

#### **Keywords:**

Reactive transport - Porous media - Physicochemical - Mass transport equations - Chemical reactivity – Reactivity at solid-liquid interfaces

#### **Objective:**

- Introduction to reactive transport in porous media with respect to the physicochemical reactivity by taking into account the mass transport equations and the chemical interaction mechanisms in the liquid phase and at the interfaces, mainly the solid-liquid ones

#### Main part of the courses:

- Some hydrodynamic considerations
- Physicochemical mechanisms affecting solute transport
- Relationships between sorption term and aqueous concentration
- Experimental setup used for reactive transport at different scales
- Application of the non-linear chromatography theory
- Modelling of reactive transport applied trace contaminants: coupling chemistry and multicomponent transport (speciation coupling methods limits)
- Introduction and use of software: VminteqA2 (case studies)
- Colloidal transport

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**Control:** 1 written exam + report from tutorial

#### Lecturers:

Prof. Philippe Behra (INPT – philippe.behra@ensiacet.fr)

## Some references

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More generally, Darcy velocity:

$$v = -\frac{\overline{k}}{\mu} \nabla \cdot \left[ P - \rho g \right]$$

with  $\overline{k}$  permability tensor [m<sup>2</sup>], expressed in darcy (1 darcy = 0,987 10<sup>-12</sup> m<sup>2</sup>),  $\mu$  dynamic viscosity of moving fluid [Pa.s], P pressure [Pa],  $\rho$  fluid density [kg m<sup>-3</sup>], and g gravity [m s<sup>-2</sup>]

Generalization of Darcy's laws for non water saturated porous media or multiphasic systems:

Darcy's law for each phase

Remarque: use of Darcy's law in filtration or in chromatographic systems, but different words









# Sorption Processes and Reactive Transport

Sorption processes

Isotherm relationships

Ionic exchange processes

Classical surface complexation model

Surface precipitation model

Electrostatic model of surface charge

Other surface complexation models

Relationship between surface complexation and basic isotherm

## Sorption Processes and Reactive Transport

Some inputs into reactive transport modelling

Reactive transport of Cd and Pb

Modelling of reactive transport in saturated medium:

Principles, methods and perspectives

Some conclusions and recommendations



















## **MODELLING OF REACTIVE TRANSPORT**

Definition: coupling between hydrodynamics (mass transport equation) and chemistry (chemical reactions at equilibrium and/or kinetic laws)

Transient advective-dispersive mass transport equation in homogeneous saturated porous media

Differential partial equation (DPE) as mass balance equation:

$$\frac{\partial \mathbf{C}}{\partial t} = \nabla \cdot (\mathbf{D} \cdot \nabla \mathbf{C}) - \nabla \cdot (\mathbf{u} \mathbf{C})$$

with C solute concentration [mol L<sup>-1</sup>], u mean pore velocity (u = v/ $\epsilon_c$ ) [m s<sup>-1</sup>], **D** dispersion tensor [m<sup>2</sup> s<sup>-1</sup>]

D: function of u and dispersivity,  $\alpha$  [m], intrinsic property of porous medium;  $\epsilon_c$  kinematic porosity [-], *i.e.* ratio: interconnected pore volume and total volume

## **MODELLING OF REACTIVE TRANSPORT**

Transient advective-dispersive mass transport equation in homogeneous saturated porous media

Mass transport equation (for water and inert tracer) for a mono-directional (1D) flow:

 $\partial[C]/\partial t = D \partial^2[C]/\partial x^2 - u \partial[C]/\partial x$ 

Chemical or reactive terms (reactive chemicals):

 $\rho_s \partial \{C_s\}/\partial t$ ;  $\lambda([C] + \rho_s \{C_s\})$ 













































































Surface Complexation Model			
Values of points of zero charge, pH <sub>pzc</sub> , of some "pure" solids			
Material	pH <sub>pzc</sub>	Material	рН <sub>рzc</sub>
$\alpha$ -Al <sub>2</sub> O <sub>3</sub> (corindon)	9.1	$\beta$ -MnO <sub>2</sub> (birnessite)	7.2
$\alpha$ -Al(OH) <sub>3</sub> (gibbsite)	5.0	SiO <sub>2</sub> (amorphous, quartz)	2.0-3.0
γ-AlOOH (boehmite)	8.2	TiO <sub>2</sub> (anatase, rutile)	6.3
BeO	10.2	ZrO <sub>2</sub>	6.4
CuO (tenorite)	9.5	ZrSiO <sub>4</sub> (zircon)	5.0
Fe <sub>3</sub> O <sub>4</sub> (magnetite)	6.5	Albite	2.0
α-FeOOH (goethite)	7.8	Chrysolite	>10
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> (hematite)	8.5	Feldspars	2-2.4
FeOOH (amorphous)	8.1	Kaolinite	4.6
MgO	12.4	Latex	8.0
δ-MnO <sub>2</sub> (vernadite)	2.8	Montmorillonite	2.5
Remark: Indicative values depending on estimation methods They are not fully comparable			


















Example: Adsorption of Pb(II) on hematite surface							
	Adsorption reactions of Pb <sup>2+</sup> on hematite surface:						
	$ \begin{array}{cccc} \equiv & FeOH_2^+ & \rightleftharpoons & \equiv & FeOH + & H_{^+} \\ \equiv & FeOH & \rightleftharpoons & \equiv & FeO^- + & H_{^+} \\ \equiv & FeOH + & Pb^{2+} & \rightleftharpoons & \equiv & FeOPb^+ + & H_{^+} \end{array} $	$K_{a1}^{s} intr = 10^{-7.25}$ $K_{a2}^{s} intr = 10^{-9.75}$ $K_{1}^{s} intr = 10^{4.0}$					
	Specific surface area: Surface site per kg: Concentration of hematite: Ionic strength:	a = 4 $10^4 \text{ m}^2 \text{ kg}^{-1}$ S <sub>tot</sub> : 3.2 $10^{-1} \text{ mol kg}^{-1}$ $\rho_s$ = 8.6 $10^{-6} \text{ kg L}^{-1}$ I = 5 $10^{-3} \text{ M}$					







# Sorption of a divalent cation M<sup>2+</sup> onto an amorphous Fe(III) (hydr)oxide (HFO or FeOOH<sub>(s)</sub>) (for more details on surface precipitation model, see K.J. Farley, D.A. Dzombak & F.M.M. Morel [*J. Coll. Interface Sci.* **106**, 226, 1985]) 1<sup>st</sup> step: Formation of a surface complex $= Fe - OH + M^{2+} + H_2O \iff FeOOH_{(s)} + = M - OH + H^+$ $*K^s_{M,1} = \frac{|FeOOH_{(s)}| \{= M - OH\}[H^+]}{\{= Fe - OH\}[M^{2+}]|H_2O|}$ with {=S-OH} in mol g<sup>-1</sup>, [M<sup>2+</sup>] in mol L<sup>-1</sup> and |H\_2O| and |FeOOH\_{(s)}| activities of H\_2O and FeOOH\_{(s)}, respectively







Formation of an Electric Double Layer Total surface charge,  $\sigma_p$ :  $\sigma_p = \sigma_s + \sigma_H + \sigma_{is} + \sigma_{os}$   $\sigma_d$  : counter-ion charge contribution Electroneutrality:  $\sigma_p + \sigma_d = \sigma_s + \sigma_H + \sigma_{is} + \sigma_{os} + \sigma_d = 0$   $\sigma_p = (8RT \varepsilon \varepsilon_0 c * 10^3)^{1/2} \sinh\left(\frac{Z\psi_0 F}{2RT}\right)$   $\varepsilon$ : dielectric constant for water: 78.5 at 25 °C; F: Faraday constant c: electrolyte concentration (I);  $\psi_0$ : surface potential  $\varepsilon_0$ : vacuum permitivity: 8.854 10<sup>-2</sup> C V<sup>-1</sup> m<sup>-1</sup>; Z: charge For low potential:  $\sigma_p \approx \varepsilon \varepsilon_0 \kappa \psi_0$ with  $\kappa$  (Debye's parameter):  $\kappa = \left(\frac{2F^2I * 10^3}{\varepsilon \varepsilon_0 RT}\right)^{1/2} [m^{-1}]$ inverse of double layer thickness

## Formation of an Electric Double Layer

```
\sigma_{p} = (8RT\epsilon\epsilon_{0}c \times 10^{3})^{1/2} \sinh(Z\psi_{0} F/2RT)
```

at 25 °C

 $\sigma_{\rm p} = 0.1174 \ c^{1/2} \sinh(19.46 \ Z \psi_0) \qquad [C \ m^{-2}] \label{eq:sigma_p}$ 

or for low potential

 $\sigma_p$  = 2.3 I<sup>1/2</sup>  $\psi_0$  [C m<sup>-2</sup>]

κ = 3.29 10<sup>9</sup> l<sup>1/2</sup> [m<sup>-1</sup>]

Examples of double layer thickness:

 $\begin{array}{ll} \mbox{for 1 mM NaCl} & \kappa^{-1} \approx 10 \mbox{ nm} \\ \mbox{for sea water (I} \approx 0.7 \mbox{ M}) & \kappa^{-1} \approx 0.4 \mbox{ nm} \end{array}$ 













## Complexation Model with Charge Distribution of Surface Sites (CD-MUSIC)

In the previous models: charge of inner-sphere complexes located in one point only

**Case of charge distribution:** taking into account of the molecule size with a part of the molecule engaged with its charge in the surface structure, the second part being located in the "Stern layer"

Positive charge of a cation or those of a ligand: charge distribution over the overall ligands or cations sorbed onto the surface (respectively)

Base: Pauling's rule

Definition of a formal valence for binding, "v": v = Z/CN with Z cation charge and CN its coordination number











## **Relationship between Surface Complexation** and Basic Isotherm (3) Aqueous total concentration of TBT: $TBT_{aq} = [TBT^+] + [TBTOH] + [TBTNO_3] + [TBTIm^+]$ (viii) or: $TBT_{aq} = [TBT^{+}] (1 + K_{a,TBT} [H^{+}]^{-1} + K_{NO3} [NO_{3}^{-}] + K_{I} [Im])$ (ix) $TBT_{a\alpha} = [TBT^+] \alpha^{-1}$ (x) with $\alpha = (1 + K_{a,TBT} [H^+]^{-1} + K_{NO3} [NO_3^-] + K_1 [Im])^{-1}$ (xi) Mass balance for surface sites: $S_{tot} = \{\equiv S-OH_2^+\} + \{\equiv S-OH\} + \{\equiv S-O^-\} + \{\equiv S-OTBT\}$ (xii) Taking (i) and (ii) into (xii) : $S_{tot} = \{\equiv S-OH\} ([H^+] K_{a1.s}^{-1} + 1 + K_{a2.s} [H^+]^{-1}) + \{\equiv S-OTBT\}$ (xiii)





## Relationship between Surface Complexation and Basic Isotherm (6)

## **Conclusion**:

Do not forget that the Langmuir-type constant,  $K_L$ , depends on important environmental factors such as pH, ligand concentration, surface acidity and thus on the type of surface material, and call  $K_L$  as a coefficient and not a constant

Can be generalised to more conditions

## **Application to TBT Transport: Parameter Estimation (1)**

First, from eq. (xviii),  $K_L$  can be estimated and then the surface complexation constant,  $\log^* K_1^{s}$ , from isotherm à pH 8

What is known:

\* surface acidity constant logK<sub>a1,s</sub> = -4; logK<sub>a2,s</sub> = -8

- \* aqueous equilibrium constant p $K_{a,TBT}$  = 6.25; log $K_{NO3}$  = 0.62; log $K_{Im}$  = 3.91 & p $K_{a,Im}$  = 7
- \* ligand concentration  $[NO_3^-]_{tot} = 100 \text{ mM et } [Im]_{tot} = 1 \text{ mM}$





Estimated parameters

From isotherm,

 $S_{tot} = 0.65 \ \mu mol \ kg^{-1}$ , &

 $K_{L} = 16.2 \ \mu M^{-1}$ 

Thus by taking into account aqueous speciation and surface acidity, from equation (xviii):

 $\log^{*}K_{1}^{s} = 1.3$ 

Second, breakthrough curves can be calculated by using non-linear chromatography theory







 $R = 1 + \rho_s \left(\frac{\partial \{C_s\}}{\partial [C]}\right)$ 

For Langmuir-type relationship:

 ${C_s} = S = S_{max}(pH).f(pH,[Ligands]).[C]/(1 + f(pH,[Ligands]).[C])$ 





# Two physical steps: External transfer Whatever the flow rate of mixing, existence of immobile liquid layer at the solid-liquid interface due to viscosity Thickness of the boundary limit: function of the mean pore velocity, u Sorption on solid after molecular diffusion of the solute through the layer by following the Fick's law Internal transfer In contact of the solid phase, possible sorption only after migration of the solute in the interstitial pores of the solid phase Flux function of the tortuosity Methods the step: physical-chemical reactions





## External mass transfer constant, k<sub>e</sub>

$$k_{e} = \frac{D_{m}a_{p}}{\delta V_{p}}$$

with D<sub>m</sub> molecular diffusion coefficient in solution;  $a_p$  particle surface area;  $v_p$  particle volume;  $\delta$  layer thickness (external diffusion layer)

Sherwood number, Sh

Sh = 
$$\frac{a_p}{\delta}$$
 = 2 + 1.8 Re<sup>1/2</sup> Sc<sup>1/3</sup>

with Re Reynolds number =  $(u d_p)/v$ ; Sc Schmidt number =  $v/D_m$ ; and v kinematic viscosity of fluid  $[m^2 s^{-1}]$ 













## What about colloid transport or their potential scavenging role in contaminant transport?

### letters to nature

Re and Al<sub>2</sub>O<sub>3</sub> were heated with laser beams from both sides. Acting like planar heat sources, the two 'hot plates' eliminate the axial temperature gradient in the sample between the plates. Temperature variation is less than 3% within roughly 30  $\mu m$  diameter at 2,500 K. Before the melting experiments, the sample was scanned with a laser beam and heated to about 2,000 K to reduce the pressure gradient and to produce a high-pressure solid-phase assemblage. For stable and smooth temperature control, temperatures were increased by adjusting an aperture placed near the beam exit, stepwise, instead of by adjusting power. Each step corresponds to a 50-100K increase. A 30-µm spot was homogeneously heated by opening the aperture (increasing the step). At the onset of melting, temperature remains constant or drops slightly with the step increment, and then drastically increases (>400K) within one step. To ensure the reliability of the melting criteria used in this study, we conducted melting experiments at pressures (16–27 GPa) overlapped by the multi-anvil apparatus and the diamond-anvil cell, using the san ne starting material, and obtained consistent melting temperatures (Fig. 3). We also used the same melting criteria to determine the melting temperature of MgSiO3-perovskite previously studied by other investigators, and our results agree with these recent determinations  $^{13,14}$  (Fig. 3). The temperature runaway phenomena near the onset of melting observed in simple and complex samples were probably a result of the latent heat of melting, followed by melt migrating away from the heated spot because of the large thermal pressure and, finally, the Re foils would have been heated without sample in between. No chemical reaction between Re and sample was observed in the multi-anvil experiments on a scale of 1 µm. The

## Migration of plutonium in ground water at the Nevada Test Site

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<sup>1</sup> Isotope Sciences Drivision, PO Box 806, 1:-251, Lawrence Livermore National Laboratory, Livermore, California 94550, USA <sup>†</sup> Chemical Science and Technology Division, MS J514, Los Alamos National Laboratory. Los Alamos. New Mexico 87545, USA

Mobile colloids—suspended particles in the submicrometre size range—are known to occur naturally in ground water<sup>1,2</sup> and have the potential to enhance transport of non-soluble contaminants through sorption<sup>3</sup>. The possible implications of this transport mechanism are of particular concern in the context of radionuclide transport. Significant quantities of the element plutonium have been introduced into the environment as a result of nuclear weapons testing and production, and nuclear power-plant accidents. Moreover, many countries anticipate storing nuclear waste underground. It has been argued that plutonium intro-

## Nature 397, 56-59 (7 January 1999)





Modelling of reactive transport in saturated medium:

TRANSPORT OF Cd and Pb THROUGH A NATURAL POROUS MEDIUM: INFLUENCE OF THE SOLID-LIQUID INTERFACE PROCESSES





SOLID PHASE					
Natural quartz sand from Alsace (Kaltenhouse, France)					
	Mineralogical composition of the sand				
	QUARTZ		> 99 %		
	POTASSIC FELDSPARS		$\approx 1 \%$		
	CLAYS		≈ 0.1 %		
	(Kaolinite, Illite, Smectite)				
	OXIDES/HYDROXIDES		traces		
	Al,Fe,Mn				
N	ledium diameter:	<b>d</b> <sub>50</sub>	= 0.65 mm		
C	haracteristic diameter:	<b>d</b> <sub>10</sub>	= 0.43 mm		
S	pecific Surface Area:	0.1	6 m² g <sup>-1</sup>		


































## Modelling of reactive transport in saturated medium: Principles, methods and perspectives

Part of Ph.D. work of Jérôme Carrayrou (2001) PhD supervisor: Philippe Behra & Robert Mosé

- Carrayrou, J., Mosé, R. & Behra, Ph., 2002. A new efficient algorithm for solving thermodynamic chemistry. *AIChE J.* **48**, 894-904.
- Carrayrou, J., Mosé, R., Behra, Ph., 2003. Modélisation du transport réactif en milieu poreux : schéma itératif associé à une combinaison d'éléments finis discontinus et mixtes-hybrides. *C. R. Mécanique* **331**, 211-216.
- Carrayrou, J., Mosé, R., Behra, Ph., 2004. Comparison of mass balance errors in operator-splitting procedures for reactive transport. *J. Contaminant Hydrol.* **68**, 239-268.





























Solving methods for coupling chemistry and transport

> Global approach Operators splitting





















































































		$H^{+}$	$Al^{3+}$	$H_{3}L$	$\log(K)$
	$H^+$	1	0	0	0
Gallic	$Al^{3+}$	0	1	0	0
A • 1	$H_{3}L$	0	0	1	0
ACIO	$OH^-$	-1	0	0	-14
	$H_2L^-$	-1	0	1	-4,15
	$HL^{2-}$	-2	0	1	-12,59
	$L^{3-}$	-3	0	1	-23,67
	$AlHL^+$	-2	1	1	-4,93
	AlL	-3	1	1	-9,43
	$AlL_2^{3-}$	-6	1	2	-21,98
	$AlL_3^{6-}$	-9	1	3	-37,69
	$Al_{2}(OH)_{2}(HL)_{3}^{2-}$	-8	2	3	-22,65
	$Al_2(OH)_2(HL)_2L^{3-}$	-9	2	3	-27,81
	$Al_2(OH)_2(HL)L_2^{4-}$	-10	2	3	-32,87
	$Al_{2}(OH)_{2}L_{3}^{5-}$	-11	2	3	-39,56
	$Al_4L_3^{3-}$	-9	4	3	-20,25
	$Al_{3}(OH)_{4}(H_{2}L)^{4+}$	-5	3	1	-12,52
	Total (M)	PH = 5,8	10-3	10-3	
	Solution (M)	1.58 10-6	2.03 10-5	2.59 10 <sup>-7</sup>	





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8.0 <sup>2</sup> 2 0.5 0 2 -22.5
δ <sub>1</sub> αζ <sup>2</sup> 4 -2 0 3 -146,1
<u>家人</u> 学 D 40,65 U 4
$\frac{FC}{Mmmur} = \frac{4}{m} + \frac{4}{2} + \frac{1}{2} +$
<i>μ</i> <sub>6</sub> (αν) <sub>λ</sub> -2 0 1 0 -12,90
Pa(GW), -2 0,25 1 0 2,63
νεί δαζή τ μο τ μ΄ 14,77 να δα μ΄ μαλά το μια
ρ <sub>60</sub> -
- ταυΣ. Ganahina -2 0,25 I 0 7,95
Manazanna -4 0.5 ? 0 16,87
Adadem na ú ú í i 2,35
βητήε 2 -3,5 I 2 -217,40 Βραγλαρίας β -2 I I -124.45
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Total (M) 2 10" -3,5 10" 1 10" 2 10"
Traitisa (M) 100° 110° vanable
Equilibre transitoire (M) 1.85 10° 3.61 10° 9.51 10° 2.12 10°
Equilibre (M) 9,24 10° 1,10 10° 2,24 10° 6,22 10°









- Transport : advection dispersion
- Chemical kinetics
- Instantaneous equilibrium

## Modelling of processes

- Basic description
- Possible application to other scientific domains

## Solving methods

- Coupling chemistry and transport
- Solving chemical and transport operators




For chemical speciation, in aqueous solution, precipitation-dissolution, gas exchanges, solid-liquid-gas interfaces, natural waters and effluents, with high ionic strength (developed for US Geological Survey) Phreeqcl Version 3.3.7-11094 (April 21, 2016) Site : http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqci/	
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## Conclusions

Integration of interface knowledge into trace contaminant transport models?



## Conclusions

Some questions for discussion:

From batch or column studies of pollutant migration through solid phases, adsorption often assumed as a very fast mechanism whereas desorption more often assumed kinetically limited

However, is this assumption so trivial?





## CONCLUSIONS

## Objective: "Field" application

Considering the spatial and temporal variations of exchanges and heterogeneity of complex systems (no need of purification of solid phases or fractionation of organic matter) by taking into account the **true speciation** both in the aqueous solution and at the surface (plus the gaseous phase if necessary), the **effective hydrodynamics** and the **effective surface reactivity** 



