lecture n°13:
Cesium retention on « resins » and porous engineered materials

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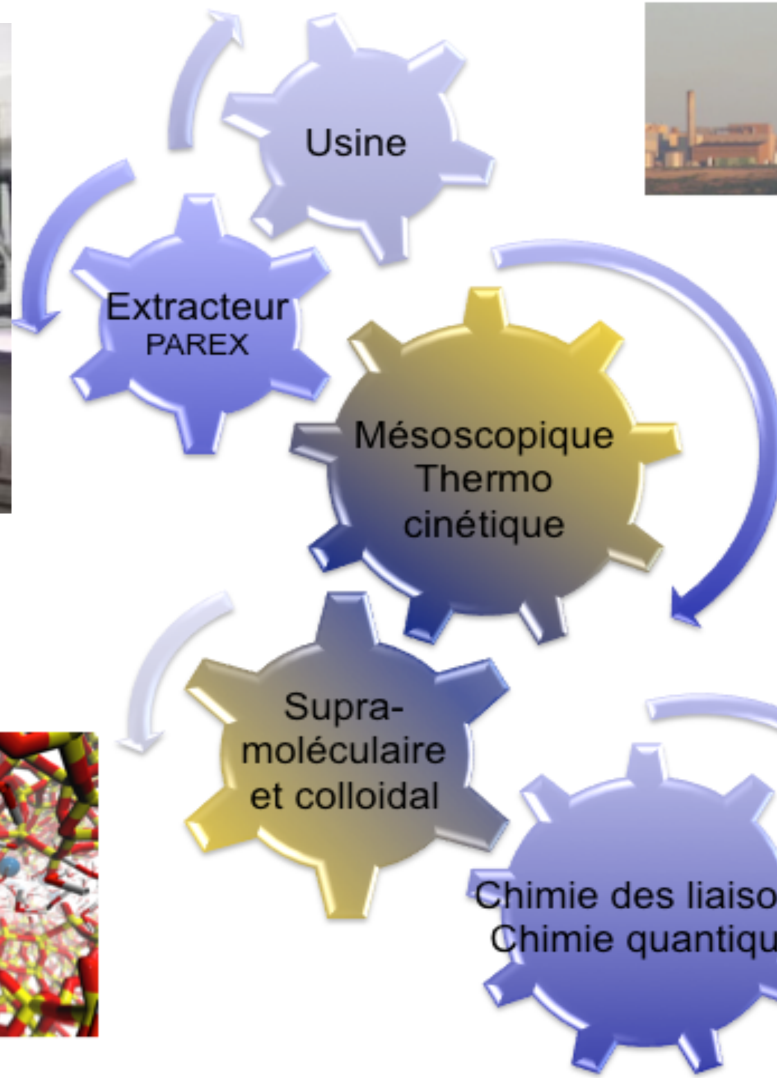
DEN/DTCD

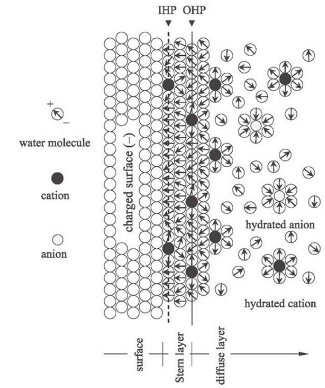
Thomas Zemb (for the audio channel)

2014-2015

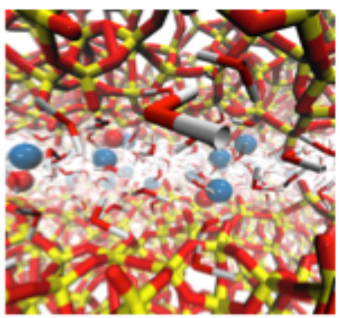
An intrinsic multi-scale approach :

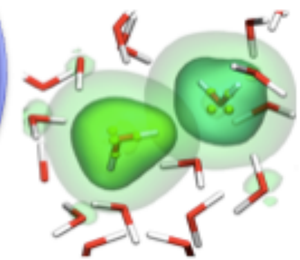
AG N° 24





JFD N° 14





1/ CONTEXT AND METHODOLOGY

Aqueous effluents decontamination

EFFLUENTS PRODUCTION

Pretreatment (membrane processes, oxydation advanced processes)

Effluent simplification

Specific chemical treatment (co-precipitation, innovative adsorbants)

Reduce the radioactivity

Trace treatment (ionic exchange, reverse osmotic membranes, electrocapture..)

« zero reject »

WASTES

RECYCLING

Decontamination of nuclear liquid wastes

Two situations :

1.Production operations. In this case liquid wastes processing facilities are integrated in the global production scheme of the plant and the volumes to be processed are known.

2.Processing of liquid wastes resulting from a temporary situation like:

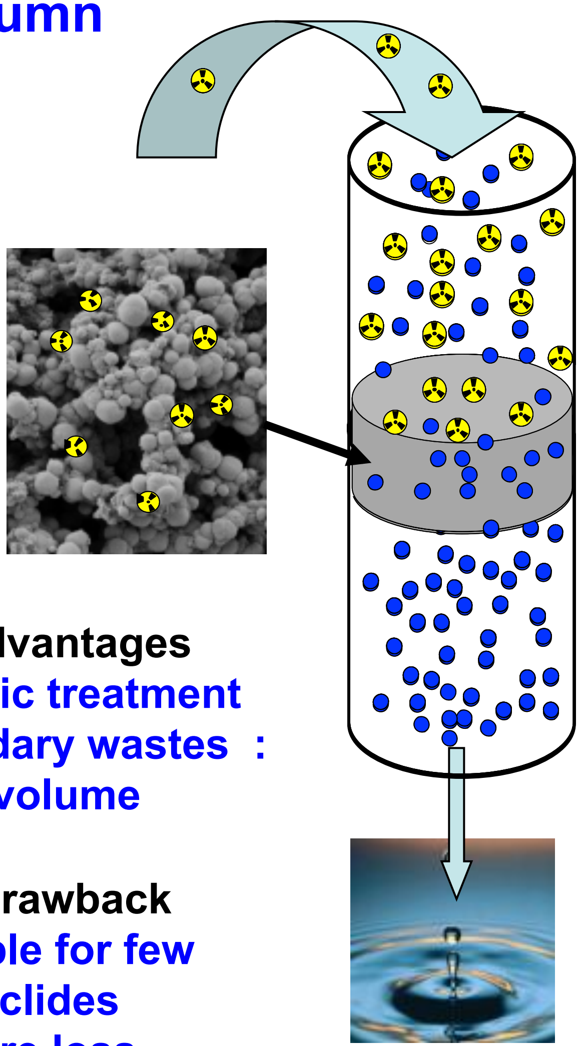
- **Decontamination or dismantling project.**
- **Incidental or accidental situation (like in Fukushima).**

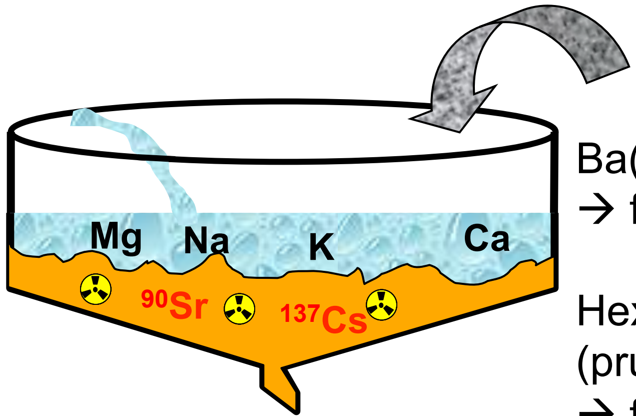
- **Research is carried out optimizing and , evaluating various processes :**
  - **Co-precipitation,**
  - **Ion exchange,**
  - Membrane separation,
  - Photocatalysis.

Ion exchange versus coprecipitation

Which process ?

Column **versus** **Bulk (coprecipitation)**





$Ba(NO_3)_2 + Na_2SO_4$
→ for Sr

Hexaferrocyanates
(prussian blue)
→ for Cs

Advantages

- **Dynamic treatment**
- **Secondary wastes : limited volume**

Drawback

- **Available for few radionuclides**
- **Pressure loss, pretreatment**

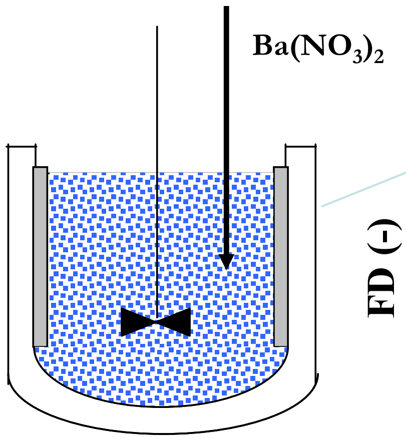
Advantages

- **Robust : can be applied to any type of aqueous effluents**
- **Easy to process**

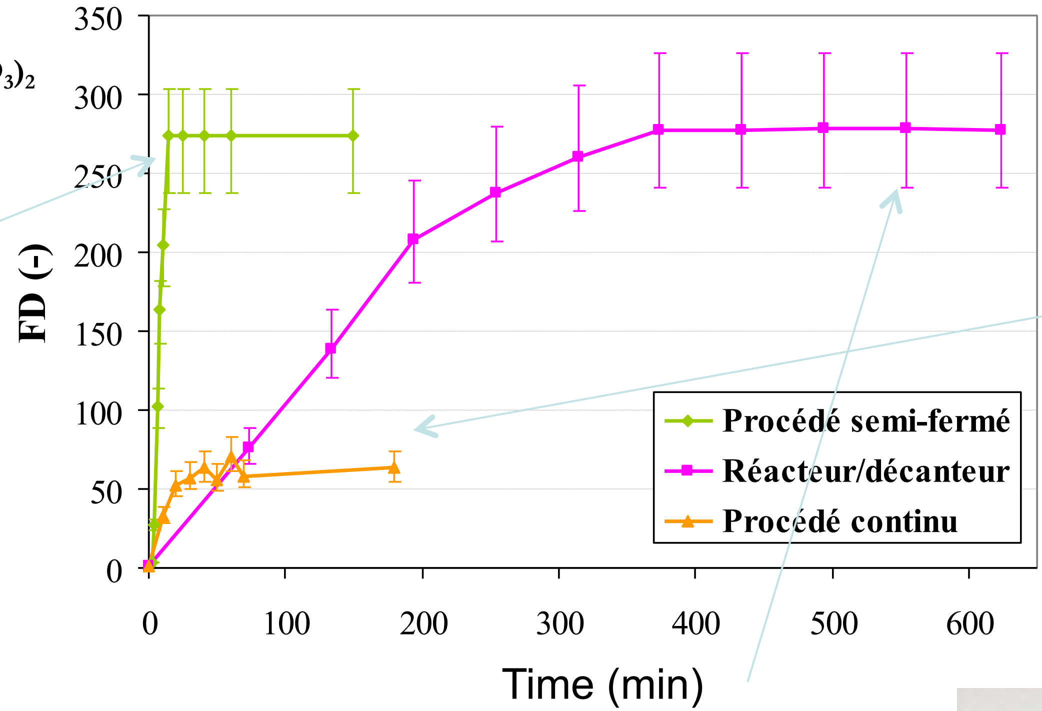
Drawback

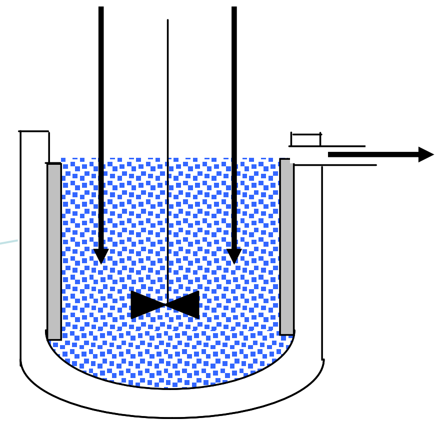
- **Production of large amount of sludge**

Efficiency of coprecipitation processes

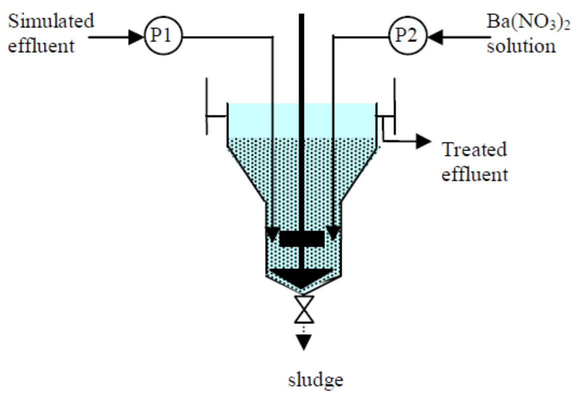


Batch reactor

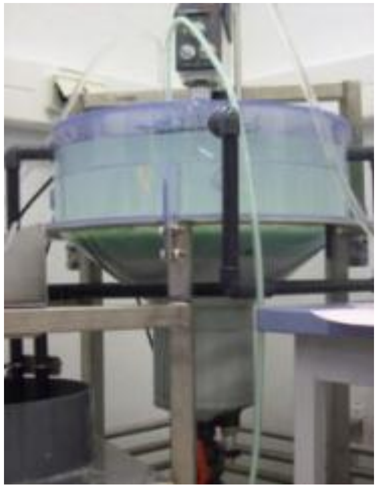




Continuous reactor



New reactor design

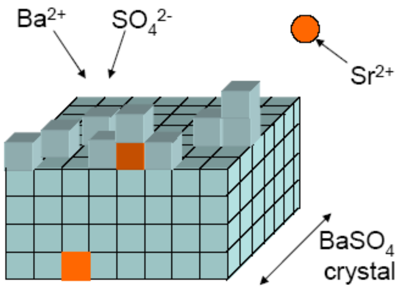


Optimization of coprecipitation process

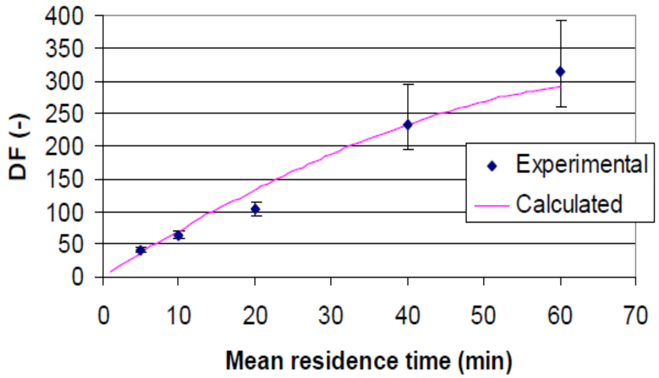
Goals

- **Achieve significant reactor size reduction**
- **Minimization of solid wastes**

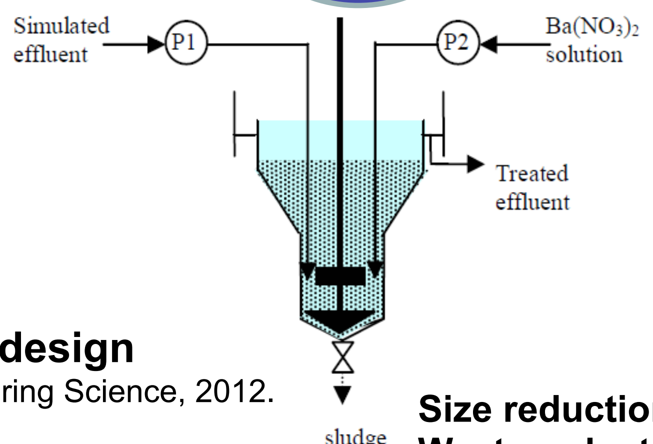
$$DF = \frac{T_E}{T} = 1 + \frac{6k\phi_V r_N G^3 \tau^4}{1 + \frac{3\phi_V kG}{k_d \phi_S}}$$



Modeling of crystallization-adsorption phenomenon
International Journal of Chemical Reactor Engineering, 2008. **6**: p. 17



Prediction of efficiency
Chemical Engineering Research & Design, 2010. **88**(9A): p. 1142-1147.



New reactor design
Chemical Engineering Science, 2012. **77**: p. 176-183.

Size reduction ~10
Waste reduction ~2

- **CHOICE OF THESE ADSORBANTS**

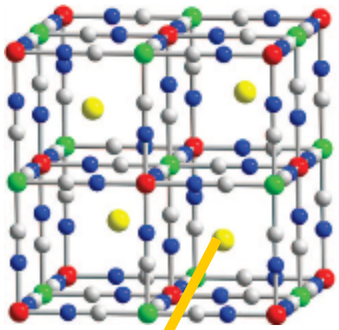
For

ADSORPTION/ION EXCHANGE PROCESSES:

« volume » adsoprtion by charge exchange

Specific for Cs:

Prussian Blue Analogous (PBA)



Exchange K⇔ Cs

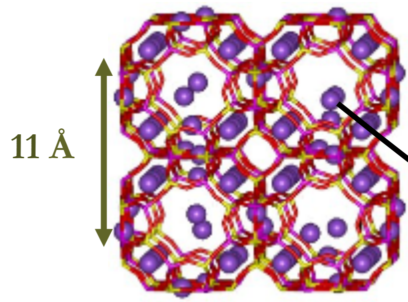
High selectivity towards other ions

Kd = 10^6 mL/g sea water enriched by ^{137}Cs

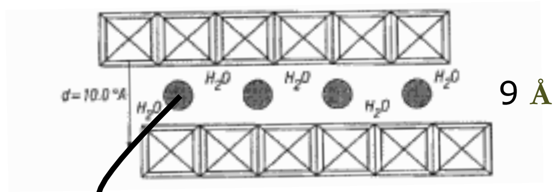
29000Bq/L → < 100Bq/L (with 1g/L of solid)

Specific forSr:

Zeolithe A



Titanate



Exchange $2Na^{+}$⇔ Sr^{2+}

High competition with Ca , Sr and Ba, especially in sea water

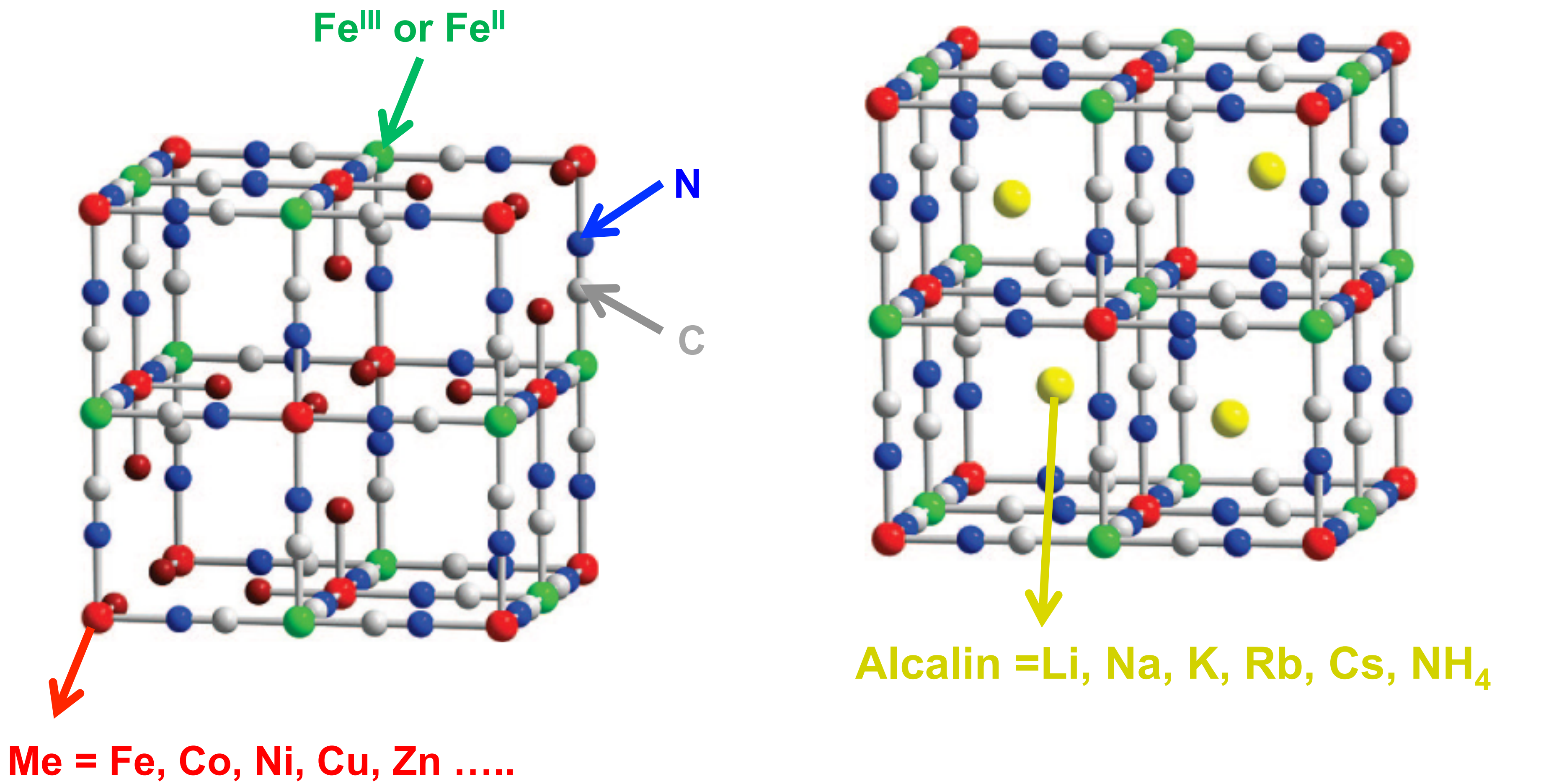
Ion exchange: sorption into the grain volume

- ⇔ Capacity linked to the echangeable ions
- ⇔ Irreversibility
- ⇔ High selectivity
- ⇔ Low kinetics (volume) -> nanostructuration to improve kinetics

Adsorption, (2011) 17, 967-975.
Separation and Purification Technology, 96 (2012), 81-88

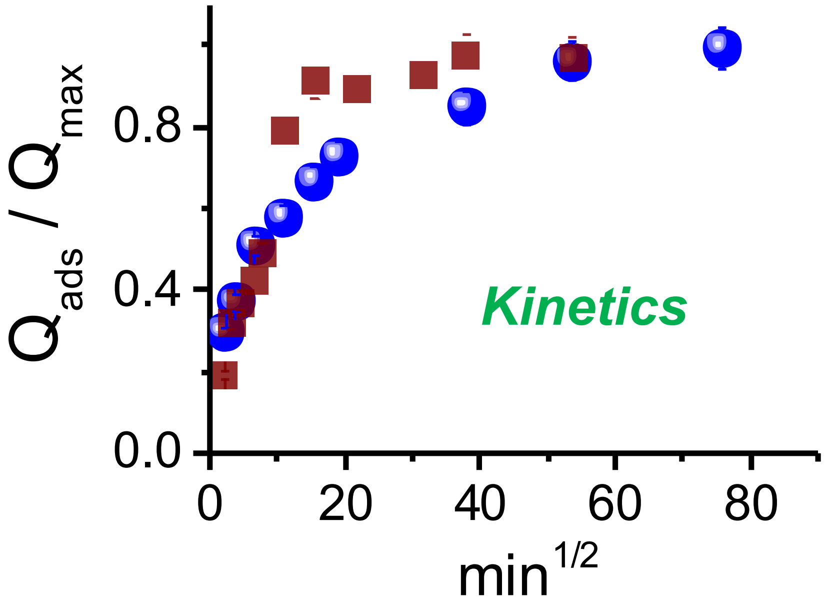
Prussian Blue Analogous

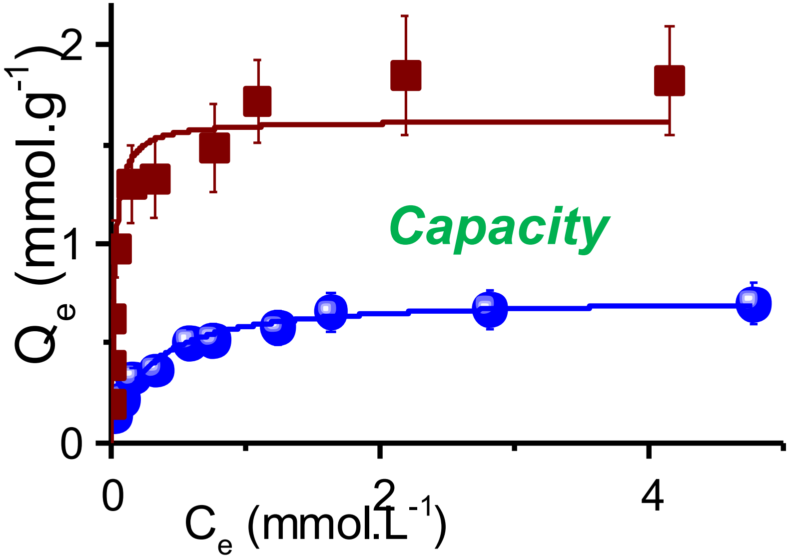
high selectivity for Cs



How to choose?

Sorption kinetics and exchange capacity of PBA





$Ni_3[Fe(CN)_6]_2$

Exchange Cs <-> Metal
+ insertion into the network

Slow kinetics
Low capacity

$K_2Ni[Fe(CN)_6]$

Exchange Cs <-> K

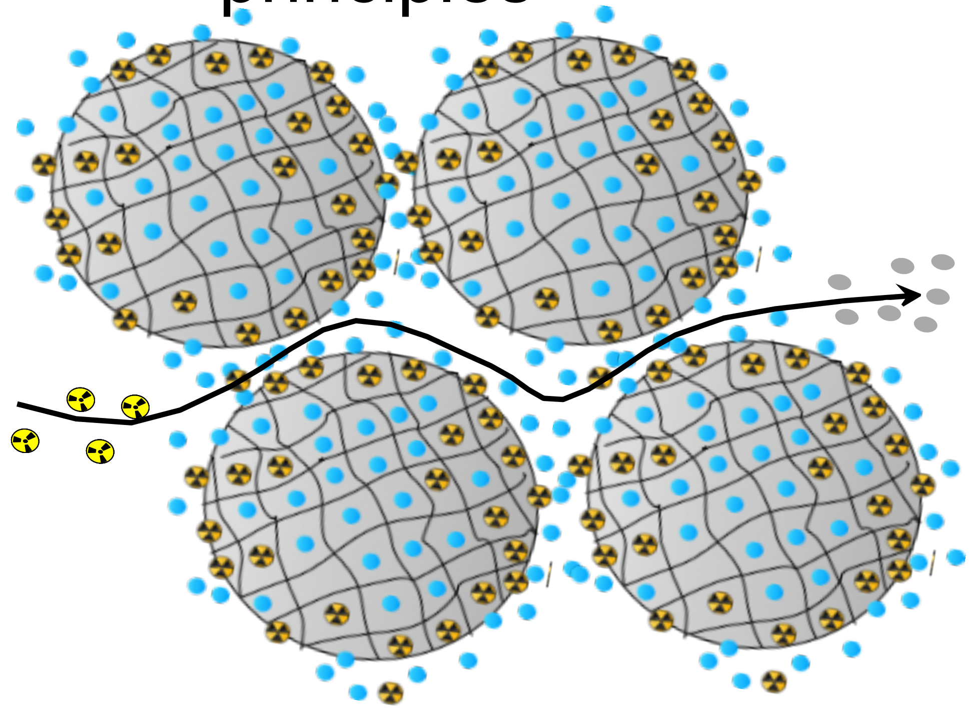
Fats kinetics
High capacity

Volume sorption : ion exchanges principles

Partial or total ion dehydration (of host ion from aqueous phase)

« Relatively » high adsorption energies

Closely linked to the presence or not of compete ions in the aqueous phase

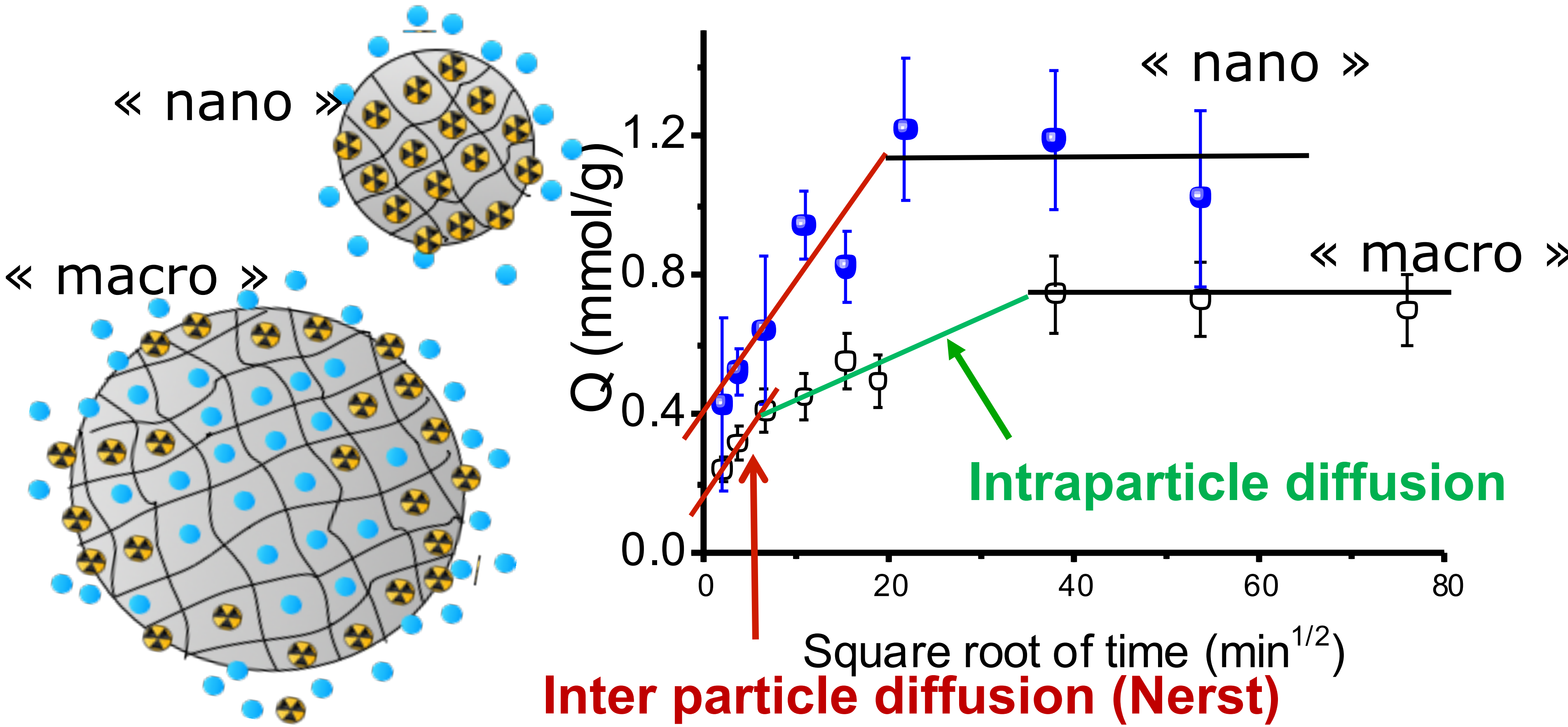


Slow mechanisms : diffusion betwen the sorbant particles (surface sorption, fast) + volume diffusion (linked to the grain size of the sorbant particles)

High selectivity: size of the « network cage » which matches well with the host ion to be extracted

« nano » effect

Nanostructuration : increase the sorption kinetics and increase the capacity because more exchangeable ion are accessible.



RSC Advances 2 (2012), 5707-5716
Chem. Mater, 25 (2013) 4447-4445
J. Materials Chemistry A, 2 (2014) 9461
Microporous Mesoporous Mater., 197 (2014) 83-91

Selectivity towards K (et Na): adsorption energy

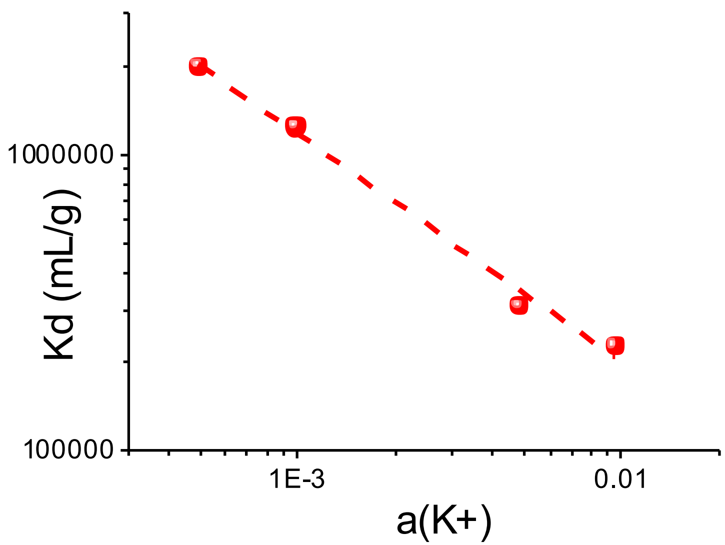
$$\overline{K^+} + {}^{137}Cs^+ \leftrightarrow K^+ + \overline{{}^{137}Cs^+}$$

$$K_{eq} = \frac{a(K^+).\overline{[Cs^+]}}{\overline{[K^+]}.a(Cs^+)}$$

In trace concentration (radioactif) $a(Cs^+) = [Cs^+]$
Activity coefficient of K^+ : Debye Hückel

$$Kd = \frac{\overline{[Cs]}}{[Cs]} = K_{eq} \cdot \frac{CEC}{a(K)}$$

$$\log Kd = cte - \log(a(K))$$



$$\Delta G^{K \rightarrow Cs}_{echange} = -RT \ln(K_{eq}) = -15 kJ/mol$$

See : « A tale of models » : E. Leontidis et al. (2009)

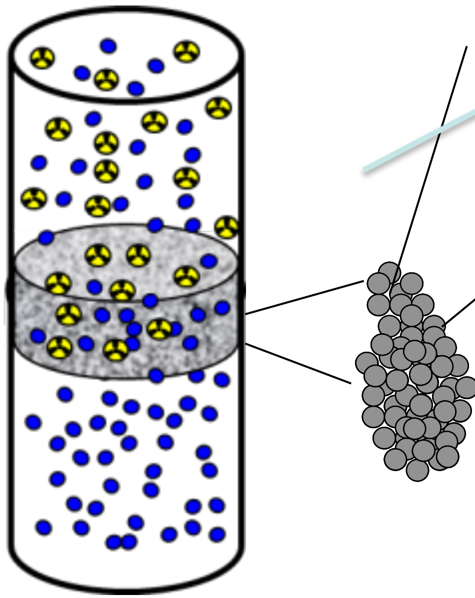
ADSORPTION/ION EXCHANGE PROCESSES:

3/ USAGE IN A FLOW PROCESS :

CONSTRAINTS AND EXAMPLES

3/ USAGE IN A FLOW PROCESS :

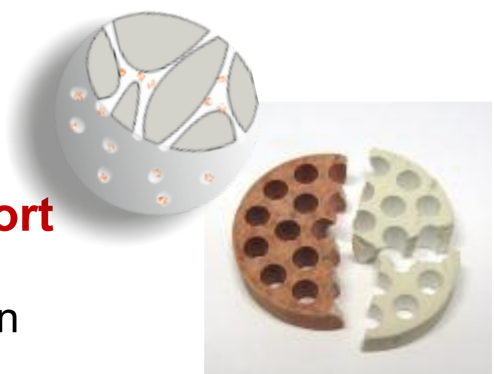
Process used



Powder sorbent?

- Grain size must be high enough to avoid drop pressure
- Mechanical behaviour?
- Ultimate waste?

insertion of sorbent nanoparticles onto a support designed for the in-flow process chosen



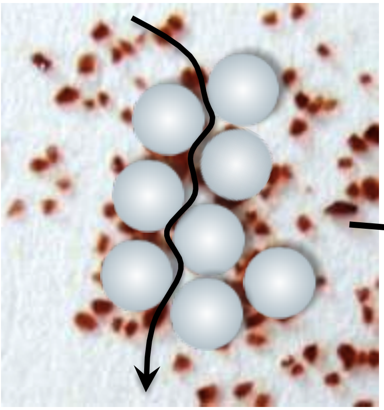
Shape and nature of the support

-Grains : glass pearls, silica gel…
-Membranes : filtration and extraction

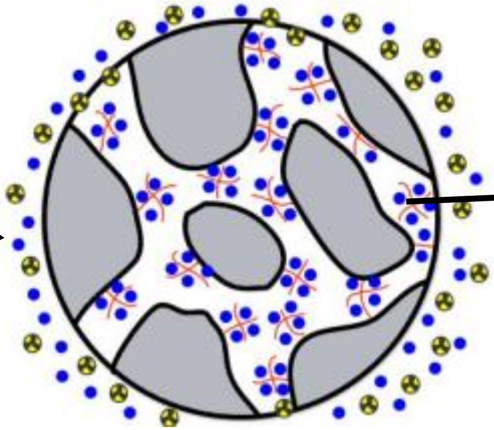
Inorganic porous support loaded with PBA

INTERFACES : multiscale diffusion and transport

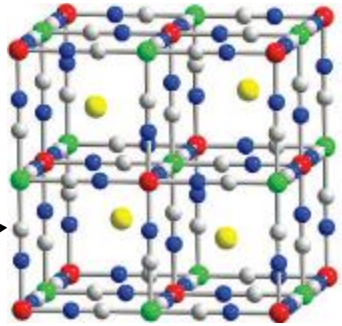
Example : support : porous silica grain (column process)



Macroscopic scale :
Grain size scale
(~ 500µm for column process or ~ 50µm for fluidized bed process)



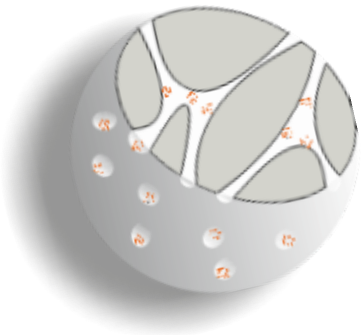
Mesoscopic scale :
Porosity scale
(10-30 nm)



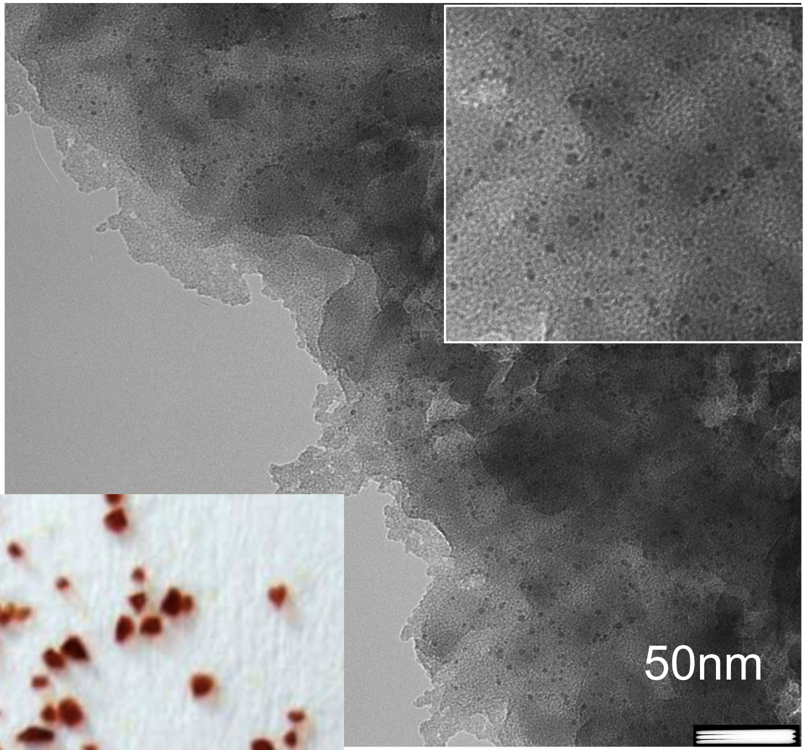
Nanoscopique scale:
Adsorbent scale (extractant « function »)
(<1nm)

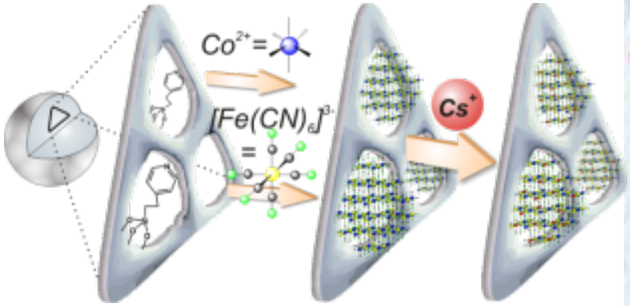
RSC Advances 2 (2012), 5707-5716
Microporous Mesoporous Mater., 197 (2014) 83-91

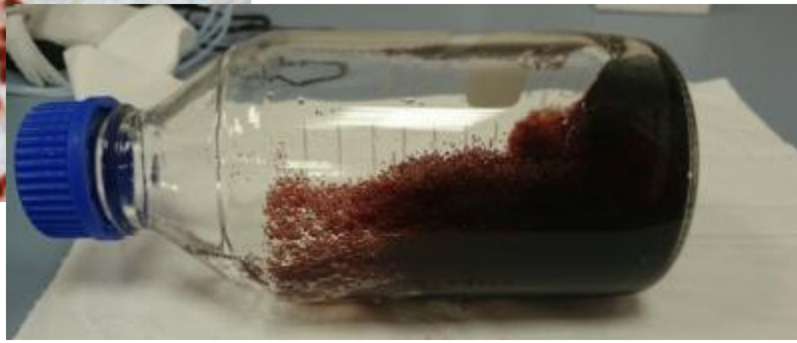
Example : synthesis of a nanocomposite of Prussian Blue and its analogs

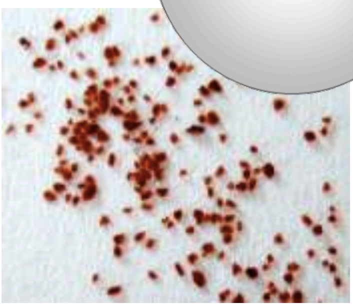


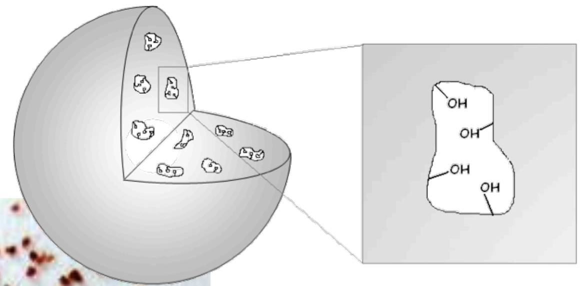
Porous glass beads
Ø = 300 to 500 µm
Pores = 30 nm



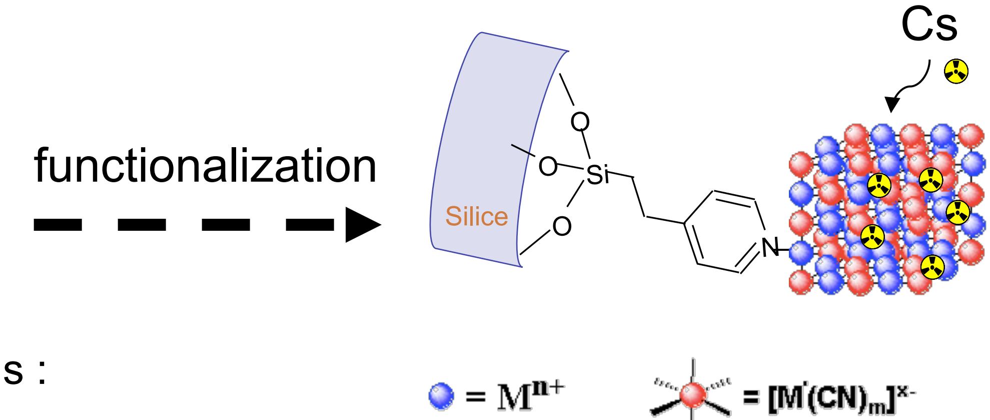








Porous glass beads :
Ø = 200 to 300µm
Pores = 30 nm



Prussian Blue Analogous

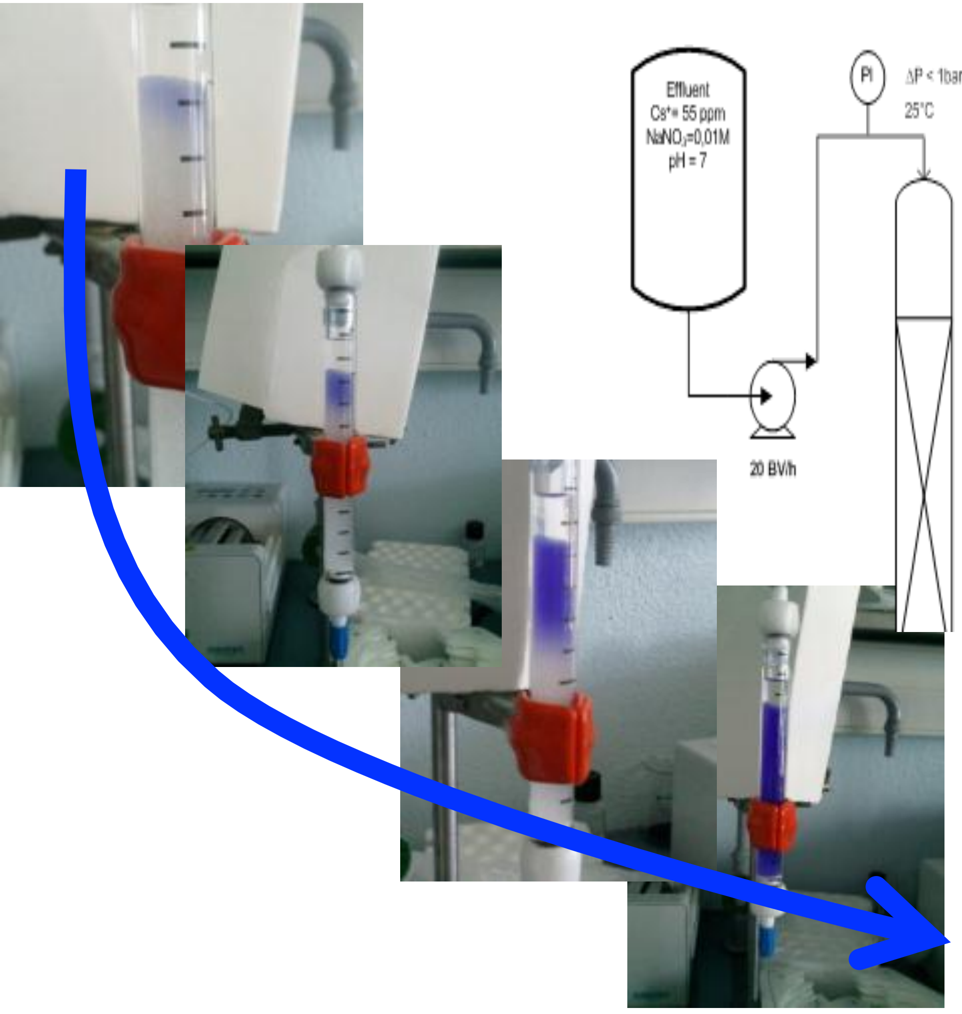
RSC Advances, 2 (2012), 5707-5716
Patent FR 2945756, *WO2010133689 A2 20101125*

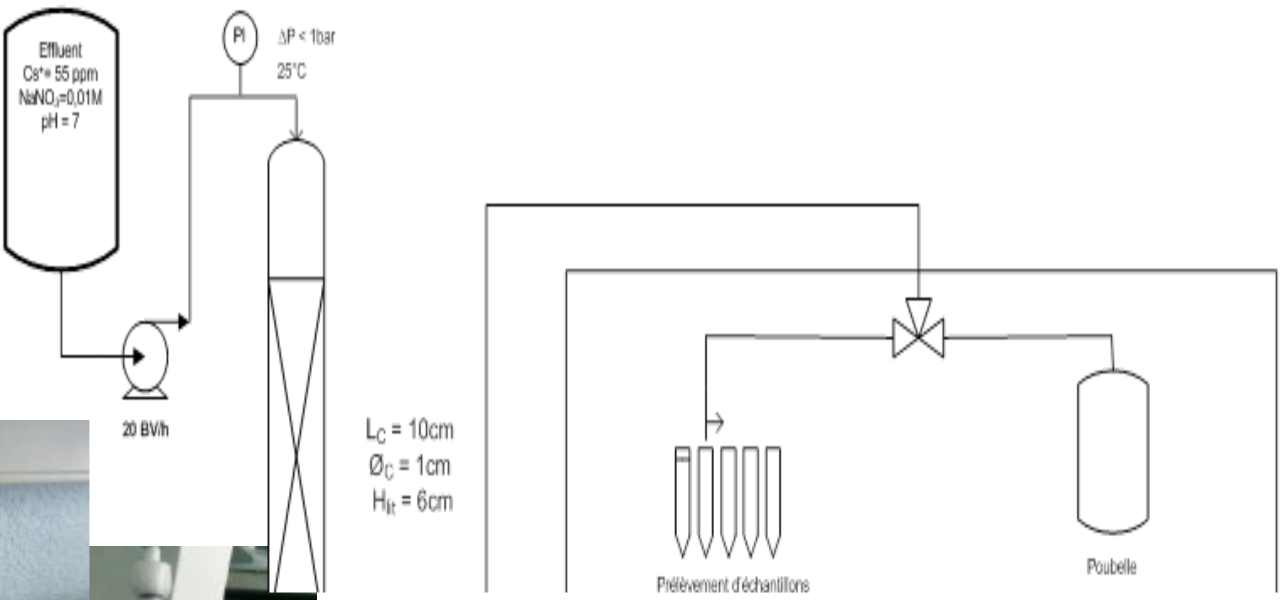
Real test with sea water (Na/CS competition) : « Fukushima »
FD= 180 with 0.5g of solid and 1L of contaminated water ^{137}Cs (29000Bq/L → 160Bq/L)

Sorbent	K_d (sea water Cs 10 ppm) $mL.g^{-1}$	K_d (radioactive sea water Cs 29 $kBq.L^{-1}$) $mL.g^{-1}$
CoFC bulk	$>10^4$ *	$6 \cdot 10^5$
Nanocomposite 1	**$>10^4$ ***	**$8 \cdot 10^5$**
Nanocomposite 2	**10^3**	**$3 \cdot 10^5$**

Similar K_d: capacity of new material is close to coprecipitated ferrocyanates

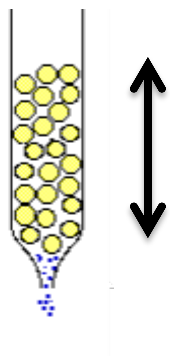
column loading : breakthrough curves





Optimizing column process

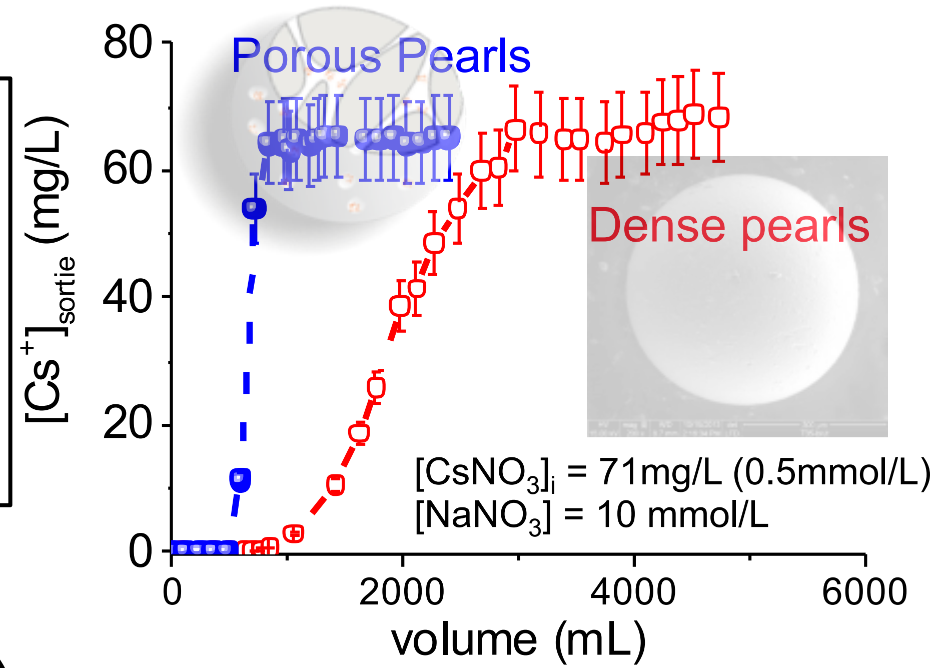
V = 3.9mL



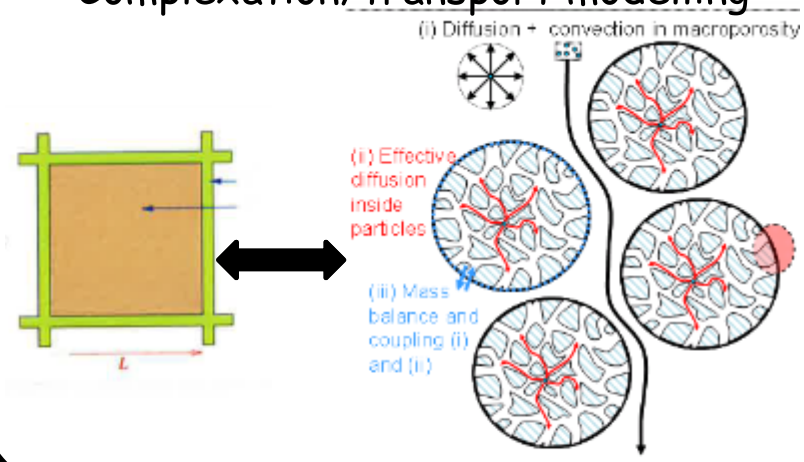
With Kd=10^6ml/g,

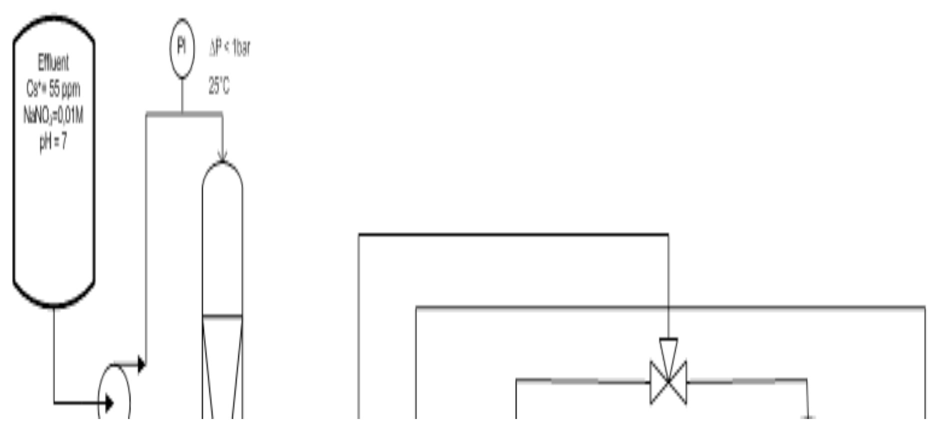
$2m^3$ of effluentcan be treated with a column of 4mL

Flow rate up to 0.4L/h

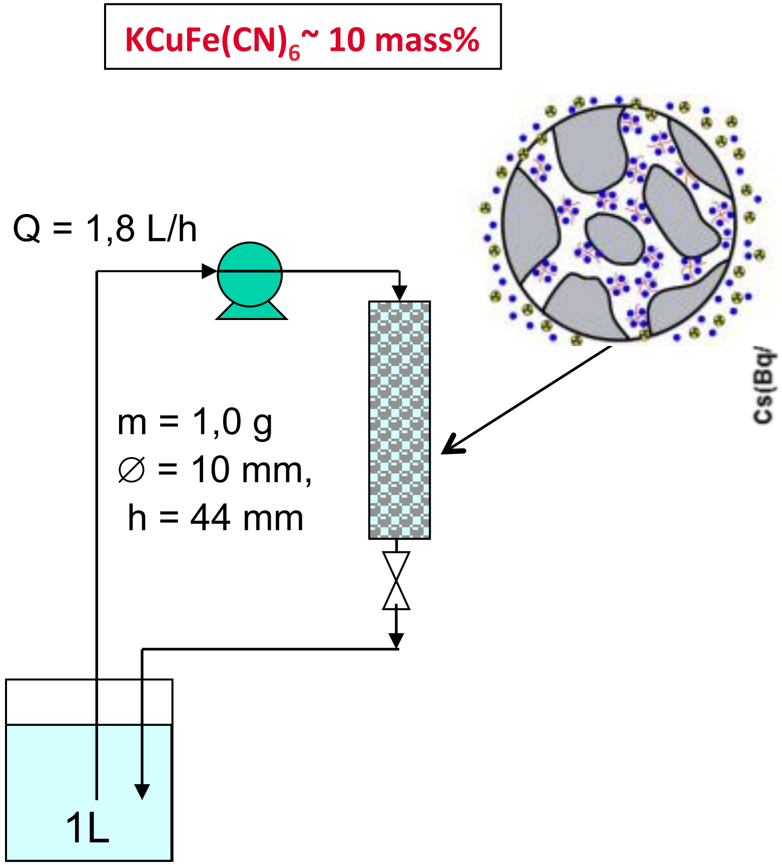


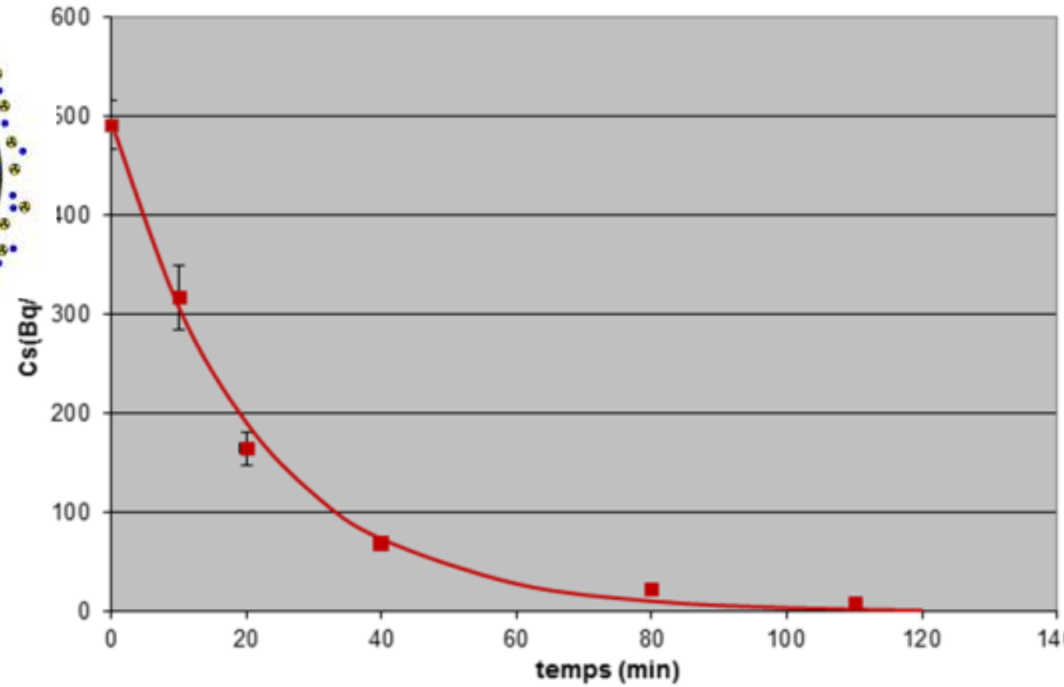
Complexation/transport modelling





Serial re-processing in "closed circuit" mode





$^{137}Cs < 5$ Bq/L

Contaminated seawater :
$^{137}Cs = 500$ Bq/L

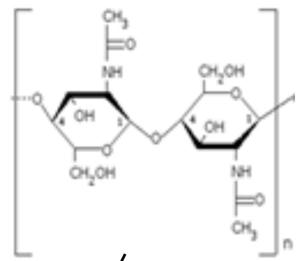
Faisibility to treat about 20m^3 of contaminated sea water (FD=10) in about 16h

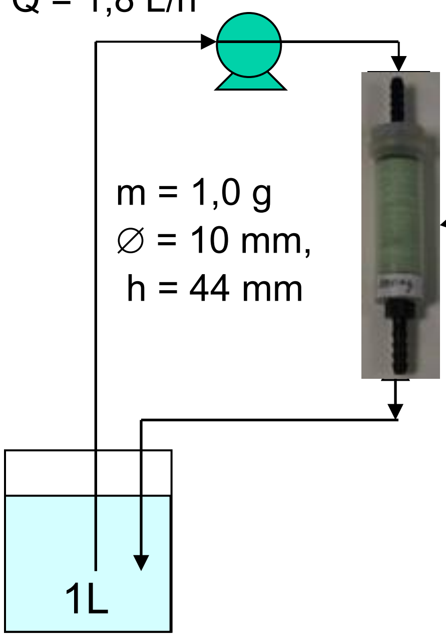
Column process in "close circuit" mode

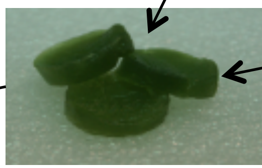
Immobilization of Ni-K ferrocyanide in porous discs of chitin

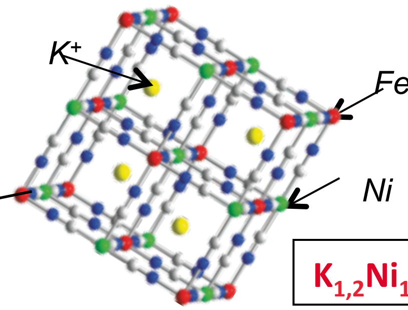
J. Mat. Chem. A, 2 (2014), 10007-10021
Chem. Eng. J., 236 (2014), 202-211

Polysaccharide biopolymer : chitin



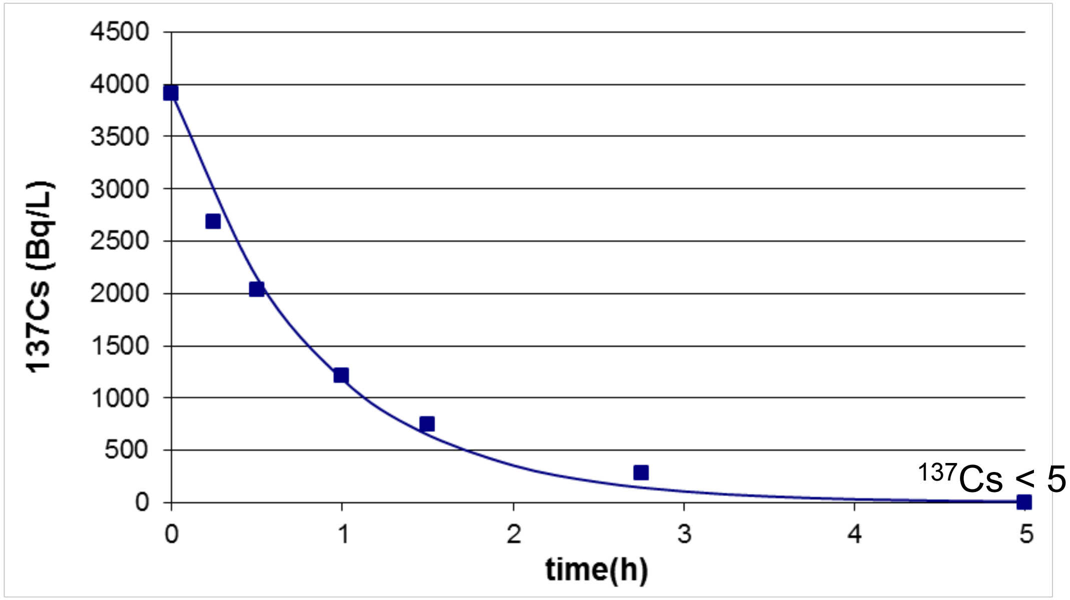






$K_{1,2}Ni_{1,2}Fe(CN)_6$ ~ 50 mass%

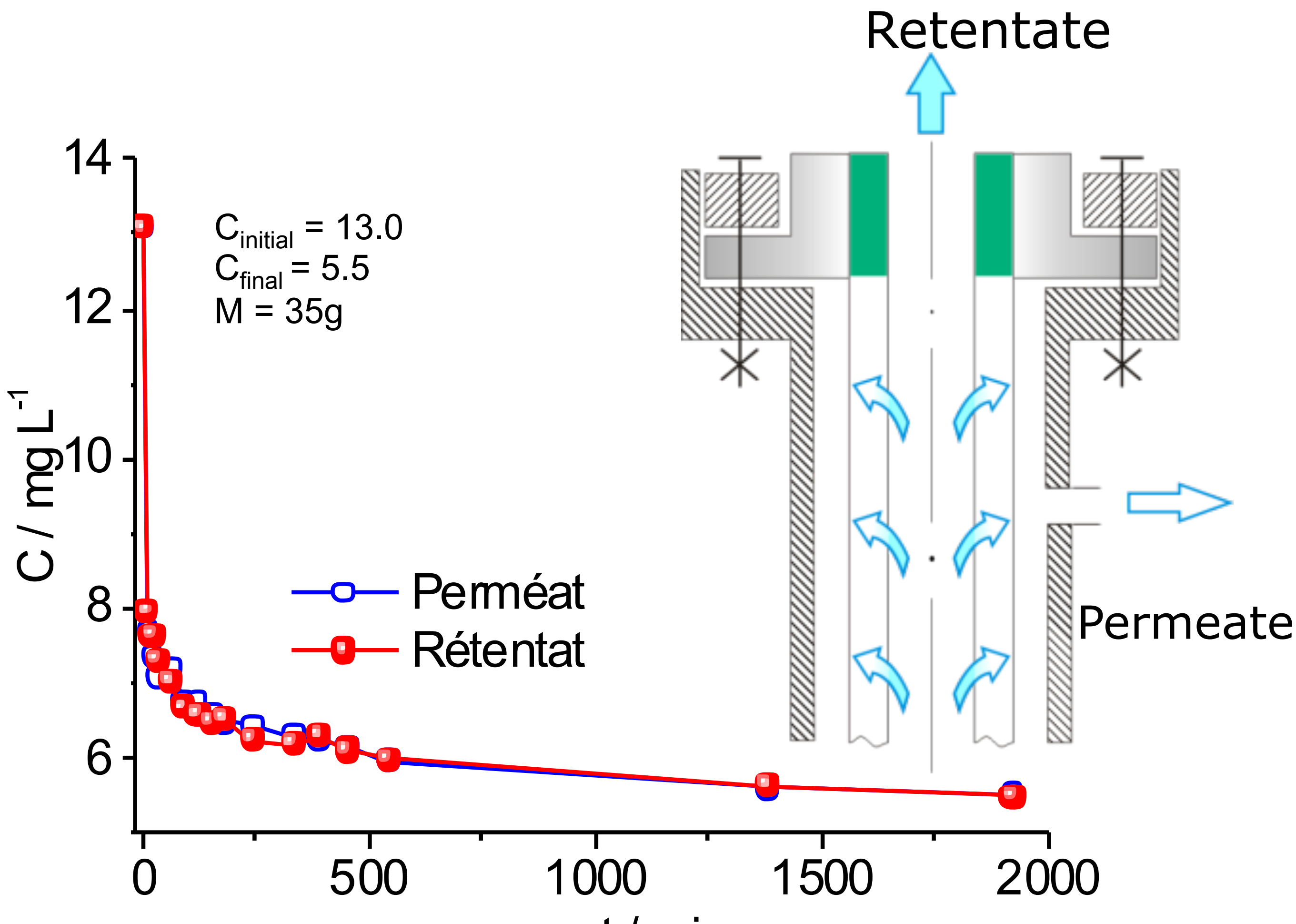
Contaminated seawater :
^{137}Cs = 4000 Bq/L



…..Using porous membranes

Inorganic membrane loaded with PBA : filtration + adsorption

Collaboration CTI/OTND/CNRS [Brevet CEA-CTI-CNRS-UM2]



Meso-scale basis of the decontamination by ion exchange in colloids/nanoparticles

Ion exchange/adsorption Na/Cs competition on the surface of a nanopartivle colloid

… diffusion inside a nanoparticle: « loading »

.. Combining fluid transport and non electrostatic effects

Scientific basis :

Ions interacting charged interfaces

-seen from the surface : surface charge regulation

-seen from the ion: dehydraion competing with surface complexation: equilibrium between ions in the bilk and ions adsorbed at the interface