FROM RESEARCH TO INDUSTRY

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6TH IGD-TP EXCHANGE FORUM (EF6)
WG3 – Cement Organics Radionuclides Interactions - CORI

TOPIC: "MOBILITY OF ORGANICS-RN COMPLEXES IN A CEMENTITIOUS ENVIRONMENT"

NOVEMBER 3-4, 2015
LONDON, UK

SCHEME OF THE CORI PROJECT

Work Packages

Degradation of organics - result of hydrolysis and radiolysis

↓

Mobility of organics in cementitious environment and their interaction with Fe

↓

Mobility of organics-RN complexes in a cementitious environment

↓

WP "Modelling, upscaling, application to PA

→ + Management Team & Training/Dissemination

"MOBILITY OF ORGANICS-RN COMPLEXES IN A CEMENTITIOUS ENVIRONMENT" (1/2)

Context

- In ternary systems (Cements-Organics-RNs), the mobility of RNs can be influenced by several processes
  - RN complexation in the aqueous phase by organic molecules acting as ligands
  - competition effects for the surface adsorption sites of cement-based materials
  - or synergic processes

- In PA exercise, this influence is usually considered as a phenomenon decreasing the adsorption (K_d) of RNs onto solid surfaces
  - using adsorption "reduction factors" (and also solubility enhancement factors)
  - applied to the sensitive RNs
  - strongly linked to the nature and amount of organics released into the system, their complexation properties as well as their own mobility

→ Link to TOPICS "Degradation" & "Mobility of Organics"

"MOBILITY OF ORGANICS-RN COMPLEXES IN A CEMENTITIOUS ENVIRONMENT" (2/2)

Objectives

- As part of the CORI Project, this TOPIC is dedicated to strengthen the understanding on organics/RNs complexes mobility in cement-based systems
  - Assess and quantify the mechanisms that take place at microscopic scale in relevant ternary systems
  - Provide new data on adsorption and radionuclide transport at macroscopic scale to be used in the integrated modelling approach

→ Link to TOPIC "Modelling, upscaling, application to PA"

GLOBAL REQUIREMENTS

From WMOs priorities and expectations

WMOs	Materials	Organic species	Radionuclides
ANDRA NAGRA ONDRAF.NIRAS RWM SKB SURAO **Data needed** • Description of chemical interactions • Transport parameters • In anoxic conditions	• CEM I/II • CEM V • Armoured concrete systems • Influence of materials degradation	Priorities towards complexing capacity Monocarboxylic acids Dicarboxylic acids Aromatic carboxylic acids Aminocarboxylic acids Hydrocarboxylic acids Influence of organic mixtures (no ^{14}C bearing molecules in this TOPIC)	**Transition elements** **Lanthanides** **Actinides** **Toxic element**

→ The challenge is to select a set of relevant systems to be studied among all the possibilities

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TEAMS THAT HAVE EXPRESSED THEIR INTEREST

Two meetings (March/Sept.) and one questionnaire (June)

- 14 Organizations / Universities have shown interest and/or proposed some work
  - Amphos 21
  - CEA (proposed as TOPIC Leader)
  - Juelich
  - KIT-INE
  - SCK.CEN
  - Subatech
  - TERAMED
  - University CTU
  - University Heidelberg
  - University Loughborough
  - University Mainz
  - University Manchester
  - University Potsdam (UPPC)
  - University Sheffield

→ Collaboration not closed, new partners are welcome

ATTEMPT TO SELECT ORGANIC SPECIES

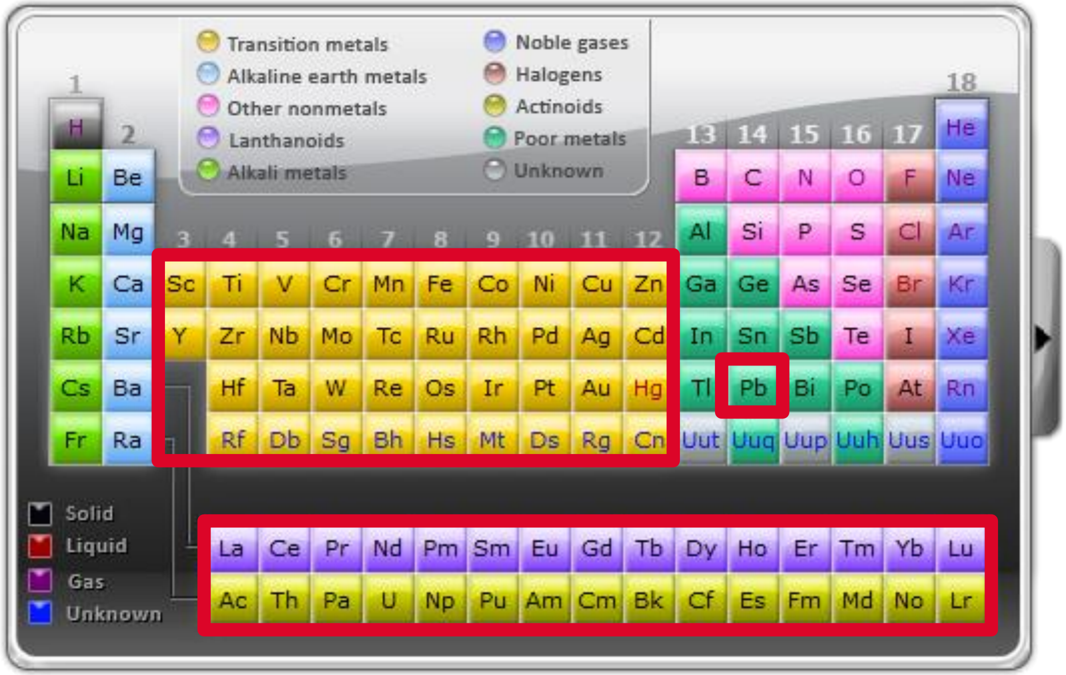
Discussion from WP “Mobility of Organics”

- to remind the tentative selection of representative organic ligands

Organic	Subgroup	Representation	Analogies
acids/alcohols and/or aldehydes C1-C2	Cationic and Anionic resins/ ^{14}C-bearing organic compounds	Short-chained acids, alcohols and /or aldehydes	Malonic, Succinic…
Adipic acid	PVC/PUR	Long-chained dicarboxylic acid	Glutaric, Pimelic, Suberic…
Phthalic acid	PVC	Aromaticdicarboxylic acid	Succinic
ISA	Cellulosic wastes	Hydroxicarboxylic acid	Citric, Gluconic
Acetic	PCE/CAE	Mono(poly)carboxylic acid	Formic, Butyric, Acetic
EDTA	Decontamination and cleaning	Aminocarboxylicacid	DTPA, NTA

ATTEMPT TO SELECT RADIONUCLIDES (1/2)

Transition elements/Lanthanides/Actinides/Toxic element



- From expectations (focused on cationic species)
  - attempt to reduce the list by highlighting specific elements (non exclusive list)

→ Ni, Pb, Am, Ln(III), Pu, U selected as a 1st set of interesting elements

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ATTEMPT TO SELECT RADIONUCLIDES (2/2)

Partners' proposals so far

Team	Radionuclides proposed	Type of experiments proposed
Amphos21	Ni, Eu, U / Cs, Se, Th	Batch sorption experiments
CEA	Cs, Ni, Eu, Se, Pu, U, Th	Batch sorption experiments/Diffusion experiments
Juelich	Ra, Sn, Tc, Se, Mo, Ni, ^{14}C	Batch sorption experiments
KIT-INE	Pu, Tc	Batch sorption experiments/Diffusion experiments
SCK.CEN	Transition metals, La/Ac	Diffusion experiments
Subatech	U, Se, actinides, Sr, Ni	Batch sorption experiments/Diffusion experiments / Computational molecular modelling
Univ. CTU	Ra, Th, U, Ac, Am, Cm, Cl, ^{3}H	Diffusion experiments
Univ. Loughborough	Ni, U, Am, Pu…	Diffusion experiments
Univ. Manchester	U, Tc, Np, Pu, I, Am, Sr, Cs, ^{14}C	Batch sorption experiments/Column systems
Univ. Potsdam	Ln(III), U	Characterization of surface complexes and alteration
Univ. Sheffield	U, Tc, Np, Am, Pu, non-radioactive e.g. Cs, I, Cl	Batch sorption experiments/Single-pass flow through

- no particular difficulty identified to meet the needs

→ We should be able to build a set of complementary studies

DESCRIPTION OF ACTIVITIES IN THIS WP (1/2)

Work on dispersed cement-based materials

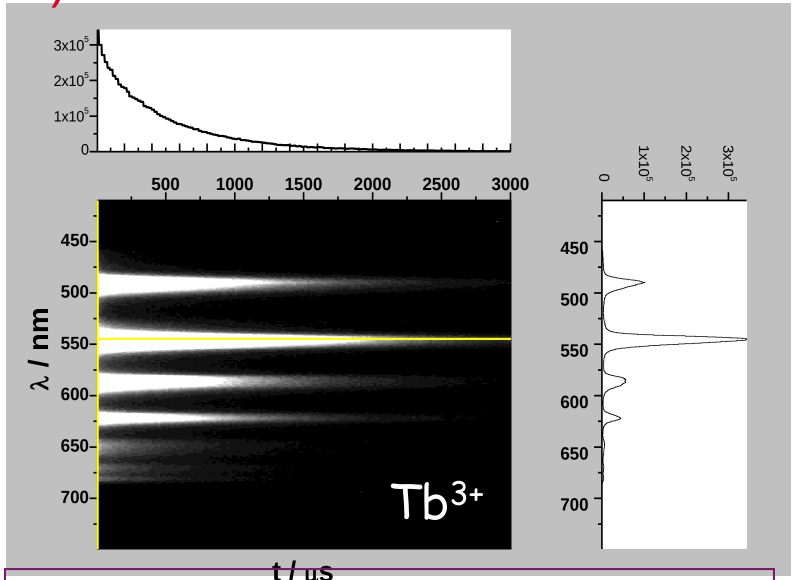
- **Physicochemical interactions** between RNs and cementitious materials in presence of organic compounds, emphasis on
  - interactions with **single cement phases** and **bulk** systems (HCP)
  - **solubility/speciation** of RNs in cement porewater in presence of organic compounds
  - effect of materials **degradation**
  - investigation of **solid surfaces** after interaction
  - adsorption **kinetics** and **isotherms**
  - effect of single organics / cocktails of organics and role of iron
  - molecular modelling (MD techniques)

→ Mechanistic description and quantitative adsorption models

→ Input data for TOPIC “Modelling, upscaling, application to PA”

Speciation analysis of organic-lanthanide complexes on cement (CSH-phase or other…) surfaces

- Lanthanide(III)-ions (as analogs)
  - Tb^{3+}, Sm^{3+}, Dy^{3+}, Eu^{3+}
  - (Uranyl)
- System parameters
  - pH
  - Ionic strength (up to sea water)
  - (pCO_2)
- Methods
  - Time resolved laser fluorescence spectroscopy
  - Steady state luminescence spectroscopy
  - Raman spectroscopy
  - SFG spectroscopy



- time-resolved luminescence (µs – ms time scales)
- site-selective luminescence spectroscopy
- luminescence spectroscopy on mineral surfaces

DESCRIPTION OF ACTIVITIES IN THIS WP (2/2)

Work on compacted cementitious materials

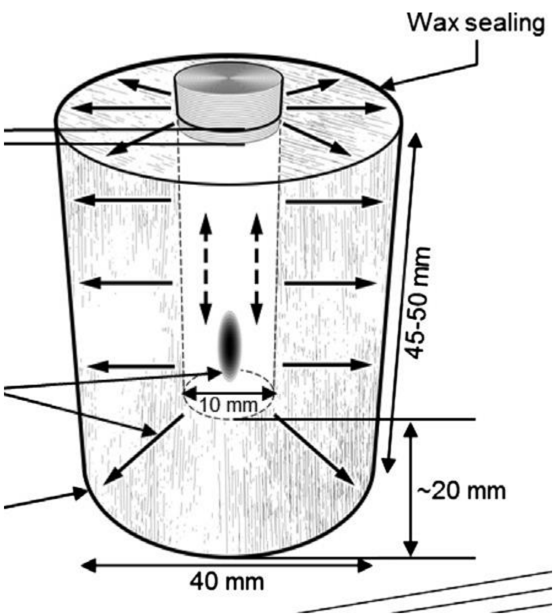
- **Migration experiments** of RNs in cementitious materials in presence of organic compounds
  - **in or through-diffusion** experiments depending on the theoretical mobility of the RNs studied
  - **column** experiments
  - solution analyses → **diffusive fluxes, elution curves**
  - images or **profile measurements** in the solid
  - effect of material degradation
  - effect of single organics / cocktails of organics

→ Quantitative transport models

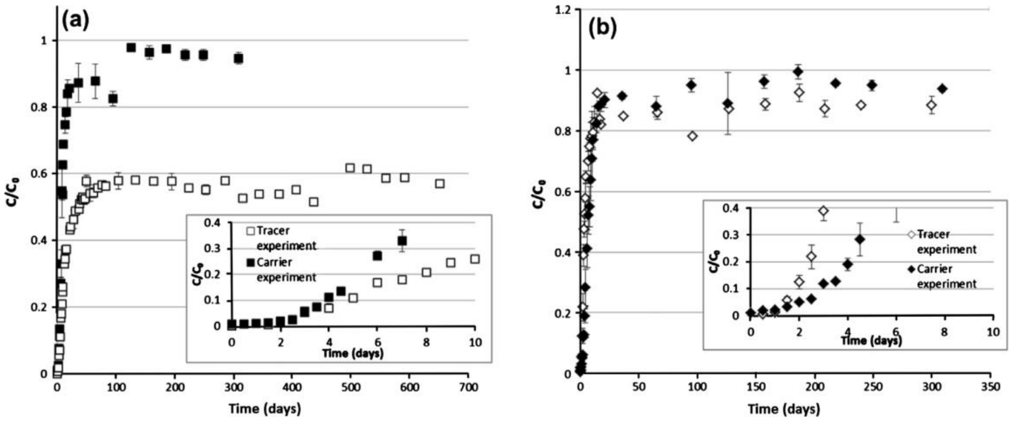
→ Input data for TOPIC “Modelling, upscaling, application to PA”

AN EXAMPLE
(DIFFUSION EXPERIMENT)

Radial diffusion through cement cylinder

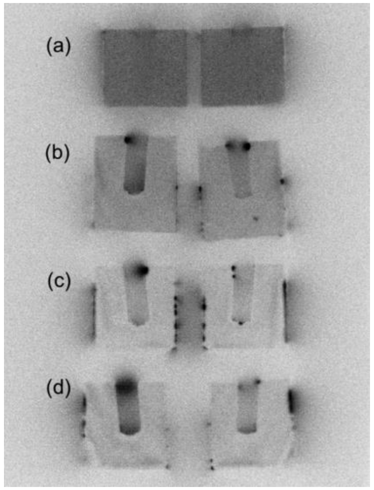


Design of the experiment



Elution curves of Cs at tracer (^{137}Cs) and carrier levels ($^{137}Cs + CsNO_3$)
(a) without organic Cellulose Degradation Product
(b) in the presence of CDP

Digital laser-photostimulated storage phosphor imaging autoradiograph of the distribution of ^{137}Cs in the NRVB blocks



→ Extraction of transport parameters

→ Possible analysis/imaging of the solid afterwards

Felipe-Sotelo et al. (2014). Radial diffusion of radiocaesium and radioiodide through cementitious Backfill. Phys. Chem. Earth **70–71** , 60–70

Thank you for your attention !

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