



**Deliverable 3.4**  
**CORI - Training Materials UPDATE**  
Work Package 3, CORI

The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 847593.



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## Executive Summary

This document contains the Deliverable on CORI Training Materials D3.4.

The key Training Activity by CORI within EURAD is documented in this Deliverable. On 12<sup>th</sup> December 2023, CORI had organized a 1-hour contribution to the Lunch & Learn Sessions in EURAD. This event was open to all EURAD partners and especially the PhD and early career researcher involved. The Lunch & Learn session organized by CORI was done by video conferencing tools and was attended by about 80 persons. At the Training Event CORI was providing information relevant in the context of the CORI Workpackage with the aim to (i) introduce the basic scientific facts and concepts underlying the research on Cement-Organics-Cement-Interactions, (ii) explain the relevance of CORI in view of enhancing Safety, and (iii) present selected technical highlights from this EURAD WP. D3.4 makes available the presentation files shown at this Training Event.

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## 1. CORI Training – Lunch & Learn Session 12<sup>th</sup> Dec. 2023

CORI has contributed to the Training activities organised within EURAD by organising a Lunch & Learn Session on December 12<sup>th</sup> 2023. The 4 Tasks in CORI were presenting information on the topics investigated in CORI with the aim to address a broad audience in EURAD and especially the PhD and early career researcher involved. This event was the key training event organised by CORI. About 80 persons were attending the 1-hour event. Positive feedback confirmed the usefulness of using the Lunch & Learn Sessions for Training Events.

The Session consisted of four connected presentations from the 4 Tasks in this WP. Task 1 was providing a general introduction to CORI, Task 2 introduced the work in CORI on organics degradation, Task 3 focused on the organic retention on cement and Task 4 on the ternary system radionuclides-organic-cement.

Further information on the work performed in CORI is given in the public Deliverables D3.5 (Final Report) and the combined Deliverables D3.5,7,8 (Technical Report on Task Level).

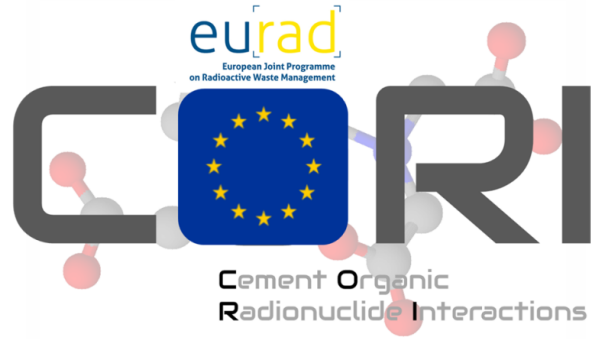
### Scope of CORI:

*CORI has improved the knowledge on the organic release issues, which can accelerate the radionuclide migration in the context of the post closure phase of geological repositories for ILW and LLW/VLLW, including surface/shallow disposal. CORI addressed topics in the context of cement-organic-radionuclide interactions. Organic materials are present in some nuclear waste and as admixtures in cement-based materials and can potentially influence the performance of a geological disposal system. This potential effect of organic molecules is caused by the formation of complexes in solution with radionuclides which can potentially increase radionuclide solubility and/or decrease radionuclide sorption. Organic substances require increased attention since a significant quantity exists in the waste and in the cementitious materials, with a large degree of chemical diversity. Cement-based materials are degraded with time in the context of waste disposal inducing a large range of alkaline pH conditions. Alkaline pH provides specific conditions under which the organics can degrade, which contributes to increasing their potential impact on repository performance. The new scientific results from WP CORI are providing new quantitative and qualitative data as well as improved process understanding to support RWMD implementation needs and safety.*

## 2. Annex – Presentation slides provided at the Training Event

In the following Annex, the presentation slides used by CORI during the Lunch & Learn Session are given. Separate series of slides are provided for the different Tasks:

- **General introduction (M. Altmaier)** – Slides Task 1
- **Organic materials and degradation (D. Ricard)** – Slides Task 2
- **Organic-Cement-Interactions (P. Henocq & D. García)** – Slides Task 3
- **Cement Organic Radionuclide Interactions (T. Missana & N. Macé)** – Slides Task 4



## **CORI Lunch and Learn, 12<sup>th</sup> December 2023**

# **CORI** **cement-organic-radionuclide-interactions**

### ***Part I: General introduction***

**M. Altmaier**



# Lunch & Learn Session



## Presentations today

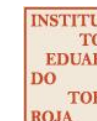
- 1) General Introduction**
- 2) Organic Degradation**
- 3) Organic-Cement-Interactions**
- 4) Radionuclide-Organic-Cement-Interactions**

# CORI Participants

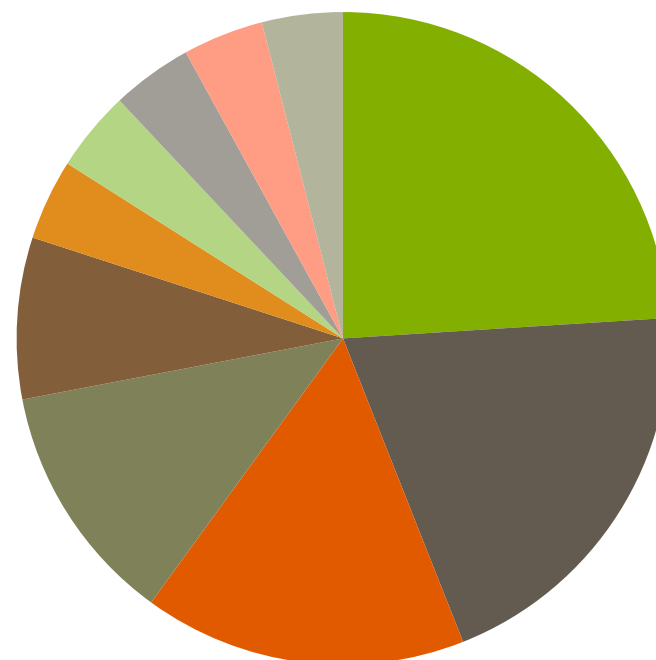


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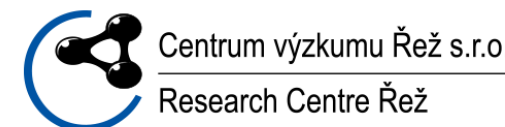
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- Belgium
- Cyprus
- Finland





# Participants - LUNCH

- Google based evaluation:





# CORI - motivation

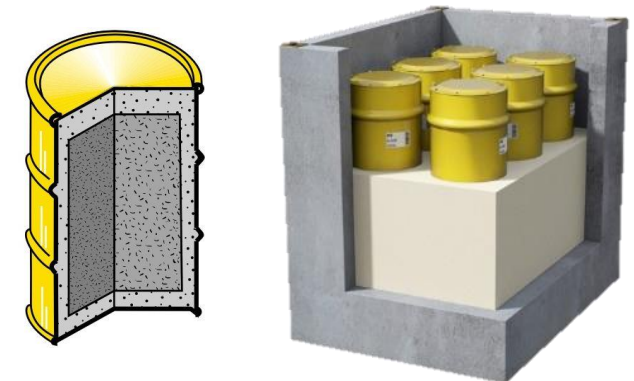


- ▶ Improve the knowledge on the organic release issues which can influence the radionuclide behaviour in geological repositories for nuclear waste (ILW and LLW/VLLW, incl. surface/shallow disposal).
- ▶ **Cement-based materials** will be **degraded** with time in the context of waste disposal inducing a large range of **alkaline pH conditions** according to their degradation state. **Cement alteration phases** can be important factors for retaining organic molecules and radionuclides by **sorption processes**.
- ▶ **Organic materials** are present in some nuclear waste and as admixtures in **cement-based materials** and can potentially influence the performance of a geological disposal system. **Alkaline pH** provides **specific conditions** under which the organics can degrade, which contributes to **increasing their potential impact** on repository performance.
- ▶ **Critical open topics and data needs required to better assess and quantify cement-organic-radionuclide-interactions are reflected in the three R&D CORI Tasks:**
  - ▶ **Organic Degradation**
  - ▶ **Organic-Cement-Interactions**
  - ▶ **Radionuclide-Organic-Cement-Interactions**

# Learn...

## Cement as a important part of the multi-barrier system

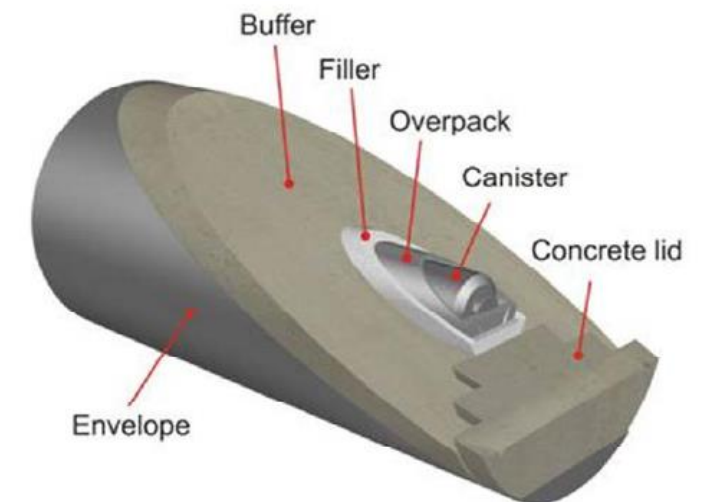
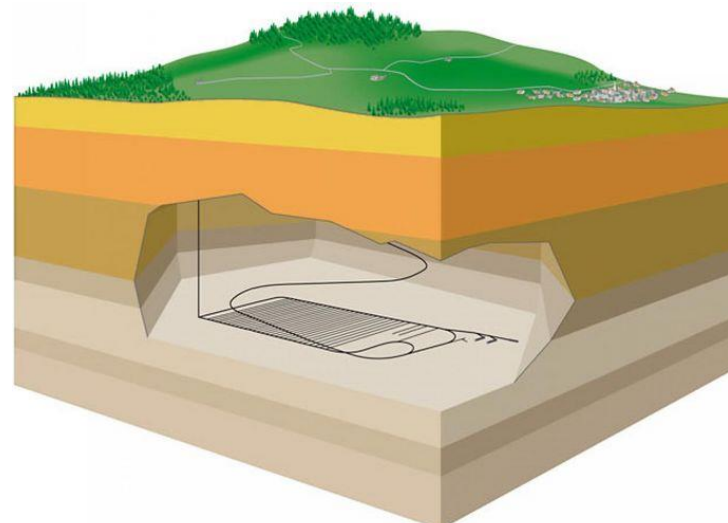
Cementitious materials are used for conditioning of the waste and for the construction of the engineered barrier system in different repository concepts, including LLW, L/ILW and HLW.



**Low level waste**  
*Near-surface disposal*

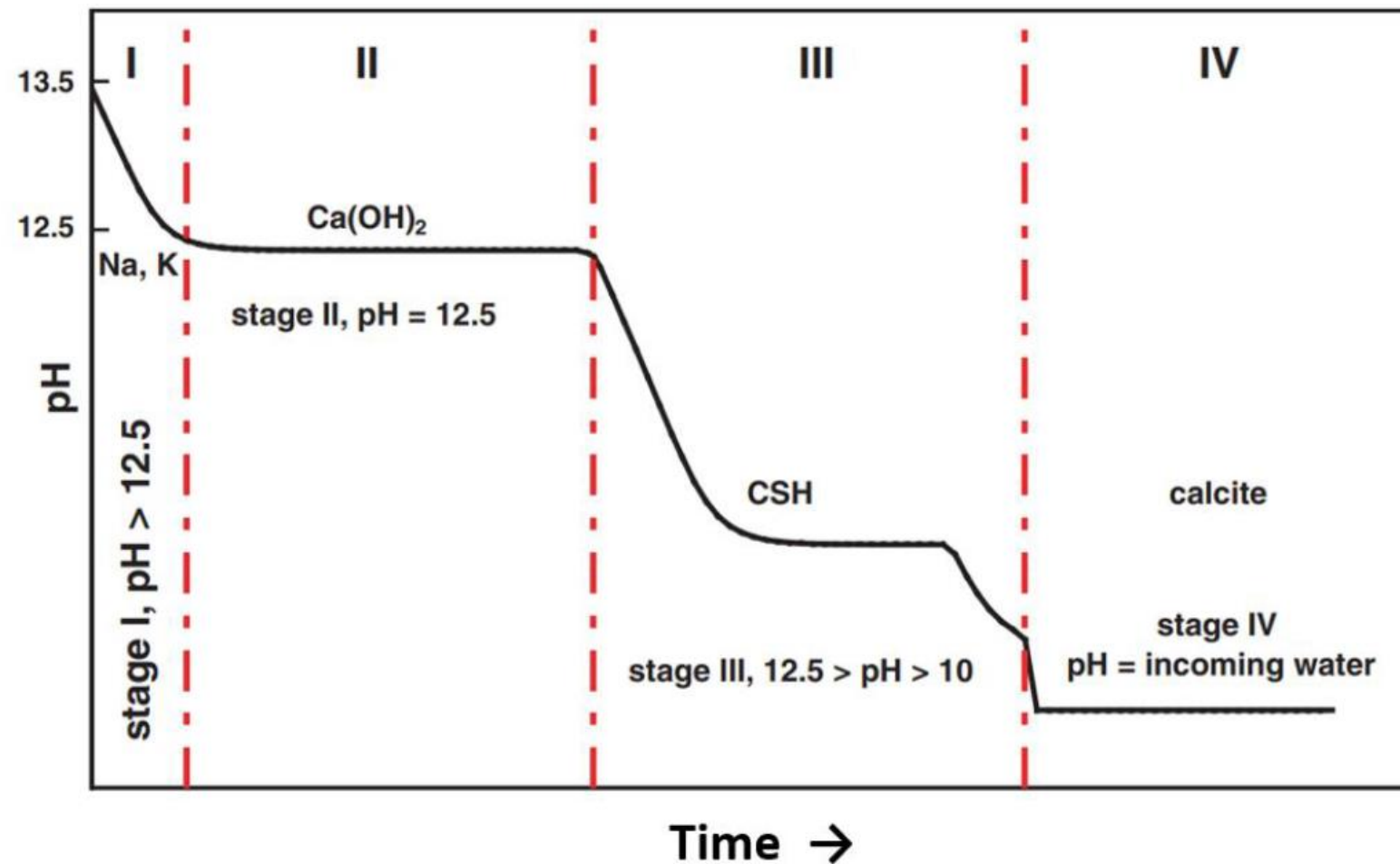
### **Low- and intermediate level waste**

*Underground disposal*



**High level waste**  
*Supercontainer concept*

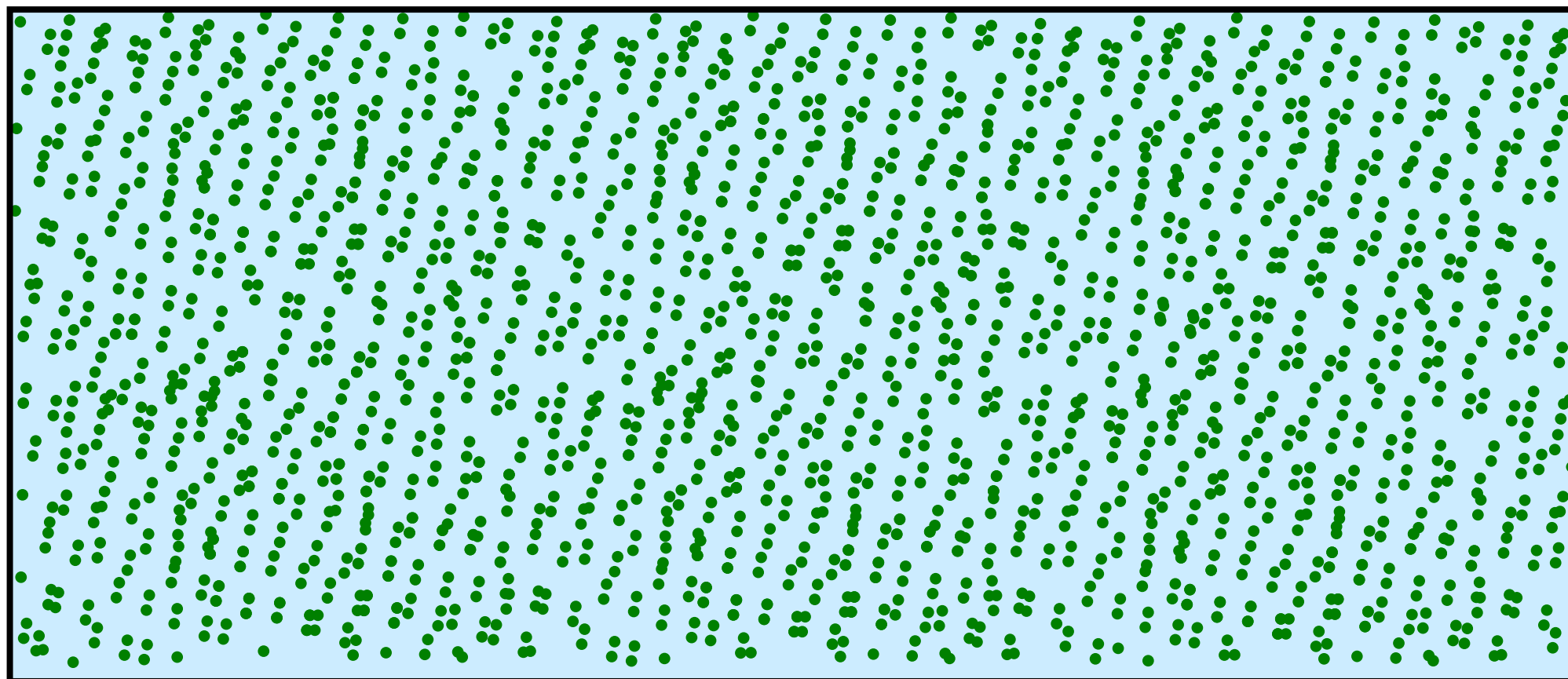
## Degradation of cement-based materials



- System with high intrinsic complexity generated. High pH!
- Specific cement phases (CSH...) controlling RN retention...

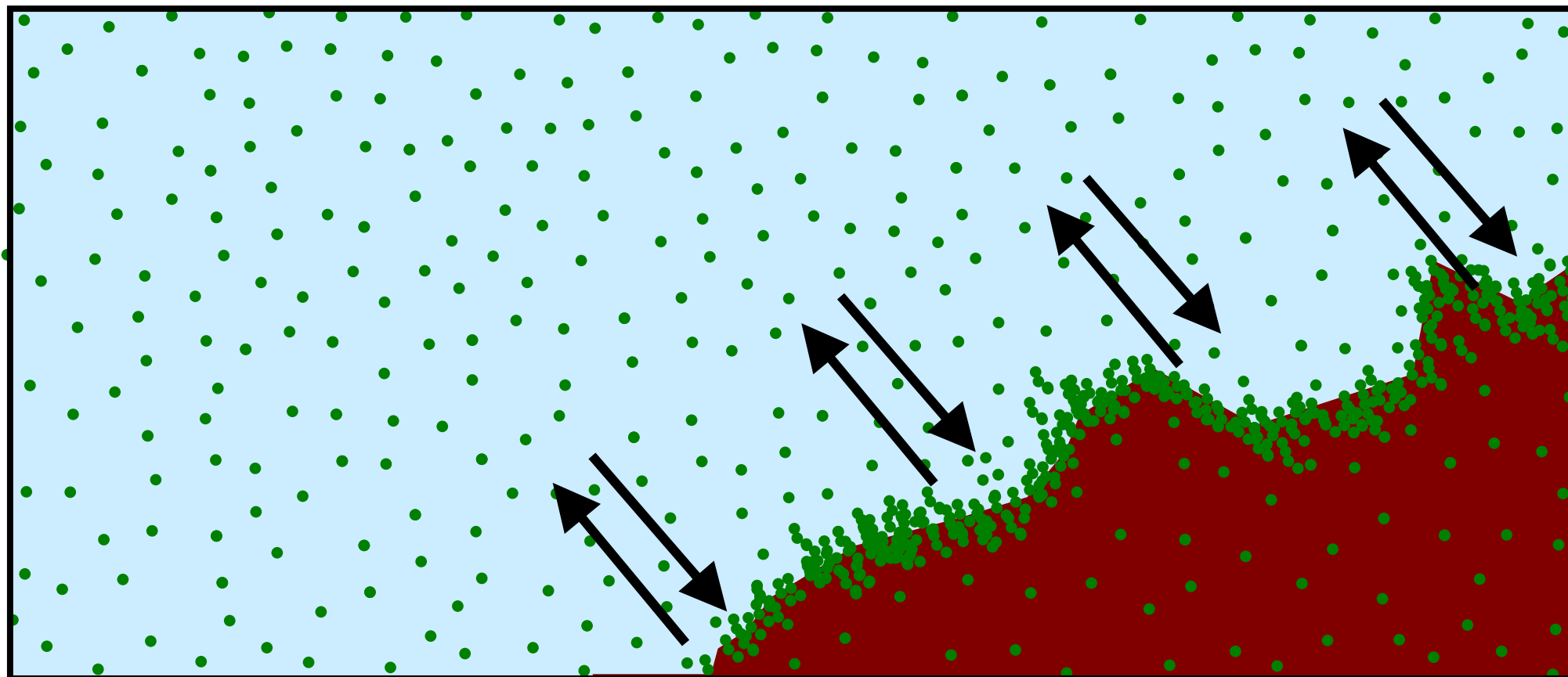
# Learn...

## Radionuclides in aqueous phase are potentially mobile...



- RN solubility and speciation controlled by geochemical conditions, pH, Eh, components of the electrolyte system

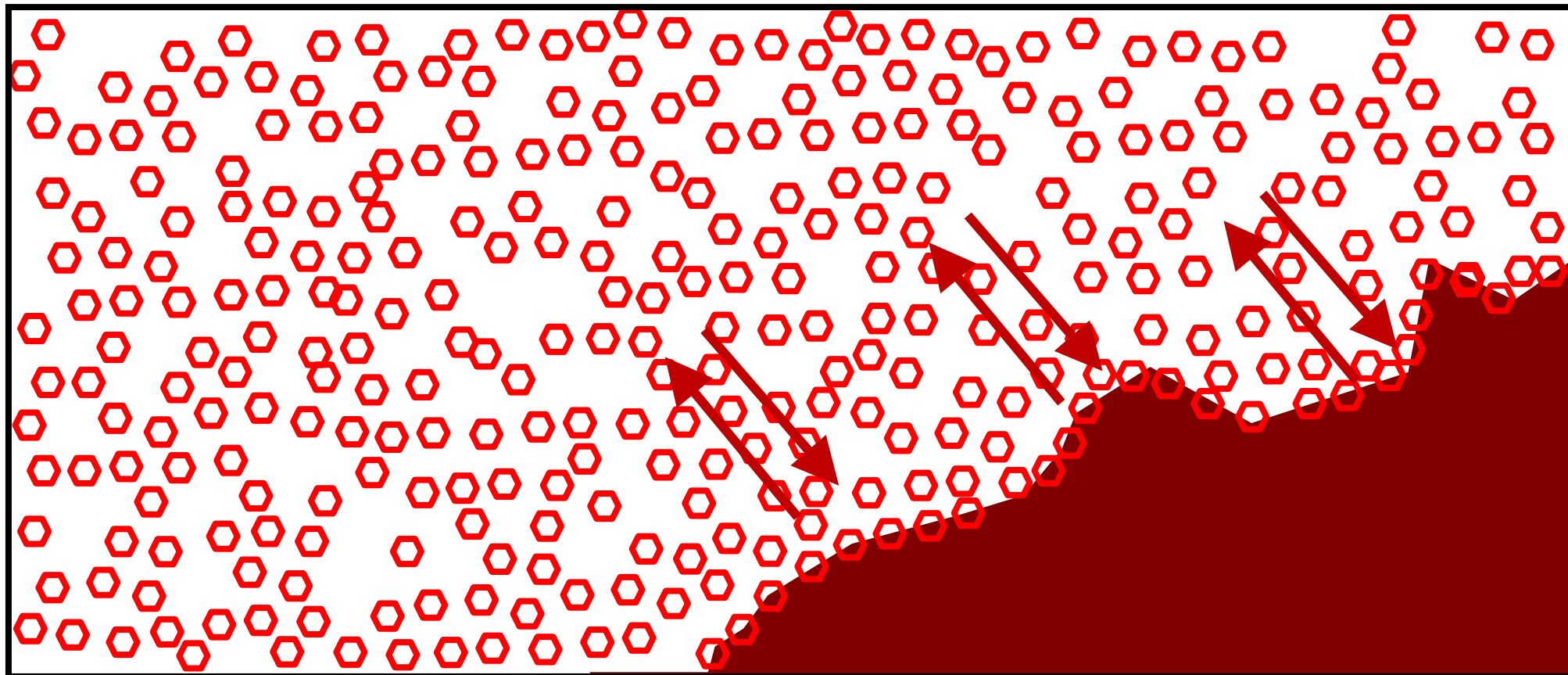
Interaction of radionuclides with mineral surfaces (“cement”) can lead to retention processes with the solid phase.



- Distribution ratio (RN-solution vs RN-solid) characteristic key value ( $K_d$ ,  $R_d$ )
  - Good understanding for many relevant materials and systems



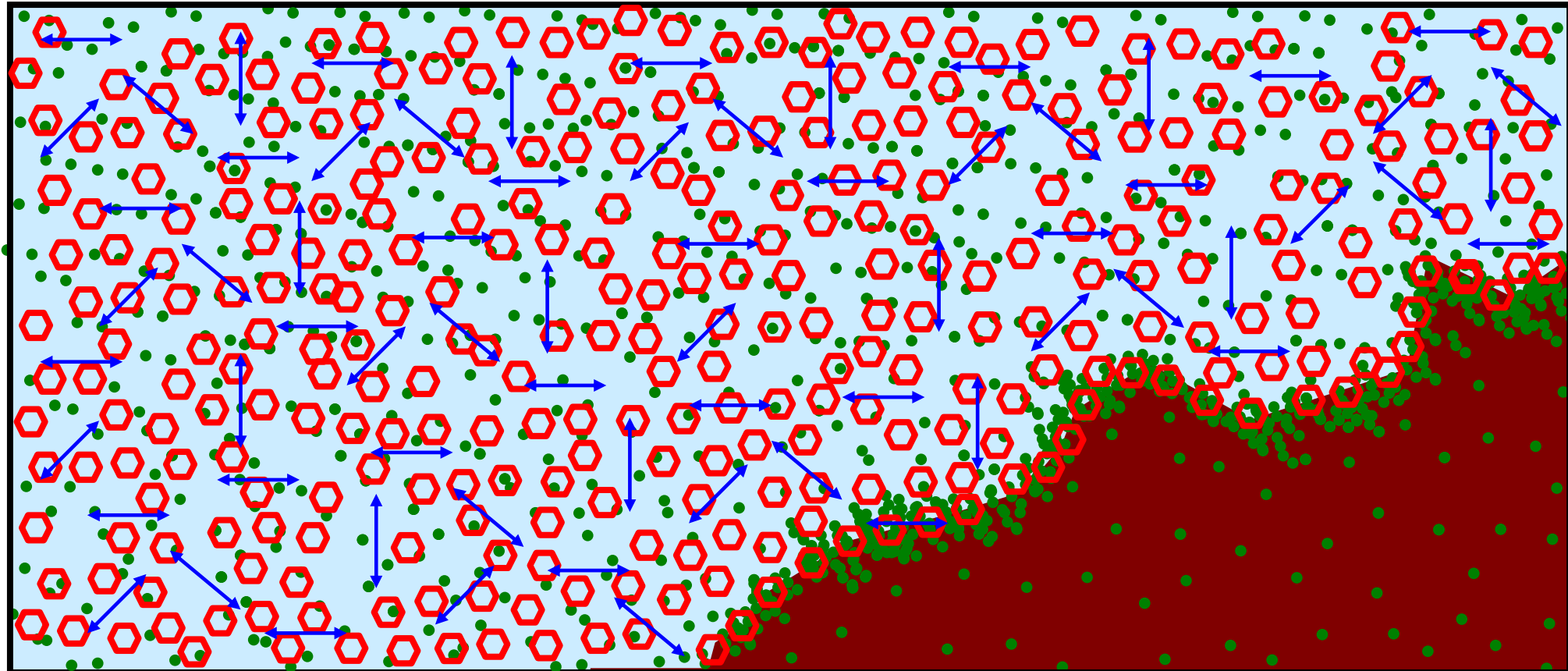
**Adding organic materials adds complexity. Organics may interact with solids and surfaces as well as with radionuclides**



- CORI: organics generated from degradation of complex materials
- Description of organics retention (distribution solution vs. solid)

# Learn...

=> full system with cement-organics-radionuclides present.  
Potential interaction processes in the aqueous phase and on the cement/mineral surface.



CORI: quantification of retention processes, identification of systematic trends, development of improved process understanding!

# CORI - impacts



Improved quantification of radionuclide solubility and sorption phenomena in cementitious environments to provide input for improved predictions of radionuclide transport. **YES!**

Regarding RWM implementation needs. Issues of interest / repository scale Improved scientific basis for the Safety Case for L/ILW waste repositories featuring high organic content. **YES!**

Co-storage of waste: support decisions on whether or not a mix of various wastes (organics, soluble salts, exothermic waste) can be foreseen. **YES! Option for the future...**

Optimization of vault design: limitations of interactions between the vaults regarding their content. CORI will provide information on the organic plume by characterizing the transfer behaviour in cement-based materials. **YES! Option for the future.**

# CORI - impacts

## Regarding safety

Characterizing the effect of the organic plume on the behavior of radionuclides in terms of:

**Solubility** (limitation of solubility increase), **YES!**

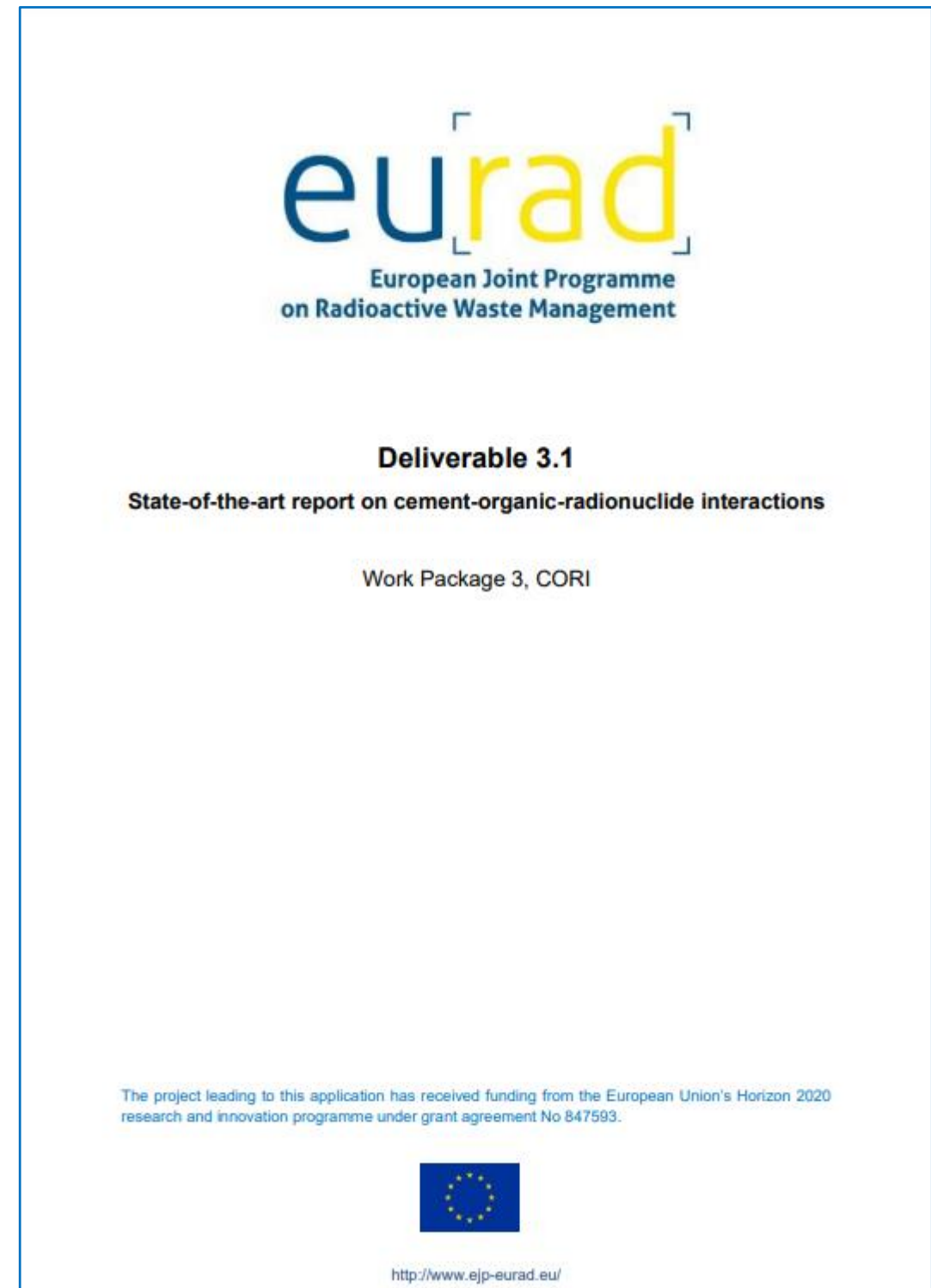
**Sorption** (limitation of retention decrease) in terms of  $K_d$  values. **YES! Many examples from Task 4.**

Retention of potentially  $^{14}\text{C}$ -bearing organic molecules (determined in CAST project) in cementitious environments in the case of specific waste. **YES!**  
**Examples form Task 3.**

- Improve the knowledge on the known organic molecules present in degradation solutions (not considered so far) with their complexing properties: better definition of the organic inventory regarding the waste and the concrete vault (geological and surface repositories). **YES! “Investigation of real leacheates”.**
- Reduce the uncertainties on the current knowledge, which is mainly based on  $K_d$  values. **YES!**

# Further information...

- **Further background information on CORI available via initial SOTA document**
- [https://www.ejp-eurad.eu/publications/eurad-d3 I-cori-sota-cement-organic-radionuclide-interactions-content-ilw-disposal](https://www.ejp-eurad.eu/publications/eurad-d3%20I-cori-sota-cement-organic-radionuclide-interactions-content-ilw-disposal)
- **Deliverable 3.1**




The image shows the cover page of a report titled 'Deliverable 3.1: State-of-the-art report on cement-organic-radionuclide interactions'. The page features the eurad logo at the top, followed by the title and subtitle. At the bottom, there is a small European Union flag and the website URL <http://www.ejp-eurad.eu/>.

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**Deliverable 3.1**  
State-of-the-art report on cement-organic-radionuclide interactions

Work Package 3, CORI

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<http://www.ejp-eurad.eu/>

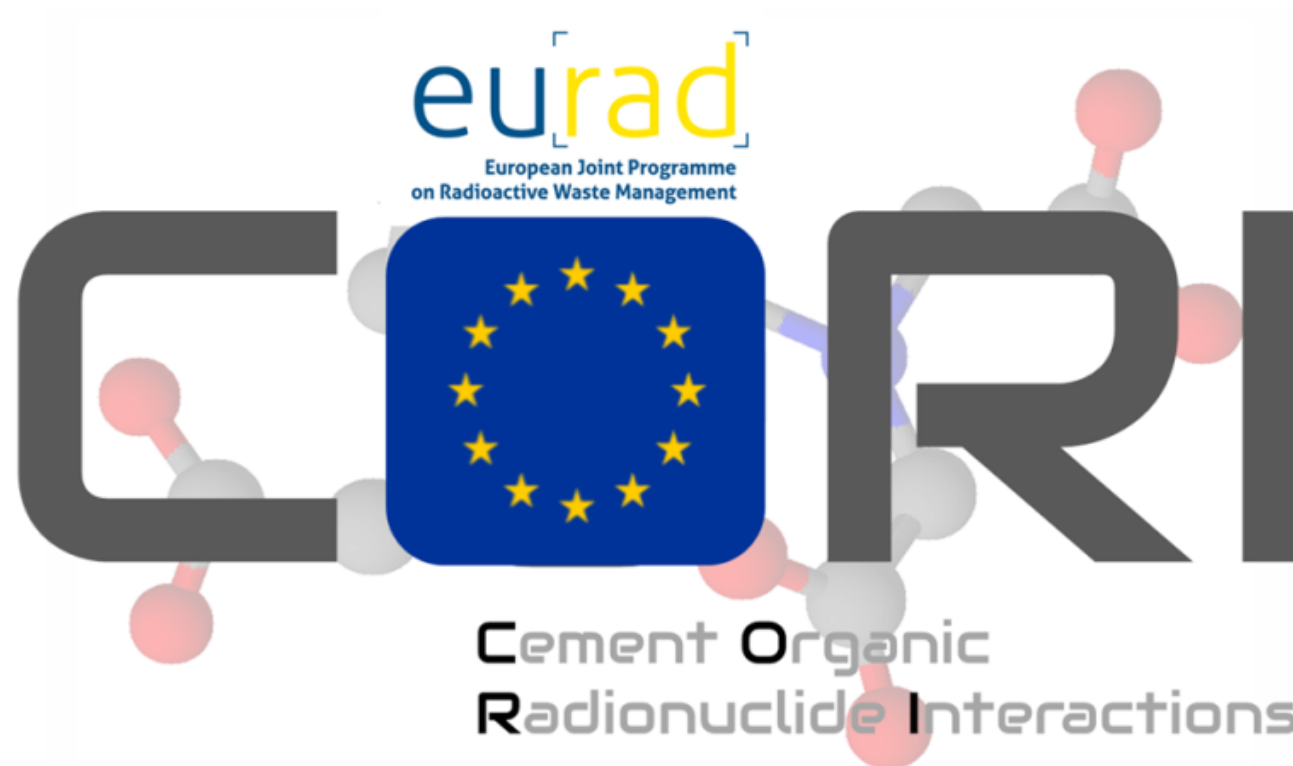
# Lunch & Learn Session



## Presentations today

- 1) General Introduction**
- 2) Organic Degradation**
- 3) Organic-Cement-Interactions**
- 4) Radionuclide-Organic-Cement-Interactions**

**Thank you for your attention !!!**



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## **CORI Lunch and Learn, 12<sup>th</sup> December 2023**

# **CORI** **cement-organic-radionuclide-interactions**

### ***Part II: Organic materials and degradation***

**D. Ricard**

12th December 2023



# Summary



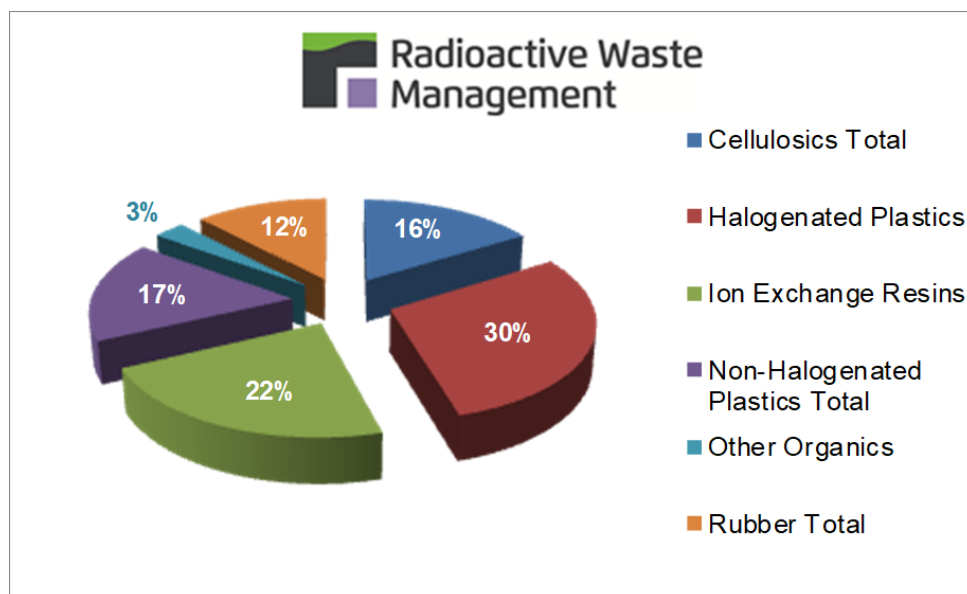
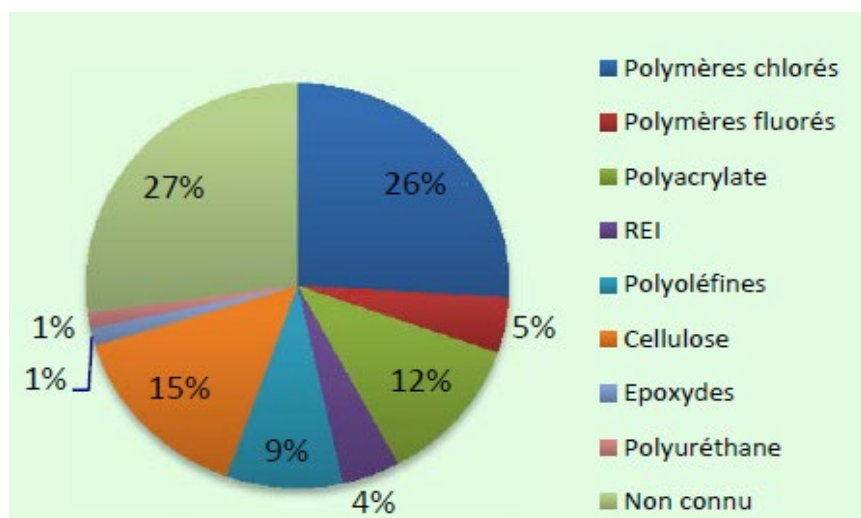
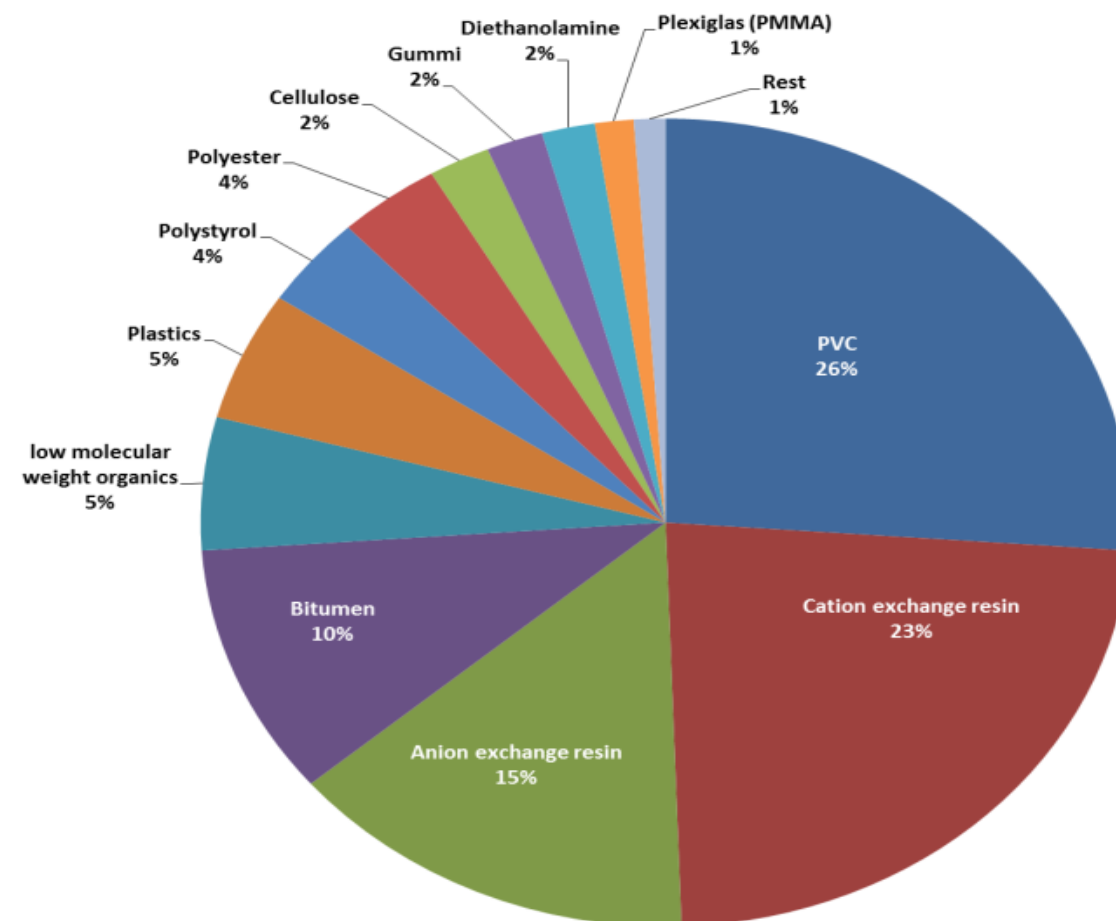
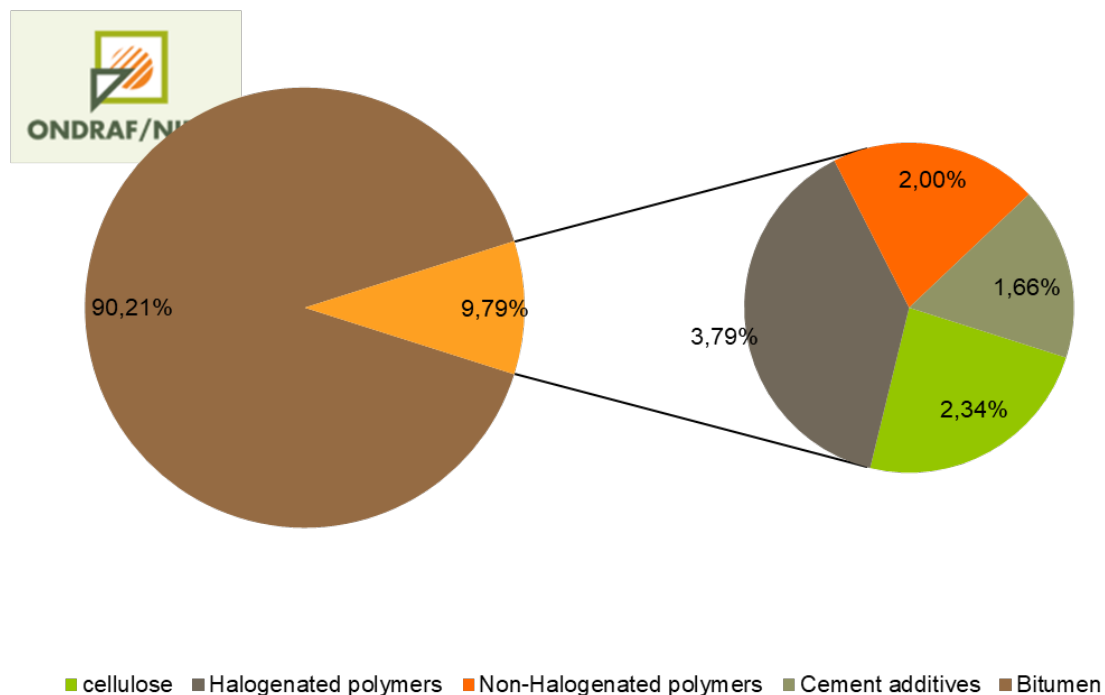
- Nature of organic materials in disposal inventories
- Organic degradation in disposal
- CORI Task 2
  - Studied materials
  - Example of results acquired

# Organic materials in disposal

- ▶ Embedding matrix:
  - ▶ Bitumen, Epoxy, Polyester...
- ▶ Technological wastes: Wastes produced during operations of maintenance and intervention in the nuclear installations
  - ▶ Different nature of polymers (papers, gloves, clothes, bottle, pipes, cables, bags, ion exchange resins...)
- ▶ Additives of cementitious materials (superplasticizers)
- ▶ Small molecular weight molecules: substances coming from effluents
  - ▶ EDTA, TBP...



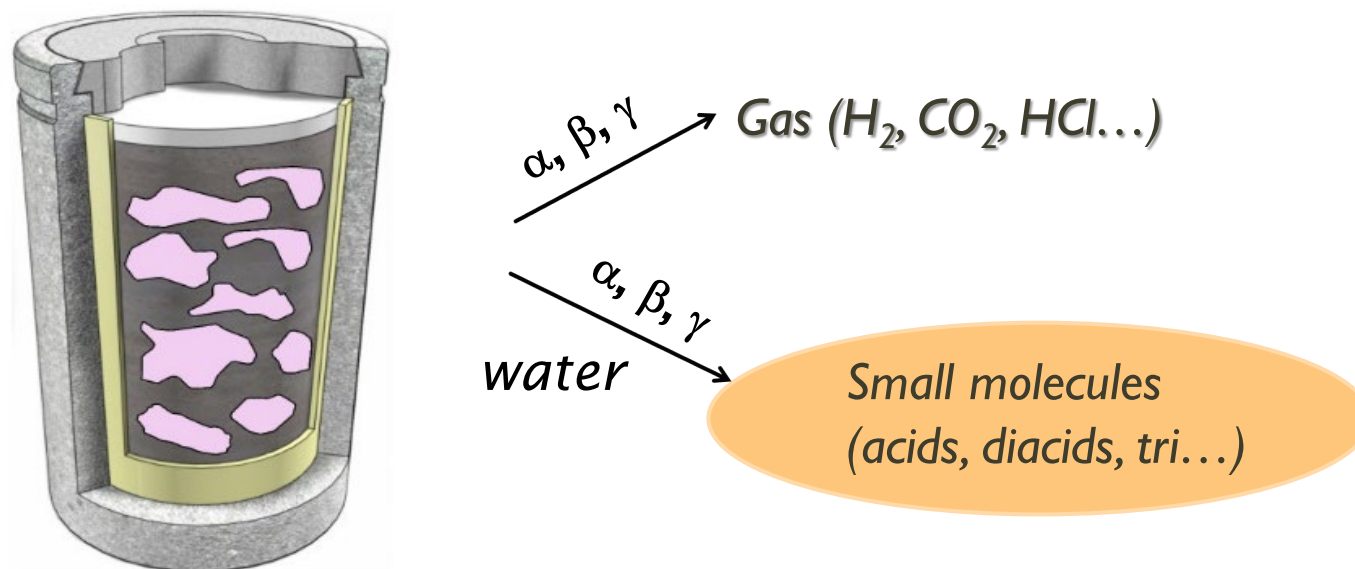
# WMO Organic matter inventories



nagra

# Degradation of organic materials in deep geological disposal

- ▶ Organic materials can undergo different kinds of degradation:
  - ▶ Radiolysis by auto-irradiation (radionuclides contamination)
    - ▶ under oxygen
    - ▶ without oxygen
  - ▶ Hydrolysis in presence of water (basic conditions)
  - ▶ Biodegradation



Technological wastes containing polymer wastes

# Degradation products – Some issues



- ▶ Gas production
  - ▶ Issues
    - ▶ Evaluate risk of explosion of H<sub>2</sub>
    - ▶ Evaluate risk of corrosion of metallic containers by corrosives gases (HCl et HF)
  
- ▶ Release of organic soluble species
  - ▶ Issues
    - ▶ Complexation and modification of behaviour of radionuclides in solution
    - ▶ Interaction and degradation of disposal materials

# Task 2



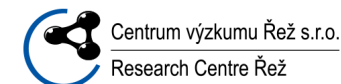
- ▶ Main objectives:
  - ▶ Improve knowledge of degradation of organic wastes in conditions representative of disposal facilities;
  - ▶ Provide characterization and quantification of degradation products, namely soluble organic species.

- ▶ Organic degradation process studied :

- ▶ Radiolytic degradation
- ▶ Hydrolytic degradation



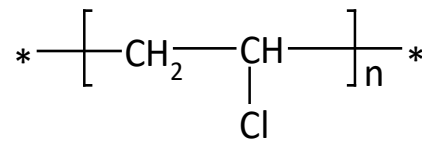
Coupled process



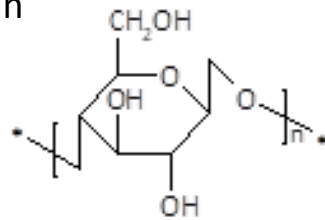
# Organic materials selected for Task 2 studies

- ▶ Selection was based non WMO inventories and needs about characterization of degradation products

- ▶ PVC



- ▶ Cellulose

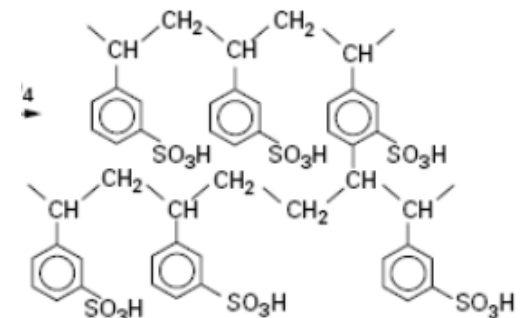
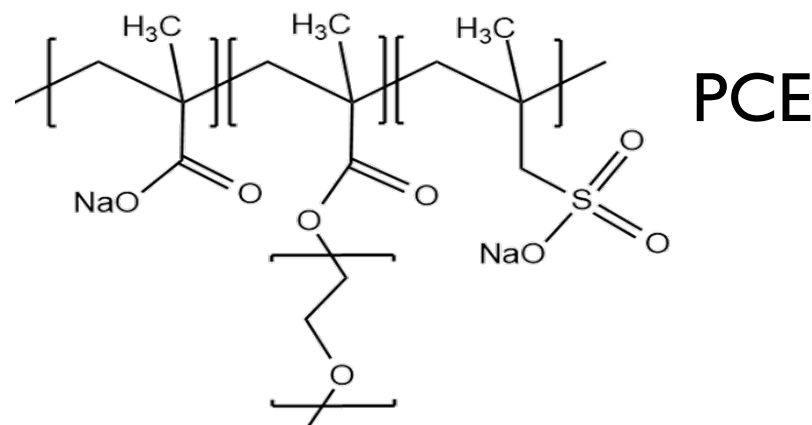


- ▶ Ion Exchange Resins (IER)

- ▶ Cross-linked polystyrene skeleton with a sulfonic functional group
- ▶ Polyacrylic skeleton with a carboxylic (COOH) functional group

- ▶ Superplasticizers

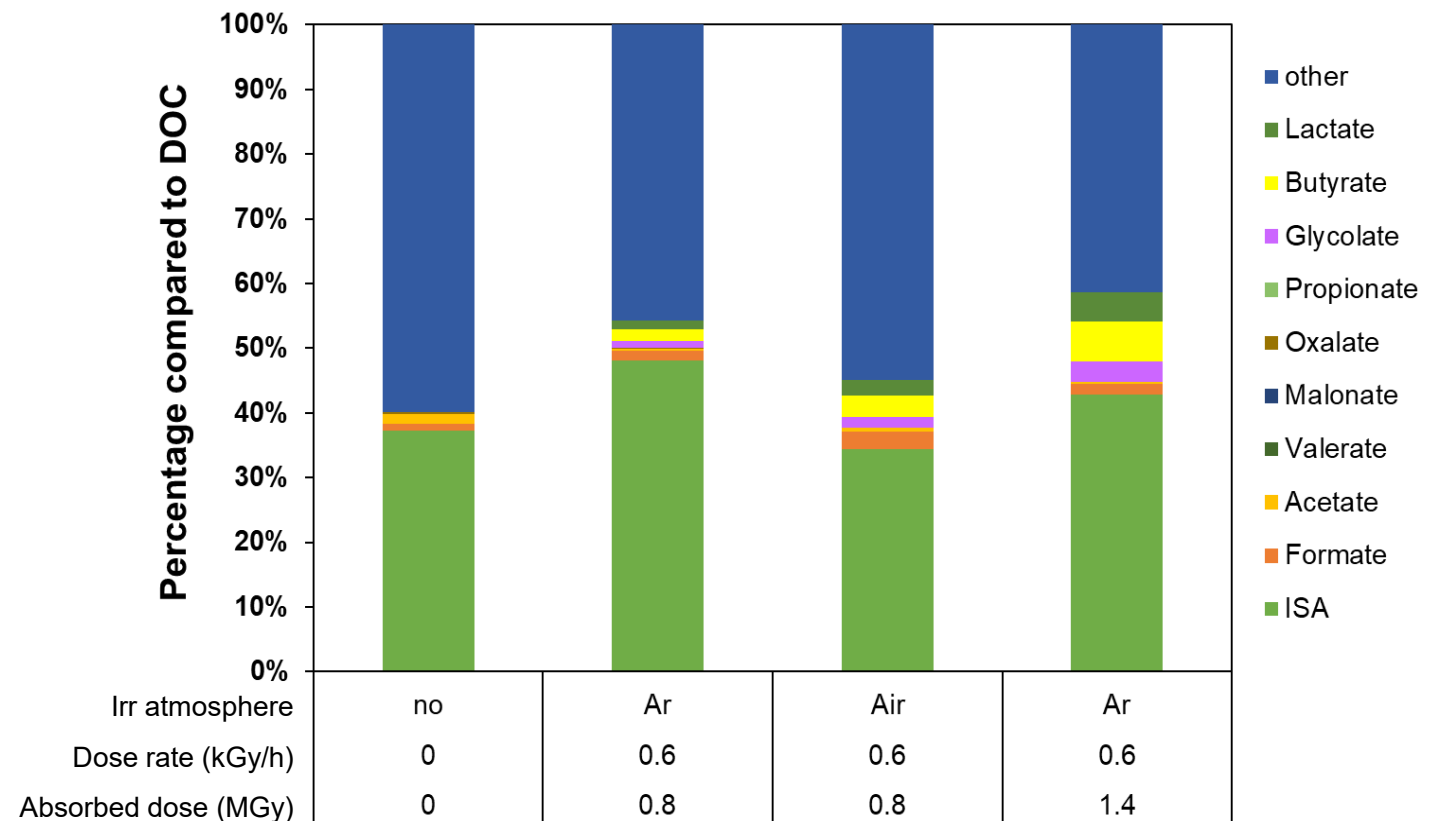
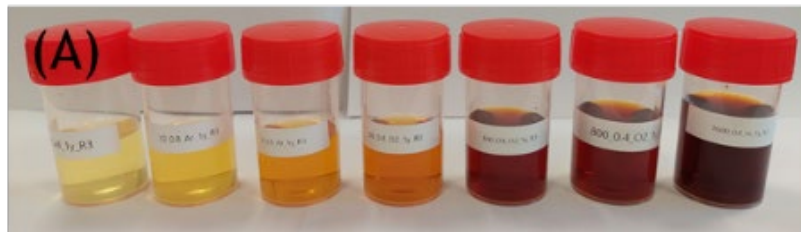
- ▶ PCE
- ▶ LignoSulfonate
- ▶ PolyMelamine Sulfonate





# Organic degradation studies

- ▶ Example: cellulose tissues degradation by radiolysis followed by hydrolysis in basic conditions
  - ▶ Ion chromatography results to determine carboxylic acids (after 1 year of hydrolysis)
    - ▶ ISA = dominant degradation product

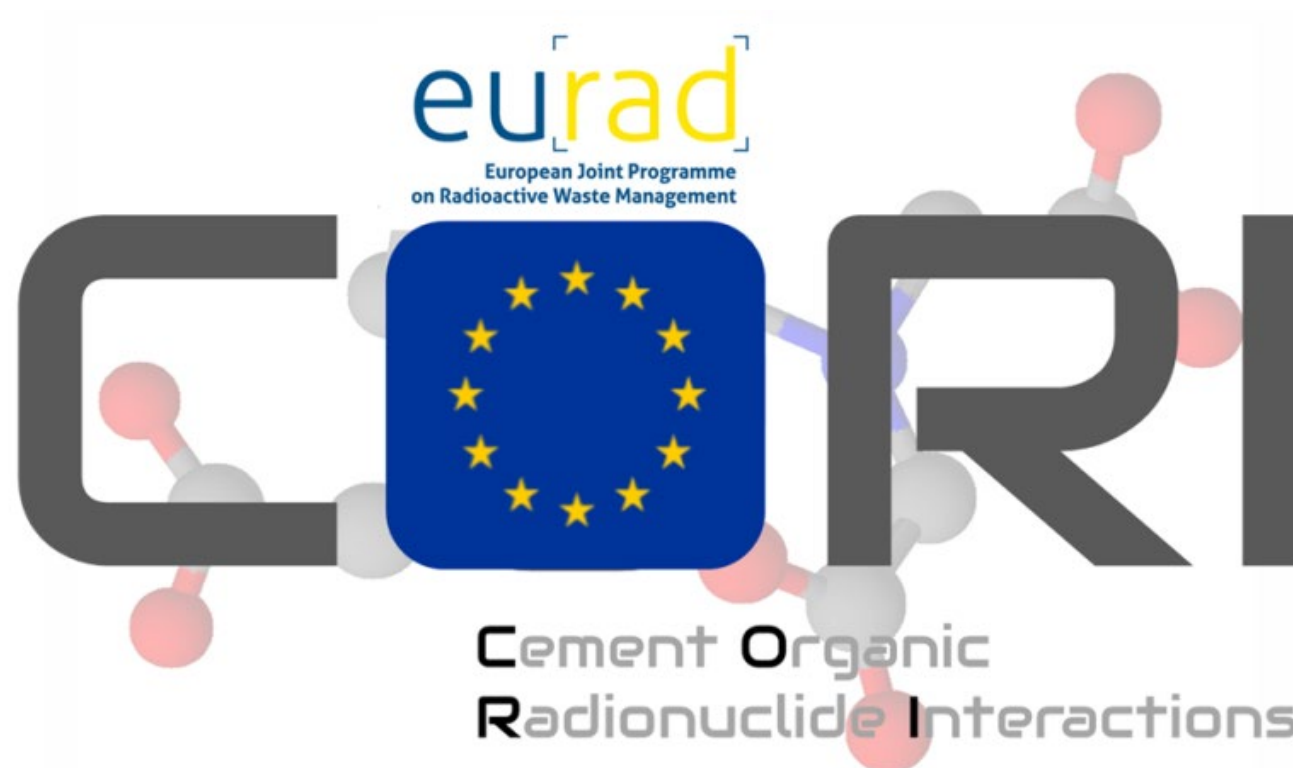


Some degradation products and degraded solutions are studied in Task 3 and 4

Cement and Radionuclides interactions



**Thank you for your attention !!!**



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**10** *research and innovation programme under grant agreement No 847593.*

**12th December 2023**



## **CORI Lunch and Learn, 12<sup>th</sup> December 2023**

**CORI**  
**cement-organic-radionuclide-interactions**


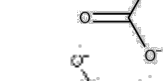
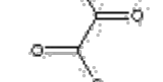
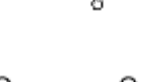
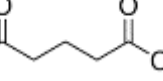

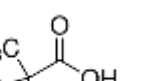
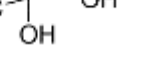
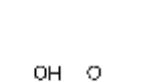
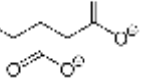

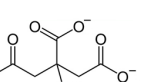
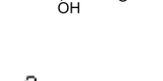
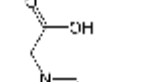
***Task 3 : Organic-Cement-Interactions***

**P. Henocq & D. García**

## Provide knowledge on interactions between organic molecules and cement-based materials

- Studies focus on investigating the **mobility** of selected **organic molecules** in cement-based materials. Mobility of organic molecules includes **retention** and **transport** properties.
- **Complexing agents**: ISA, Phthalate, EDTA, NTA, and other degradation products (link to Task 2)
- Organics will also include small **<sup>14</sup>C** bearing **molecules** as identified in CAST.
- Cement hydrates (**C-S-H, AFms**) and cement-based materials (**HCP**)
- Analysing the fate of the organics in cementitious environments is a key requirement to understand/model the radionuclide behavior in Task 4.

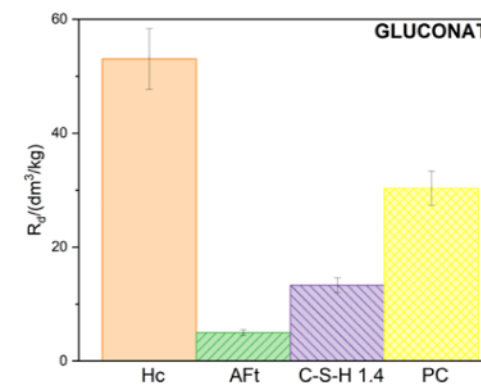
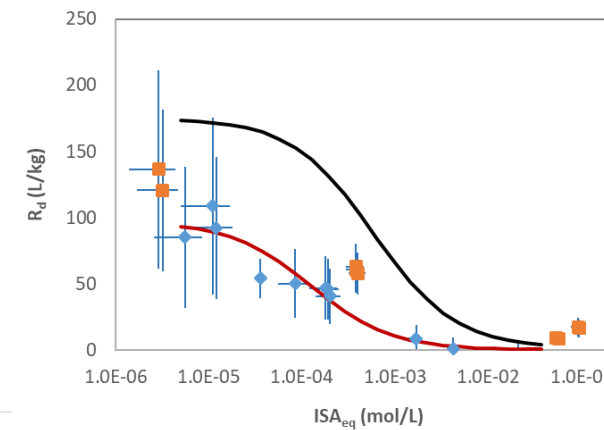
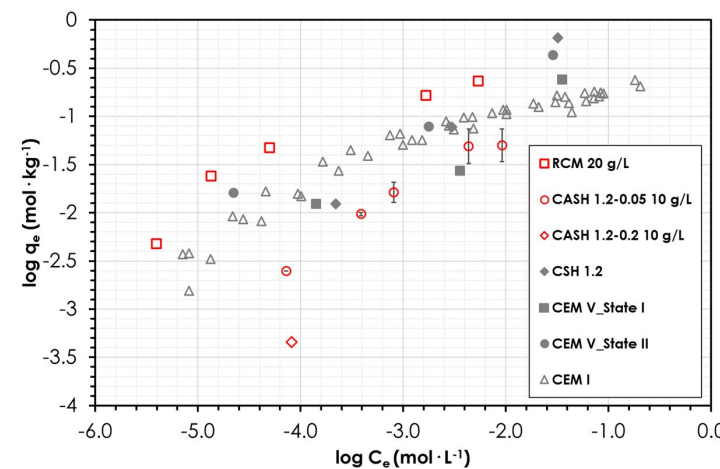
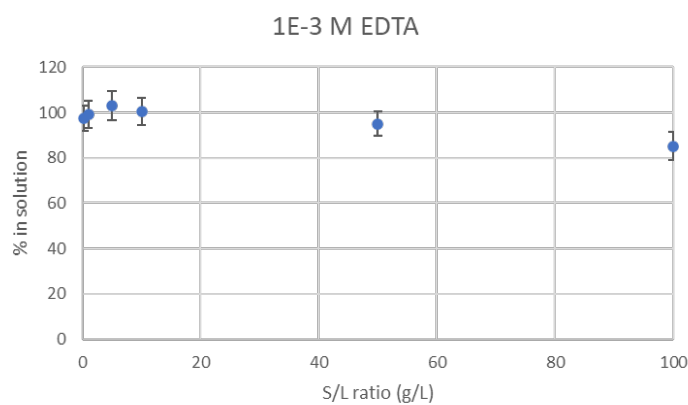
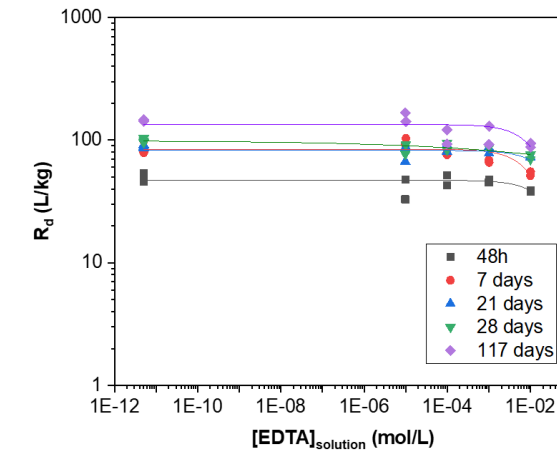
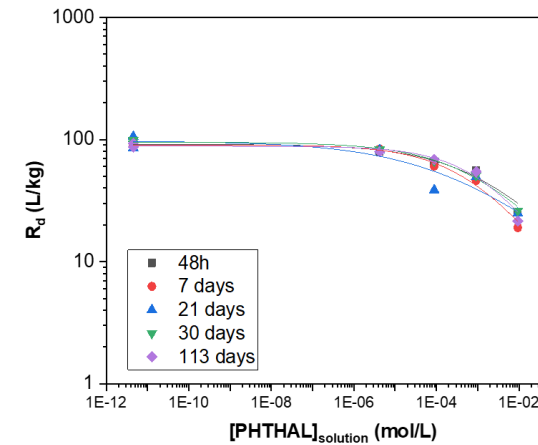
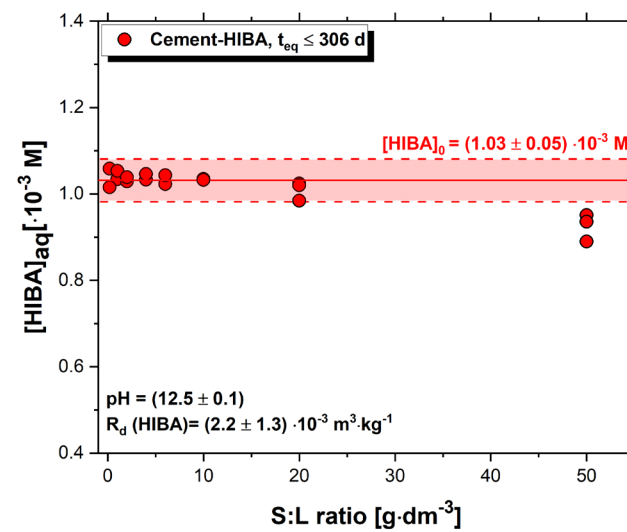
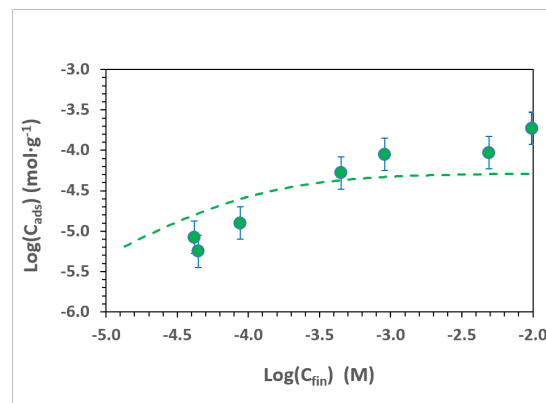
# Investigated systems

	CSH	CAS H	Ca(OH) <sub>2</sub>	AFm	AFt	HCP (F)	HCP (St. II)	HCP (St. III)	
	KIT/EMPA			KIT/EMPA	KIT/EMPA		CTU, UJV, RATEN	RATEN	<chem>CC(=O)[O-]</chem>
							UJV		<chem>CC(=O)[O-]</chem>
							CTU		<chem>C1=CC=C(C=C1)C(=O)C(=O)O</chem>
		A2I							<chem>CCCCC(=O)O</chem>
							KIT		<chem>CCCCC(=O)O</chem>
		A2I					Andra, CEA, CTU	CEA	<chem>C1=CC=C(C=C1)C(=O)OC(=O)C1=CC=C(C=C1)</chem>
							KIT		<chem>CC(C)(O)C(=O)O</chem>
							KIT		<chem>CCC(O)C(=O)O</chem>
	KIT/EMPA			KIT/EMPA	KIT/EMPA				<chem>OC(CC(=O)O)(CC(=O)O)C(=O)O</chem>
					KIT/EMPA				<chem>OC(CC(O)C(O)C(O)C(=O)O)C(=O)O</chem>
	CIEMAT	A2I	CIEMAT		CIEMAT		Andra, IETcc-CSIC	SCK-CEN	<chem>C1=CC=C(C=C1)C(=O)OC(=O)C1=CC=C(C=C1)</chem>
							CEA, CTU, IETcc-CSIC, JSI	CEA, JSI	<chem>C1=CC=C(C=C1)C(=O)OC(=O)C1=CC=C(C=C1)</chem>
							JSI	JSI	<chem>C1=CC=C(C=C1)C(=O)OC(=O)C1=CC=C(C=C1)</chem>
	CIEMAT		CIEMAT			CIEMAT	CIEMAT, IETcc-CSIC		<chem>C1=CC=C(C=C1)C(=O)OC(=O)C1=CC=C(C=C1)</chem>

# Type of experiments

- Solubility tests (i.e. CEA)
- Kinetic batch sorption tests (i.e. KIT-INE)
- Batch sorption (isotherms) and desorption (leaching) tests (i.e. JSI)
- Conventional diffusion tests (i.e. SCK-CEN)
- Electromigration diffusion tests (i.e. Helsinki University)

# Type of results

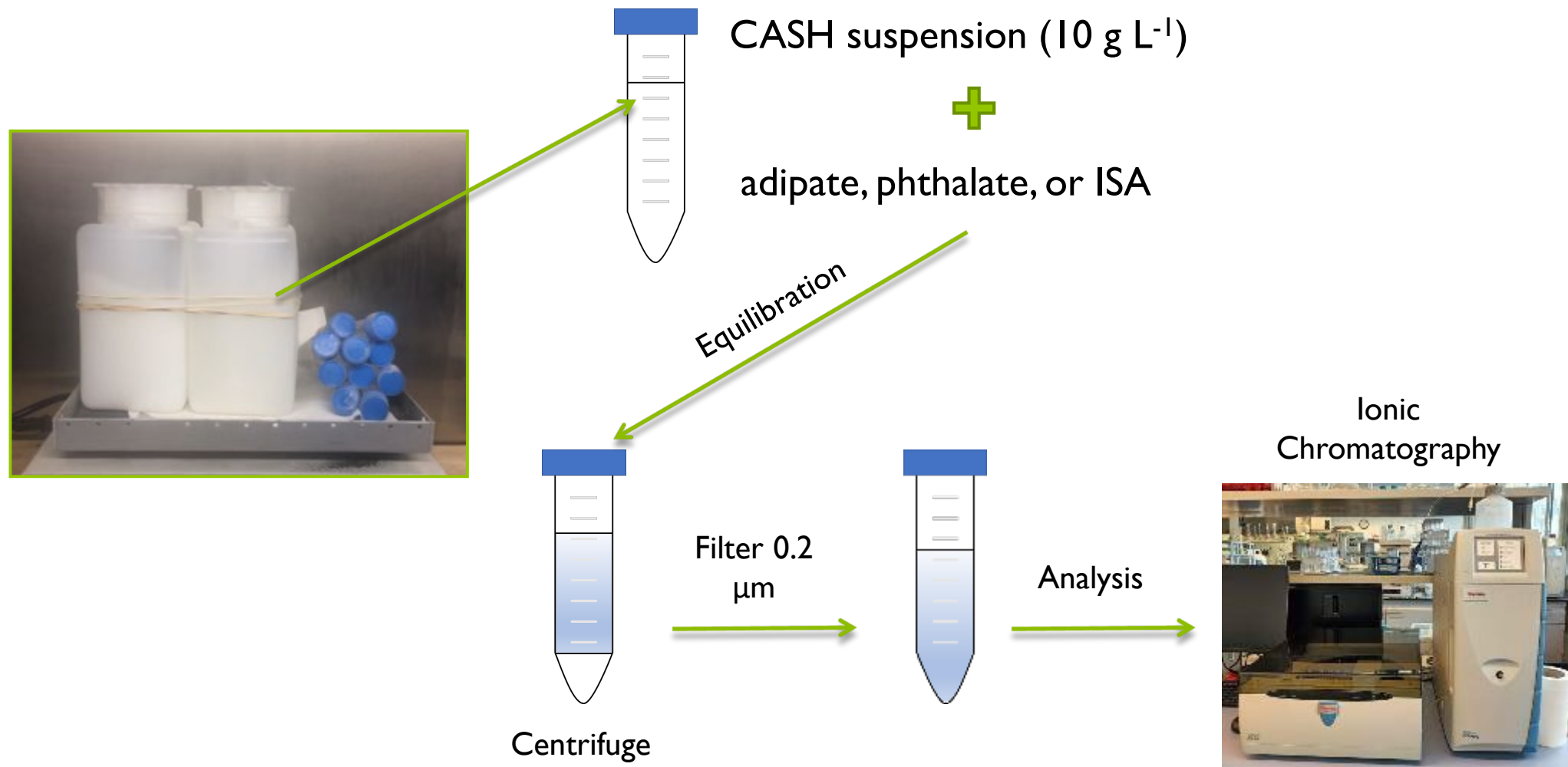


# Examples

- Example 1, sorption on simplified cementitious systems:
- Sorption of adipate, phthalate, and ISA to calcium alumina silicate hydrates, from Amphos 21.
- Example 2, sorption on hardened cement pastes:
- Interaction of the degradation products of a PAN-based (UP2) resin with Portland cement CEM I (degradation stage II), from KIT-INE
- Example 3, diffusion on hardened cement pastes
- Diffusion of Radiotracers and Organic Molecules in Cement Samples by Electromigration Technique, from Helsinki University & Andra

# Example 1

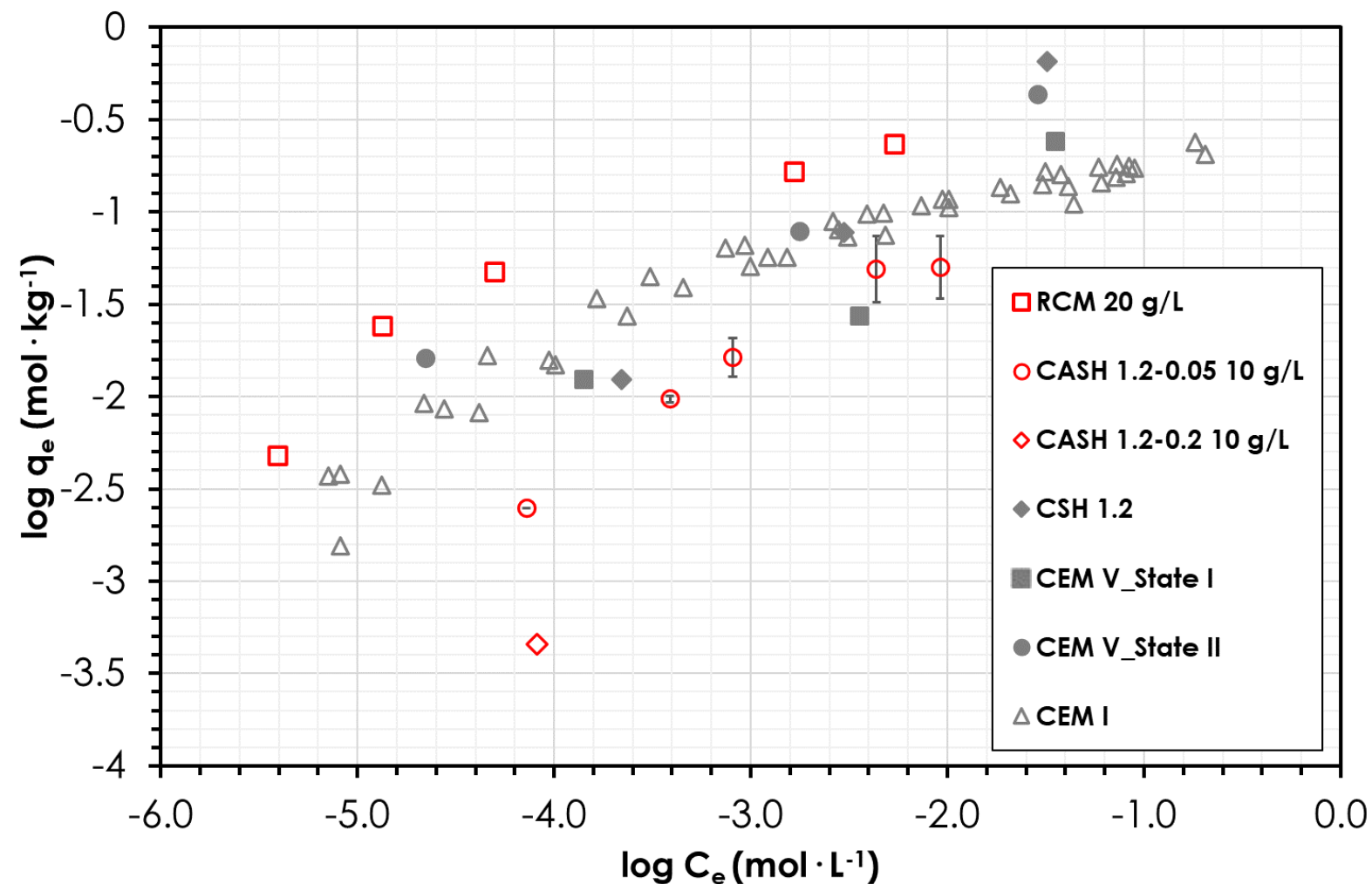
## Sorption of adipate, phthalate, and ISA to calcium alumina silicate hydrates





# Example 1

## Sorption of adipate, phthalate, and ISA to calcium alumina silicate hydrates



- ▶ No sorption of adipate or phthalate to C-A-S-H phases.
- ▶ Low sorption of ISA to C-A-S-H solids.

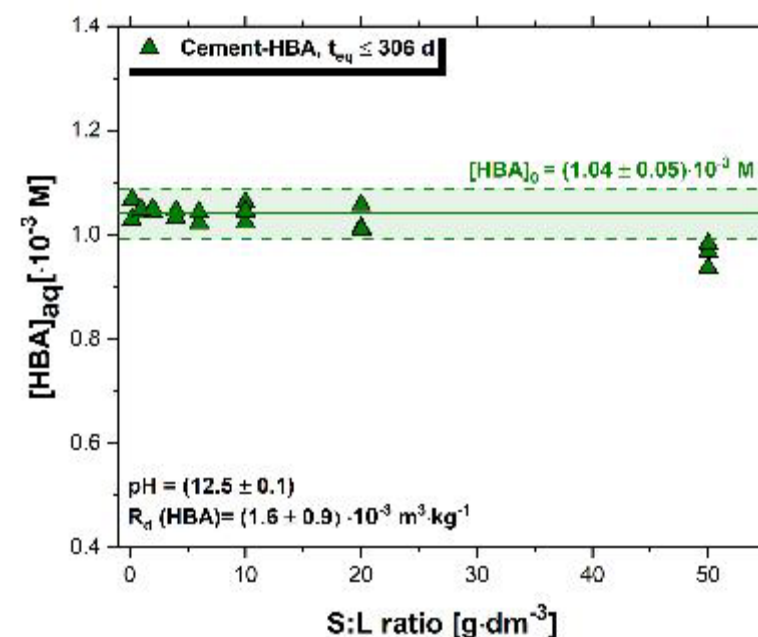
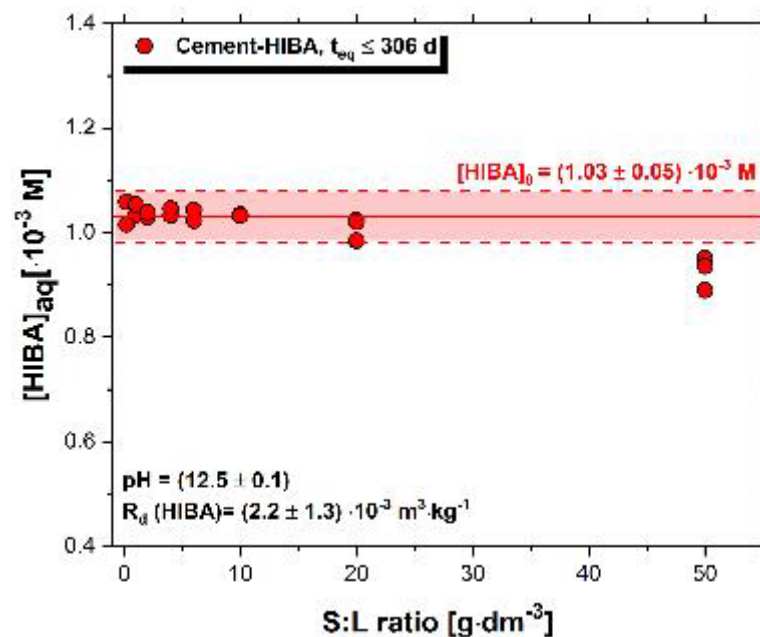
# Example 2

## Interaction of the degradation products of a PAN-based (UP2) resin with Portland cement CEM I (degradation stage II)

- All experiments performed under Ar atmosphere
- Batch sorption experiments with equilibrium pore water at degradation stage II ( $\text{pH} \approx 12.5$ ,  $[\text{Ca}]_{\text{tot}} \approx 0.02 \text{ M}$ ) and fresh cement powder: CEM I 42.5N BV/SR/LA type (provided by SKB)
- Sorption experiments with proxy ligands (defined by degradation leachates of UP2):
  - $10^{-6} \text{ M} \leq [\text{L}]_0 \leq 0.1 \text{ M}$  (GTA; HIBA; HBA),  $\text{S:L} = 4 \text{ g} \cdot \text{L}^{-1}$
  - $0.2 \text{ g} \cdot \text{L}^{-1} \leq \text{S:L} \leq 50 \text{ g} \cdot \text{L}^{-1}$  cement phase;  $[\text{L}]_0 = 10^{-3} \text{ M}$
- Sorption experiments of  $^{14}\text{C}$ -labeled GTA:
  - $15 \text{ g} \cdot \text{L}^{-1} \leq \text{S:L} \leq 50 \text{ g} \cdot \text{L}^{-1}$  cement phase;  $[\text{C}^{14}\text{-GTA}]_0 = 10^{-7} \text{ M}$
  - $10^{-5} \text{ M} \leq [\text{GTA}]_0 \leq 0.1 \text{ M}$ , spiked with  $[\text{C}^{14}\text{-GTA}]_0 = 10^{-7} \text{ M}$ ,  $\text{S:L} = 20 \text{ g} \cdot \text{L}^{-1}$
- Prior centrifugation was applied with  $0.1 \mu\text{m}$  Teflon syringe and 10 kD filtration
- Characterization of the aqueous phase:
  - NPOC, pH, LSC, Zeta potential analyzer

# Example 2

## Interaction of the degradation products of a PAN-based (UP2) resin with Portland cement CEM I (degradation stage II)



- ▶ Slight decrease of  $[L]$  observed at high S/L ratios.
- ▶ Observations differ significantly from previous sorption studies with polyhydroxocarboxylic acids, e.g. ISA or GLU<sup>[1,2]</sup> → Role of multiple OH-groups in uptake of organic ligands by cement

# Example 2

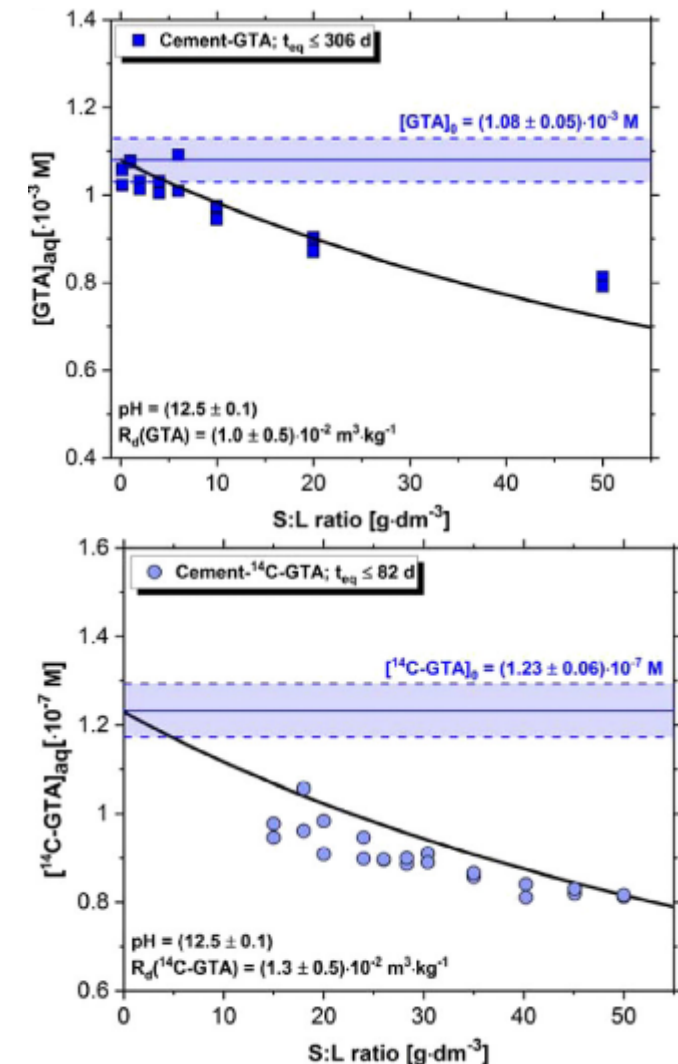
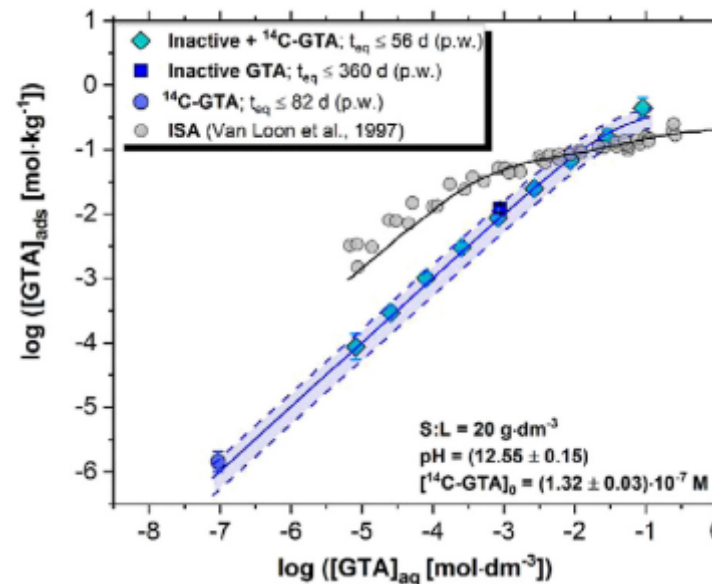
## Interaction of the degradation products of a PAN-based (UP2) resin with Portland cement CEM I (degradation stage II)

- One-site Langmuir isotherm explains well all experimental observations, including inactive and <sup>14</sup>C-labelled GTA

$$[GTA]_{\text{sorbed}} = \frac{K \cdot q \cdot [GTA]_{\text{aq}}}{1 + K \cdot [GTA]_{\text{aq}}}$$

$$q = (0.45 \pm 0.12) \cdot \text{mol} \cdot \text{kg}^{-1}$$

$$K = (22.5 \pm 6.1) \cdot \text{dm}^3 \cdot \text{mol}^{-1}$$



Weak uptake of HIBA and HBA by HCP. Slightly stronger uptake of GTA

# Example 3

## Diffusion of Radiotracers and Organic Molecules in Cement Samples by Electromigration Technique

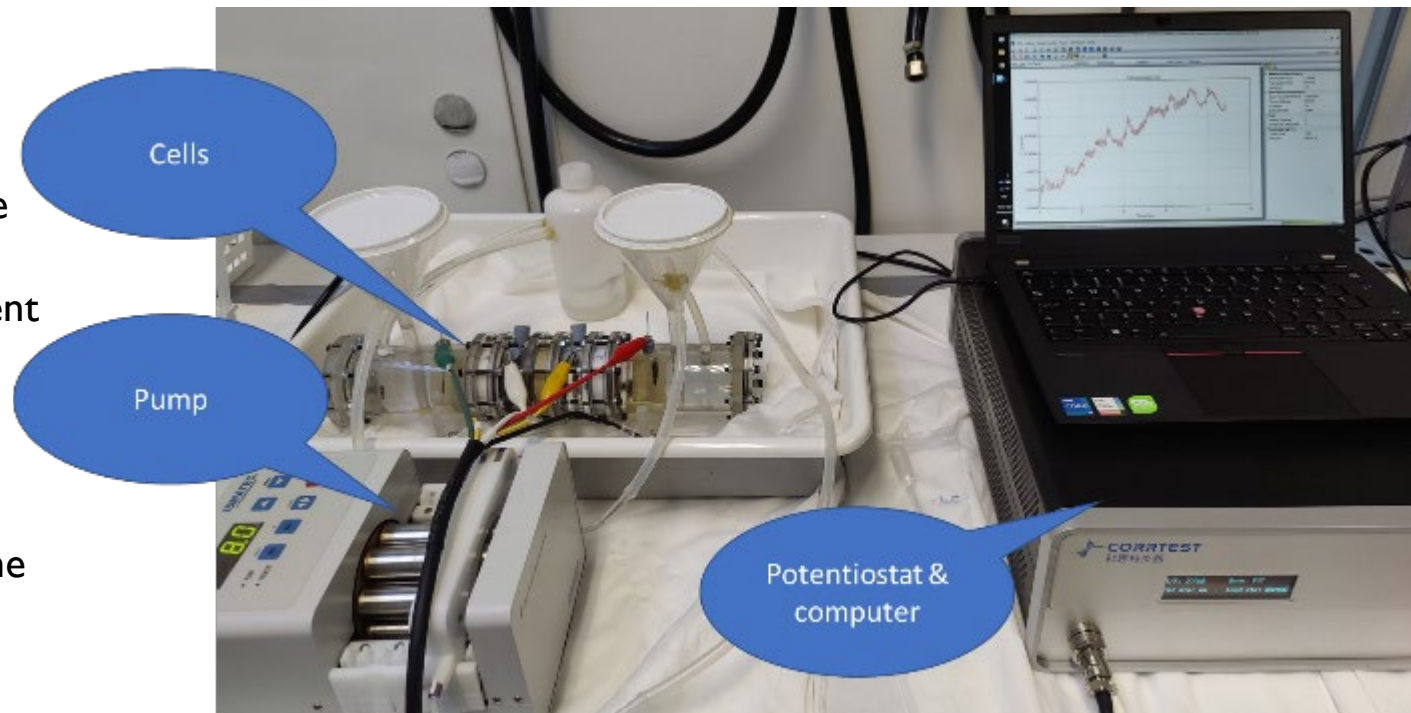
### Part I: Computer & potentiostat

- provide and control voltage applied to the cells ( $\pm 0.01$  V)
- Record current flowing through the cement sample

### Part II: Pump

- Neutralise  $H^+$  and  $OH^-$  produced from electrolysis reactions that happened on the anode and cathode

### Part III: Electromigration cell





# Example 3

## Diffusion of Radiotracers and Organic Molecules in Cement Samples by Electromigration Technique

Tracers:

Tracers	Form	Measurement method
HTO	Neutral	Beta (Tricarb)
Cl-36	Negative ion (-1)	Beta (Tricarb)
Cs-137	Positive ion (+1)	Beta (Tricarb)
Gluconate (C-14)	Organic molecular	Beta (Tricarb)
ISA	Organic molecular	TOC or IC (?)

Samples:

CEMV HCP (degradation states I and II) samples

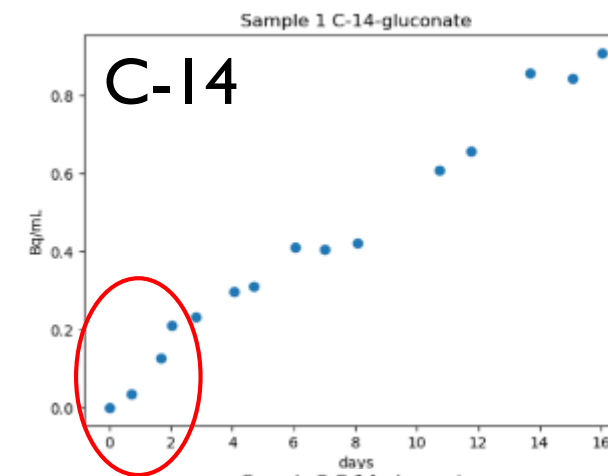
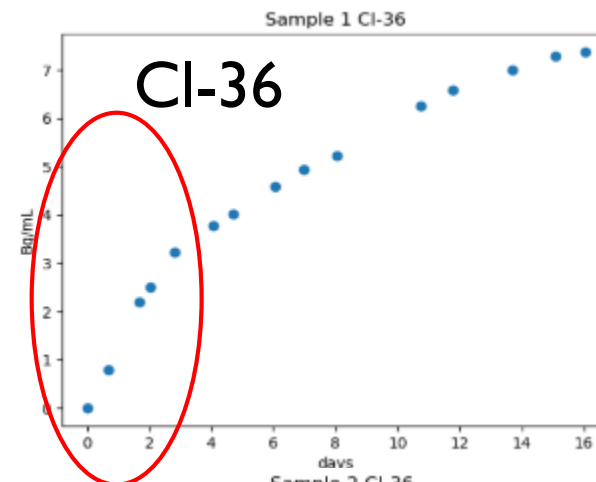


# Example 3

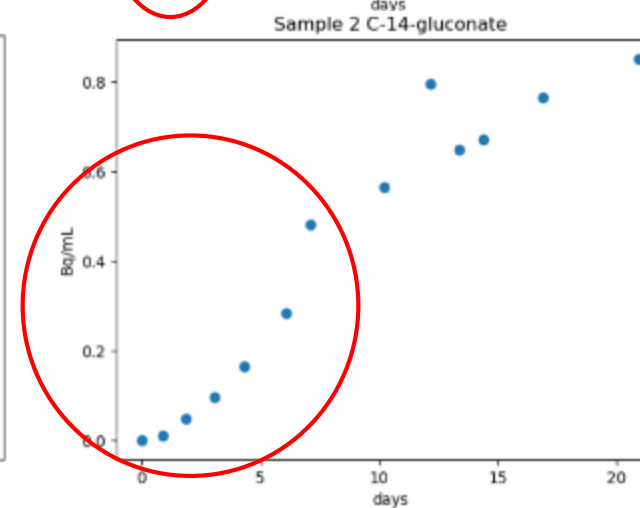
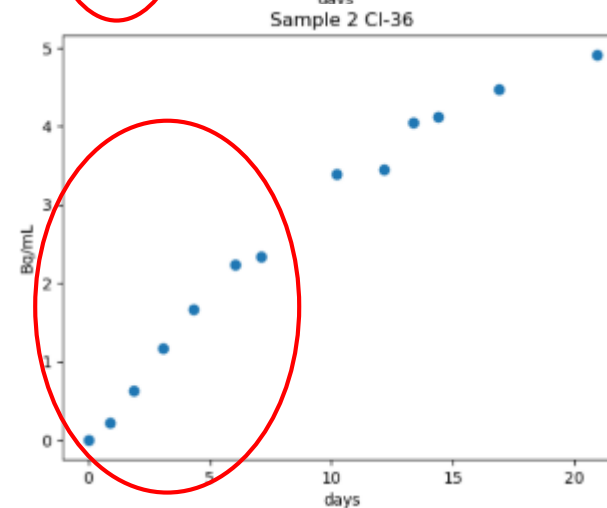
## Diffusion of Radiotracers and Organic Molecules in Cement Samples by Electromigration Technique

### Outlet breakthrough curve

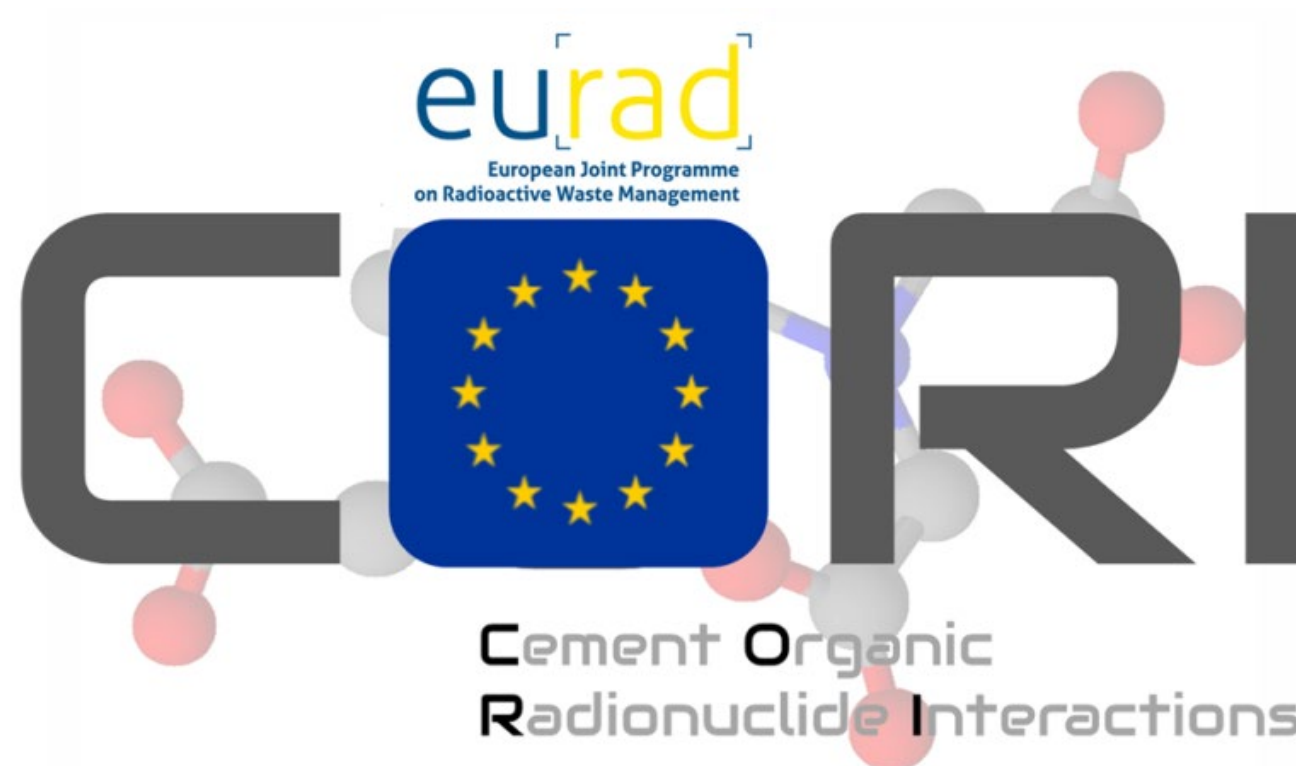
Sample No. 6.6 →



Sample No. 3.4 →



**Thank you for your attention !!!**



*The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 847593.*





## **CORI Lunch and Learn, 12<sup>th</sup> December 2023**

### **EURAD WP3: CORI** **cement-organic-radionuclide-interactions**

#### ***Task 4: Cement Organic Radionuclide Interactions***

**Tiziana Missana and Nathalie Macé**

# OBJECTIVE

**CORI (Task 4) addresses topics in the context of cement – organic - radionuclide-interactions (CEM-RN-ORG).**

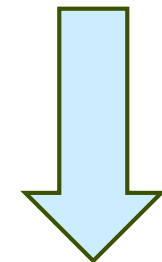
**To improve the knowledge on the organics which may enhance RN migration in the post closure phase of VLL / LL / IL waste, including surface – shallow disposals.**



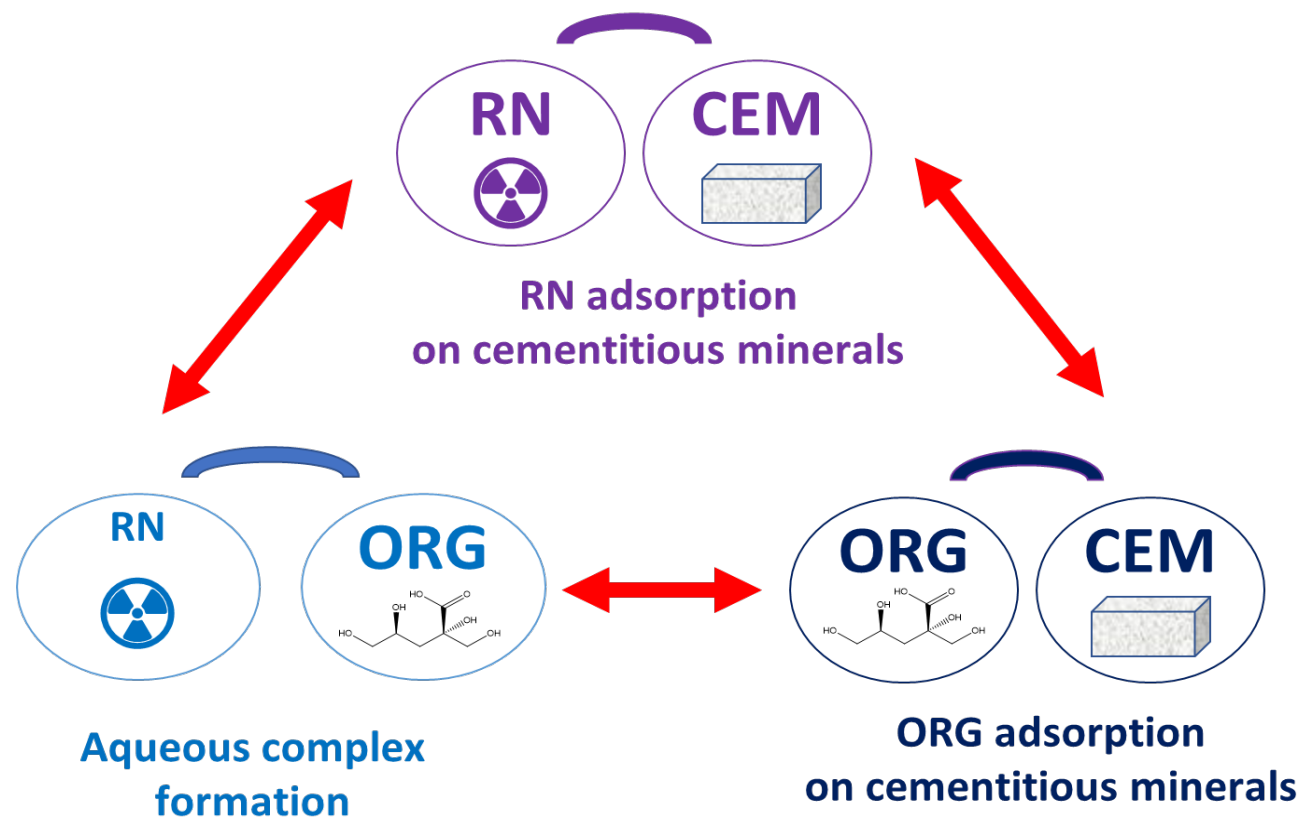
**Cement materials widely used for stabilizing and conditioning radioactive waste in these types of disposals.**

# TASK 4 (mechanistic understanding)

- Radionuclides incorporation → analysis of ternary systems  
(Cementitious Materials, Organics, RN)



Analysis of the ternary system



Analysis of binary systems with radionuclides

→ CEM & RN -- ORG & RN

Incorporating information from Task 3

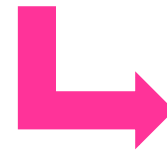
→ CEM & ORG



# ORGANIC LIGANDS SELECTION



- ❑ Tissues, papers → cellulose
- ❑ Plastics (PVC), filters
- ❑ Resins (IER)
- ❑ Chelates (decontamination processes), EDTA, NTA
- ❑ Additives (superplasticizers, SP)
- ❑ ...



Degradation  
products

DEGRADATION (Task 2)

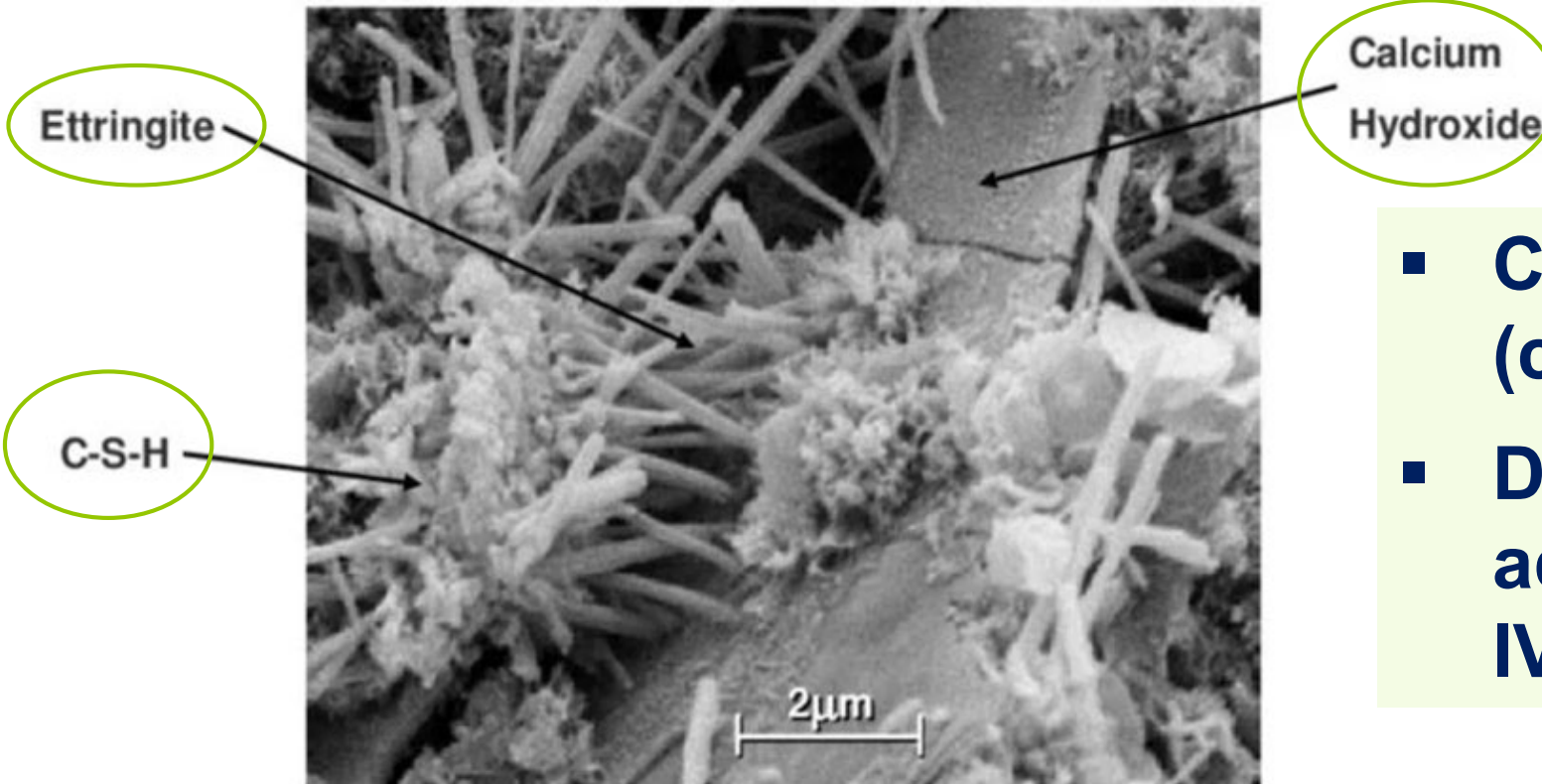
Hydrolysis

(high pH)

Radiolysis

- Many possible systems to be considered in Task 4 → including real degradation products (RDP) from Task 2.
- Specificity of CEM-ORG-RN interactions → materials and physico-chemical conditions.

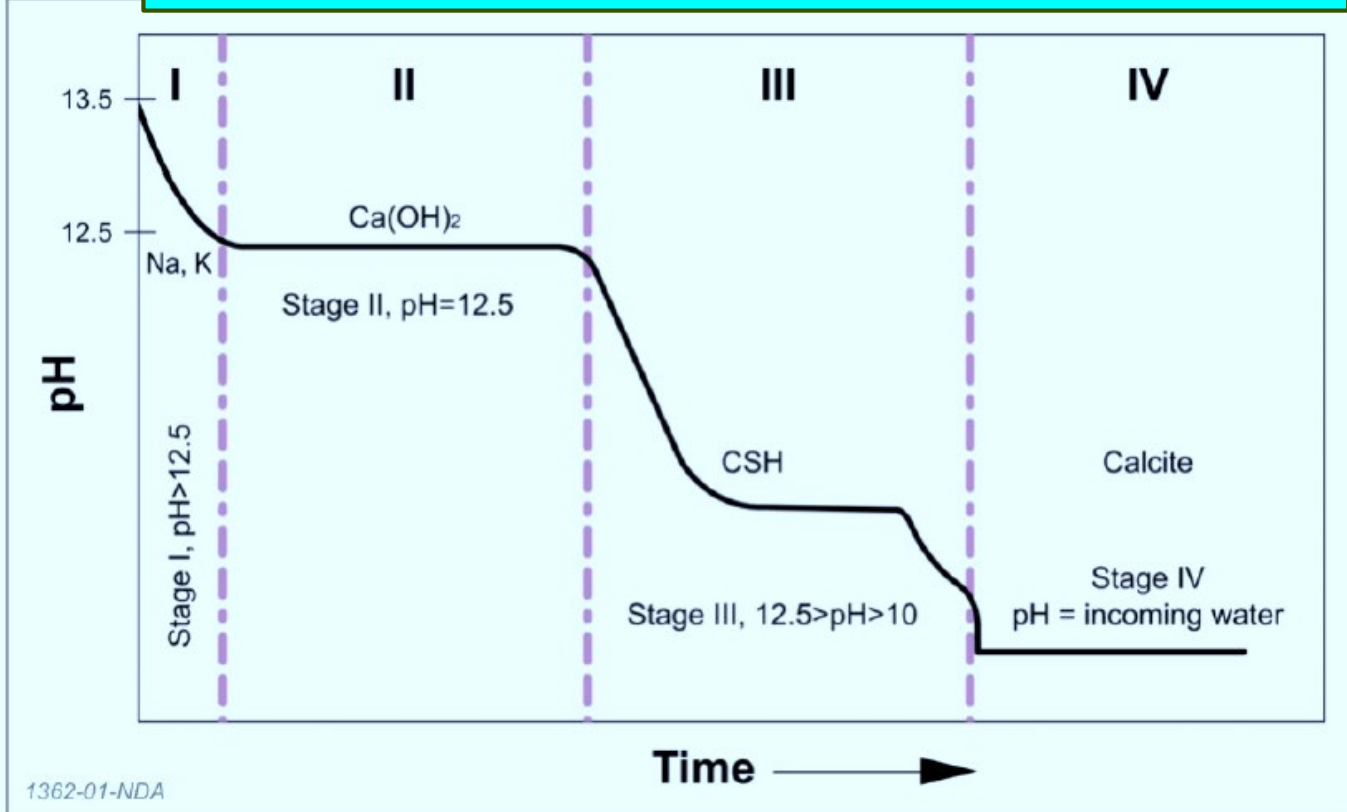
# CEMENT & CEMENTITIOUS MATERIALS SELECTION



**COMPLEX**

- Complex mineral system (cement, hydrated phases)
- Different compositions and additives. CEM I, CEM II, CEM IV, CEM V...

**Stages I to IV →→→→→**



**EVOLVING**

- Hyper-alkaline conditions
- Cement degradation → chemical evolution / solids and porewater (pH, salinity).
- Different stages, different CEM-ORG-RN interactions.

# OVERVIEW OF THE STUDIED SYSTEMS in CORI TASK 4

\*RCM: reference cement material

## ORGANICS

EDTA, NTA

ISA, GLU

IER & GTA, HIBA,  
HBA

CITRATE, FORMATE,  
ADIPATE, PHTHALATE

Superplasticizers

REAL ORGANIC  
DEGRADATION  
PRODUCTS  
(TASK 2)

## CEMENTITIOUS MATERIALS

CEMENT  
MINERALS

CSH, CASH, AFm, Aft, Port

CEM I (RCM\*), CEM III, CEM IV,  
CEM V

HCP  
(CEM)

Stage (I, II, III/IV)

## TESTS

Solubility

Retention

Diffusion

## RADIONUCLIDES

U (VI), Ni,  
Pb

Trivalent  
Actinides /  
Lanthanides

Tetravalent  
Actinides

HTO

## □ Solubility data.

- Operational solubility: difference between adsorption / (co)precipitation processes

OS

## □ Adsorption data (binary and ternary systems).

- Batch sorption tests in powdered materials (also in small coupons)

$K_d$  ( $R_d$ )

SRF

## □ Diffusion data (binary and ternary system) → more realistic conditions → complicate tests (time consuming, chemical equilibrium,...).

- IN-DIFFUSION / THROUGH-DIFFUSION TESTS

$D_a / D_e$

$\varepsilon$

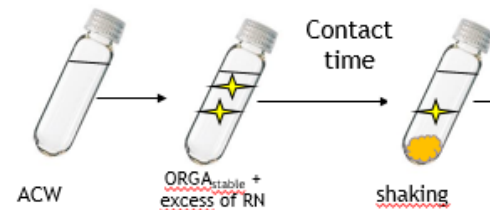
Lot of results obtained in Task 4...Only few examples...



# Chelates (EDTA)

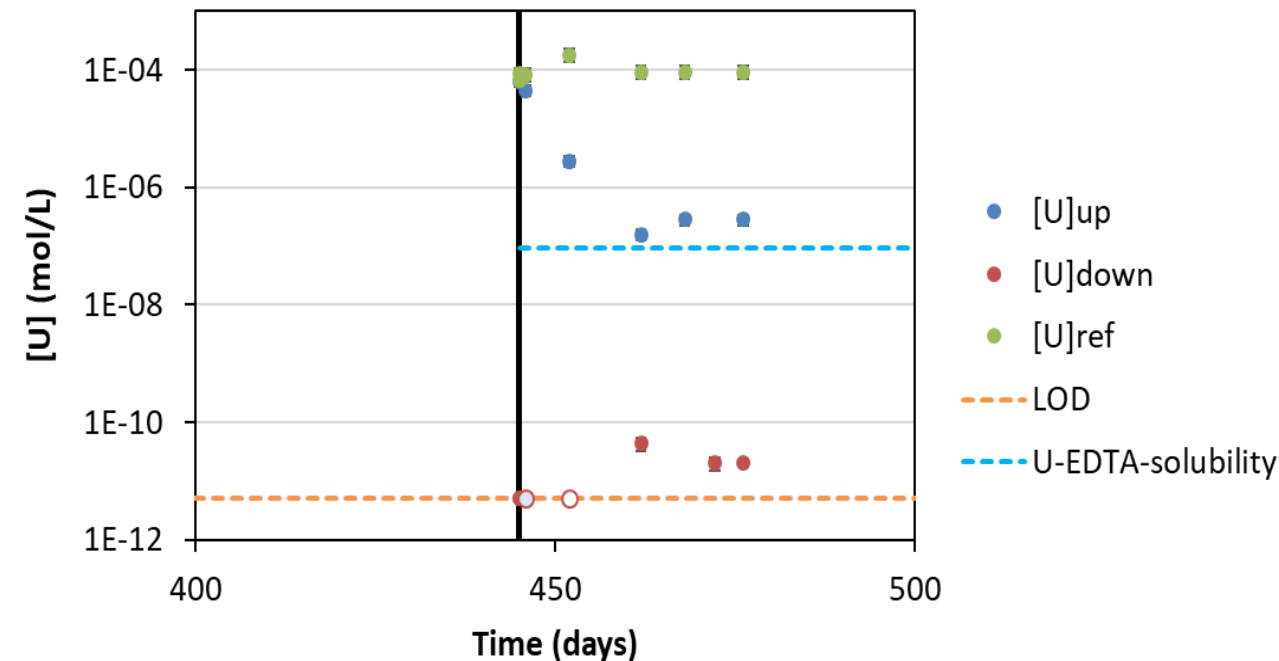
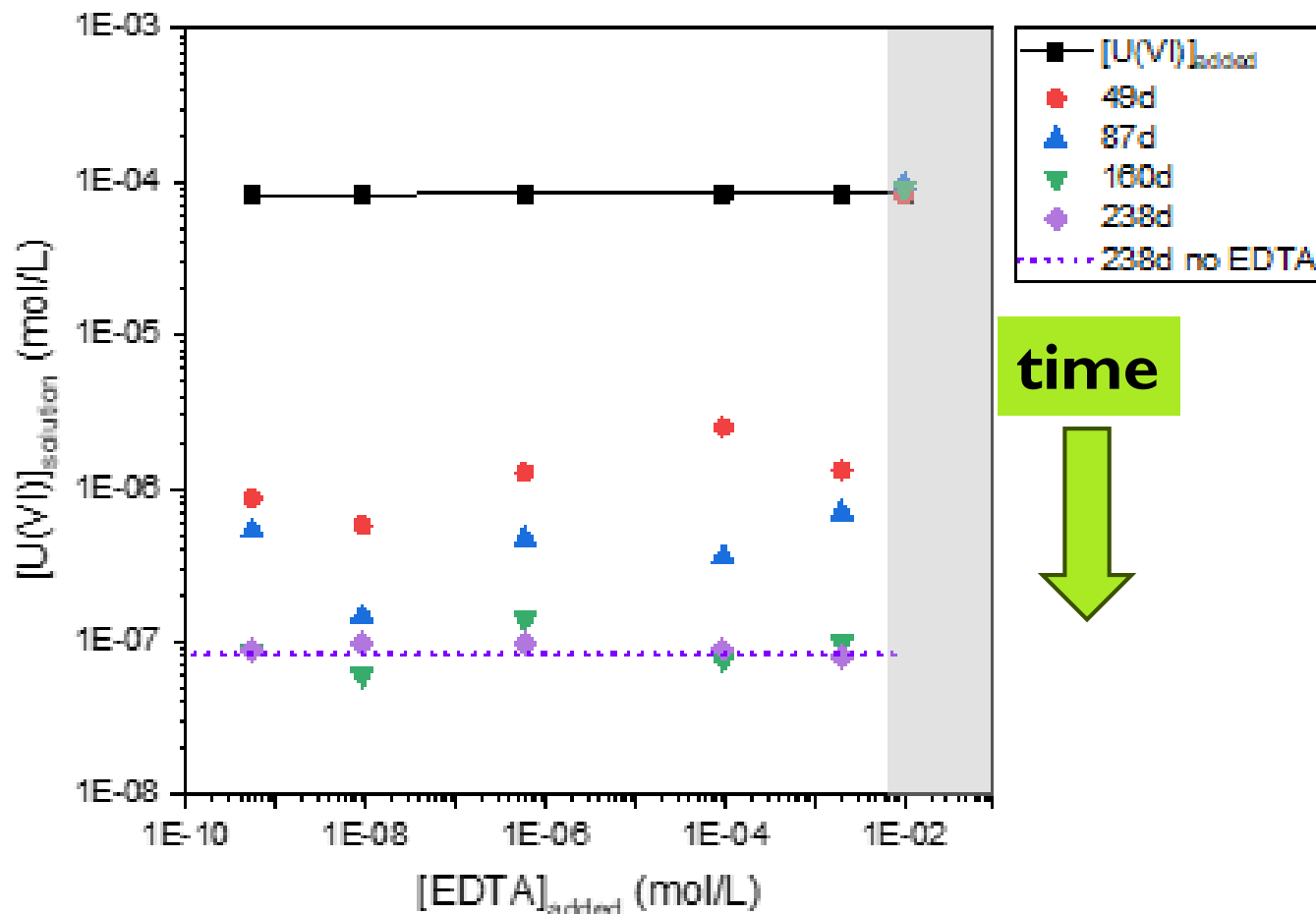
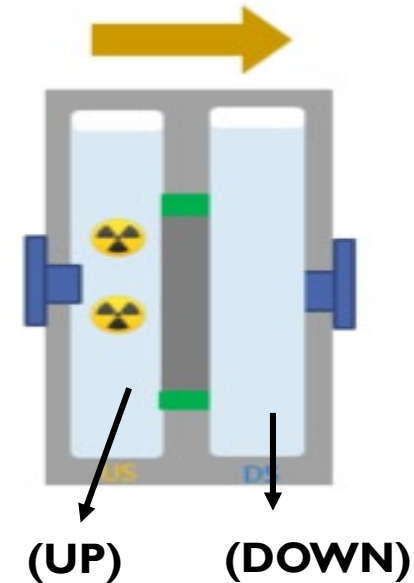
## U(VI) migration in presence of EDTA in CEM (Stage II) pH 12.5

### Operational solubility



vs.

### Diffusion experiments



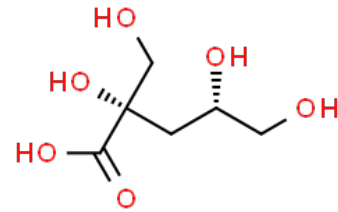
- Similar evolution of [U(VI)] solution in both experiments
- Solubility limit  $\sim 10^{-7}$  M  $\rightarrow$  minor effect of EDTA



# Cellulose degradation products (CDP)

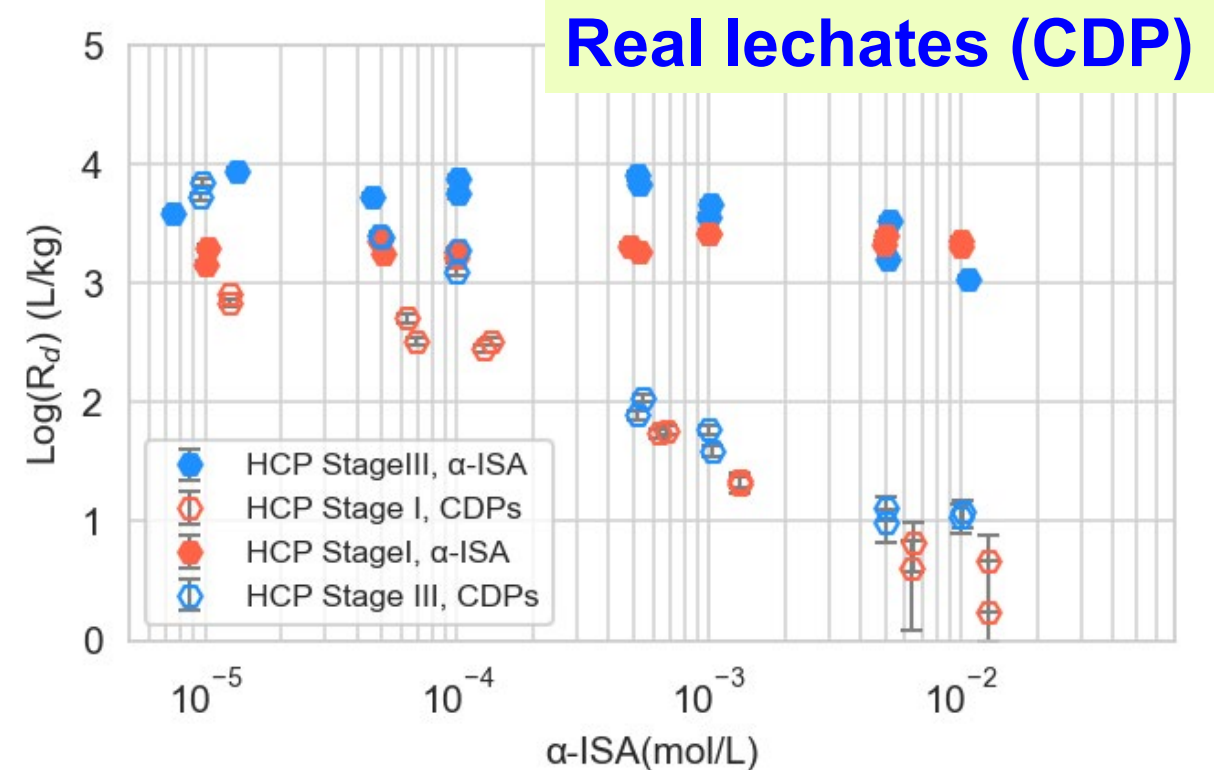
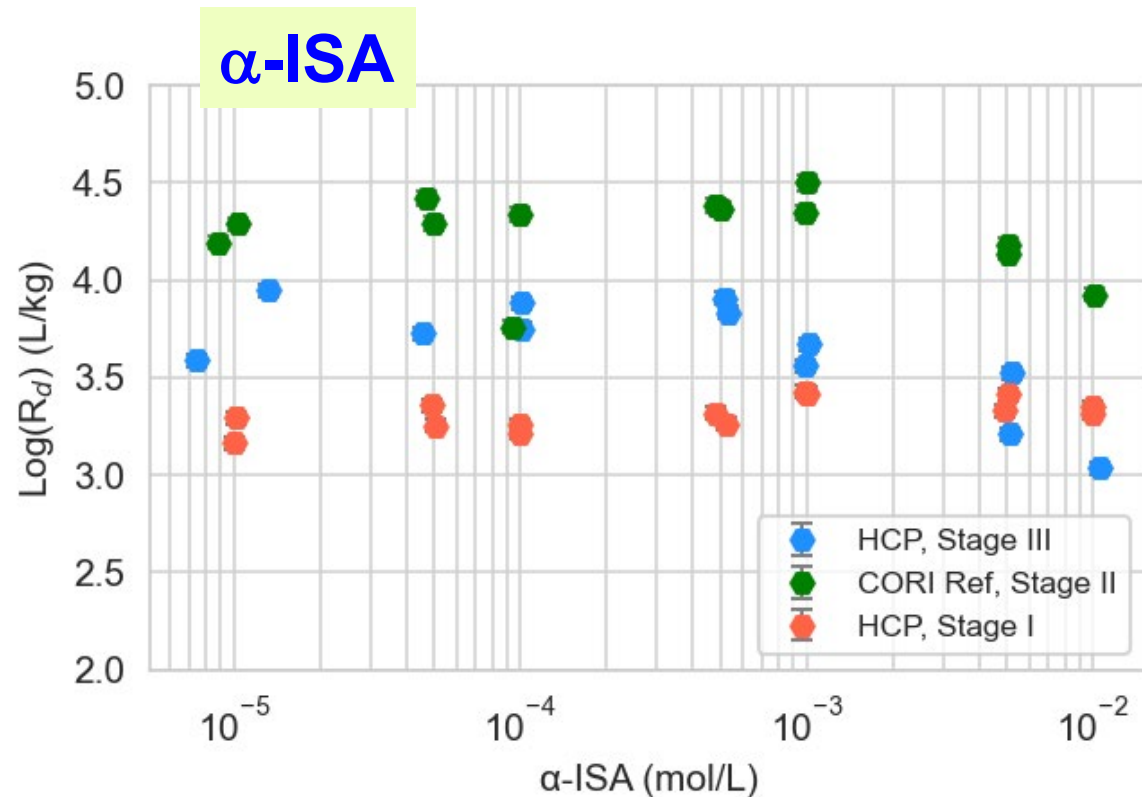
## Ni(II) adsorption in CEM (Stage I, II and III) in the presence of CDP.

- Main CDP: Isosaccharinic acid (ISA).
- $\alpha$ -ISA complexing properties. Widely studied, easy synthesis.



VS.

- Task 2 CDP → Radiolysis + Hydrolysis.
- Different cellulosic materials → cocktail of CDP (mainly  $\alpha$ -ISA, but also others).



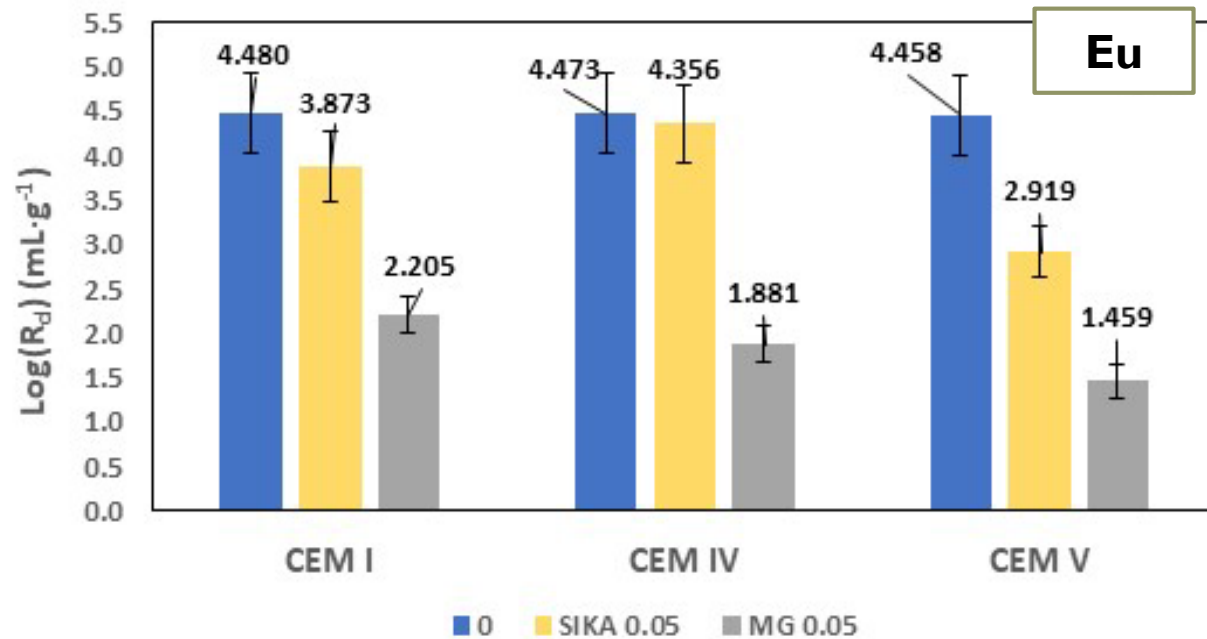
- No effects of  $\alpha$ -ISA on Ni adsorption in HCP
- Also in-diffusion tests.

- “Real” CDP affects Ni adsorption in HCP (same  $\alpha$ -ISA content)

# Superplasticizers

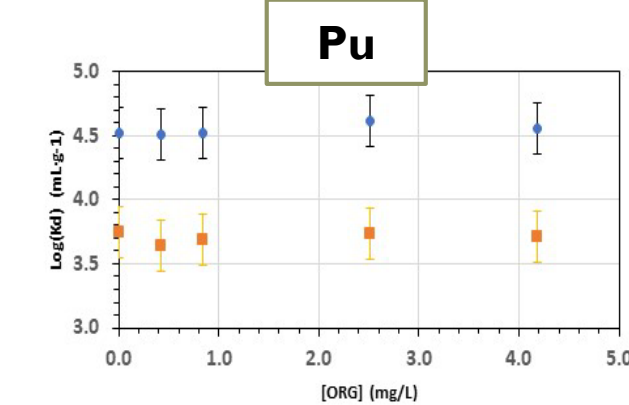
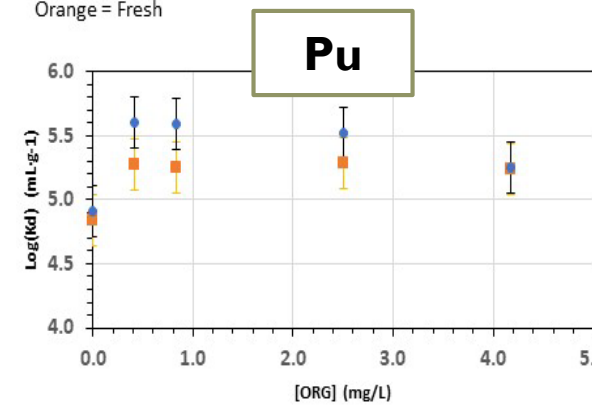
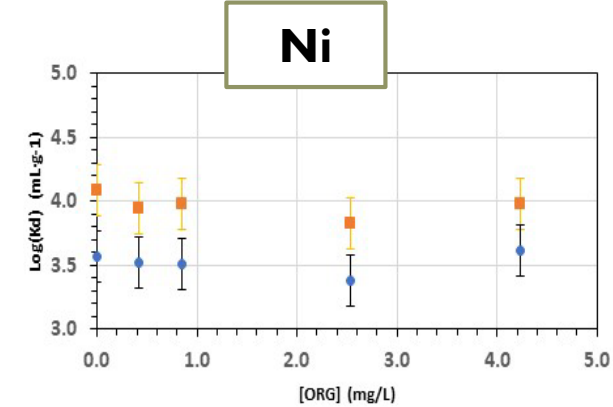
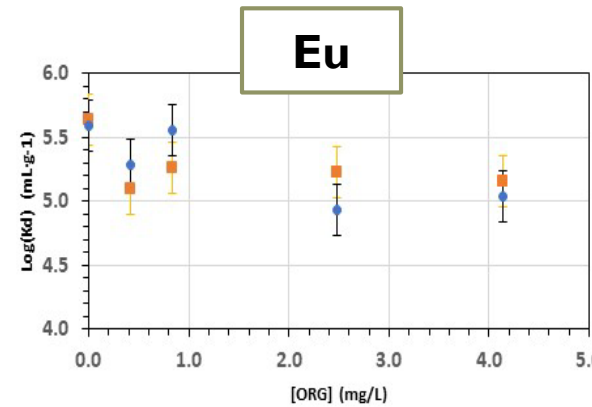
## RN adsorption in CEM in the presence of SPs (Ni, Eu, U, Pu)

Batch sorption experiments CEM (Stage I) + Commercial SPs - 5 wt %, added to water



- Ni & SPs in the solid: no different leaching properties or diffusivity were observed.
- Sorption tests with SPs in water → No clear effects on K<sub>d</sub>.
- Eu with MG(PCE) → real, colloid pcpc?
- To be checked with diffusion tests.

## Task 2 : Hydrolysed PCE by BGRM Sorption tests with CEM (Stage I & II)



### High variability in the market:

- Polycarboxylate, PCE, Master Glenium (MG)
- Melamine based (SIKA)

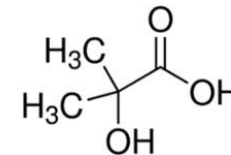
Low quantity (1 - 5 wt %) in CEM (and in PW )?

# Resins (filters)

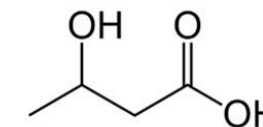
## RN solubility and adsorption on CEM (Stage II) in the presence of UP2W

- UP2W: polyacrylonitrile-based polymer (PAN) used as filter aid in nuclear power plants. **vs.**
- Real degradation products of UP2W (Task 2)

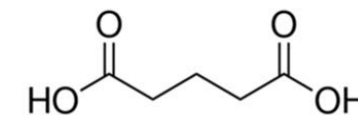
**HIBA**



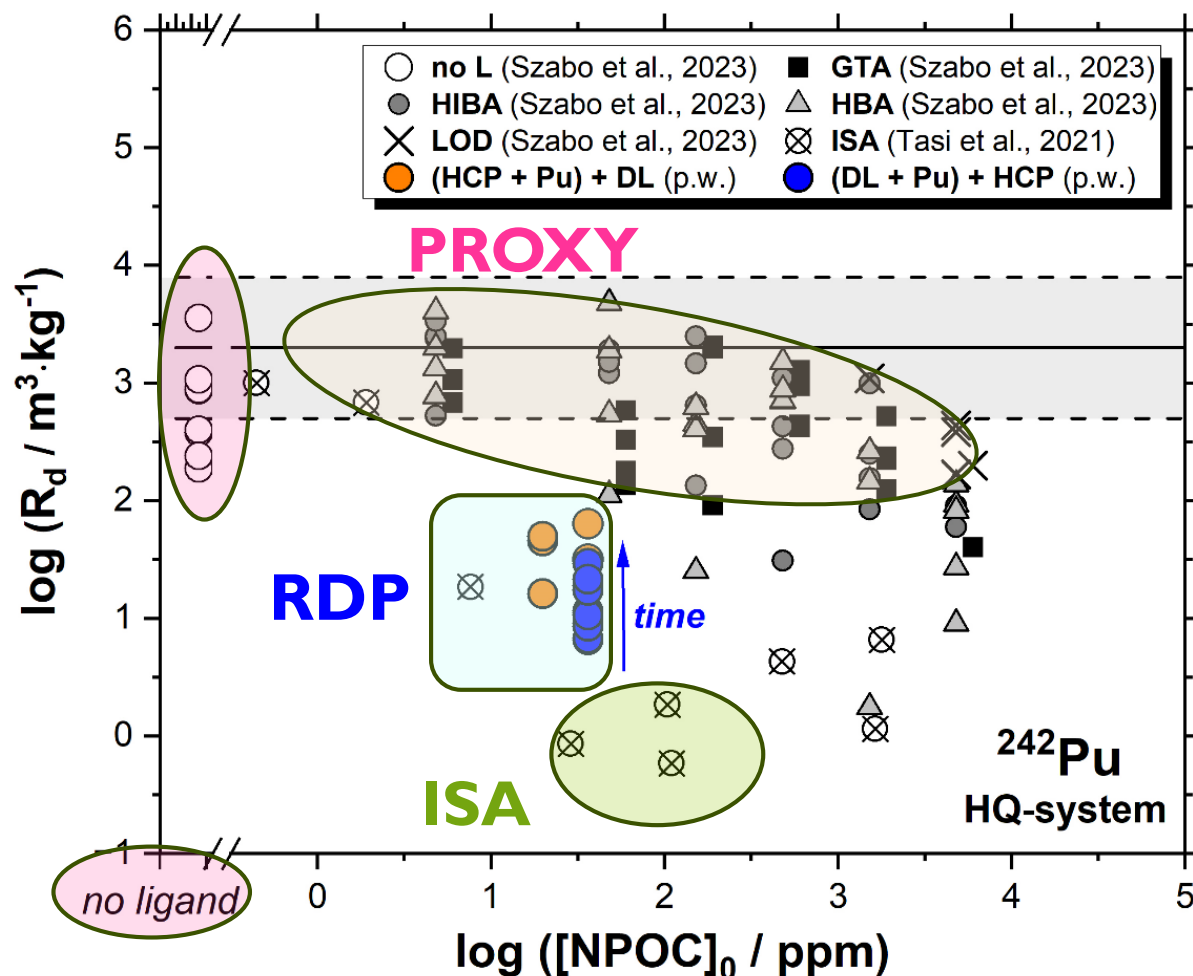
**HBA**



**GTA**



Proxy ligands:  $\alpha$ -hydroxyisobutyric acid (HIBA); 3-hydroxybutyric acid (HBA) and glutaric acid (GTA).



- Proxy ligands: no significant impact on Ca(II), Nd(III) or Pu(IV) solubility. Slight increase of Ni(II) solubility at  $[L] = 0.1 \text{ M}$ .
- $^{63}\text{Ni(II)}$ ,  $^{152}\text{Eu(III)}$  and  $^{242}\text{Pu(III/IV)}$  uptake slightly affected by proxy ligands. Cf. ISA.
- RDP: decrease in the uptake of  $^{63}\text{Ni(II)}$ ,  $^{152}\text{Eu(III)}$  and  $^{242}\text{Pu(IV)}$  by HCP  $\neq$  proxy ligands.

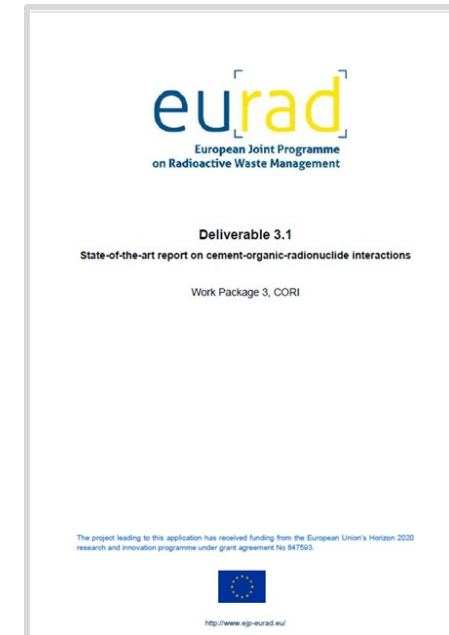
Importance of studying RDP



# Conclusions

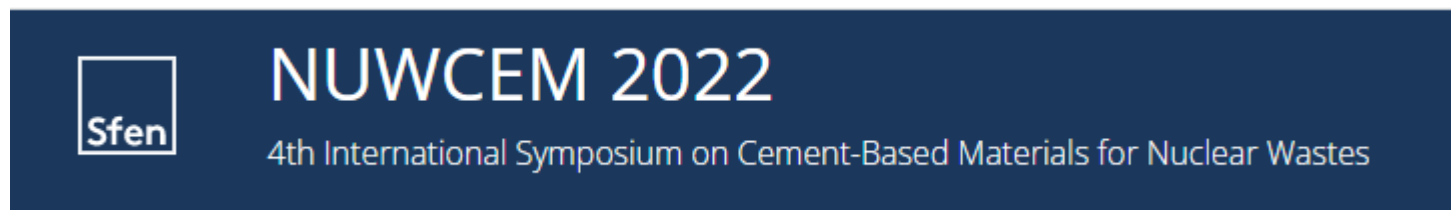
Many different systems have been studied; many new data available!

**PLEASE SEE: Contributions (oral + posters) in international conferences, internal reports, articles + EC reports available onto CORI project place website**



Mechanisms and Modelling of Waste/Cement Interactions

FISA 2022 – EURADWASTE '22



SBNWM 2023

47th Scientific Basis for Nuclear Waste Management Symposium

6 - 10 November 2023 | Cologne, Germany



Conference website	Second Announcement	
<p><b>6th International Workshop on Mechanisms and Modelling of Waste / Cement Interactions</b></p> <p>PRAGUE, CZECH REPUBLIC NOVEMBER 20th – 22nd, 2023</p> <p>For information or questions regarding the workshop on "Mechanisms and Modelling of Waste / Cement Interactions", please contact: <a href="#">Peter Večerník (ÜV Ret)</a></p>	<p><b>EURAD WP CORI Final Internal Workshop</b></p> <p>PRAGUE, CZECH REPUBLIC NOVEMBER 23rd, 2023</p> <p>Information on the Final Workshop of the WP CORI integrated in EURAD HERE will be made available at a later time. For information on CORI please contact the project coordinator <a href="#">Marcel Altmajer (KIT)</a></p>	<p><b>Excursions optional</b></p> <p>NOVEMBER 24th, 2023</p> <p>Laboratories: CTU, ÚJV, CVR, SÚRAO facilities</p>

# Thanks

## Organizations actively contributing to Task 4



Amphos21, Spain

Andra, France

CEA, France

CIEMAT, Spain

CPST, Lithuania

CTU, Czech Republic

HZDR, Germany

JGU INC (UMainz), Germany

FZJ, Germany

KIT, Germany

RATEN, Romania

SCK-CEN, Belgium

Subatech, France

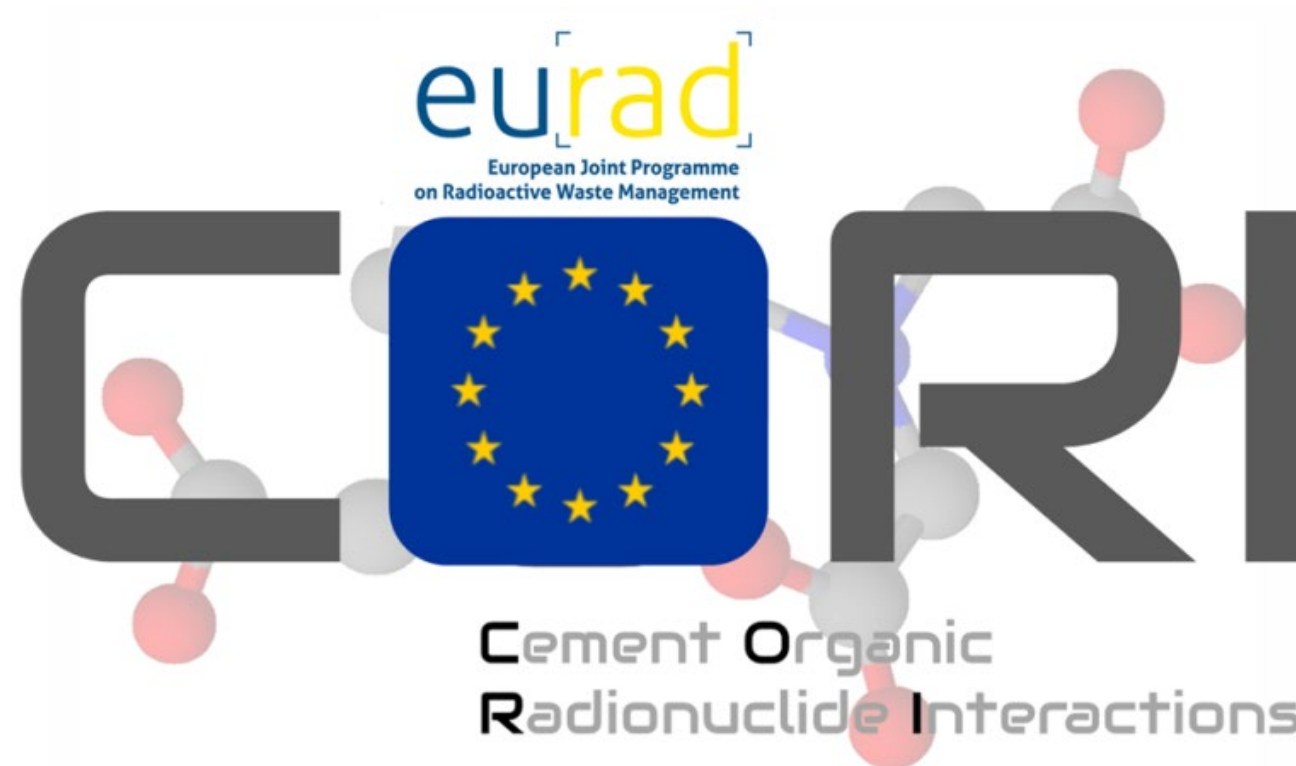
SÚRAO, Czech Republic

UCY, Cyprus

UJV, Czech Republic

Upotsdam, Germany

**Thank you for your attention !!!**



*The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 847593.*