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
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
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”
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”
From WMOs priorities and expectations

<table>
<thead>
<tr>
<th>WMOs</th>
<th>Materials</th>
<th>Organic species</th>
<th>Radionuclides</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANDRA</td>
<td>• CEM I/II</td>
<td>• Priorities towards complexing capacity</td>
<td>Transition elements</td>
</tr>
<tr>
<td>NAGRA</td>
<td>• CEM V</td>
<td>Monocarboxylic acids</td>
<td>Lanthanides</td>
</tr>
<tr>
<td>ONDRAF.NIRAS</td>
<td>• Armoured concrete systems</td>
<td>Dicarboxylic acids</td>
<td>Actinides</td>
</tr>
<tr>
<td>RWM</td>
<td>• Influence of materials degradation</td>
<td>Aromatic carboxylic acids</td>
<td>Toxic element</td>
</tr>
<tr>
<td>SKB</td>
<td></td>
<td>Aminocarboxylic acids</td>
<td></td>
</tr>
<tr>
<td>SURAO</td>
<td></td>
<td>Hydrocarboxylic acids</td>
<td></td>
</tr>
</tbody>
</table>

Data needed
- Description of chemical interactions
- Transport parameters
- In anoxic conditions

→ The challenge is to select a set of relevant systems to be studied among all the possibilities
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
Discussion from WP “Mobility of Organics”

to remind the tentative selection of representative organic ligands

<table>
<thead>
<tr>
<th>Organic</th>
<th>Subgroup</th>
<th>Representation</th>
<th>Analogies</th>
</tr>
</thead>
<tbody>
<tr>
<td>acids/alcohols and/or aldehydes C1-C2</td>
<td>Cationic and Anionic resins/ $^{14}$C-bearing organic compounds</td>
<td>Short-chained acids, alcohols and/or aldehydes</td>
<td>Malonic, Succinic…</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>PVC/PUR</td>
<td>Long-chained dicarboxylic acid</td>
<td>Glutaric, Pimelic, Suberic…</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>PVC</td>
<td>Aromatic dicarboxylic acid</td>
<td>Succinic</td>
</tr>
<tr>
<td>ISA</td>
<td>Cellulosic wastes</td>
<td>Hydroxicarboxylic acid</td>
<td>Citric, Gluconic</td>
</tr>
<tr>
<td>Acetic</td>
<td>PCE/CAE</td>
<td>Mono(poly)carboxylic acid</td>
<td>Formic, Butyric, Acetic</td>
</tr>
<tr>
<td>EDTA</td>
<td>Decontamination and cleaning</td>
<td>Aminocarboxylic acid</td>
<td>DTPA, NTA</td>
</tr>
</tbody>
</table>
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
### Partners’ proposals so far

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

- no particular difficulty identified to meet the needs

→ **We should be able to build a set of complementary studies**
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
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”
Radial diffusion through cement cylinder

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

Thank you for your attention!