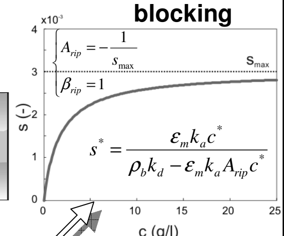
clean bed





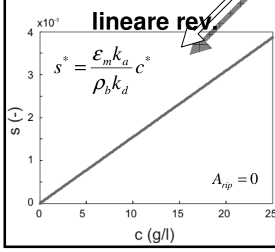


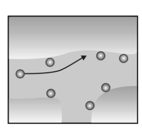
blocking

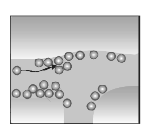


$$\rho_b \frac{\partial s}{\partial t} = \varepsilon_m \left(1 + A_{rip} s^{\beta_{rip}}\right) k_a c - \rho_b k_d s$$

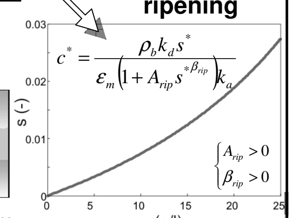
lineare rev.







ripening

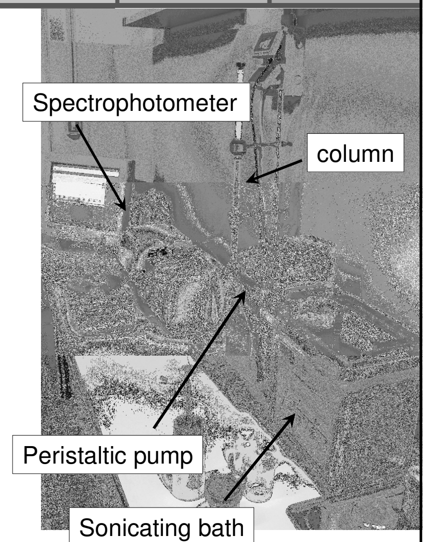


Sethi R., Tosco

Experimental setup Laboratory scale

DITAG POLITECNICO DI TORINO

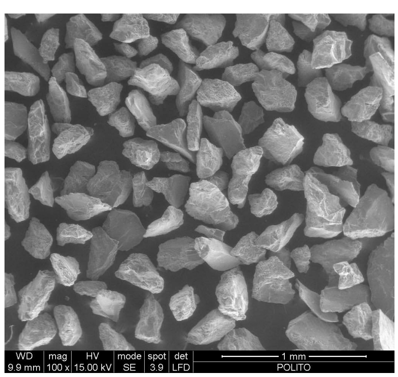
- 1D system, saturated porous medium
- Colloidal particles: latex, d=2 µm
- Porous medium: sand, d_{50}=250 µm
- Column:
  - d_{int} = 1.6 10^{-2} m
  - L = 0.1 m
  - n = 0.42
  - a_L = 5.8 10^{-4} m
- Water:
  - q = 7.9 10^{-5} m/s
  - pH = 7.0
  - Ionic strength = 0 - 300 mM

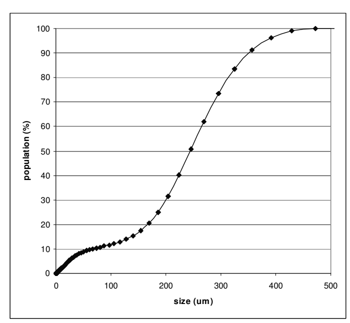


Column tests: Materials

DITAG POLITECNICO DI TORINO

- **Silica Sand**



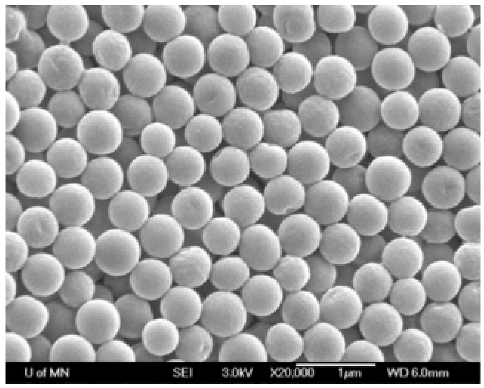


- *SEM image* *Particle Size distribution*

DITAG
POLITECNICO DI TORINO

Column tests: Materials

- Particles: latex microspheres

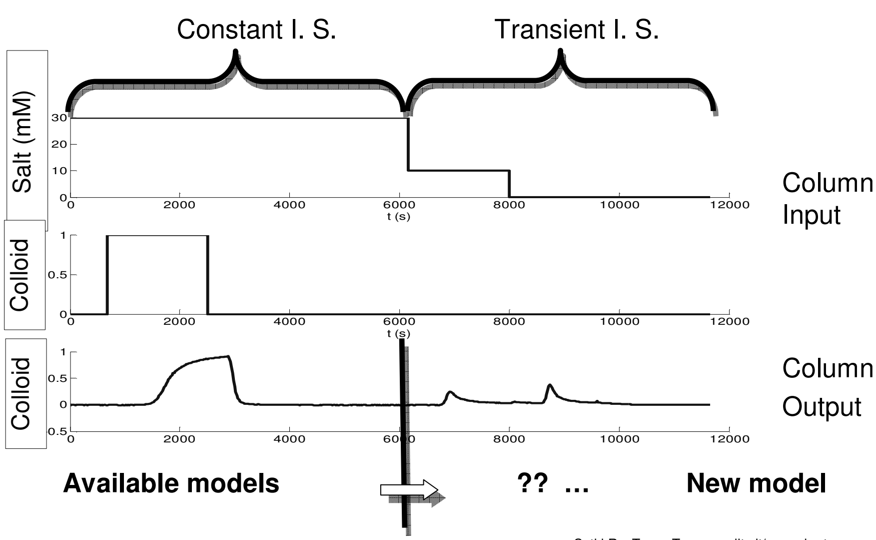


Sethi R., Tosco T. www.polito.it/groundwater

25

DITAG
POLITECNICO DI TORINO

Column tests: Design

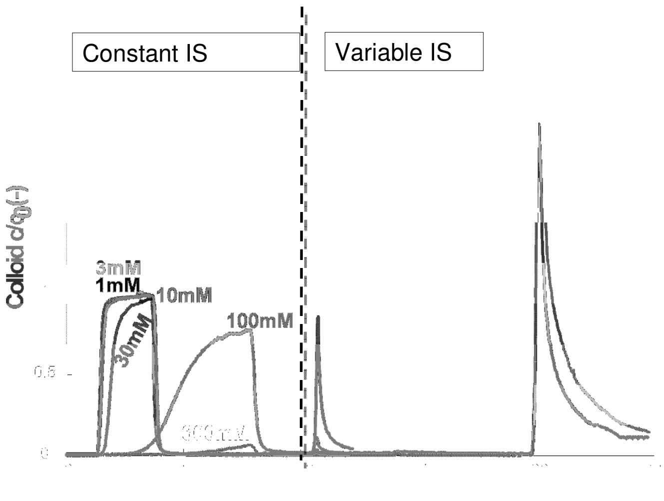


Sethi R., Tosco T. www.polito.it/groundwater

26

DITAG
POLITECNICO DI TORINO

Column tests: Results



DITAG
POLITECNICO DI TORINO

One site model

- One-site models are usually presented in these forms:

$$\begin{cases} n\dfrac{\partial c}{\partial t} + \rho_b \dfrac{\partial s}{\partial t} = nD\dfrac{\partial^2 c}{\partial c^2} - v\dfrac{\partial c}{\partial x} \\ \rho_b \dfrac{\partial s}{\partial t} = nk_a c - \rho_b k_d s \end{cases}$$

Linear attachment function

$$\begin{cases} n\dfrac{\partial c}{\partial t} + \rho_b \dfrac{\partial s}{\partial t} = nD\dfrac{\partial^2 c}{\partial c^2} - v\dfrac{\partial c}{\partial x} \\ \rho_b \dfrac{\partial s}{\partial t} = n\left(1 - \dfrac{s}{s_{\max}}\right)k_a c - \rho_b k_d s \end{cases}$$

Langmuirian attachment function

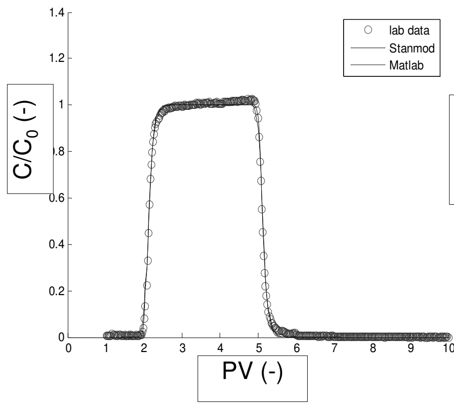
These models can be useful in many cases, but did not proved to be satisfactory when modeling our column experiments.

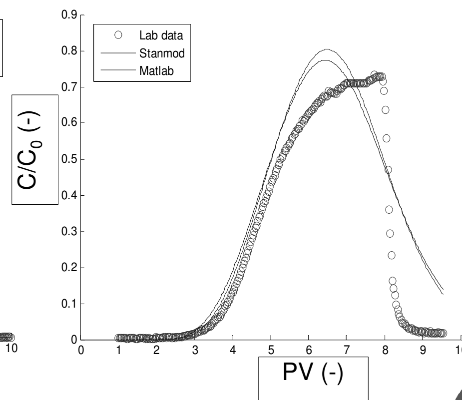
DITAG
POLITECNICO DI TORINO

One-site model…

- Can't fit experimental curves at high IS

F.I. = 1mM — F.I. = 100 mM



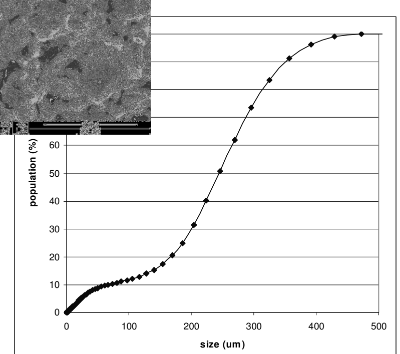


DITAG
POLITECNICO DI TORINO

Column tests: Materials

- **Heteroneous silica sand + feldspar**

SEM image



Size distribution

DITAG
POLITECNICO DI TORINO

Two sites model

- Differential equations for the two-interaction-site model:

$$
\begin{cases}
n\dfrac{\partial c}{\partial t}+\rho_b\dfrac{\partial s_1}{\partial t}+\rho_b\dfrac{\partial s_2}{\partial t}=nD\dfrac{\partial^2 c}{\partial c^2}-v\dfrac{\partial c}{\partial x} \\
\rho_b\dfrac{\partial s_1}{\partial t}=n\left(1-\dfrac{s_1}{s_{\max,1}}\right)k_{a,1}c-\rho_b k_{d,1}s_1 \\
\rho_b\dfrac{\partial s_2}{\partial t}=nk_{a,2}c-\rho_b k_{d,2}s_2
\end{cases}
$$

blocking attachment function (second equation)

linear attachment function (third equation)

- **Model implementation** (**MNM1D** www.polito.it/groundwater):
  - Matlab code, finite-differences approach
  - Non linear-problem, solved with an iterative scheme
  - Code validated with well-established analitycal (Stanmod) and numerical (Hydrus1D) solutions

DITAG
POLITECNICO DI TORINO

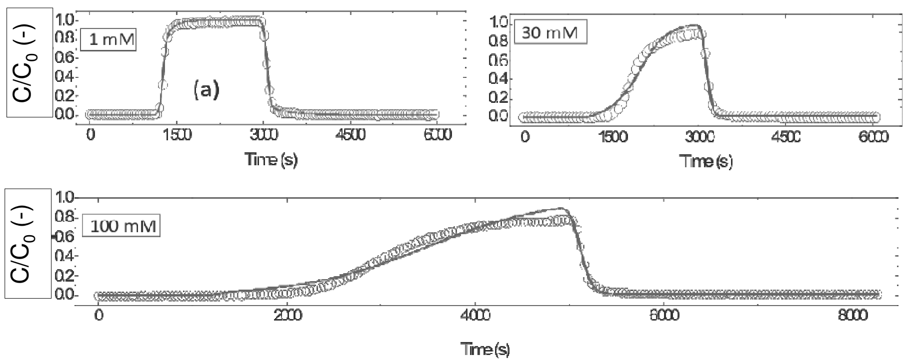
Colloids in porous media: modeling the influence of I.S.

- MNM1D (Micro-and Nanoparticle transport Model in porous media in 1D geometry):
  - Development of the model at CONSTANT ionic strength
  - Fitting of the first part of experimental curve (I.S. 1 – 300 mM);
  - Definition of semi-empirical relationships for attachment/detachment coefficients VS ionic strength
  - Development of the model in TRANSIENT ionic strength
  - Application of MNM1D for the fitting of the whole experimental curves

Colloids in porous media: modeling the influence of I.S

DITAG
POLITECNICO DI TORINO

- Fitting of the first part of the breakthrough curves, at constant ionic strength (1 – 300 mM)



Sethi R., Tosco T. www.polito.it/groundwater

33

Colloids in porous media: modeling the influence of I.S.

DITAG
POLITECNICO DI TORINO

- MNM1D (Micro-and Nanoparticle transport Model in porous media in 1D geometry):
  - Development of the model at CONSTANT ionic strength
  - Fitting of the first part of experimental curve (I.S. 1 – 300 mM);
  - Definition of semi-empirical relationships for attachment/detachment coefficients vs ionic strength
  - Development of the model in TRANSIENT ionic strength conditions
  - Application of MNM1D to the whole test

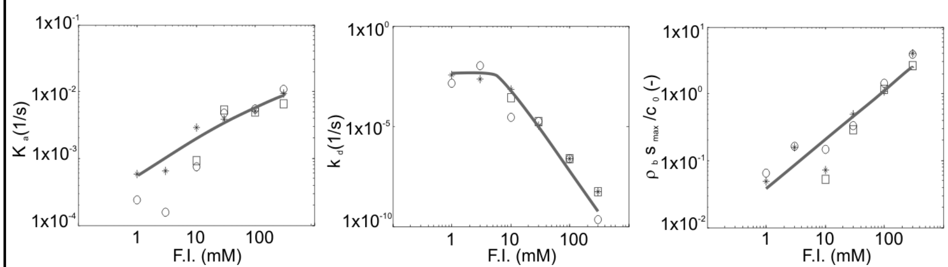
Sethi R., Tosco T. www.polito.it/groundwater

34

DITAG
POLITECNICO DI TORINO

Two sites model: influence of the IS

- Dependence of coefficients on IS:



$$k_{a,1} = \frac{k_{a1,\infty}}{1+\left(\frac{CDC_1}{c_t}\right)^{\beta_{a,1}}} \qquad k_{d,1} = \frac{k_{d1,0}}{1+\left(\frac{c_t}{CRC_1}\right)^{\beta_{d,1}}} \qquad s_{\max,1} = \alpha_{s,1} c_t^{\beta_{s,1}}$$

DITAG
POLITECNICO DI TORINO

Colloids in porous media: modeling the influence of I.S.

- MNM1D (Micro-and Nanoparticle transport Model in porous media in 1D geometry):
  - Development of the model at CONSTANT ionic strength
  - Application for the fitting of the first part of experimental (I.S. 1 – 300 mM);
  - Definition of semi-empirical relatioships for attachment/detachment coefficients VS ionic strength
  - Development of the model in TRANSIENT ionic strength conditions
  - Application of MNM1D to the whole test

DITAG
POLITECNICO DI TORINO

Colloids in porous media: modeling the influence of I.S. MNM1D

- A further PDE is added to account for the evolution of IS:

$$\begin{cases} n\dfrac{\partial c_t}{\partial t} = nD\dfrac{\partial^2 c_t}{\partial x^2} - v\dfrac{\partial c_t}{\partial x} \\ n\dfrac{\partial c}{\partial t} + \rho_b\dfrac{\partial s_1}{\partial t} + \rho_b\dfrac{\partial s_2}{\partial t} = nD\dfrac{\partial^2 c}{\partial x^2} - v\dfrac{\partial c}{\partial x} \\ \rho_b\dfrac{\partial s_1}{\partial t} = n\left(1-\dfrac{s_1}{s_{max,1}(c_t)}\right)k_{a,1}(c_t)c - \rho_b k_{d,1}(c_t)s_1 \\ \rho_b\dfrac{\partial s_2}{\partial t} = n k_{a,2}(c_t)c - \rho_b k_{d,2}(c_t)s_2 \end{cases}$$

Conservative tracer

$$k_{a1} = \frac{k_{a1,\infty}}{1+\left(\dfrac{CDC_1}{c_t}\right)^{\beta_{a1}}}$$

$$k_{d1} = \frac{k_{d1,0}}{1+\left(\dfrac{c_t}{CRC_1}\right)^{\beta_{d1}}}$$

$$s_{max1} = \alpha_{S1} c_t^{\beta_{S1}}$$

DITAG
POLITECNICO DI TORINO

Two sites model + IS dependence

$$\begin{cases} \varepsilon_m\dfrac{\partial c_t}{\partial t} = \varepsilon_m D\dfrac{\partial^2 c_t}{\partial x^2} - q\dfrac{\partial c_t}{\partial x} \\ \varepsilon_m\dfrac{\partial c}{\partial t} + \rho_b\dfrac{\partial s_1}{\partial t} + \rho_b\dfrac{\partial s_2}{\partial t} = \varepsilon_m D\dfrac{\partial^2 c}{\partial x^2} - q\dfrac{\partial c}{\partial x} \\ \rho_b\dfrac{\partial s_1}{\partial t} = \varepsilon_m\left(1-\dfrac{s_1}{s_{max,1}(c_t)}\right)k_{a,1}(c_t)c - \rho_b k_{d,1}(c_t)s_1 \\ \rho_b\dfrac{\partial s_2}{\partial t} = \varepsilon_m k_{a,2}(c_t)c - \rho_b k_{d,2}(c_t)s_2 \end{cases}$$

$$k_{a,i} = \frac{k_{ai,\infty}}{1+\left(\dfrac{CDC_i}{c_t}\right)^{\beta_{ai}}}$$

$$s_{max,1} = \alpha_{S1} c_t^{\beta_{S1}}$$

$$k_{d,i} = \frac{k_{di,0}}{1+\left(\dfrac{c_t}{CRC_i}\right)^{\beta_{di}}}$$

DITAG
POLITECNICO DI TORINO

Colloids in porous media: modeling the influence of I.S.

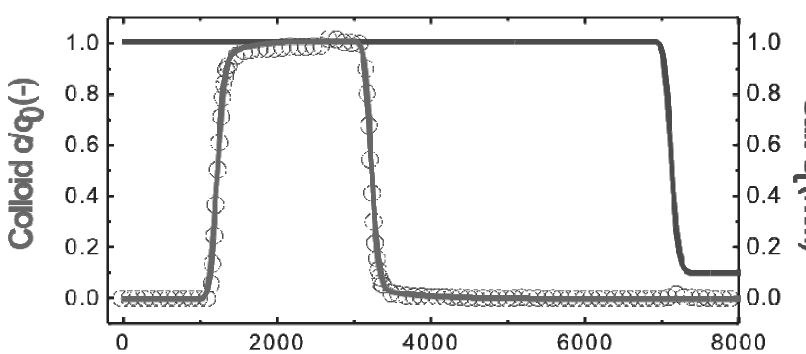
- MNM1D (Micro-and Nanoparticle transport Model in porous media in 1D geometry):
  - Development of the model at CONSTANT ionic strength
  - Application for the fitting of the first part of experimental (I.S. 1 – 300 mM);
  - Definition of semi-empirical relatioships for attachment/detachment coefficients vs ionic strength
  - Development of the model in TRANSIENT ionic strength
  - MNM1D can be downloaded from: http://areeweb.polito.it/ricerca/groundwater/software/MNM1D.html

DITAG
POLITECNICO DI TORINO

Colloids in porous media: modeling the influence of I.S.

- Fitting of the complete column test

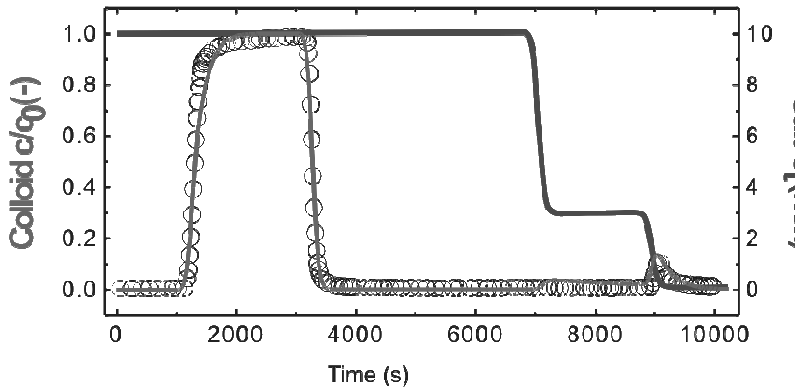
I.S. = 1mM



Colloids in porous media: modeling the influence of I.S.

DITAG
POLITECNICO DI TORINO

- Fitting of the complete column test
  I.S. = 10mM



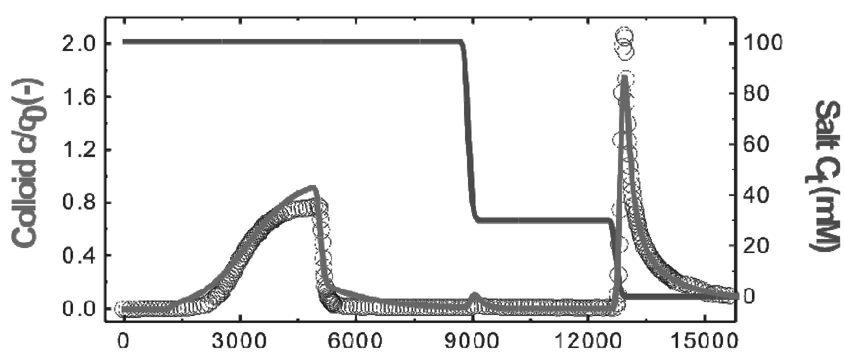
Sethi R., Tosco T. www.polito.it/groundwater

41

Colloids in porous media: modeling the influence of I.S.

DITAG
POLITECNICO DI TORINO

- Fitting of the complete column test
  I.S. = 100mM



Sethi R., Tosco T. www.polito.it/groundwater

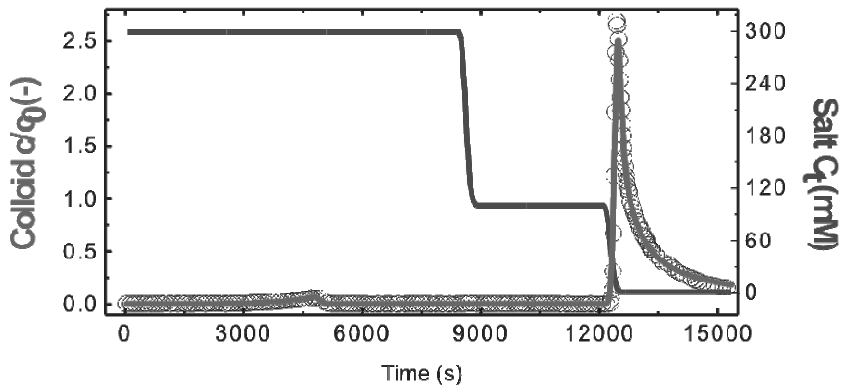
42

Colloids in porous media: modeling the influence of I.S.

DITAG POLITECNICO DI TORINO

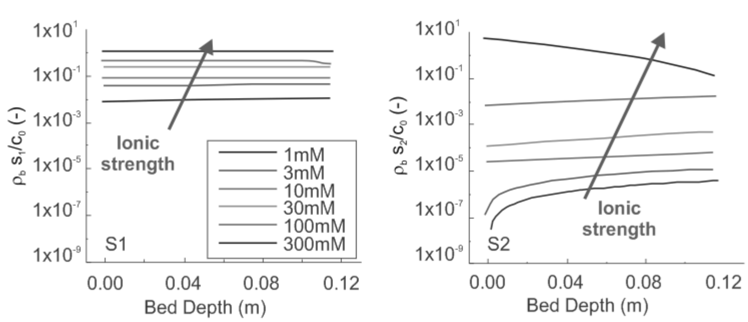
- Fitting of the complete column test

I.S. = 300mM



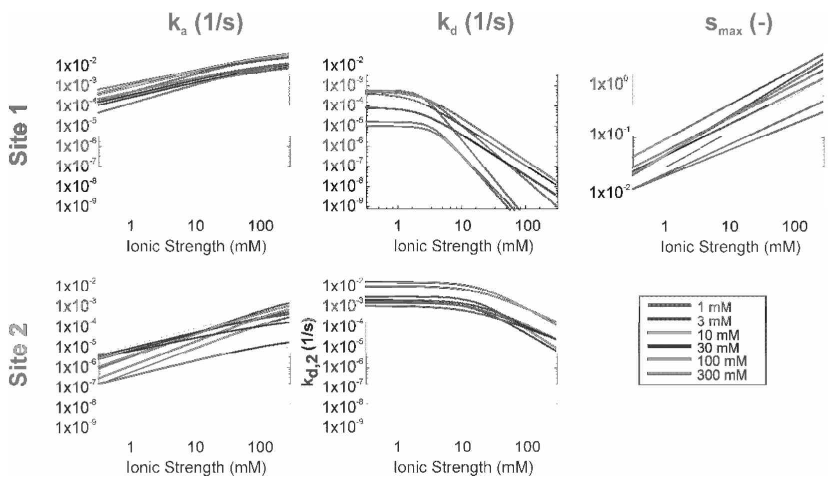
Solid phase concentration

DITAG POLITECNICO DI TORINO



DITAG
POLITECNICO DI TORINO

Colloids in porous media: modeling the influence of I.S.



DITAG
POLITECNICO DI TORINO

References

- Tosco, T.; Tiraferri, A.; Sethi, R. Ionic Strength Dependent Transport of Microparticles in Saturated Porous Media: Modeling Mobilization and Immobilization Phenomena under Transient Chemical Conditions. *Environmental Science & Technology* **2009**, *43*(12), 4425-4431.
- Tosco, T.; Sethi, R. MNM1D: a numerical code for colloid transport in porous media: implementation and validation. *American Journal of Environmental Sciences* **2009**, *5*(4), 517-525.
- Tiraferri, A., T. Tosco, e R. Sethi (2010), Transport and Retention of Microparticles in Packed Sand Columns at Low and Intermediate Salinities: Experiments and Mathematical Modeling. *Environmental Earth Sciences* (submitted) **2010**.
- Tiraferri, A.; Chen, K.L.; Sethi, R.; Elimelech, M. Reduced aggregation and sedimentation of zero-valent iron nanoparticles in the presence of guar gum. *Journal of Colloid and Interface Science* **2008**, *324*(1-2), 71-79.
- Tiraferri, A.; Sethi, R. Enhanced transport of zerovalent iron nanoparticles in saturated porous media by guar gum. *J Nanopart Res* **2009**, *11*(3), 635-645.