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

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An intrinsic multi-scale approach:
Aqueous effluents decontamination

Pretreatment (membrane processes, oxydation advanced processes)

Specific chemical treatment (co-precipitation, innovative adsorbants)

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

Effluent simplification

Reduce the radioactivity

« zero reject »

1/ CONTEXT AND METHODOLOGY

EFFLUENTS PRODUCTION

WASTES

RECYCLING
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

Advantages
- Dynamic treatment
- Secondary wastes: limited volume

Drawback
- Available for few radionuclides
- Pressure loss, pretreatment

Bulk (coprecipitation)

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

Drawback
- Production of large amount of sludge

Ba(NO₃)₂ + Na₂SO₄ → for Sr

Hexaferrocyanates (prussian blue) → for Cs
Efficiency of coprecipitation processes

Batch reactor

Ba(NO₃)₂

Continuous reactor

Time (min)

Efficiency of coprecipitation processes

Procédé semi-fermé

Réacteur/décanteur

Procédé continu

New reactor design
Optimization of coprecipitation process

Goals

• Achieve significant reactor size reduction
• Minimization of solid wastes

Modeling of crystallization-adsorption phenomenon

Prediction of efficiency

New reactor design

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

Size reduction ~10
Waste reduction ~2
2/ INTRINSIC PROPERTIES OF ADSORBANT

➢ CHOICE OF THESE ADSORBANTS
For
ADSORPTION/ION EXCHANGE PROCESSES:
Specific for Cs:
Prussian Blue Analogous (PBA)

Specific for Sr:
Zeolithe A

Titanate

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

Ion exchange: sorption into the grain volume

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

Exchange $K \equiv Cs$

High selectivity towards other ions

$K_d = 10^6 \text{ mL/g sea water enriched by } ^{137}\text{Cs} \ 
29000 \text{Bq/L} \rightarrow < 100 \text{Bq/L} \ (\text{with 1g/L of solid})$

Exchange $2Na^+ \Leftrightarrow Sr^{2+}$

Adsorption, (2011) 17, 967-975.
Separation and Purification Technology, 96 (2012), 81-88
Prussian Blue Analogous
high selectivity for Cs

Me = Fe, Co, Ni, Cu, Zn .....  

Fe$^{III}$ or Fe$^{II}$

Alcalin = Li, Na, K, Rb, Cs, NH$_4$

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$_2$Ni[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 between 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
2/ ADSORBANT PROPERTIES

« nano » effect

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

Intraparticle diffusion

Inter particle diffusion (Nerst)

Square root of time (min$^{1/2}$)

Q (mmol/g)
Selectivity towards K (et Na): adsorption energy

\[
K^+ + ^{137}Cs^+ \rightleftharpoons K^+ + ^{137}Cs^+
\]

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

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

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

\[
\log K_d = cte - \log(a(K))
\]

\[
\Delta G_{\text{exchange}}^{K \rightarrow Cs} = -RT \ln(K_{eq}) = -15kJ / mol
\]

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

Shape and nature of the support
- Grains: glass pearls, silica gel...
- Membranes: filtration and extraction

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
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)

Nanoscopic 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
**Grafted glass beads - Sorption of $^{137}$Cs from seawater**

**Porous glass beads:**
- $\varnothing = 200$ to 300$\mu$m
- Pores $= 30$ nm

**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 $\rightarrow$ 160Bq/L)

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>$K_d$ (sea water Cs 10 ppm) mL.g$^{-1}$</th>
<th>$K_d$ (radioactive sea water Cs 29 kBq.L$^{-1}$) mL.g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFC bulk</td>
<td>$&gt;10^4$ *</td>
<td>6$\cdot10^5$</td>
</tr>
<tr>
<td>Nanocomposite 1</td>
<td>$&gt;10^4$ *</td>
<td>8$\cdot10^5$</td>
</tr>
<tr>
<td>Nanocomposite 2</td>
<td>$10^3$</td>
<td>3$\cdot10^5$</td>
</tr>
</tbody>
</table>

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

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*Prussian Blue Analogous*

RSC Advances, 2 (2012), 5707-5716
Patent FR 2945756, WO2010133689 A2 20101125
column loading: breakthrough curves
V = 3.9mL

With Kd=10^6ml/g,

2m³ of effluent can be treated with a column of 4mL

Flow rate up to 0.4L/h

[Cs⁺]_{sortie} (mg/L)

[CsNO₃]_i = 71mg/L (0.5mmol/L)
[NaNO₃] = 10 mmol/L

Flow rate up to 0.4L/h

Complexation/transport modelling

Effluent

Flow rate up to 0.4L/h

Optimizing column process
Serial re-processing in "closed circuit" mode

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

- $m = 1.0 \text{ g}$
- $\varnothing = 10 \text{ mm}$
- $h = 44 \text{ mm}$

$Q = 1.8 \text{ L/h}$

$K\text{CuFe(CN)}_6 \sim 10 \text{ mass\%}$

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

Faisibility to treat about $20 \text{ m}^3$ of contaminated sea water (FD=10) in about 16h
Contaminated seawater: $^{137}\text{Cs} = 4000 \text{ Bq/L}$

$m = 1.0 \text{ g}$
$\varnothing = 10 \text{ mm}$,
$h = 44 \text{ mm}$

$Q = 1.8 \text{ L/h}$

Column process in “close circuit” mode

Immobilization of Ni-K ferrocyanide in porous discs of chitin

$\text{K}_{1,2}\text{Ni}_{1,2}\text{Fe(CN)}_6 \sim 50 \text{ mass%}$

Polysaccharide biopolymer: chitin

$J. \text{Mat. Chem. A, 2 (2014), 10007-10021}$
$Chem. \text{Eng. J., 236 (2014), 202-211}$

Using a biopolymer as support for active colloids
Inorganic membrane loaded with PBA : filtration + adsorption

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

Using porous membranes

\[ C_{\text{initial}} = 13.0 \]
\[ C_{\text{final}} = 5.5 \]
\[ M = 35 \text{g} \]
Meso-scale basis of the decontamination by ion exchange in colloids/nanoparticles

Ion exchange/adsorption Na/Cs competition on the surface of a nanoparticle 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: dehydration competing with surface complexation: equilibrium between ions in the bulk and ions adsorbed at the interface