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DE LA RECHERCHE À L'INDUSTRIE
cea

Design of optimised chelating agents for cesium extraction in supercritical CO_2

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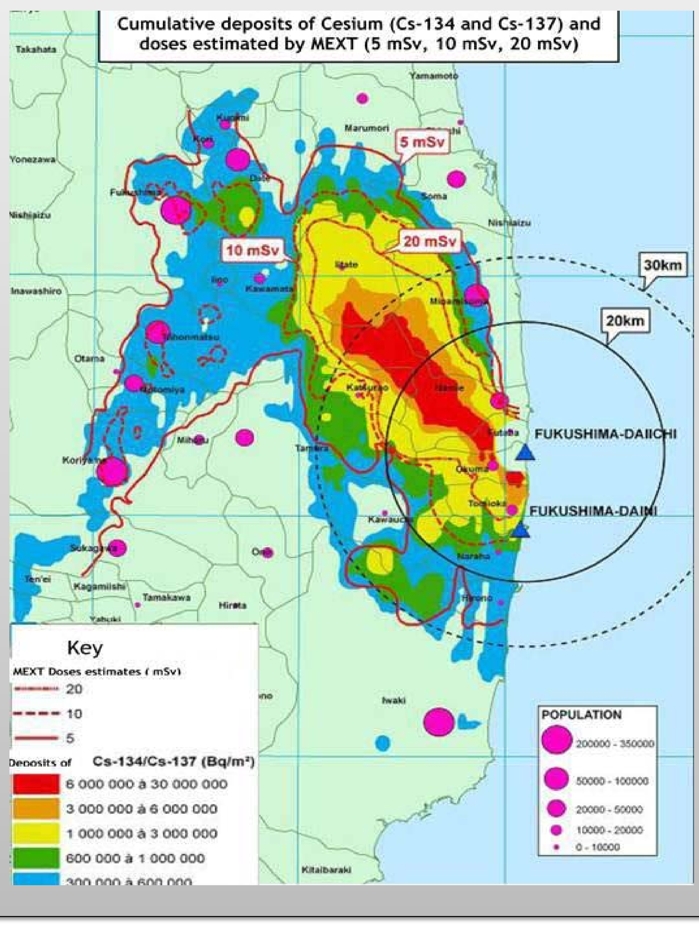
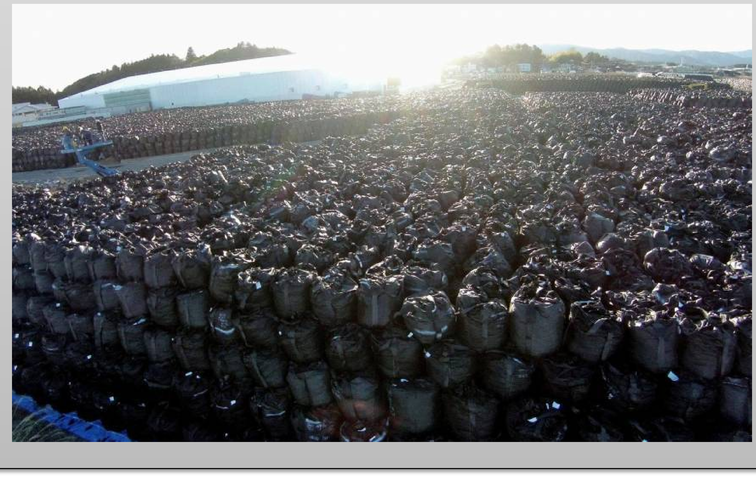
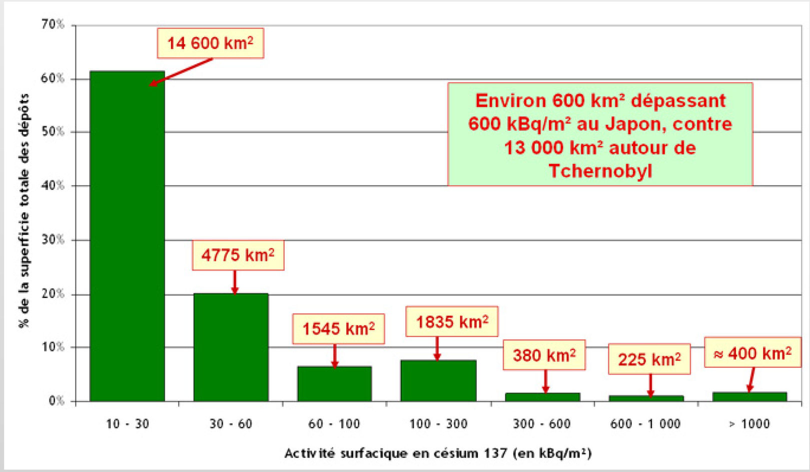


Context: In March 2011, the earthquake and subsequent tsunami resulted in severe damage of the Fukushima-Daiichi Nuclear Power Plant. This accident led to the release of large quantities of radioactivity, mainly the volatile fission products such as cesium (estimated around 15 PBq of ^{137}Cs). The presence of ^{137}Cs in the natural environment is a radiological concern as it causes significant external and internal radiation exposures of living beings.





Area of the territories received cesium 137 deposits in the accident of Fukushima Daiichi (IRSN)

Unique features of contamination:

- Processing volumes outsized
- Unusual substrates
- Spatial heterogeneity of contamination

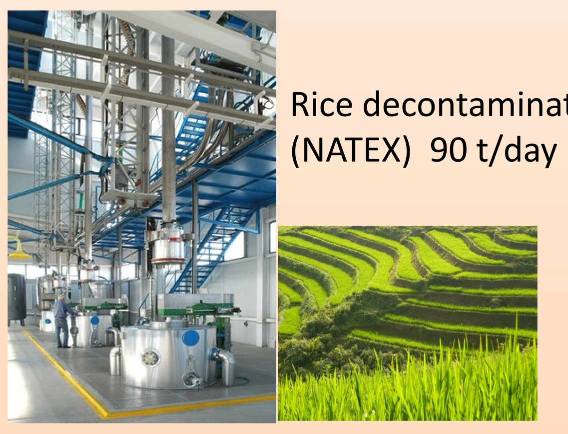
In this context, **developing new green processes** for the extraction of **cesium** to clean up contaminated soil remains a major challenge for the nuclear industry:

- ✓ by restoring sustainable agricultural land
- ✓ by reducing population exposure
- ✓ by limiting the residual waste

DEMETERRES

= **DE**veloppement de **M**éthodes bio- et **E**co-**T**echnologiques pour la **R**emédiation **R**aisonnée des **E**ffluents et des **S**ols contaminés

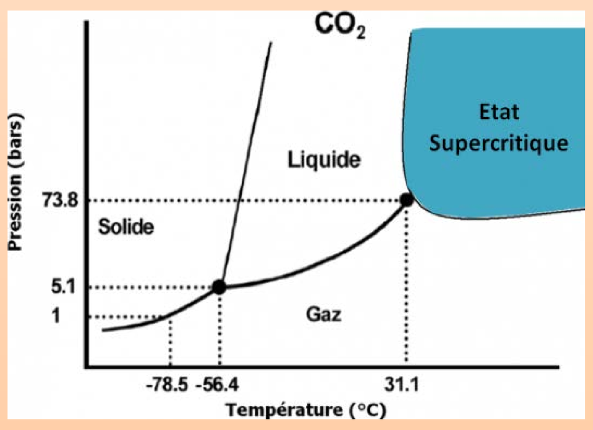
Supercritical CO_2 – a solvent like no other:



Rice decontamination (NATEX) 90 t/year

Cap taste extraction (DIAM Bouchage) 5000 t/year

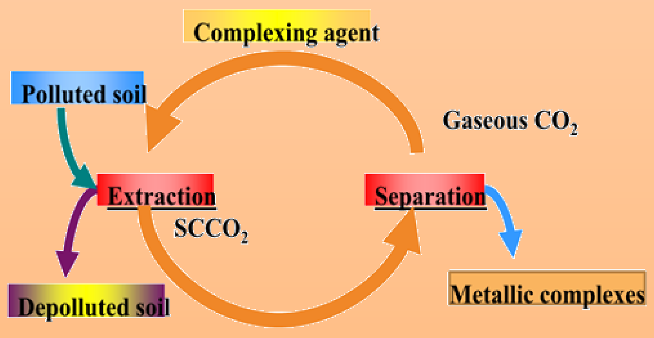
Mature technology



- Easily accessible supercritical properties
- Easy tuning of solvent properties by adjusting P and T (density, viscosity, ..)
- Abundant, non toxic, non inflammable
- No solvent waste, green solvent
- Difficult solubilisation of polar compounds
- pH = 2.9 in presence of water

Interesting alternative to classic diluents used in liquid/liquid extraction

- ✓ Direct extraction of organic molecules
- ✓ Inefficient direct extraction of metal ions

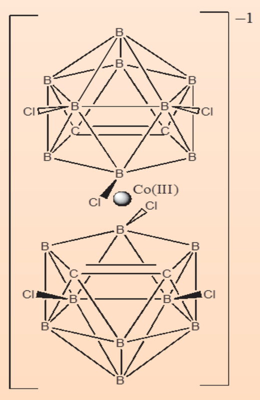


Introduction of an organic chelating agent (extractant):

- soluble in sc CO_2
- formation of a stable complex
- Efficient at pH = 2.9

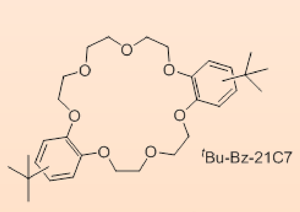
The efficiency of a supercritical CO_2 metal extraction process depends on the extractant efficiency

Which chelating agents for cesium extraction?



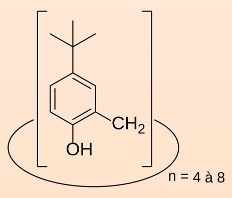
Dicarbollide

- Interact with M^+ through ion-pairing
- Good extraction of cesium
- Moderate selectivity (vs Na, K)



Crown-Ether

- Extraction mechanism: solvatation
- Selectivity dependent of macrocycle size
- Good extraction of cesium
- Moderate selectivity (vs Na, K)

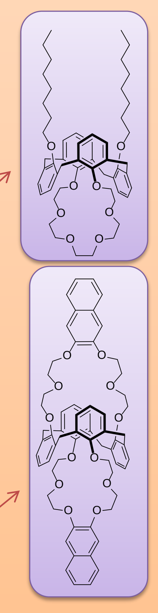


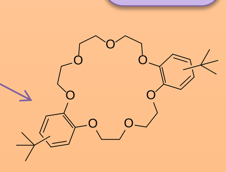
Calix[n]arene

- Extraction mechanism: solvatation
- Selectivity based on macrocycle size
- **Excellent extraction** of cesium with functionalised calix[4]arene

Compounds	D_{Na}	D_{Cs}	α(Cs/Na)
Calix[4] arene dimethoxy-crown-6	3 × 10^{-3}	4 × 10^{-2}	
Calix[4] arene hydroxy-ethoxy-crown-6	4 × 10^{-3}	4.2	> 4200
Calix[4] arene dipropoxy-crown-6	2 × 10^{-3}	19.5	9750
Calix[4] arene diisopropoxy-crown-6	< 10^{-3}	28.5	> 28500
Calix[4] arene di-*n*-octyloxy-crown-6	< 10^{-3}	33	> 33000
Calix[4] arene di-*n*-octyloxy-(dibenzo-crown-6)	< 10^{-3}	31	> 31000
Calix[4] arene dimethoxy-crown-7	4 × 10^{-3}	7 × 10^{-3}	
Calix[4] arene *bis*-crown-5	2 × 10^{-3}	0.4	
Calix[4] arene *bis*-crown-6	1.3 × 10^{-2}	19.5	1500
Calix[4] arene *bis*-crown-7	< 10^{-3}	0.3	–
Calix[4] arene *bis*-*p*-benzo-crown-6	< 10^{-3}	2 × 10^{-2}	–
Calix[4] arene *bis*-*o*-benzo-crown 6	1.7 × 10^{-3}	32.5	19000
Calix[4] arene *bis*-(dibenzocrown-6)	< 10^{-3}	23	> 23000
Calix[4] arene *bis*-naphthyl-crown 6	< 10^{-3}	29.5>	> 29000
Calix[4] arene *bis*-diphenyl-crown-6	< 10^{-3}	7 × 10^{-2}	–
n-decylbenzo-21-crown-7	1.2 × 10^{-3}	0.3	250
Tert-butylbenzo-21-crown-7	1.2 × 10^{-3}	0.3	250

Aqueous feed solution: MNO_3 5 × 10^{-4} M; HNO_3 1 M.
Organic solution: 10^{-2} M extractant in 1,2-nitrophenylhexylether (o/a = 1; t = 25°C)
(Dozol, *J Incl Phenom Macro* **2000**, 38, 1-22)





Calix[n]arene

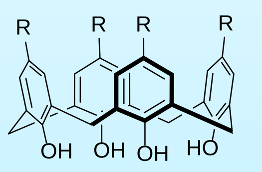
- Stable under strong acidic, basic or irradiating conditions
- Excellent extraction of Cs
- Good selectivity (vs Na)
- Poorly soluble in sc CO_2

Molecular characteristic for a « CO_2-philic » function:

- ✓ Weak self-interactions
- ✓ Specific interactions with CO_2 (LH, AL/BL)
- ✓ High flexibility with high free volume.

Beckman, E. J. *Chem. Comm.* **2004,** 17, 1885.

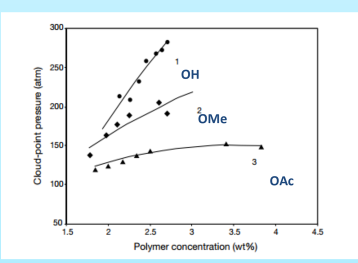
Fluorous functions



Glennon, J. D. *Analytical Chem.* **1997**, 69, 2207.

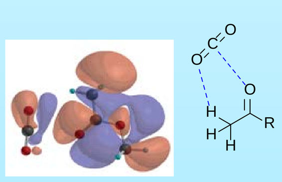
R	Solubility (60°C, 200 bar)
t-butyl	0.62 mmol/L
$(CH_2)_3$-S-$(CH_2)_2$-$(CF_2)_7$-CF_3	> 120 mmol/L

Oxygenated functions



poly(propylene glycol) diol (curve 1)
poly(propylene glycol) monobutyl ether (curve 2)
poly(propylene glycol) acetate (curve 3)
each with 31 repeat units at 22°C in CO_2 sc.

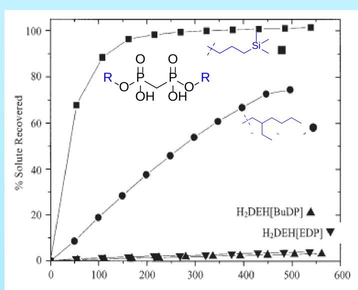
Beckman, E. J. *Nature* **2000,** 405, 165.



The HOMO for the optimized geometry of the CO_2-methyl acetate complex . The C-H…O hydrogen bond acts cooperatively with the LA-LB interaction (CO_2-carbonyl) introducing further stabilization.

S. L. Wallen, *J. Am. Chem. Soc*, **2002**, 124, 7274

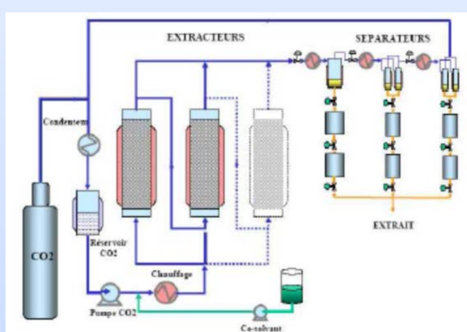
Silyl functions

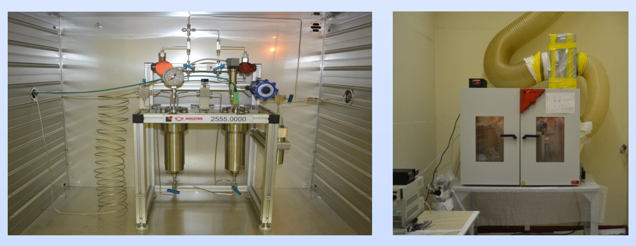


% recovery of extractant from glass beads at 250 bar, 60°C

Alister, D. R. *Sep. Sci. Technol.* **2004**, 39, 761.

First experimental results using sc CO_2: solubility and assays on contaminated soil





Experimental device

Determination of the chelating agent solubility by dynamic gravimetric measurement

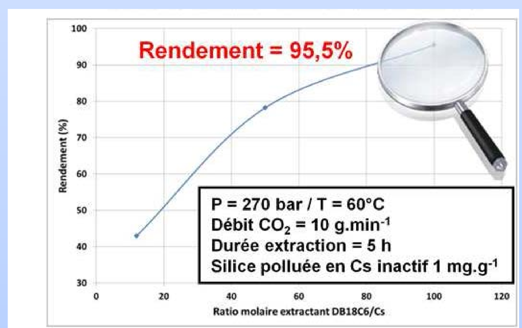
Chelating agent	Solubility (40°C, 270 bar)
DB21C7	5.3 +/- 0.6 10^{-4} g/L
4-tbu-calix[4]arene	0.7 +/- 0.6 10^{-4} g/L

Solvating Extraction Mechanism

⇓

Need of an acid counter ion to extract a stable complex from the solid matrix.

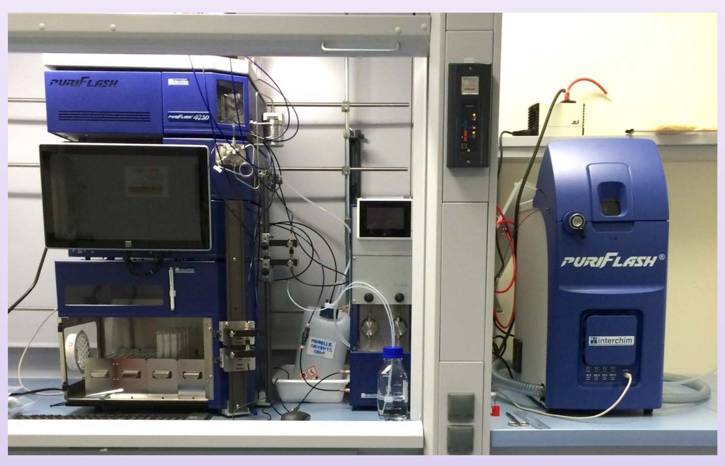
Cs + calix + HA = [Cs(calix)A] = H



sc CO_2 process using silica as model soil

Limitation: Weak solubility of the extracted complex in sc CO_2
Feasability of the process demonstrated on silica
Need of innovative cesium chelating agents optimised for the sc CO_2 extraction!

Objective:



Puri Flash coupled with MS

DESIGN, SYNTHESIS and EVALUATION of new Cs-selective extractants efficient in the sc CO_2 process

by coupling the results obtained in SX experiments for the extraction of cesium with sc CO_2 process requirements.

CO_2-philic function — Chelating agent + Acid counter ion

- ✓ Synthesis of new extracting agents combining the efficiency of Cs chelating agents with CO_2-philic functions
- ✓ Liquid/Liquid extraction test using ^{137}Cs to validate the affinity and selectivity for Cs
- ✓ Solubility experiments in sc CO_2
- ✓ Tests on contaminated solid matrixes

First optimised extractants synthesised gave promising results in the sc CO_2 process

Experiments

Parallel synthesis

Microwave reactor

Radleys

Overview of the laboratory

Acknowledgements:

INVESTISSEMENTS D'AVENIR
RECHERCHE EN MATIERE DE SURETE NUCLEAIRE ET DE RADIOPROTECTION (RSNR)

DEMETERRES

AREVA