



## **Deliverable 3.5**

# **CORI – Final Report integrating the R&D performed in CORI, including application to the Safety Case**

Work Package 3, CORI

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## Executive Summary

The Workpackage CORI in EURAD has improved the knowledge on the organic release issues which may 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 has 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, especially in the context of low and intermediate level waste disposal. This potential effect of organic molecules is caused by the formation of complexes in solution with radionuclides of interest (actinides and lanthanides, but also other metal cations like Ni which can (i) increase the radionuclide solubility and/or (ii) decrease the 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 will be degraded with time in the context of waste disposal inducing a large range of alkaline pH conditions according to their degradation stage. Alkaline pH provides specific conditions under which the organics can degrade, which contributes to increasing their impact on repository performance. The RD&D was performed in the three technical Tasks, Task 2 - Organics Degradation, Task 3 - Organic-Cement Interactions, and Radionuclide-Organic-Cement Interactions.

This final report summarizes main technical achievements in CORI generated in the RD&D Tasks 2, 3, and 4 (which are presented in the combined CORI Deliverable D3.6,7,8 in much more detail). Task 2 has provided new results on the organic source terms for several types of organic materials: polyvinyl chloride PVC, cellulose, ion exchange resins (IER) and superplasticizers (cementitious additives). New information is available on degradation processes and mechanisms but also on the chemical characteristics and production yields over time. Results from Task 3 provide new quantitative information on the retention of selected organic molecules on different cement materials and cement alteration stages and contribute to an improved definition and assessment of the organic plume. Main results from Task 4 show how selected radionuclides (with often diverse chemical characteristics) are retained on the investigated cement materials in the presence of a variety of different organic molecules. Results for the many investigated systems show a rather large variation of radionuclide retention, highlighting systems where radionuclide retention is strongly impacted by the organics and others where there is no apparent discernible impact of a certain organic molecule on radionuclide retention. The large variation in CORI regarding radionuclides, cement materials / degradation stages, and organics provides a significantly improved database and scientific understanding to assess these processes. In addition, the potential impact of CORI is discussed in view of application oriented activities and the Safety Case, also reflected at the national levels of the groups involved in CORI. This Deliverable is not intended to comment on any specific existing Safety Case but rather explain the broader context in which CORI results may be used. Impact is also generated in CORI by improving scientific/technical networking in Europe, enhancing interactions with interested stakeholders including civil society representatives, educating and training young researcher as future experts in the field. CORI contributes to European integration and vision.

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## Glossary

An	Actinide(s)
AFm	Monosulfoaluminate
AFT	Trisulfoaluminate
C-A-S-H	Calcium aluminium silicate hydrate
C-S-H	Calcium silicate hydrate
CAST	Carbon-14 Source Term, EC project
CEM 1-5	Cement degradation stages
CORI	Cement Organic Radionuclide Interactions
DIOP	Diisooctyl phthalate
DOC	Dissolved organic carbon
EDTA	Ethylenediaminetetraacetic acid
EUG	End User Group
GLU	Gluconate
GTA	Glutaric acid
HPC	Hardened cement paste
HBA	3-Hydroxybutyric acid
HIBA	$\alpha$ -Hydroxyisobutyric acid
ICS	Interactions with civil society in EURAD
ILW	Intermediate level waste
S.I.	International system of units
IER	Ion exchange resins
ISA	Isosaccharinic acid
LS	Ligninsulphonates
LLW/VLLW	Low-level waste / Very low-level waste
LILW-LL	Long lived low and intermediate level waste
NTA	Nitrilotriacetic acid
MG	Master Glenium SKY 886 (BASF)
OPC	Ordinary Portland cement
ORG	Organic species
PAE	Polyaryl ether
PAN	Polyacrylonitrile
PBTC	2-phosphonobutane-1,2,4,-tricarboxylate
PCE	Polycarboxylate ether
PMS	Polymelamine sulfonate
PVC	Polyvinyl chloride
RCM	Reference cement material in CORI, HCP based on CEM II
RDP	Real degradation products
RWMD	Radioactive waste management and disposal
RN	Radionuclide(s)
RD&D	Research development and demonstration
SIER	Spent ion exchange resins
SOTA	State of art report
SP	Superplasticiser(s)
SRF	Sorption reduction factors
NEA-TDB	Thermochemical database project of the OECD-NEA



## EURAD Deliverable 3.5 – CORI – Final Report

TBP	Tri-butyl-phosphate
TMA	Tri-methyl-amine
TOC	Total organic carbon
TBP	Tributyl phosphate
UP2W	polyacrylonitrile-based polymer
WAC	Waste acceptance criteria
WMO	Waste management organisation



## 1. Introduction to WP CORI

The Workpackage CORI in EURAD has improved the knowledge on the organic release issues which under certain conditions may 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 has addressed topics in the context of cement-organic-radionuclide interactions. Organic substances are present in some nuclear waste and as admixtures in cement-based materials and can potentially influence the performance of a geological disposal system, especially in the context of low and intermediate level waste disposal. This potential effect of organic molecules is caused by the formation of complexes in solution with radionuclides of interest (actinides and lanthanides, but also other metal cations like Ni which in some cases can (i) increase the radionuclide solubility and (ii) decrease the 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 omnipresent in disposal concepts and may be degraded with time inducing a large range of alkaline pH conditions according to their degradation stage. Alkaline pH provides specific conditions under which the organics can degrade, which contributes to increasing their impact on repository performance. The most critical open topics and data needs required to better assess and quantify cement-organics-radionuclides interactions were reflected in the three experimental RD&D oriented CORI Tasks. There is a clear conceptual and methodologic link between the Tasks, which build up on each other. CORI worked on the identification of the organic source term (Task 2) focusing on the type and amount of organic molecules. CORI then proceeded to assess the mobility and retention of organics in a cementitious environment (Task 3) in order to better characterise the characteristics of the organic plume. Finally, CORI analysed the impact of the organics on radionuclide mobility in the ternary system including organics, radionuclides and cement materials (Task 4). Quantification of the impact of organic molecules on radionuclide retention requires the knowledge of all these related processes.

**CORI Task 2 - Organics Degradation.** Focus was put on the characterization of soluble organic species generated by radiolytic and hydrolytic degradation of selected organics (PVC, cellulose, resins, superplasticizers). Studies also included the analysis of degradation/stability of small organic molecules such as carboxylic acids. Determination of degradation rates of polymeric materials and small molecular weights molecules was also performed.

**CORI Task 3 - Organic-Cement Interactions.** Studies focused on investigating the mobility of selected organic molecules in cement-based materials. Understanding the mobility of organic molecules requires knowledge on retention and transport properties. Organics also include small  $^{14}\text{C}$  bearing molecules as identified in the previous EC funded project CAST. Both retention on individual cement minerals and actual cementitious systems were investigated. Analysing the fate of the organics in cementitious environments is a key requirement to understand and model the radionuclide behaviour in single and complex systems.

**CORI Task 4 - Radionuclide-Organic-Cement Interactions.** Processes of radionuclide migration were studied in the ternary system. The role of organic molecules on the transfer properties of radionuclides were investigated through retention and transport experiments, covering a range of experimental conditions (relative amounts of radionuclide–cement–organics solutions). Radionuclides cover a range of chemical characteristics and redox states relevant for the expected conditions in L/ILW disposal.

In the CORI Workplan it was considered essential to focus. It was therefore decided from the start that CORI will not study other related topics like microbial degradation of organics, bitumised waste, iron corrosion in cementitious environments, work related to the conditioning of waste in cement materials or studies on natural organics present in certain host-rocks. Studies primarily targeting to derive new thermodynamic data for databases were likewise not included. The limited modelling performed within CORI is necessary to analyse and systematize the new experimental data and findings from CORI in the RD&D Tasks. CORI did not perform any PA related modelling studies. These limitations regarding the scope of CORI is also reflected in this Final Report.



## 2. Technical Progress and Results on Task level

In this chapter, the scientific and technical progress achieved in the three RD&D Task in CORI are summarized. It should be noted that the experimental program in CORI was significantly impacted by the Covid crisis which led to a disruption of work and prolonged lab-shutdowns in several cases. Owing to the flexibility in EURAD, which allowed a neutral-cost extension of CORI for one year (until PM 60), the Covid related negative impacts on CORI were successfully mitigated.

Short summaries of the main technical outcome is given below for the three Tasks (i) Organic degradation, (ii) Organic-Cement Interactions, and (iii) Radionuclide-Organic-Cement Interactions. CORI has investigated the degradation of four main types of organics (PVC, cellulose, ion exchange resins, superplasticizer) and a large variety of radionuclides which potentially undergo interactions with complexing organic molecules. The cement materials considered in CORI likewise exhibit a certain diversity. The investigated cement-based materials also considered different degradation stages of the cement materials as well as individual cement phases. Cement-based materials are known to degrade under repository relevant conditions (see chapter 5.5 in D3.2 CORI SOTA update [1] for details), leading to specific degradation products and related geochemical conditions which both may impact radionuclide retention. The investigation of several different degradation stages and cement-based materials is a specific feature in CORI and provided valuable information.

Fundamental information on the investigated topics can be found in the public CORI Deliverables D3.2 [1] (final State-of-the-Art Report), and the combined Deliverable D3.6, D3.7 and D3.8 [2] (detailed technical reports on the research performed at Task level).

### 2.1 Organic degradation (CORI Task 2)

Studies in CORI Task 2 were analysing the degradation processes of selected organics and identifying soluble organic degradation species. The experimental studies were strongly relying on (i) irradiation experiments of organic materials, and (ii) wet-chemistry investigations of hydrolytic degradation. The chemical identity and quantity of the organic molecules formed via the degradation processes were analysed and quantified using complementary analytical methods. Conditions were especially adopted allowing to assess the effect of irradiation and the presence of alkaline pore water (as is relevant for cementitious environments) on the degradation processes. These degradation processes also might occur in nuclear waste disposal; the first being associated to self-irradiation owing to the presence of radionuclides in organic rich waste and the second one associated to presence of pore water after disposal saturation in cementitious environments.

Groups active in CORI Task 2 were [Andra] [CNRS (SUBATECH)] [SCK-CEN], [Andra (BRGM)] [CNRS (UOrléans)] [FTMC] [JSI] [FZJ] [KIT] [PSI] [SURAO (CTU)] [SURAO (UJV)] [CVREZ] [SCK-CEN].

The following organic materials were studied in Task 2 of EURAD-CORI: (i) cellulose, (ii) polyvinyl chloride (PVC), (iii) ion exchange resins (IER) and (iv) superplasticizers (SP). The selection of these materials was based on relevant high abundance in the WMO's inventories and/or the lack of knowledge regarding the organics degradation.

**Cellulose materials** are often present in high abundance in LLW/ILW inventories considered by WMOs. Cellulose material is historically used in the nuclear industry as tissue for smear-testing potentially radioactive particles but also be found in paper textile, filters, wood, and cardboard materials. The degradation of cellulose materials can lead to the formation of isosaccharinic acid (ISA) which features complexing properties for several radionuclides. As the degradation of cellulose materials has been investigated in the past mainly regarding the alkaline degradation process, the scope of CORI extends beyond the initial state-of-the-art.



In the framework of Task 2, the radiolysis of cellulose tissues and the effect of pre-irradiation on the alkaline degradation of this material were investigated. At the start of CORI, there was very few information about this coupled degradation process (radiolysis and alkaline hydrolysis in alkaline conditions) available from literature. The long-term alkaline hydrolysis of cellulose materials (up to 28 years!) were studied in Task 2, as well as the effect of Fe(0) powder on the hydrolytic degradation of cellulose and the stability of the ISA molecule.

*The main outcomes from the cellulose related degradation studies are:*

- Pre-irradiation of cellulose tissues leads to a significant formation of degradation products other than those observed for non-irradiated tissues. This leads to a significantly faster DOC and ISA production during subsequent hydrolytic degradation in artificial cement water. The pre-irradiation of cellulose tissues does not seem to alter the alkaline degradation pathways, but rather accelerates the overall degradation process. The model previously proposed by PSI [3, 4] to predict cellulose degradation and ISA production is still applicable.
- Long-term alkaline hydrolytic degradation of cellulose (up to 28 years) at ambient temperature confirms that cellulose degradation slowly progresses after a rather short (~3 years) first phase of fast removal ("peeling-off") of glucose units from the reducing end of the cellulose chain. The subsequent secondary slow phase of peeling-off is assumed to proceed via the same reaction paths as the fast process.
- Hydrolytic cellulose degradation studies also indicated that the presence of portlandite and Fe(0) powder have no significant influence on the degradation rate nor on the type of degradation products formed. Furthermore,  $\alpha$ -ISA is stable in artificial cement water at pH = 13.3 under reducing conditions and a temperature of 90°C over a period of up to 120 days, both in absence and in presence of portlandite and Fe(0) powder.

**PVC**, a chlorinated polymer, is one of the most abundant polymers to be emplaced in LLW/ILW repositories. Depending on the specific application of the PVC material their chemical composition differs. Soft commercial PVC, primarily present in the waste as bags, glove box sleeves for example, has a high concentration of plasticizers in its formulation, namely phthalates. On the other hand, hard PVC, used i.e. as filter casings or ventilation filter seals, have lower contents of plasticizers and are also formulated with other kinds of additives. Studies were reported in the literature about the degradation and identification of degradation products of soft commercial PVC. In framework of Task 2, the degradation of hard commercial PVC under specific conditions characterised by radiolysis and alkaline hydrolysis were studied.

*The main outcomes from the PVC degradation studies are:*

- Degradation of hard PVC under radiolysis followed by hydrolysis shows similar results as described in the literature for soft PVC. The main difference is that phthalate is one the most important degradation product of soft PVC and not found as degradation product of hard PVC.
- Carboxylic acids produced in solution from the radiolytic degradation of PVC are:
  - organic acids with long carbon chains (C16 and C18) which were observed during solid analysis, and
  - small organic acids (acetic, chloro- and dichloroacetic, succinic) formed and transferred to the solution. Alcohols, ketones, and carboxylic acids formed during hydrolysis of pre-irradiated materials. Succinic acid is mainly released into solution from the degradation of PVC.

**Ion Exchange Resins (IER)** are an abundant material in some LLW/ILW inventories of relevance to WMOs. IERs are primarily used by the nuclear industry for treating and decontaminating the water used in spent fuel unloading and storage pools. IERs can be made by several types of polymer skeletons, including for example, a polystyrene or polyacrylic skeleton. In framework of Task 2, the degradation of the UP2W filter aid based on polyacrylonitrile (PAN) was studied. UP2W filter aid is widely used in nuclear plants for particle removal and as support material for ion exchange resins.

The results obtained in Task 2 showed that the alkaline hydrolytic degradation of PAN based material (UP2W filter aid and IERs) leads to the degradation of the material. For UP2W filter, the release of organic molecules in solution clearly increases after a contact time of ca. 800 days. Three proxy ligands were proposed to simulate the chemical characteristics of the degradation products: glutaric acid,  $\alpha$ -hydroxyisobutyric acid and 3-hydroxybutyric acid. A real leachate was produced in Task 2 which then also fed into Task 3 and Task 4.

Several types of **superplasticizers** have been used in cement formulations to reduce the water content in the mixture and to increase the early strength of the concrete whilst improving their flow characteristics. A great amount of cement materials is expected in disposal, as cementitious matrix of wastes, waste containers or part of the disposal structures. The categories of superplasticizers studied in the framework of Task 2 were (i) polycarboxylate ether (PCE), (ii) lignosulfonate (LS), (iii) polyaryl ether (PAE) and (iv) polymelamine sulfonate (PMS). These substances were selected in order to reflect different kinds of superplasticizers used or expected to be used in the formulation of cementitious materials used in nuclear waste disposal.

Irradiation of the different kinds of superplasticizers investigated in Task 2 showed that superplasticizer backbones cross-linked under irradiation when experiments were performed in solution. This crosslinking lead to difficulties in characterization. Furthermore, this behaviour cannot be extrapolated to bulk cement under disposal conditions. In the actual cement system, superplasticizer will be present in lower concentration and be immersed in a cement matrix. Cement particles would then be expected to reduce the possibility that significant amounts of superplasticizers could come into contact to allow crosslinking processes.

The dilution of superplasticizers in solution seems to avoid chain crosslinking, favouring degradation of the polymer chains and formation of small molecules in solution. Analysis of the soluble fractions of partially cross-linked systems seems to indicate a limited degree of degradation of superplasticizers and the release of low molecular weight molecules into the solutions. Radiolytic degradation of “homemade” PCE lead to the release of formate and acetate.

To summarize in brief, the studies performed in Task 2 allow to increase the knowledge about the degradation of organic materials and the identification of degradation products for the selected organic materials. Real degraded solutions were generated and provided to Task 3 and 4 in order to analyse the effect of real leachates on the interaction with cement materials and radionuclides.

## 2.2 Organic-Cement interactions (CORI Task 3)

Task 3 of WP CORI provides knowledge on interactions between organic molecules and cement-based materials. Specifically, the studies focused on investigating the mobility of selected organic molecules in cement-based materials, including both their retention and transport properties. The experimental investigations performed in Task 3 were frequently relying on batch sorption studies, often performed under inert atmosphere to exclude interactions of the cementitious materials with carbonate. The organic concentration resulting from the retention processes were quantified with several analytical methods, including the use of radiolabelled compounds to reach very low detection limits. The chemical characteristics of the cement-based materials likewise analysed in detail. Diffusion studies were performed in order to study the organics retention and transport properties in a non-static experimental

setup which ultimately enables a better transfer of data and results to more complex and “intact” real systems.

Processes of organic molecules or radionuclides at the water/cementitious materials interface (e.g. sorption processes) are controlled by the chemical characteristics of (i) the molecule in solution and (ii) the specific chemical characteristics of the mineral surface. The measured  $K_d$  can be envisaged as the distribution coefficient of a given molecule between the aqueous and the solid phase for the investigated geochemical conditions. A high  $K_d$  value indicates that most molecules will be present/sorbed at the mineral surface and not be present in solution; argumentation accordingly is going the other way for low  $K_d$  values where the largest portion of the radionuclides will be found in solution. In order to provide data on sorption processes and provide the scientific process understanding to support the measured data, it is hence required to (i) use reliable analytical tools to measure the concentration of a molecule or radionuclide in solution and/or on the solid phase, and (ii) use spectroscopic techniques to identify the chemical characteristics of the molecules in solution and/or on the solid phase as well as the identity of the mineral (surface) itself.

Groups active in CORI Task 3 were [Andra] [KIT (Amphos21)] [CEA] [CNRS (SUBATECH)] [CIEMAT (CSIC)] [CVREZ] [JSI] [KIT] [PSI (EMPA)] [RATEN] [SCK-CEN] [SURAO (CTU)] [SURAO (UJV)] [UHelsinki].

The list of organic molecules investigated includes small, large and complex molecules such as ISA, phthalate, EDTA, HIBA, HBA, adipate, citrate, NTA,  $^{14}\text{C}$  bearing molecules, superplasticizers and real degradation products (obtained from CORI Task 2). Regarding the cementitious systems under investigation, cement hydrates (C-S-H, C-A-S-H, AFms, Aft, Portlandite...) as well as different types (I, III, V) of cement-based materials (HCP) at different degradation stages were investigated. A brief summary of results generated by the different partners of the project and the synthesis of main results are presented below.

Regarding the investigation of retention properties of selected organic molecules, a substantial amount of new data were generated in CORI, increasing the knowledge of the different systems beyond the initial state-of-the-art. One of the main outcomes from CORI Task 3 are the apparent discrepancies between the types of organics in terms of  $K_d$  values (see Figure 1). ISA and gluconate are significantly sorbed while glutaric acid (GTA), citrate and formate exhibit very weak sorption under the investigated conditions. This finding confirms previous work on binary systems including organics and cement and supports  $K_d$  values to describe organics retention on the cement-based materials used in the context of safety assessments.

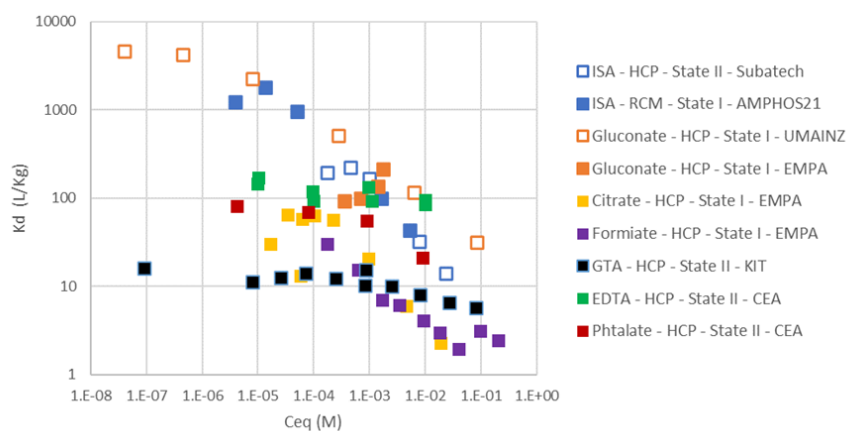


Figure 1:  $K_d$  values for selected organic molecules on HCP at different degradation stages (I and II).

The sorption results of ISA, EDTA and phthalate for HCP at degradation stage III compared to stage I and/or stage II show that sorption is generally lower at the degradation state III (*Figure 2*). Also, the trend in retention as a function of the equilibrium organic concentration ( $C_{eq}$ ) remains the same whatever the degradation stage. Indeed, for ISA, the  $K_d$  value decreases as  $C_{eq}$  increases from  $C_{eq} = 10^{-5}$  M at stage I and stage III while for EDTA the  $K_d$  only slightly evolves for stage II and stage III/IV. Apparently, the chemical degradation of the cement-based materials does not modify the threshold concentrations related to the decrease of the sorption due to the possible saturation of the adsorption sites. This observation, however, should be confirmed by speciation calculations and modelling for the various aqueous systems.

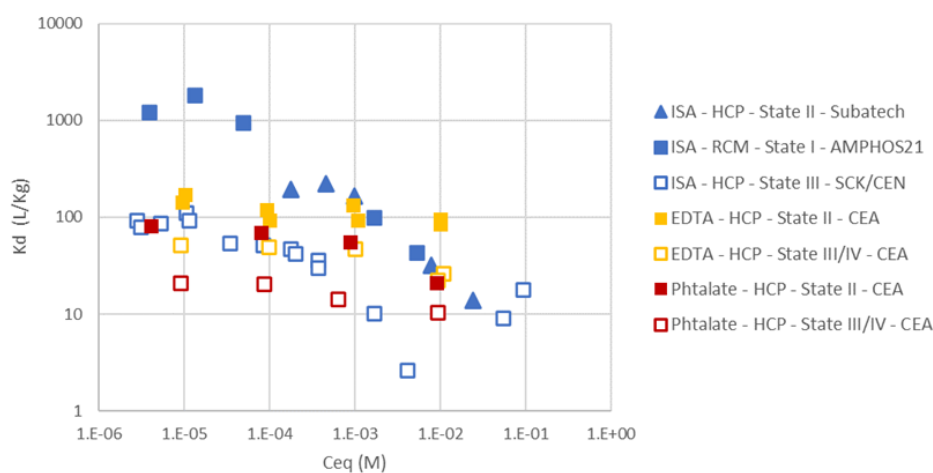


Figure 2:  $K_d$  measurements for selected organic molecules in HCP at different degradation stages.

ISA has been one of the most studied molecules due to the high amount of cellulose in the chemical inventory of radioactive waste (considering low level to intermediate level waste). All  $K_d$  values obtained for ISA on the different cement-based materials investigated in CORI can be associated with a general trend regarding the evolution of  $K_d$  values as a function of the ISA concentration. It should be noted that there is also a remarkable agreement with existing data.

The measurements of gluconate sorption on C-S-H phases provided by [KIT] in CORI agree very well with previous results. This observation validates the acquired data on C-S-H but also on the other cement hydrates investigated.

One key outcome from CORI Task 3 is the determination of sorption properties for several cement hydrates other than C-S-H phases. Indeed, CORI results clearly show that AFm/AFt phases and portlandite can sorb organic molecules (as in the case of citrate and ISA) with high affinities (*Figure 3*). Sorption properties of individual phases (for example AFm, HC) can show similar  $K_d$  values like C-S-H. This outcome confirms and explains the higher  $K_d$  values in HCP compared to C-S-H. It provides consistent information in terms of mechanistic knowledge and understanding the processes controlling the sorption of organic molecules in cement-based-materials.

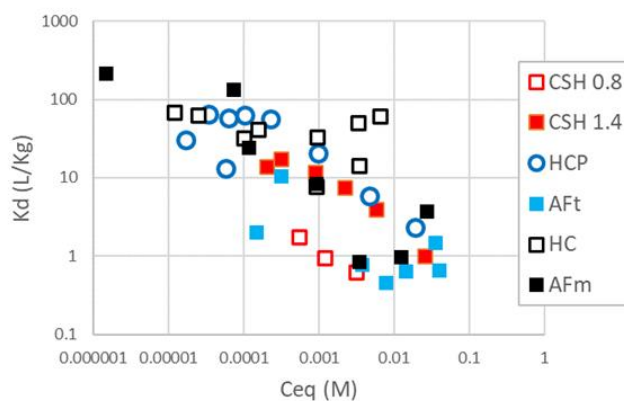


Figure 3: Sorption of citrate on selected cement hydrates and CEM I HCP.

The effect of sorbed organic molecules or superplasticizers on cement surface properties were also investigated in CORI. The evolution of the zeta potential of HCP particles in presence of HIBA, HBA and glutaric acid in comparison with ISA were investigated in the frame of Task 3. The conditions of the study corresponds to the degradation stage II (pH=12.5). The measurements showed that HBA and HIBA molecules have no effect on the zeta potential and then further on the surface charge of HCP particles. Contrary to HBA and HIBA, however, glutaric acid has a significant effect on the zeta potential, comparable to ISA at higher concentrations.

Important insights from CORI Task 3 concern the superplasticizers which were particularly studied in selected cementitious systems. Two commercial superplasticizers were considered: the first (SIKA) is based on modified melamine (SIKAMENT™ 200 R, Sika, Spain), and the second product (MG) is the Master Glenium SKY 886 (BASF). The latter is an innovative superplasticizer based on latest generation of polycarboxylate ether (PCE) polymers. Zeta potential measurements of individual cement phases, C-S-H and portlandite were obtained in the presence of this superplasticizers. These results indicate that the surface charge is significantly modified, changing from positive to negative values. The surface of these cement hydrates becomes negatively charged, with the superplasticizer SIKA showing a higher effect.

In terms of organic transport, diffusion tests were conducted by several partners in CORI at different cement degradation stages. Classical through-diffusion cells, in-diffusion tests and novel electro-migration tests were used by the different organizations involved in CORI. The obtained results confirmed the previously observed trends, indicating that organic diffusion is an extremely slow process. Even after four years of experimental tests, organic compounds have not been detected in the downstream cells of the experimental setups.

### 2.3 Radionuclide-Organic-Cement interactions (CORI Task 4)

The work performed in Task 4 of CORI features experimental studies on binary systems (radionuclides + cement) and ternary systems (radionuclides + organics + cement). Studies in the binary system are required to assess the specific effect of organic compounds in the higher complexity ternary systems. Similar to CORI Task 3, the experimental studies in Task 4 were largely relying on batch sorption studies under protective atmosphere complemented by selected experiments using setups to investigate diffusion processes. The chemical characteristics of the investigated cement-based materials were monitored. Several analytical tools were used to quantify the radionuclide concentrations, including radiometric and mass-spectrometry based methods. To provide additional information to support improved process understanding on the specific interaction processes, several complementary

spectroscopic investigations were performed to provide molecular level information on the chemical form and speciation of the radionuclides.

Groups active in CORI Task 4 were [CEA] [CIEMAT] [Andra] [CNRS (SUBATECH)] [FTMC] [FZJ (HZDR)] [KIT (Amphos21) (UMAINZ) (UPOTSDAM)] [SURAO (CTU) (UJV)] [RATEN] [SCK-CEN] [UCY], [UHelsinki].

The new studies in CORI have extended knowledge beyond the already published data and state-of-the-art documented in the literature. It needs to be highlighted that the results from CORI Task 4 clearly confirm that interactions between organic molecules and radionuclides in a cementitious environment can significantly influence radionuclide retention. It was demonstrated that the effect of organics on radionuclide retention depends on the type of organic and the type of radionuclide. The cement type and degradation stages likewise influence retention behaviour. Results from Task 4 show that there are certain systems particularly sensitive to the impact of organic molecules, like for example in the Pu-ISA case, while others show only limited interactions or none at all. Task 4 provides significant new information on the systems studied, however, the relevance of findings also strongly depends on the type and concept of a repository and the inventory of organic waste and radionuclides which define specific boundary conditions. Considering the high complexity of the ternary systems studied in CORI Task 4 and the several variations regarding the investigated radionuclides, organic ligands and cement(phase) types, it is not straightforward to present results in an integrated short summary overview and thus they are presented below for the several individual systems in a more detailed way.

In the subsequent sub-chapters focusing on specific groups of radionuclides, the new data and improved process understanding generated in CORI Task 4 are described along the investigated types of organics. More detailed information can be found in the combined Deliverables D3.6,7,8 [2].

Main **general observations** regarding radionuclide retention in the ternary system RN-organic-cement derived from the work in CORI are as follows:

- As there are important cases, like in the case of Pu-ISA interactions (leading to reduced Pu retention), which show a strong impact of organics on radionuclide retention, in many investigated cases the **effect of organic species** on the solubility or sorption of RNs was zero or minor.
- New **quantitative data** on radionuclide retention on cement-based materials under presence of organics were derived. The strong variations used in CORI regarding cement, degradation stages, organics and radionuclides open perspectives **to systematize findings into material/radionuclide groups** having expected „weak“, „moderate“, „strong“ potential to reduce sorption retention. (See also the subsequent sub-chapters).
- **A strong effect of dissolved calcium** on the chemical speciation, reaction mechanisms and quantification was observed. Ca can interact both with species in solution and/or the mineral surface and thus strongly impacts the investigated chemical processes. This fundamental observation provides new input for a more realistic description of the chemical system. It should be emphasized, that a **comprehensive understanding of speciation** (supported by thermodynamics) is **essential** for in-depths data interpretation.
- Differences between the **real leachates** from Task 2 and the **proxy ligands** were observed regarding impact on radionuclide retention. The organic substances from the real leachates tend to cause a stronger decrease in radionuclide sorption, which is also related to the organic concentrations.

The **radionuclides** studied in Task 4 were:  $^{134}\text{Cs}$ ,  $^{36}\text{Cl}$ , Pb(stable),  $^{63}\text{Ni}$ ,  $^{152}\text{Eu}$ , Nd(stable),  $^{241}\text{Am}$ ,  $^{248}\text{Cm}$ ,  $^{232,234}\text{Th}$ ,  $^{238,239}\text{Pu}$  and  $^{233,238}\text{U}$ , spanning a wide range of chemical characteristics. For the discussion of Cl and Cs, the reader is referred to CORI D3.6,7,8 [2]. **Cement materials** investigated in Task 4 were CEM I, CEM III, CEM IV and CEM V hardened cement paste (HCP) at various degradation stages. Pure solid phases such as portlandite, C-A-S-H, AFt and AFm-phases were investigated to improve process understanding. Some studies were performed using the “reference cement” material (RCM) defined in CORI, which is a CEM I HCP, (producer CEMEX Prachovice, Czech Republic) provided by the Czech team in CORI. A large variety of **organic molecules** was investigated in CORI Task 4, including ISA, EDTA, NTA, Citrate, formate, oxalate, acetate, phthalate, gluconate but also more complex mixture such as superplasticizer, real degradation product of cellulose, PCE or IER.

### Results obtained in CORI for U(VI)

In binary systems (radionuclides + cement), the retention of U(VI), expressed as distribution ratio  $R_d$ , is significant ( $R_d > 10^5$  L/kg) at low U concentration in solution for all matrices investigated. The nature of cement (RCM vs. HCP CEM V/A) has less effect than the alteration state of the matrix. The maximum retention of U(VI) is observed for stage II of cement degradation, where the Ca concentration in solution is buffered by portlandite *i.e.* at around 22 mM for pH 12.5. Desorption experiments performed for stage II and stage III reveal a reversible uptake mechanism. These results confirmed what was also observed in literature. Uranium shows an extremely strong binding affinity to all investigated forms of C-A-S-H ( $R_d = 10^{5.5}$  L/kg), *i.e.* with Ca/Si and Al/Si ratios: 1.2-0.05 (pH= 11.3 ± 0.2) and 1.2-0.02 (pH= 10.2 ± 0.1). For C-S-H (Ca/Si = 0.8), the affinity of U(VI) is similar ( $R_d = 10^{5.1}$  L/kg). From long term diffusion experiments (*i.e.* 505 days), a limited penetration depth of around 40 µm was determined for HCP at stage II in absence of organics. These results are consistent with a migration behaviour of U(VI) dominated by strong sorption and/or very slow diffusion processes.

The effect of organics on U(VI) retention depends on the nature of the organic ligand and on its concentration in the ternary system (CEM-ORG-RN). This is discussed in more detail below.

**$\alpha$ -ISA:** No large effect is observed regarding the  $R_d(\text{U(VI)}/\text{C-A-S-H})$  value in presence of  $\alpha$ -ISA, while a minor increase of the solubility of U(VI) in presence of  $10^{-3}$  M of ISA is measured in similar solution. For the ternary system U(VI)-ISA-HCP, one main result is the existence of a threshold value for ISA concentration in solution ( $[\text{ISA}]_{\text{eq}} = 2 \times 10^{-4}$  mol L<sup>-1</sup>) above which uranium uptake strongly decreases. The same behaviour was reported in literature for CEM I HCP at stage I and III for which the ISA threshold concentration is in the same order of magnitude or slightly higher, *i.e.* about  $10^{-3}$  mol L<sup>-1</sup> compared to  $2 \times 10^{-4}$  mol L<sup>-1</sup>. Similar observations have been recently reported in literature for the uptake of Nb(V) (CEM I HCP stage I) and Pu(IV) (CEM I HCP stage II). Studies in CORI also observed a slight increase of U(VI) adsorption in portlandite, which can be explained by the formation of ternary U(VI)-ISA-portlandite complexes. From diffusion experiment in HCP at stage III, first data are consistent with a deeper penetration of uranium inside the degraded zone of the HCP which could be (at least partly) linked to the change of mineralogy in the degraded zone and the presence of ISA. The effect of presence of cellulose RDP onto U(VI) sorption was also investigated on fresh and stage II RCM samples. A clear decrease in  $R_d$  was observed for the degraded RCM (two orders of magnitude at the higher total ISA content ( $\alpha$ -ISA and  $\beta$ -ISA) of  $3 \times 10^3$  M in the cellulose RDP). The effect of the RDP on uranium adsorption in fresh RCM was negligible.

**GLU and PBTC:** The influence of GLU and PBTC on U(VI) retention by C-S-H with a C/S ratio of 0.8 was investigated. For a concentration of  $10^{-2}$  M of GLU, the  $\log(R_d)$  of U(VI) decreases from 5.1 in absence of GLU to  $4.8 \pm 0.1$ . Regarding the U(VI) uptake, no clear trend can be seen in the tests with different addition sequences of U(VI) and GLU, thus indicating that GLU has only a very small influence on the U(VI) retention by C-S-H under these conditions. Concerning PBTC, the U(VI) retention by C(A)SH decrease when PBTC species are present at relatively high concentrations.





**EDTA:** For solutions reflecting the degradation stage II of cement, the solubility of U(VI) in presence of EDTA after long contact time is similar to the one without organics ( $\sim 10^{-7}$ M). Under similar conditions, the U(VI) sorption is still significant ( $R_d \sim 10^5$  L/kg) for HCP CEM V/A independently of the introduced EDTA concentration and contact time in the ternary system. At stage III/IV and for initial EDTA concentrations up to  $10^{-3}$ M, the  $R_d$  value tends to decrease, suggesting a saturation of sorption sites. In spectroscopic investigations, the U(VI) fluorescence spectra evolution suggest that the EDTA interacts with U(VI) complexes at the highest concentration. Characterisation of the C-S-H-U(VI)-EDTA system showed an effect of the presence of carbonate. Under  $N_2$  atmosphere the presence of EDTA in solution caused (slightly) lower  $R_d$  values due to stabilization of U(VI) in solution in the form of EDTA complexes. However, higher  $K_d$  values were observed when EDTA solutions were contacted with the C-S-H-U(VI) phase, because of the formation of ternary C-S-H-U(VI)-EDTA surfaces complexes, which stabilize U(VI) onto the C-S-H phase. On the other hand, under ambient atmosphere, U(VI) carbonate complexes govern the U(VI) chemistry in solution, resulting generally in lower  $R_d$  values. Similarly, under 1%  $CO_2$  U(VI)-carbonate complexes govern the U(VI) chemistry in solution and result in the formation of ternary carbonate solid phases. EDTA ligand forms stable complexes with U(VI) in aqueous C-S-H suspensions.

**Phthalate:** The presence of phthalate had no significant effect on the retention of U(VI) on HCP CEM V/A at stage II or III/IV, similarly to what was observed for U(VI) retention in portlandite.

**Superplasticiser:** The number of studies performed with superplasticisers and U(VI) were limited. Two different commercial products were used for the experiments. The first one (SIKA) is based on modified melamine (SIKAMENT™ 200 R, Sika, Spain) and the second one (MG) is the Master Glenium SKY 886 (BASF), an innovative superplasticizer based on the latest generation of polycarboxylate ether (PCE) polymers. Batch sorption tests were carried out with “realistic” concentrations of superplasticizers (5% wt). Under these conditions, the effect of superplasticizers in the C-S-H was negligible. The presence of SIKA also slightly affected U(VI) sorption in fresh cements (CEM I, CEM IV and CEM V), whereas MG produced a decrease of 20% and 10% in the  $\log(R_d)$  in CEM IV and CEM V, respectively.

### Results obtained in CORI for Th(IV)/Pu(IV)

Th(IV) and Pu(IV) strongly sorb on fresh HCP under reducing and hyperalkaline conditions in the absence of organic ligands.

**$\alpha$ -ISA:** ISA clearly affects the uptake of Th(IV) and Pu(IV) as can be shown in adsorption experiments (with 2 orders of magnitude less uptake). The decrease of Pu(IV) adsorption in the presence of ISA was also observed in portlandite. Diffusion experiments also show up to 2.5 mm deeper Pu(IV) in-diffusion in the presence of ISA within 118 days.

**EDTA:** The HCP-An(IV)-EDTA system with fresh HCP leads to a quantitative uptake of Th(IV) and Pu(IV) on HCP. Almost no difference is observed regarding the order of RN ligand addition, indicating negligible influence of EDTA on the retention of Th(IV) or Pu(IV) on HCP after 72 hours of contact time.

**GLU:** Concerning the HCP-Pu(IV)-GLU system, much lower  $R_d$  values for Pu(IV) are obtained in the ternary system compared to the binary HCP-Pu(IV) system. When Pu(IV) was added first, the uptake was higher than with initial GLU present, but lower compared to the binary system. This may be an indication that Pu(IV) desorbs after GLU addition. The order of addition affects Pu(IV) uptake on HCP, suggesting GLU occupies sorption sites, acting as a competitive element for the actinide retention. The order of additions of An(IV) and GLU have significantly influence of the uptake of An(IV) on HCP ( $pH > 13$ ) during short contact times (72 h).

Further concerning the effect of GLU, the Pu(IV)-C-S-H-GLU and Pu(IV)-(AFm-ettringite)-GLU systems were investigated. At  $[GLU] > 10^{-4}$  M, the Pu(IV) uptake is decreased in both C-S-H phases with high (1.4) and low (0.8) Ca:Si ratio and presence of redox buffer (*i.e.* HQ and Sn(II)). In the case of Pu(IV)-(AFm-ettringite)-GLU system, Pu uptake by AFm phases and ettringite has been observed, with  $\log R_d$  of  $(5.6 \pm 1.0)$  and  $(5.7 \pm 1.1)$  (with  $R_d$  values reported in L/kg), respectively. Similar effects were observed



for the uptake of Pu(IV) by AFm phases and ettringite: the presence of GLU at concentrations higher than  $10^{-4}$  M decreases the  $R_d$  of Pu(IV). The impact of GLU on the retention of Pu(IV) by AFm phases and ettringite was stronger than that observed for C-S-H phases.

**UP2W degradation products:** The solubility of Pu(IV) in cement porewater solutions was moderately affected by the presence of HIBA, HBA or GTA. The uptake of  $^{242}\text{Pu(III/IV)}$  by HCP in the degradation stage II was investigated in the absence and presence of the proxy ligands (HIBA, HBA or GTA) and the UP2W degradation leachate generated in Task 2. The presence of proxy ligands slightly decreased the distribution ratios for  $^{242}\text{Pu(III/IV)}$  for  $[\text{L}]_{\text{tot}} > 10^{-2}$  M. However, this effect is less evident due to the dispersion of the data and the increase of the detection limits for plutonium with increasing ligand concentrations. As for  $^{63}\text{Ni(II)}$  and  $^{152}\text{Eu(III)}$ , the presence of the degradation leachate induces a moderate decrease in the uptake of  $^{242}\text{Pu(IV)}$  by HCP, as compared to the sorption in the presence of the proxy ligands.

**Superplasticiser:** Pu(IV) sorption tests on fresh cements were done with Pu(IV) and presence of MG or SIKA (5 wt.%). The presence of SIKA significantly decreased Pu(IV) sorption in CEM V (47%), but the effect was also notable in CEM I (20%) and CEM IV (9%). The effect of MG was stronger decreasing the  $\text{Log}(R_d)$  of 41%, 44 % and 61 % for CEM I, CEM IV and CEM V, respectively. Batch sorption tests with Pu(IV) on portlandite and fresh and degraded (stage II) RCM in the presence of variable concentration of superplasticizers, confirmed the potential of decreasing the retention of the actinide, which can be also attributed to the non-negligible adsorption of the additives on the solid surface.

### Results obtained in CORI for Eu(III)/ Cm(III)/ Pu(III)

**$\alpha$ -ISA:** A significant decrease in  $R_d$  values was previously observed for Eu(III) and Pu(III) in the presence of  $\alpha$ -ISA synthesized in the laboratory. The effects of cellulose RDP degraded by radiolysis and hydrolysis on the adsorption of Eu(III) and Pu(III) on fresh and stage II RCM were investigated. In the case of Eu(III) and Pu(III) no large difference between the two stages was observed. The RDP have a non-negligible effect on the adsorption of all the studied RN. For the Eu(III)-RCM-RDP system at stage II, the effects produced by cellulose RDP on Eu(III) diffusion were depending on the TOC content of the RDP obtained either by only hydrolysis or hydrolysis and radiolysis. The effect of ISA on Eu(III) retention in portlandite is relevant (about 2 orders of magnitude). The diffusivity of Eu(III) is then higher with a factor of 250 in presence of high TOC content.

**GLU:** In the ternary  $^{152}\text{Eu(III)}$ -C-S-H-GLU system, high uptake of Eu(III) was observed on C-S-H phases in the absence of organic ligands and under hyper-alkaline conditions. GLU has a negligible effect on  $^{152}\text{Eu(III)}$  retention on C-S-H 0.8 at  $[\text{GLU}] < 10^{-2}$  M, whereas a moderate decrease in retention is observed for higher GLU concentrations  $[\text{GLU}] = 10^{-1.5}$  M and for longer equilibration times. For C-S-H 1.4, a strong decrease of Eu(III) retention was observed for  $[\text{GLU}] > 10^{-3}$  M. In the  $^{248}\text{Cm(III)}$ -C-S-H-GLU system, TRLFS analysis showed that Cm(III) is mostly incorporated in the C-S-H phase structure both in the presence and in absence of GLU. Conversely, for C-S-H 1.4, the formation Ca-Cm(III)-GLU-(OH) aqueous complexes is observed at  $[\text{GLU}] \geq 10^{-2.5}$  M, thus preventing the incorporation of Cm(III) into the C-S-H structure. The results obtained in this framework support that the retention decrease of Eu(III) on C-S-H 1.4 in the presence of GLU is due to the formation of Ca-Eu(III)-GLU-(OH) species, thus highlighting the relevant role of Ca in the formation of Ca-Ac(III)/Ln(III)-L-(OH) complexes, as previously reported in literature.

**Phthalate:** The uptake/retention and migration behaviour of  $^{241}\text{Am(III)}$  and  $^{152}\text{Eu(III)}$  in the presence of phthalate on C-A-S-H phases and HCP (CEM V) were investigated. At phthalate concentrations above  $10^{-3}$  mol kg $^{-1}$  a distinct decrease of  $R_d$  values was observed. This reduction of the  $^{241}\text{Am(III)}$  and  $^{152}\text{Eu(III)}$  uptake in the presence of phthalate is suggested to be a consequence of the destabilisation/dissolution of C-S-H/C-A-S-H due to increasing Ca-complexation by phthalate in solution. In contrast, in sorption experiments with pure synthesised C-A-S-H (Ca/Si ratio 1.6), only a minor effect of the phthalate addition on the retention behaviour of Am(III) and Eu(III) was observed. In the absence of organics and at



phthalate concentrations up to 10 mM, the  $R_d$  values of Am(III) and Eu(III) were in the order of  $10^5$  to  $10^7$  L kg<sup>-1</sup>. Only at very high phthalate concentrations ( $10^{-1}$  mol kg<sup>-1</sup>), a slight decrease in the radionuclide uptake was found.

**UP2W degradation products:** The uptake of <sup>152</sup>Eu(III) by HCP in the degradation stage II was investigated in the absence and presence of proxy ligands (HIBA, HBA, GTA) and the UP2W degradation leachate generated in CORI Task 2. The presence of proxy ligands has a negligible effect on the uptake of <sup>152</sup>Eu(III) up to  $[L]_{tot} = 0.1$  M. The presence of the degradation leachate induces a moderate decrease in the uptake of <sup>152</sup>Eu(III) by HCP, as compared to the sorption in the presence of the proxy ligands. These observations possibly reflect that the multiple functionalities (-COOH, -OH, amide groups) expected in the macromolecules (10–15 kDa) present in the degradation leachate, can offer further binding / chelating capabilities compared to the small organic proxy ligands which feature monodentate or at the most bidentate binding properties.

**Superplasticiser:** The presence of superplasticizers does not affect the retention of Pu(III) and Eu(III) in C-S-H, however a non-negligible decrease of sorption is observed in fresh HCP for these RNs in the presence of 5%wt of superplasticizers. In particular, the presence of SIKA clearly affects Eu(III) sorption in CEM I (-13% in Log( $R_d$ )) and CEM V (-33 %), but much less in CEM IV. Again MG has a larger effect in all the cements with a reduction observed in the log ( $R_d$ ) values for Eu(III) by 51%; 58% and 67% for CEM I, CEM IV and CEM V, respectively. It is of interest to further investigate the role of superplasticisers in diffusion tests with Eu(III) and Pu(III) with the superplasticizer added during casting.

**Organics with observed negligible impact:** The effect of **citrate** on the Cm(III), Pu(III) and Eu(III) adsorption on C-S-H phases, AFm phases and ettringite was investigated. Citrate has a negligible impact on Pu(III) and Eu(III) retention by C-S-H phases. It was observed to reduce Pu(III) retention by AFm phases and ettringite only at  $[CIT]_{tot} > 10^{-2}$  M. No effect of **EDTA** on Eu(III) adsorption kinetic in HCP CEM III was observed. Concerning **formate**, the effect on <sup>242</sup>Pu(III) and <sup>152</sup>Eu(III) uptake by C-S-H phases (Ca:Si = 0.8, 1.4) was negligible. The effect of formate on <sup>242</sup>Pu(III) adsorption on AFm phases and ettringite was likewise negligible. In the case of diisooctyl **phthalate** (DIOP), no significant effects were observed for sorption experiments with Pu(III/IV) and Am(III). Negligible effects regarding the presence of **adipates** or **oxalate** on Pu(III) or Am(III) adsorption on HCP CEM I at stage II were observed. Based on thermodynamic calculations, the affinity of **tri-methyl-amine** (TMA), which is a degradation product of basic anion exchange resins to form complexes with Am(III) or Eu(III) in HCP CEM V/A conditions is supposed to be low. A small effect of TMA on the mobility of these RNs is presumed and unlikely effects of TMA on Ca-bearing cement hydration phases are expected.

### Results obtained in CORI for Pb(II)/Ni(II)

**EDTA:** The sorption reduction factor values (SRF) for Pb(II) in HCP CEM I and CEM III showed a limited effect of the presence of phthalate or EDTA, while depending of the Ca:Si ratio, the affinity of Pb(II) for C-S-H is more affected the presence of EDTA. For C-S-H 1.2, a maximum of SRF is observed for EDTA concentration at  $5 \times 10^{-3}$  M.

**Formic acid:** The solubility of Ni(II) is about  $2 \cdot 10^{-7}$  M for fresh cement porewater conditions. When formic acid is added to the system, the resulting Ni(II) concentrations in solution are not significantly influenced. The <sup>63</sup>Ni(II) uptake was evaluated on non-degraded and degraded cement pastes based on CEM I and CEM V. The presence of formic acid, at a concentration of  $10^{-3}$  M was found to have an impact on <sup>63</sup>Ni(II) uptake on non-degraded CEM I HCP and to a lower extent on degraded cement, *i.e.* moderately lower  $R_d$  values were obtained for nickel sorption in the ternary systems. On CEM V HCP, the presence of formic acid, at a concentration of  $10^{-3}$  M was found to have an inverse impact on <sup>63</sup>Ni(II) uptake: higher  $R_d$  values were obtained for nickel sorption in the ternary system.

**$\alpha$ -ISA:** Ni(II) sorption on HCP was higher for advanced degradation stages than on fresh HCP. Additionally, the real degradation products (RDP) of cellulose had a much stronger impact than pure  $\alpha$ -ISA on Ni(II) retention. This result suggests that not only  $\alpha$ -ISA has a sorption reduction power but other



products from the degradation of cellulose should eventually be considered, too. The presence of cellulose RDP on Ni(II) adsorption on fresh and stage II RCM show higher effects in the case of RCM degraded at stage II compared to fresh cement. Whereas significant decreases in  $R_d$  values were previously observed for Eu(III) and Pu(III/IV) in the presence of  $\alpha$ -ISA synthesized in the laboratory, this effect was not been observed for Ni(II). This can be an indication that some of the still not identified cellulose degradation products obtained by hydrolysis and radiolysis might have stronger effects than pure  $\alpha$ -ISA on Ni retention. The adsorption behaviour of Ni was also analysed in the C-S-H phases at different Ca/Si ratios, indicating that adsorption increases as the Ca/Si decreases. The effect of the organic on radionuclide retention in the Ni-C-S-H- $\alpha$ -ISA system is quite limited. Diffusion experiments of Ni(II) in the presence/absence of  $\alpha$ -ISA in HCP stage II did not exhibit a variation in the diffusion coefficients within the experimental errors.

**EDTA and phthalate:** The HCP-Ni(II)-EDTA and HCP-Ni(II)-phthalate systems were investigated with HCP CEM V/A (or RCM) degraded at stage II and IV with a focus on investigating the solubility, sorption kinetics and performing diffusion experiments. The trends obtained with U(VI) are also observed for  $^{63}\text{Ni(II)}$ . At stage III/IV and for higher EDTA concentration, the evolution of  $R_d$  values with the organic concentration suggests a competition effect and/or a saturation of the sorption site for EDTA concentration higher than  $10^{-4}\text{M}$ . No significant effects were observed due the presence of phthalate on the retention of Ni(II) in HCP at stage II or stage III/IV. The penetration of  $^{63}\text{Ni(II)}$  (or  $^{63}\text{Ni(II)}$ -ORG complex) into the solid is quite limited and restricted to the very surface of the HCP sample. The presence of EDTA or phthalate does slightly enhance the  $^{63}\text{Ni(II)}$  diffusion.

**UP2W degradation products:** GTA, HIBA and HBA induce a slight increase in the solubility of Ni(II) at  $[\text{L}]_{\text{tot}} = 0.1\text{ M}$ , thus hinting at the formation of stable Ni(II)-GTA, -HIBA and -HBA complexes under hyperalkaline conditions. The comparison of these results with solubility data in the presence of ISA confirms the stronger complexation properties of the latter ligand. Even though HIBA and HBA are carboxylic acids containing one alcohol group, this comparison shows that additional alcohol groups are required to efficiently chelate the metal ion and outcompete hydrolysis. The uptake of  $^{63}\text{Ni(II)}$ , by HCP in the degradation stage II was investigated under the absence and presence of proxy ligands (HIBA, HBA, GTA) and the UP2W degradation leachate generated in Task 2. A slight decrease in the distribution ratios for  $^{63}\text{Ni(II)}$  was observed only at  $[\text{L}]_{\text{tot}} > 10^{-2}\text{ M}$ .

**Superplasticiser:** Sorption tests were carried out on fresh cements samples with Ni(II) in the presence of MG or SIKA (5 wt%). MG slightly affects Ni(II) adsorption, with observed variations within the experimental uncertainty. The maximum decrease in  $\log(R_d)$  was observed for CEM V in the presence of SIKA. However, a very limited effect on nickel diffusion was observed in tests carried out with cements casted in the presence of SPs. The Ni(II) leaching behaviour was similar in the cement with and without superplasticizers.

### 3. Impact and application to programs (Safety Case)

Chapter 3 summarizes how the genuine scientific/technical results generated in CORI described in the previous chapter can feed into applications in the context of nuclear waste disposal and the Safety Case. The two following subchapters first differentiate into more general aspects of the CORI impact and then provide information on how CORI results are potentially used by national programs.

#### 3.1 General impact of CORI in the applied field

The results generated in CORI offer important new scientific and technical information on the several systems studied. However, in addition they may have important application related impact, e.g. regarding the assessment of repository safety. Predicting and assessing radionuclide transport is a key topic for nuclear waste disposal applications. For radionuclide behaviour in cementitious environments

where large inventories of organic materials may be present, CORI has significantly improved the previous knowledge and state-of-the-art. The improved quantification of radionuclide solubility and retention phenomena in cementitious environments provides important input into predicting radionuclide transport.

Important application related aspects exist for the studies in each of the CORI Tasks. Task 2 provided new information on the organic source terms reflecting the specific types of organic materials studied, (for instance considering the difference between degradation products formed from hard and soft PVC). Knowing the types of organic molecules in waste inventories or formed via degradation processes is a key requirement to assess the potential impact of complexing organic molecules on radionuclide behaviour. Information on the organic source term as derived in Task 2 is needed as part of the Safety Case and can provide input to perform safety assessments. The studies in CORI related to the sorption of organics on cement-based materials (Task 3) have greatly improved the available data and established a sound database to assess the organic plume in a repository setting. This is important input in order to identify whether or not a potential impact from organics is to be expected. The work performed in Task 4 of CORI has demonstrated that there are certain systems in a cementitious environment containing radionuclides which are particularly sensitive to interactions with organics (for instance the Pu-ISA system or systems with high concentration of phthalates). Other systems, like for instance including formic acid, are less sensitive or show no impact of organic ligands on radionuclide retention at all. This shows that not all the organics present have a similar effect and that this effect is also not the same depending on the types of radionuclides. In summary it can be stated that research in CORI provided important new information to help identify the most sensitive systems where the Safety Case should pay attention. In addition, results of CORI can be used to develop reactive transport models which can be used in Performance Assessment.

In view of the initial ambition and general motivation in CORI, further impacts regarding potential implementation needs or regarding safety are reflected below.

*Regarding implementation needs:*

Issues of potential interest at the repository scale:

- Improved scientific basis for the Safety Case for L/ILW waste repositories featuring relevant organics content.
- Co-storage of waste: technical information is provided to support decisions regarding the question whether a mix of various wastes (organics, soluble salts, exothermic waste) can be foreseen.
- Optimization of vault design: CORI has provided new information on the organic plume by characterizing the transfer behavior in cement-based materials. This may contribute to assess limitations of interactions between the vaults regarding their content.
- Optimization of concrete formulations as regards the potential effect of superplasticizers on radionuclide transfer properties.

*Regarding safety:*

- New results and information are available to characterize the effect of the organic plume on the behavior of radionuclides in terms of:
  - solubility (better assessment regarding potential solubility increase),
  - sorption (better assessment of potential retention decrease) in terms of  $K_d$  values.
  - retention of potentially  $^{14}\text{C}$ -bearing organic molecules (determined in CAST project) in cementitious environments in the case of specific waste.

CORI project has in addition:

- reduced the uncertainties on the current knowledge (mainly  $K_d$  values),
- improved the knowledge on the known organic molecules present in degradation solutions (not considered so far) with their complexing properties.
- Contributed to a better definition of the organic inventory regarding the waste and the concrete vault (geological and surface repositories).

### 3.2 CORI input and relevance for national programs

A closer look at how CORI results are actually used or may potentially feed into the different national programs (considering the countries of CORI partners) goes beyond the general summary given above. In order to provide an overview, the following subsections reflect the CORI impact in view of several national programs. The respective subsections were written by authors from the countries often together with WMO representatives. The authors of the subsections are explicitly acknowledged in the end of this report.

Considering the situation in Europe, the several national programs and their particular development stages present a quite manifold picture. As for some countries CORI results may be directly used to support the Safety Case and specific results from CORI may even feed directly into applications, other countries at the present will primarily use CORI results for future planning and decision making. The following subsections are reflecting this overall diverse situation.

#### *France*

The presence of organic molecules formed as products of polymer degradation in the waste packages or initially present like some chelating agents is considered in performance assessment by taking into account (i) the properties of the organics in the cement-based materials and (ii) their effect on radionuclide behaviour.

Currently, four main organic molecules can be considered: ISA (from cellulose degradation), phthalate (from PVC degradation), and EDTA or TBP (used in some waste treatment processes). The concentration of the organics in solution and the speciation of these molecules are determined from the Thermochimie database. Only in the case of ISA, the concentration in solution is controlled by a solid ISA phase limiting its concentration at  $2 \cdot 10^{-2}$  M. The concentrations of EDTA, phthalate or TBP in solution are not limited by solubility, and accordingly, the entire amounts of these molecules are considered to be present in solution. The sorption of these molecules in the cement-based materials is taken into account using specific  $K_d$  values determined from experiments. Consequently, the total amount of organic molecules present is distributed between solutions and the cementitious matrix.

The concentration of ISA, phthalate, EDTA, and TBP in solution are then used to determine the effect of these molecules on the solubility and the sorption of given radionuclides of interest (mainly lanthanides and actinides, reflecting their complexation properties). This effect is characterized by a concentration threshold, related to each organic molecule, from which an increase of the radionuclide solubility and a decrease of the radionuclide sorption are applied. The organic plume is first evaluated at the scale of the disposal facility and the correction on the solubility and the sorption of the radionuclides is then applied in agreement with the above mentioned approach.

In the framework of CORI, new results were acquired regarding the characterisation of organic degradation products. Interesting information are namely the characterisation of degradation products of alkaline hydrolysis of pre-irradiated cellulose. It has been shown that the ISA content in the degradation solution represents about 60% of the total degradation products when radiolysis and hydrolysis are considered. Previous information available from literature and considered by Andra for modelling results from alkaline degradation, indicate 80% of ISA and 20% of additional small carboxylic

acids. In this view, the new results acquired might be useful in future modelling since ISA is a strong complexing molecule. CORI also provided new insights regarding the sorption behaviour of organic ligands in cement-based materials. The knowledge on ISA, gluconate, EDTA, or phthalate have been expanded beyond existing literature data. Moreover, new data were produced in CORI for additional organic molecules such as citrate, glutarate, adipate or NTA. The effects of these complexing agents were studied on a large range of radionuclides. These measurements revealed that: (i) the concentration threshold of phthalate is between  $10^{-4}$  M and  $10^{-3}$  M for Am and Eu in the case of HCP at pH=12.2 (before CORI, the concentration threshold was defined at  $10^{-3}$  M) while for C-S-H, no effect was found compared to HCP, (ii) gluconate has an effect on Pu sorption on AFt and AFm phases and on Eu in C-S-H confirming previous observations, (iii) glutaric acid has less effect than ISA on Pu sorption in HCP at degradation stage II, (iv) the effect of ISA on U(VI) sorption was confirmed with a concentration threshold around  $10^{-4}$  M. As some results may provide direct input to safety assessments, there likewise remain certain challenges, i.e. to further validate CORI data in specific systems and reduce present uncertainties. Additionally, the retention of selected radionuclides were studied in the presence of degradation leachates of polymers (cellulose or resins). These sorption experiments showed that the effect of these complex degradation leachates was stronger than from individual molecules such as ISA and glutaric acid, being related to cellulose and resins respectively. This outcome should be considered and deeper investigated to be considered in safety assessments.

It can be noticed that CORI has helped to define relevant experimental protocols for preparing the samples at given degradation stages and for measuring the sorption and diffusion properties as a function of ligand concentration.

### **Sweden**

Some operational wastes from Swedish nuclear powerplants contain the filter aid UP2W, a polyacrylonitrile-based polymer, which is being disposed of in the Final Repository for Short-lived Radioactive Waste (SFR). Under the conditions expected in SFR the polymer decomposes gradually and can form soluble complexes with radionuclides which may affect their solubility and sorption.

Within CORI, the degradation of UP2W was monitored under relevant conditions. Degradation kinetics were comprehensively investigated over 5 years. The influence of the degradation products on the solubility and retention properties of a few key radionuclides was studied in the presence of hardened cement paste. A moderate negative impact of the UP2W degradation products on the sorption capacity of plutonium was observed, while the impact on other studied radionuclides was minor. The results obtained through CORI are being implemented into the waste acceptance criteria for the SFR repository in terms of maximum allowed amounts of polyacrylonitrile per waste package, which ensures the correct management of the filter aid. Furthermore, the results are used to derive sorption reduction factors from already disposed polyacrylonitrile in SFR for implementation in the future safety assessments.

Additionally, extensive work was conducted within CORI on the degradation of cellulose under various conditions (hydrolysis, irradiation), which confirmed the formation of a non-negligible fraction of other degradation products besides ISA. Degradation leachates generated in the experiments were used to assess their impact on the retention of different radionuclides (e.g., Ni, Eu, U, Pu) by cement. The results complement existing literature available on the effect of ISA with a more applied perspective by using real degradation leachates. This is expected to be potentially useful for future safety assessments for the SFR and SFL repositories in Sweden.

### **Spain**

In Spain, very low, low and intermediate level radioactive waste containing organic compounds is strictly controlled and disposed within the El Cabril facility located near Cordoba, southern Spain, and operated by ENRESA. El Cabril is a surface disposal site whose engineering barriers are based on cementitious

materials. The results obtained within CORI regarding the degradation of organic materials and the effect of organic compounds on radionuclide mobility under cementitious conditions could be directly applicable to the El Cabril context, improving both the knowledge of the organic long-term stability and their potential effect on radionuclide migration under disposal conditions. In terms of safety, the information from CORI might be of high relevance to complement the current safety assessments regarding long-term facility performance (i.e. regarding the evolution of organic materials in post-closure scenarios, or by providing valuable insights on resins, PVC and cellulose tissues). The data from CORI is likewise decreasing uncertainties by complementing current assumptions on radionuclide mobility in the presence of organics (i.e. regarding the potential effect of organic degradation products on radionuclide retention, new results on radionuclide adsorption, update on certain retention values, and the investigation of real organic degradation products like obtained in CORI).

### Switzerland

Nagra's current generic repository project is based on a combined repository with two disposal areas, one for spent fuel (SF) and high-level waste (HLW) grouped in an HLW repository section, and one for low- and intermediate level waste (L/ILW) and alpha-toxic waste (ATW) placed in an L/ILW repository section. After an extensive site selection programme, Nagra selected Nördlich Lägern as the safest siting region to host a combined repository for both HLW and L/ILW at a depth of around 900 m in Opalinus Clay.

The inventory of the Swiss radioactive waste shows that more than 99% of organic substances are present in L/ILW, while less than 1% is found in the ATW. The L/ILW is the main source of organic material in the repository (i.e., ~ 95%) while conditioning materials and tunnel support contain only a very small proportion, e.g., in the form of cement additives. Ion-exchange resins, poly(vinylchloride), bitumen, polystyrene/styrene, other plastics, cellulose, poly(methyl metacrylate), polyethylene, polyester, diethanol amine and polycarboxylates are the main organic materials in term of mass, similar to other European waste management programmes.

Most of the contaminated organic materials are pressed and embedded in a cement/mortar matrix and placed in standardised 200 L drums. In the current concept, the 200 L drums will be loaded into final disposal containers made of reinforced concrete. After loading, these containers are backfilled with cement mortar and closed, before being transported to the L/ILW repository section. The concrete disposal containers will be stacked in dead-end L/ILW emplacement caverns. Once the waste emplacement has been completed for one compartment of a cavern, the voids between the containers and the cavern lining will be backfilled with a highly porous mortar.

Recently, a comprehensive literature review on the abiotic and biotic degradation of the main organics present in Swiss L/ILW under conditions relevant to a cementitious deep geological L/ILW repository was conducted at Nagra [5] to improve process understanding and define the gas generation rates used in performance and safety assessments. Due to a general lack of knowledge available in the literature on degradation processes controlling degradation of organics under anoxic and highly alkaline conditions, and their kinetics, a rather conservative approach had to be taken in terms of gas generation. The results obtained from Task 2 of the EURAD - CORI work package are a first step to fill this general lack of knowledge on degradation processes and kinetics of cellulose, poly(vinylchloride) and superplasticisers.

Optimisation of L/ILW emplacement in the repository is a topic of relevance at Nagra, where L/ILW is classified into two waste groups, depending on the concentrations of organic complexing ligands and the expected degradation stage of cement caused by the presence of CO<sub>2</sub> resulting from the degradation of organics. The results from Tasks 3 and 4 can eventually help to define the input parameters for the implementation of radionuclide diffusion models.



### **Romania**

For Romanian near surface and geological disposal facilities, the main category of organic waste to be disposed of consists in spent ion exchange resins (SIERs). RATEN ICN therefore selected to work in CORI with  $^{14}\text{C}$  labelled organic molecules that are generated by SIERs degradation.

$^{63}\text{Ni}$  is one of the safety relevant radionuclides for Romanian near surface disposal facility and the effect of organics on its mobility in the disposal zone (cementitious environment) was not considered in the preliminary performance assessment for the near surface disposal facility (DFDSMA). Furthermore, as the type of cement to be used to construct the disposal modules and disposal vaults for DFDSMA was not selected yet, RATEN ICN decided to work in the frame of CORI with CEM I and CEM V as raw materials for cement formulations to assess not only the effect of cement degradation and organics on  $^{63}\text{Ni}$  mobility in cementitious materials, but also the effect of cement composition. The CORI outcomes will be used in the optimization of concrete formulation for disposal modules and vaults and also as input data for the DFDSMA performance and safety assessment.

### **Czech Republic**

The results of the CORI project will serve to support the long-term safety assessments of both existing disposal repositories and the planned deep geological repository in the Czech Republic. The analysis of old concrete samples from the Richard repository, performed as part of the CORI project, will provide support for a project aimed at extending the lifetime of the Richard repository. The sorption and migration tests conducted on the reference CORI cementitious material and the already affected cementitious materials will also contribute to enhancing the understanding of the overall behaviour and transport of radionuclides through engineered barriers. The results obtained will be used in the preparation of documentation for the Safety Case.

### **Belgium**

Due to its early development stage, the safety case for geological disposal of LL-ILW in Belgium is still, in essence, simplistic and does not rely on cementitious barriers for its long-term safety functions. Thus, in general, the specificities of the Belgian geological and surface disposal programs limit the direct applicability of the CORI work package results at this time. Yet, the CORI results constitute a valuable expansion of the knowledge base and later may prove helpful in evolving the safety functions of the geological disposal. In theory, the results of the CORI work package could be directly relevant to surface disposal of low and intermediate-level short-lived waste because it relates to the safety functions which involve the retardation of the radionuclide migration due to the cement matrix. However, in practice, the cement formulations used in the Belgian surface disposal program (mostly CEM III/C based mortars) differ from those used in the CORI work package (mostly CEM I and CEM V). Therefore, a direct application of the results, and particularly of the sorption and diffusion results, is not straightforward. On the other hand, the progress in cellulose degradation mechanistic understanding constitutes a valuable improvement of the knowledge base. The degradation of superplasticizers (notably PCE) is interesting for further optimization of engineered barriers. Also, the PVC degradation study could be used to update the safety report's section covering the knowledge of the phenomenology of the engineered barriers in their environment. Tasks 2 and 3 of CORI constitute significant progress in the mechanistic understanding of organic degradation and organic-cement interactions. However, it seems some studies in Task 2 were not designed for direct safety assessment applications and applied radiation doses were generally higher than those expected in the surface disposal system. Task 4 constitutes a breakthrough in observing complex organic-cement-radionuclide interactions (e.g. between RN, cement and real degradation leachates rather than proxy ligands) and is a valuable starting point for more specific studies. When oriented toward the development of a safety assessment, such studies could prove highly useful given their unique representativity of a real system's behaviour.

### ***Slovenia***

Slovenia is in the construction phase of a LILW disposal facility. New iterations of the safety assessment for the operation of the facility will be done in upcoming years. The waste acceptance criteria (WAC) are already prepared for the disposal of radioactive waste.

Slovenian LILW, which will be disposed in the disposal facility, can contain small amounts of cellulose and other organic matter. Results from the CORI programme generally confirm the WAC for disposal, i.e. that small amount of organic matter does not affect sorption of RN to the concrete. From Task 3 useful information can be taken for the further development of the Slovenian Safety Case. Results from CORI will be useful for the further development of the transport model of RNs, integrating some new findings in the field of sorption. Results from the CORI programme confirms the results from the safety case for Slovenian LILW disposal facility.

### ***Lithuania***

As part of the decommissioning process for the Ignalina Nuclear Power Plant (INPP), a new Near Surface Repository (NSR) is being constructed on the INPP site. This facility is designed for the disposal of low and intermediate-level short-lived radioactive waste. The waste, which includes both liquid and solid forms, originates from operational activities, decommissioning processes at INPP, and historical as well as recent medical, industrial, and scientific sources. This waste is treated and conditioned at INPP's Cementation Facility, where it is cemented into 200-liter drums. These drums are then placed into concrete overpacks and transported to a Temporary Storage Building located on the INPP site. Prior to final disposal, the drums are immobilized with cemented grout.

The NSR has waste acceptance criteria that limit the specific and total activity of Pu and Am (among other radionuclides) in the radioactive waste. These criteria were established using a conservative approach, based on the industrial grouting technology available at the time the Cementation Facility was constructed. Efforts are ongoing to enhance the safety of the NSR during its operation. One significant avenue being explored is the development of a new matrix designed to improve the retention of long-lived actinides.

### ***Germany***

The results generated in CORI currently do not directly feed into the site-selection process in Germany for a repository for high level waste. BGE has initiated a site-selection process which currently includes all potential host rock formations in Germany (crystalline, clay, salt), to find the site that ensures the best possible safety for a million years. Within this process, the number of potential options will be subsequently narrowed down on the basis of science-based comparisons. Results from CORI can potentially be used in later stages of the German site selection process to support decision making and eventually contribute to the Safety Case.

### ***Cyprus***

There is not current direct input from CORI into decision-making in Cyprus related to radioactive waste disposal. However, results from CORI help to develop the knowledge base for the future developments and decision making.

## 4. Networking, dissemination and future perspectives

In this section, additional aspects and impacts related to the CORI project are discussed which go beyond the genuine scientific/technical results described in Chapter 2 or the application oriented aspects discussed in Chapter 3.

CORI had established an **End User Group** (EUG) from the start of the project which included WMO representatives, groups with RE status in the USA and East Asia and one TSO partner. Members of the EUG from WMOs had been involved in CORI starting from the initial preparation phase where they had a strong contribution to define the project scope and technical focus. EUG representatives participated and contributed to every Annual CORI Workshop, with a specific EUG related topical session organized in 2021. EUG followed the project progress during each of the Annual CORI Workshops and commented on the presented work, often during the technical Task level presentations. EUG members were supporting CORI by performing reviews of selected documents and Deliverables (e.g. SOTA, Del. 3.1, 3.2, 3.5, 3.6, 3.7, 3.8). Toward the end of CORI there was an ongoing involvement of EUG members to analyze and evaluate the CORI impact. EUG members were included in the preparation of the present D3.5 (Final Report) where the applicability of CORI results to the different national programs are discussed in Chapter 3.2.

Since 2021 CORI has participated in **interactions with civil society representatives** (ICS) and UMAN with the aim to perform a pluralistic dialogue process between CORI, UMAN and ICS. The interactions were structured by discussions concerning contextual case studies, in order to enlighten the impact of the work performed in CORI on reducing uncertainties and enhancing safety. Discussions were based on selected scientific cases studied by CORI. A key event was the 2.5 h plenary session at the Annual EURAD Event in March 2022, which was continued in-person at the EURAD Annual Event in Cyprus (March 2023) supported by several video meetings.

A key experience especially at the beginning of the interactions was the realization of the importance to establish a “common language” between technical/chemistry and social sciences experts. Concerning the discussions focused on the concept of safety and the rationale behind how CORI selected systems and did research with that perspective, there was fully agreement that contributing to safety is of highest importance for research in CORI and beyond in the wider field of nuclear waste disposal. In this context, CORI explained that there is research outcome in the form of new experimental data and improved numerical description of several systems investigated, which contributes to reduce uncertainties in the technical description of the systems and substantiates safety. CORI similarly highlighted the high importance to develop proper process understanding, i.e. identify and systematically characterize the underlying chemical reactions and processes which give rise to the numerical data. As the latter aspect has no direct impact on the numerical values themselves, it provides fundamental scientific justification, scientific traceability, and hence serves as essential quality assurance.

The exchange and discussions between a technical WP like CORI and the ICS group highlighted the excellent options for cross-disciplinary networking in EURAD, which clearly constitutes a step-change relative to previous EC funded projects.

CORI has been active regarding the **dissemination of project results** at conferences and in open access peer reviewed publications. Within EURAD, CORI contributed to the annual EURAD events by giving technical presentations on the research performed and actively organized CORI related sessions. CORI likewise contributed a presentation to EURADWASTE 2022 conference together with the WPs CONCORD, FUTURE and MODATS. In November 2023, CORI has co-organized the 6<sup>th</sup> International Workshop on Mechanisms and Modelling of Waste / Cement Interactions, hosted by the Czech groups in CORI in Prague and held in connection to a CORI WP meeting. Main activities by individual CORI

partners were the dissemination of the research performed in CORI in about 100 oral and poster contributions at conferences and workshops. At the end of CORI in May 2024, groups participating in CORI have prepared 19 peer-reviewed scientific publications with several others still under review with the respective journals.

The data and results produced in CORI can also be accessed via Public Deliverables. Detailed technical reports on data and results generated in the R&D Tasks 2, 3, 4 are available in the combined Deliverable D3.6,7,8 [2]. The state-of-the-art (SOTA) document D3.2 is likewise providing substantial information on topics addressed in CORI including fundamental background information. Finally, CORI has prepared a scheme to document which kind of data are available at the different partners so that CORI results can be efficiently shared and used in future studies, available from the WP leader.

CORI has strongly relied on **PhD and early career researchers**, especially in conducting the experimental program. In total, about 25 young researchers were involved in CORI, performing PhD studies, Master studies and PostDoc research. Students were supported by the Mobility Measures available in EURAD, both regarding focused research stays at other CORI partners and participation at EURAD events. Specific meetings were organized at CORI WP Meetings with a strong focus on the early career researcher. The tools offered in EURAD regarding training and education were successfully used. CORI has successfully contributed to the training and education of young researcher.

Looking ahead on the expected **future perspectives arising from CORI**, additional scientific output is expected via future peer-reviewed publications from CORI partners not fully completed so far. Within EURAD II, a provision of input data from CORI to the EURAD II RAMPEC WP is expected to support research in RAMPEC on the modeling of radionuclide behavior in cement-based environments. The interactions with civil society representatives started in CORI are expected to continue in EURAD II. As mentioned above, CORI has strongly based its R&D program on young early career researchers which in some cases have already or are expected to continue their future careers in the context of nuclear waste disposal related topics, hence meeting the general demand for qualified experts in this field. EURAD and CORI have established networking between different European partners which facilitates joint collaborative work in the future, with sharing of competence and facilities in support of working in a cost-efficient and scientifically excellent manner. Last but not a least, the networking established in EURAD and CORI contributes to European Integration and contributes to promoting and strengthening a joint European vision and research.

## 5. Literature

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Chapter 2.3: contributed by N. Macé (CEA) and T. Missana (CIEMAT)

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