Radionuclide migration studies performed with the Task 4 of CORI workpackage

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NUWCEM 2022 – 4th International Symposium on Cement-based Materials for Nuclear wastes, May 4 to 6, 2022, Avignon, France

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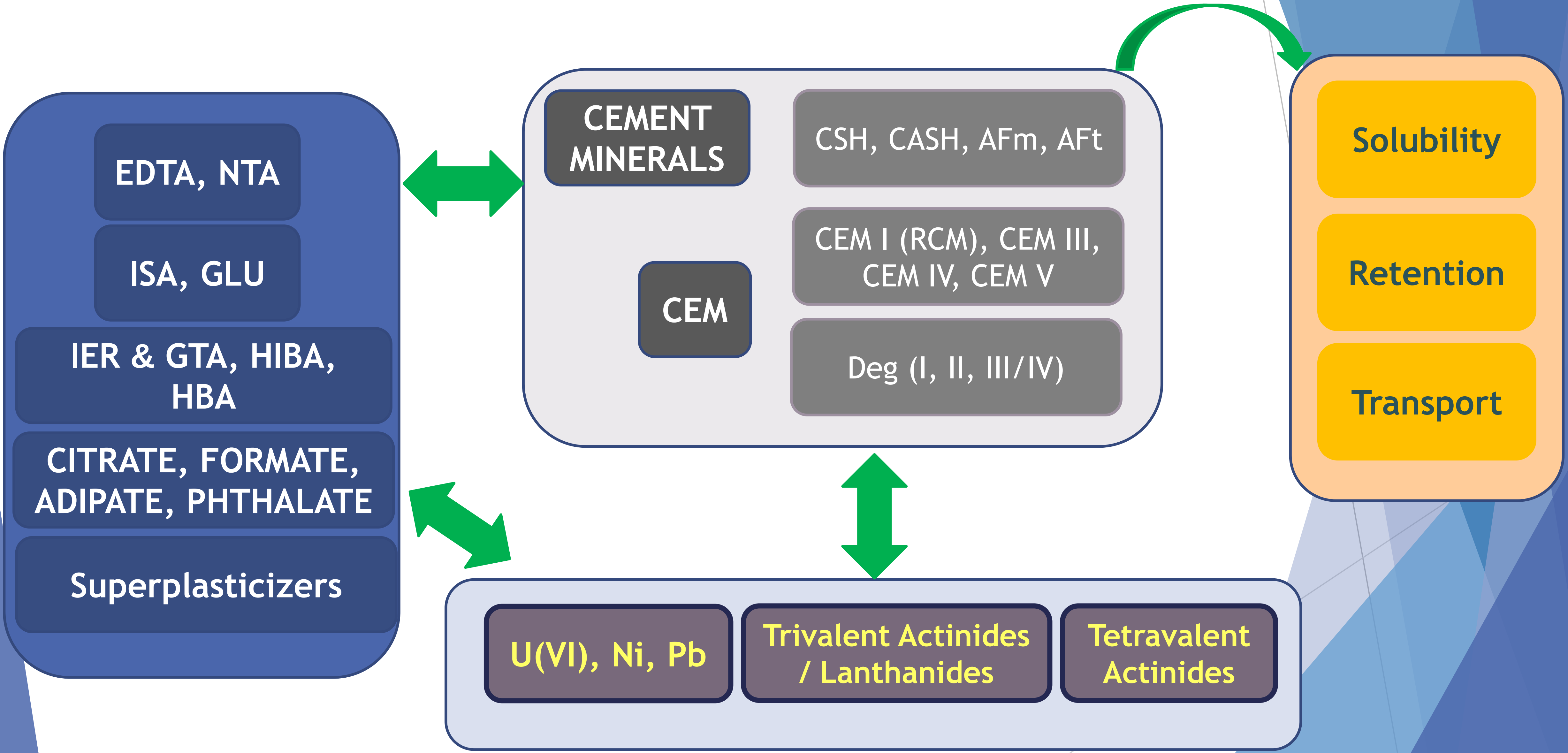
Task 4 - Radionuclide-organic-cement-interactions

- **Main objectives:**
  - Improving the knowledge on organic-radionuclide complexes mobility in cement-based systems
  - Studying the competition or synergetic effect in ternary systems (i.e. organic(s)/radionuclide/cement)
  - Providing a mechanistic understanding of radionuclide interactions and quantitative transfer data in various cementitious environments

Objective of Task 4: "Analyze the effects of organics on RN retention & transport in cementitious materials"



RCM: reference cement material

Dedicated experiments using a CEM I – RCM

Cement : CEM I 45.5R, CEMEX Prachovice, Czech republic;
HCP : water/cement = 0.45 – curing time > 28 days – portlandite saturated solution
➔ 12 participants will include RCM in their work program: retention and/or transfer experiments

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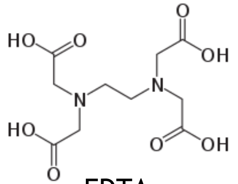
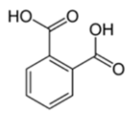
RCM: reference cement material

Example of technical work in Task 4



EDTA



Phthalic Acid

- EDTA, NTA
- ISA, GLU
- IER & GTA, HIBA, HBA
- CITRATE, FORMATE, ADIPATE, PHTHALATE
- Superplasticizers

CEMENT MINERALS

- CSH, CASH, AFm, AFt

CEM

- CEM I (RCM), CEM III, CEM IV, CEM V
- Deg (I, II, III/IV)

- Solubility
- Retention
- Transport

- U(VI), Ni, Pb
- Trivalent Actinides / Lanthanides
- Tetravalent Actinides
- HTO

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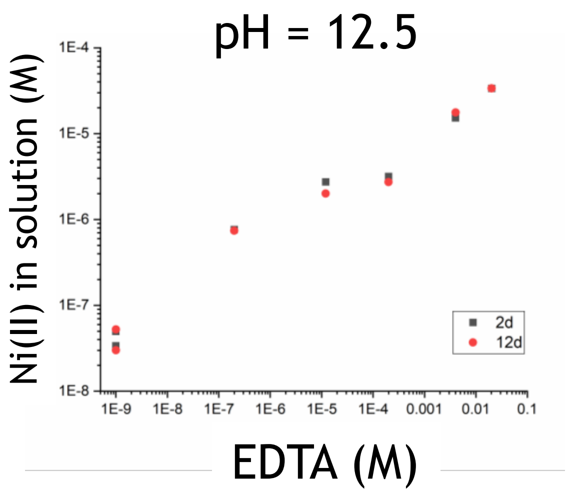
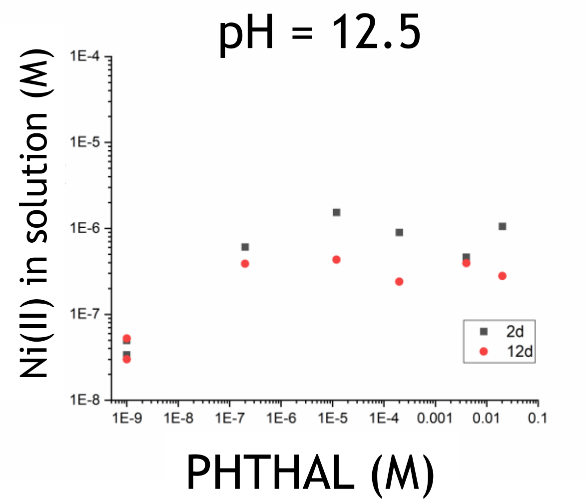
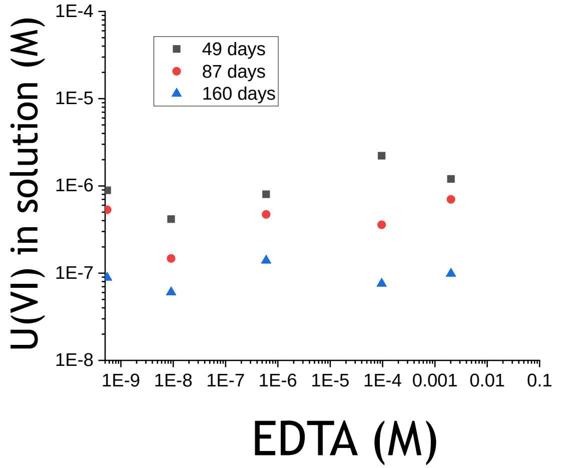
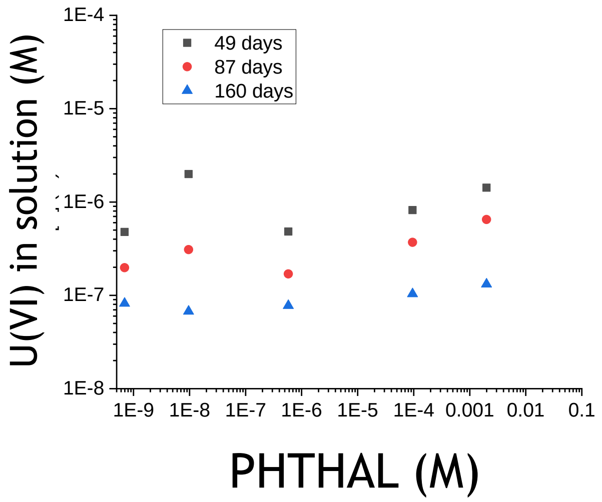
Step 1: operational solubility to size migration experiments





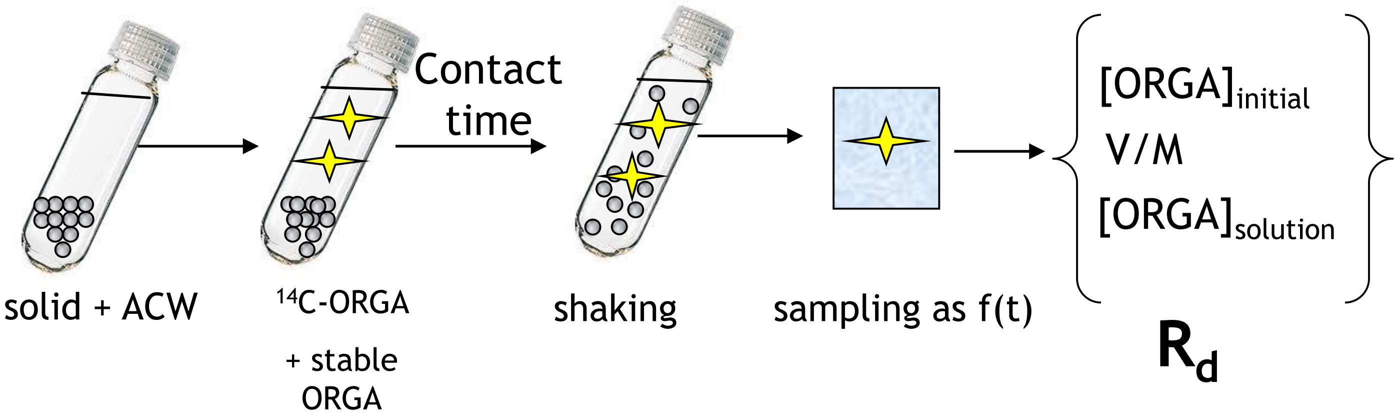




- Increase of the solubility with higher concentration of ORGA
- Solubility of Ni or U in presence of EDTA > phthalate
- Difficulties to observe ORGA-U(VI) species by TRLFS
- $[ORGA]_{ini}$ for diffusion = 10^{-2}M

Step 2: Retardation factor estimation from batch sorption experiments

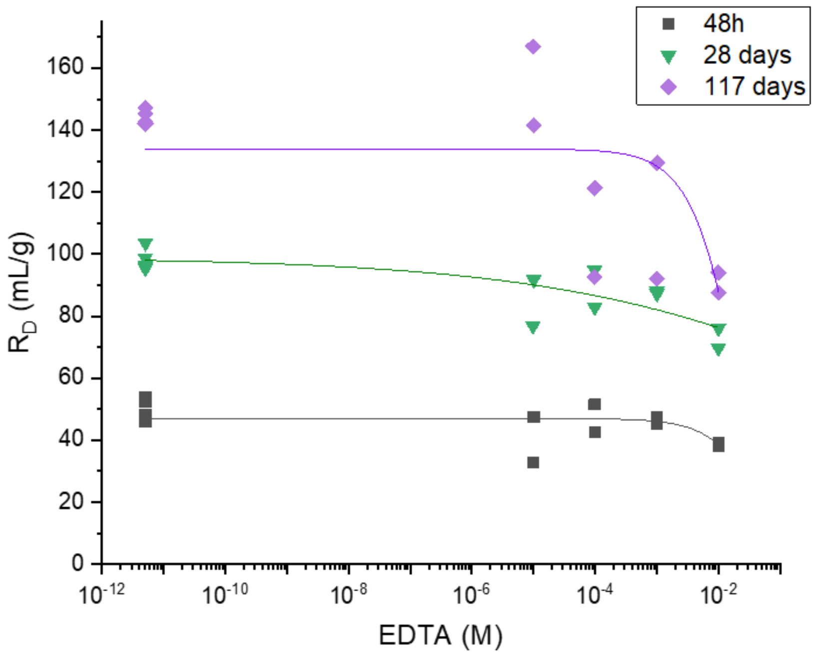
$$R_d\ (L/kg) = \frac{[ORGA]_{solid}}{[ORGA]_{solution}} = \frac{V_{solution}}{m_{dry\_solid}} \times \frac{[ORGA]_{initial} - [ORGA]_{solution}}{[ORGA]_{solution}}$$

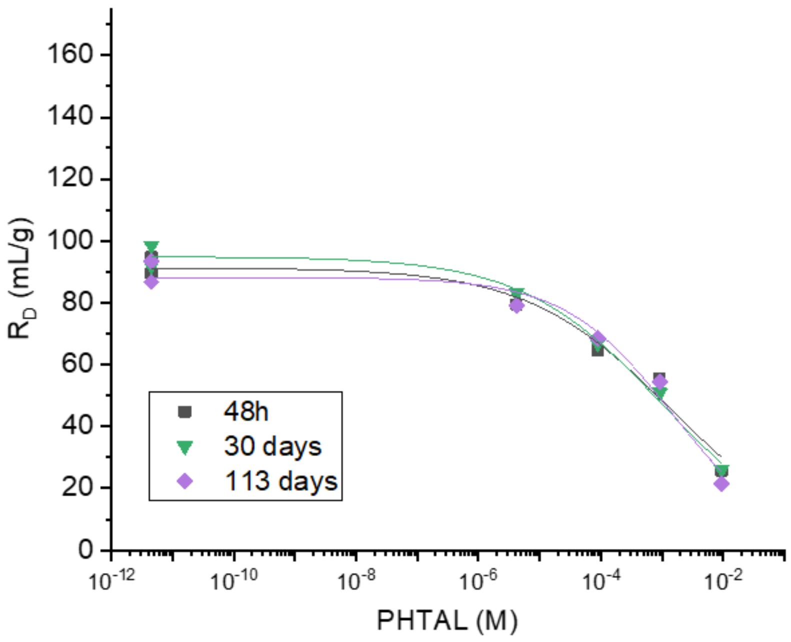


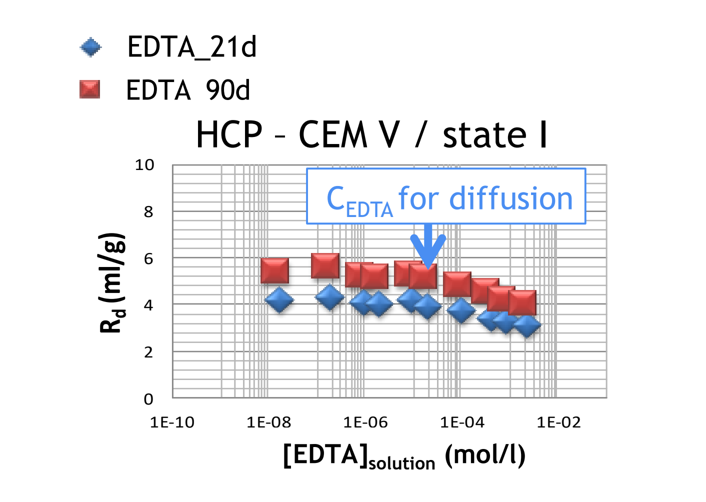
- Crushed HCP (CEM V/A, Water/Cement = 0.40) in suspension in ACW (pH 12.5)
- Use of ^{14}C-labelled species of EDTA and phthalate as ORGA radiotracers ➔ retention in binary mode (Task3)
- Use of stable ORGA + ^{63}Ni or U ➔ retention in ternary mode (Task 4)
- $[ORGA]_{initial}$ = from 10^{-5} to 10^{-2} mol/L and $[RN]_{initial}$ < solubility
- Contact time = from 48h to >3 months
- LSC technique to measure ^{14}C or ^{63}Ni in solution, ICP-MS for U
- Usual analytical techniques to measure major species in solution

Determination of R_d values as a function of [ORGA] and [RN]

Step 2: first results for binary systems with HCP state II







Macé *et al.* (2016) 4th cement workshop, Murten

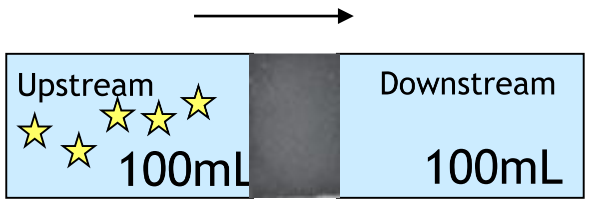
- R_d(EDTA) > R_d(PHTHAL) for higher contact time
- Sorption kinetics : R_d(EDTA) ↗ with time
- Strong decrease of R_d for [ORGA] > 10^{-5}M;
- 1 site Langmuir isotherm;
- $[ORGA]_{ini}$ for diffusion = 10^{-2}M
- Ternary systems: on going experiments with Ni and U

Step 3: On going diffusion experiments

- Configuration n°1: classical through-diffusion set-up / Sikadur® sample

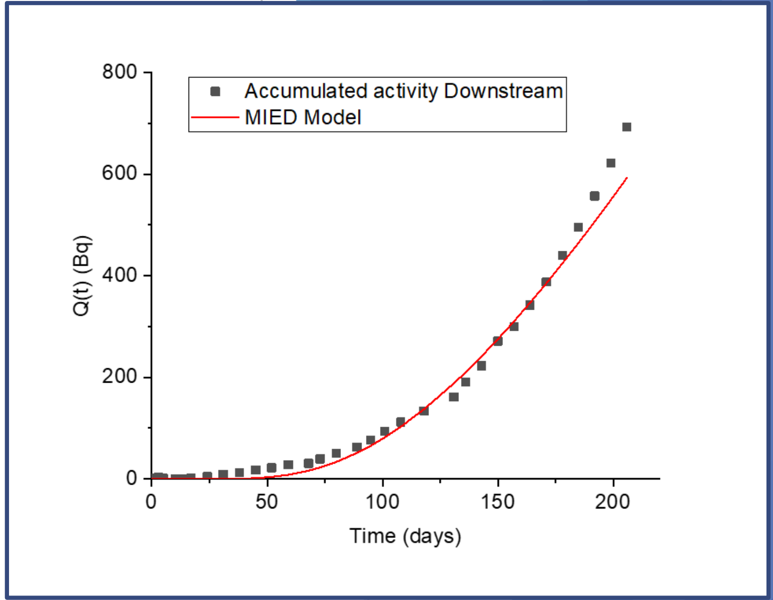
$A(HTO)_{up}$: 4500 Bq/cm^3
$A(^{14}C)_{up}$: 300 Bq/cm^3

T_{0_HTO} : 27/08/21
$T_{0\_14C\text{-}EDTA}$: 28/02/22



pH = 12.5 pH = 12.5

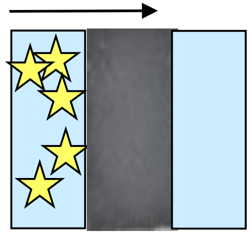
After 200d of diffusion ➔ $D_{app}(HTO) = 1\ 10^{-13}$ m^2/s
After 60d of diffusion ➔ no $A(^{14}C)$ is detected



- Configuration n°2: optimized through-diffusion set-up / HCP sample – State II

$A(HTO)_{up}$: 4500 Bq/cm^3
$A(^{14}C\text{-}EDTA)_{up}$: 5000 Bq/cm^3

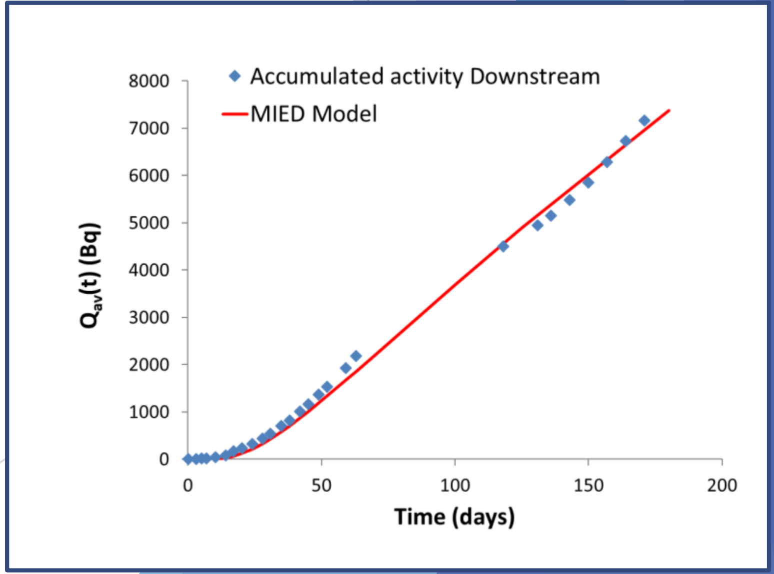
T_{0_HTO}: 27/08/21
$T_{0\_14C\text{-}EDTA}$: 15/12/21



Upstream = dowstream ≈ 10mL

pH = 12.5

After 200d of diffusion ➔ $D_{app}(HTO) = 6.3\ 10^{-13}$ m^2/s
After 90d of diffusion ➔ no $A(^{14}C)$ is detected



Conclusive remarks

ORGA: PHTALATE; EDTA
CEM: HCP (CEM I, CEM V), deg (I, II), CASH, CSH
RN: U(VI), Ni(II)

Solubility

- In portlandite saturated solution (pH = 12.5):
  - Increase of the solubility of Ni(II) with higher concentration of EDTA
  - Solubility of U(VI) or Ni(II) in presence of EDTA > phthalate
- In CASH equilibrium solution (pH= 10.3-11.3) = solubility limit of U(VI) is c.a. $4 \cdot 10^{-7}$ M (data to be confirmed)

Retention

- For HCP CEM V – state II:
  - R_d of U(VI) ~ $6\text{-}30 \cdot 10^4$ L/kg + decrease of R_d with increasing [U(VI)];
  - R_d (PHTAL/EDTA)< $1.5 \cdot 10^2$ L/kg + decrease of R_d with increasing [ORGA];
  - For [EDTA] up to 10^{-2} mol·L^{-1} decreases the resulting R_d of Ni(II) : from 10^3 to < 1 L/kg;
- For HCP CEM I - state II:
  - For [EDTA]= $5 \cdot 10^{-5}$ mol·L^{-1} no significant effect on the resulting R_d of U(VI) ~ 10^4 L/kg;
- For CSH (Ca/Si = 1), $[U]_{ini}$ = $7 \cdot 10^{-8}$ mol·L^{-1} ➔ R_d values are higher in comparison with sorption on CEM I
- For CSH (Ca/Si = 1.27), $[U]_{ini}$ = $5 \cdot 10^{-5}$ mol·L^{-1} ➔ slight decrease of R_d values with increasing [EDTA];

Diffusion

- Only HTO diffusion data in HCP – state II are available so far
- Due to high R_d values ➔ only in-diffusion for RN-ORGA can occur, as expected

➔ Puzzle is still not fully completed to be able to predict RN-ORGA interactions

Overview of Task4 technical work contributions in NUWCEM

AMPHOS 21 member of RSK

Sorption of organics and uranium to CASH
➔ presented by James D. Begg

GOBIERNO DE ESPAÑA | MINISTERIO DE CIENCIA, INNOVACIÓN Y UNIVERSIDADES | Ciemat Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

^{233}U sorption on portlandite and the effect of organic compounds
➔ presented by Oscar Almendros

KIT Karlsruher Institut für Technologie

Degradation products of UP2 filter aid material and their impact on radionuclide retention in cementitious systems
➔ presented by Xavi Gaona

Empa Materials Science and Technology

Impact of formate, citrate and gluconate on the uptake of radionuclides by cement: study of the binary and ternary systems cement-L and cement-RN-L
➔ presented by Rosa E. Guidone

ÚJV

Ni-63 interaction with cement material in the presence of organic compounds
➔ presented by Petr Vercernik

ČVUT ČESKÉ VYSOKÉ UČENÍ TECHNICKÉ V PRAZE

Interaction of europium with cementitious materials in the presence of organic substance
➔ presented by Marta Buresova

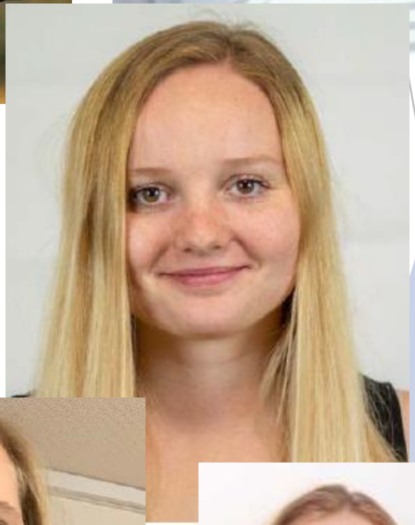
Sorption of uranium and lead on cement materials
➔ presented by Jana Kittnerova

Focus on young researchers involved in Task 4

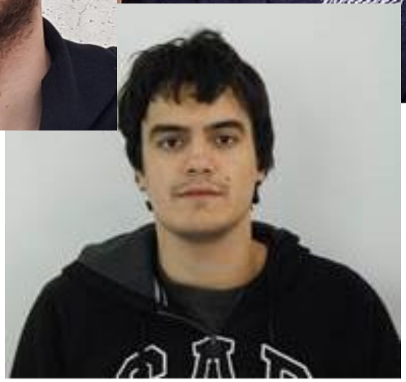








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European Joint Programme on Radioactive Waste Management

CORI

Cement Organic Radionuclide Interactions

Thank you for your attention !!!

October23-25, 2019, Barcelona, Spain

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.

Mechanisms and Modelling of Waste/Cement Interactions 6th International Workshop

Combined (back to back) with

the final CORI (eurad) meeting

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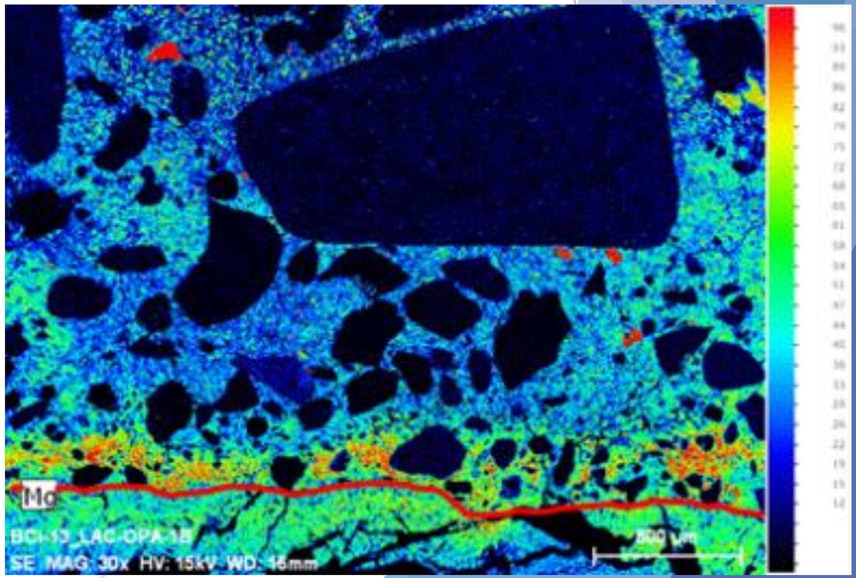
CORI

Cement Organic Radionuclide Interactions

Save the data:

November 20 to 24th 2023 in Prague



Detailed information will follow soon