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Authors	Marcus Altmaier (KIT); Tiziana Missana (CIEMAT); Norbert Maes (SCK-CEN); Nathalie Macé (CEA); Susan Britz (GRS); John Provis (PSI); Hans Meeussen (NRG); Andrés Idiart (AMPHOS 21); Jean-Charles Robinet (Andra)

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Executive Summary

Past research related to deep geological disposal of radioactive waste has established a strong understanding of radionuclide behaviour in clay, crystalline, and cementitious systems under equilibrium conditions. However, during construction, operation and post-closure of a geological disposal facility (GDF), inevitably the near field (NF) - engineered components and part of the host rock (HR) - will be subjected to “perturbations”. These perturbations can be subdivided into following effects: thermal, hydraulic, mechanical, chemical, biologic and radiation. Under perturbed conditions, the behaviour of radionuclides and, in general, dissolved species in a disposal environment (e.g. gas, chemotoxic elements, organics...) remain poorly constrained. At present, no integrated, model-based description exists for such systems, and the ability to represent the chemical evolution of *in-situ* conditions has not yet matured to the level required for mechanistic transport modelling at the near-field scale.

RAMPEC aims to address these gaps by gathering new experimental data under relevant perturbing conditions, enabling the required modelling of radionuclide retention and migration in such environments, and supporting upscaling to disposal cell–scale.

The scope of the work focuses on clay, crystalline, and cement systems, with particular attention to perturbations most relevant to each. In addition, the present initial State-of-the-Art (SOTA) report serves as a baseline against which the RAMPEC workplan has been developed. It provides a synthesis of the existing knowledge, offers comprehensive references to past projects and published results, and identifies key challenges to be addressed.

Keywords

Geological disposal – Host Rock – Radionuclides – Perturbations – Migration – Diffusion – Retention – Sorption – Speciation

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Glossary

AFm: Monosulfoaluminate

AFt: Trisulfoaluminate

C3A: tri-Calcium Aluminate

C-A-S-H: Calcium Aluminate Silicate Hydrates

CDP: Cellulose Degradation Products

C-S-H: Calcium Silicate Hydrates

D_e: Effective Diffusion Coefficient

D_a: Apparent Diffusion Coefficient

DGR: Deep Geological Repositories

EBS: Engineered Barrier Systems

EDL: Electric Double Layer

ETT: Ettringite

GDF: Geological Disposal Facility

HCP: Hardened Cement Paste

HM: Hydromechanical

HR: Host Rock

IER: Ion Exchange Resins

ILW: Intermediate Level Waste

IS: Ionic Strength

ISA: Isosaccharinic acid

LILW: Low and Intermediate Level Waste

LLW: Low Level Waste

MLW: Medium Level Waste

MSH: Magnesium Silicate Hydrates

NF: Near Field

OM: Organic Matter

OPC: Ordinary Portland Cement (CEM I type cement)

ORGA: Organic Molecules

POR: Portlandite

PVC: Polyvinyl Chloride

REEY: Rare Earth Elements and Yttrium

RN: Radionuclide

RH: Relative Humidity

SEM: Scanning Electron Microscopy

SFC: Safety Case

SP: Superplasticizer

THMCB: thermal, hydraulic, mechanical, chemical, and biological

URL: Underground Research Lab

WMO: Waste Management Organisation

1. Introduction

The present SOTA (State of the Art) document is related to the Work Package RAMPEC (radionuclide mobility under perturbed conditions) in EURAD-2. RAMPEC is investigating different aspects of radionuclide mobility with the aim of improving the predictive capacity of models for disposal system chemistry and radionuclide mobility under perturbed (temperature, chemical, partial saturation) conditions, based on a combination of new experimental and modelling studies up to the disposal cell scale. RAMPEC is projected to have a 5-year duration (2024-2029) and is performed by a group of 31 beneficiaries.

The RAMPEC structure comprises different technical Tasks as depicted in Figure 1. Task 2 is related to Knowledge Management, including Subtask 2.1 on Knowledge Capture; Subtask 2.2 on Knowledge Transfer and Subtask 2.3 dedicated to the development of retention/transport parameters databases. Task 3 implements the experimental program through studies in clay, crystalline/granitic, and cement systems (Subtasks 3.1–3.3), and is completed by Task 4 on the development of macroscopic and mechanistic models. Task 5 deals with the upscaling of data and models.

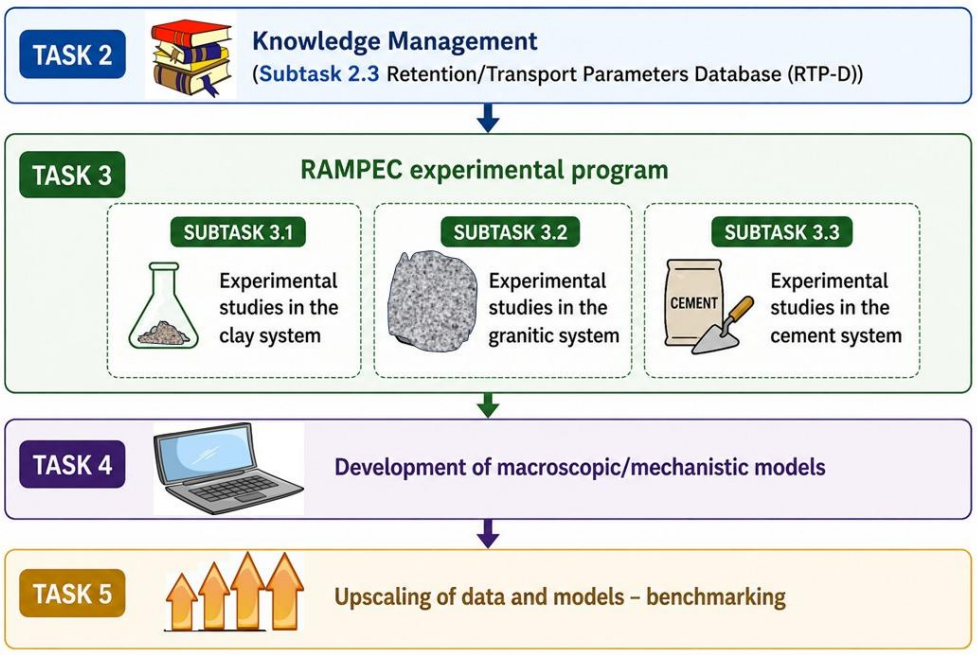

Figure 1: RAMPEC Project Structure

Good understanding of radionuclide (RN) behaviour in argillaceous, crystalline and cementitious systems under equilibrium conditions has been derived from past experimental studies in simplified reference systems. Radionuclide and gas behaviour under perturbed conditions, however, are poorly constrained and, to date, there is no integral model-based description for perturbed systems. In addition, the capability of describing the chemical evolution of *in-situ* conditions in such systems has not yet reached a necessary level of maturity to deliver deterministic reactive transport modelling of the nearfield. RAMPEC is providing improved methods and approaches both regarding mechanistic modelling of RN retention and migration on the disposal cell scale (meter to decametre scale). This is achieved using existing data from previous EURAD projects (FUTURE, CORI, …) and targeted new experimental investigations.

The present SOTA is restricted to the systems investigated in RAMPEC (clay, crystalline, cement), with a limited number of specific perturbations relevant to each system. The modelling work performed in RAMPEC is likewise reflected in the SOTA. The topics covered in this SOTA include chapters on relevant issues for clay, crystalline and cement systems and sub-systems. This is complemented by a discussion on modelling radionuclide migration in perturbed systems as well as aspects related to upscaling and disposal cell modelling. The SOTA is summarizing present knowledge and provides ample reference to previously published information and projects.

The initial SOTA document is providing fundamental information on the R&D topics addressed in RAMPEC, against which the Workplan in RAMPEC was developed. The technical chapters of this SOTA report were prepared by the respective Task and Subtask leaders in RAMPEC. The present initial state-of-the-art report in RAMPEC, which is developed early in the project, with the experimental Tasks operative for only a few months, will be updated towards the end of RAMPEC. The updated final SOTA will include main R&D achievements in the project and highlight the specific progress made in this particular R&D field.

2. Clay systems

2.1 Introduction

During construction, operation and post-closure of a geological disposal facility (GDF) inevitably the near field (NF) of the host rock (HR) will be subjected to “perturbations”. These perturbations can be subdivided into following effects: thermal, hydraulic, mechanical, chemical, biologic and radiation. These effects do not always have the same impact during the entire time span of the GDF. Hence in Safety Cases (SFC), evolution scenarios are made to see which perturbations are important in which phase and what their effects on the safety functions of the repository system can be. An example of so-called storyboards, used by ONDRAF/NIRAS illustrating the evolution of the disturbed zone during different phases of repository lifetime, is given in

Figure 2 (Wickham, 2008 & Harvey et al., 2011).

The focus of RAMPEC is on perturbations that influence the safety function “delay and attenuate the release of radionuclides (R)” and more specifically the retention function for contaminant migration (R3).

Radionuclide migration processes in clay host rocks are well studied and have reached a high level of understanding (Maes et al., 2024), but most of the effort and understanding is obtained for the undisturbed conditions, because these are the most important as they should provide the safety at long time. Even if disturbances exist and could act for a long time, there should always remain “pristine” host rock to rely on.

In a simple, often conservative approach, a “disturbed zone” in the host rock can be considered to have no retention function. However, as knowledge progresses, it becomes more desirable to abandon this conservative approach and to consider also the “retention/migration” in this disturbed region, to quantify margins, and increasing confidence in the overall system performance based on advanced system understanding.

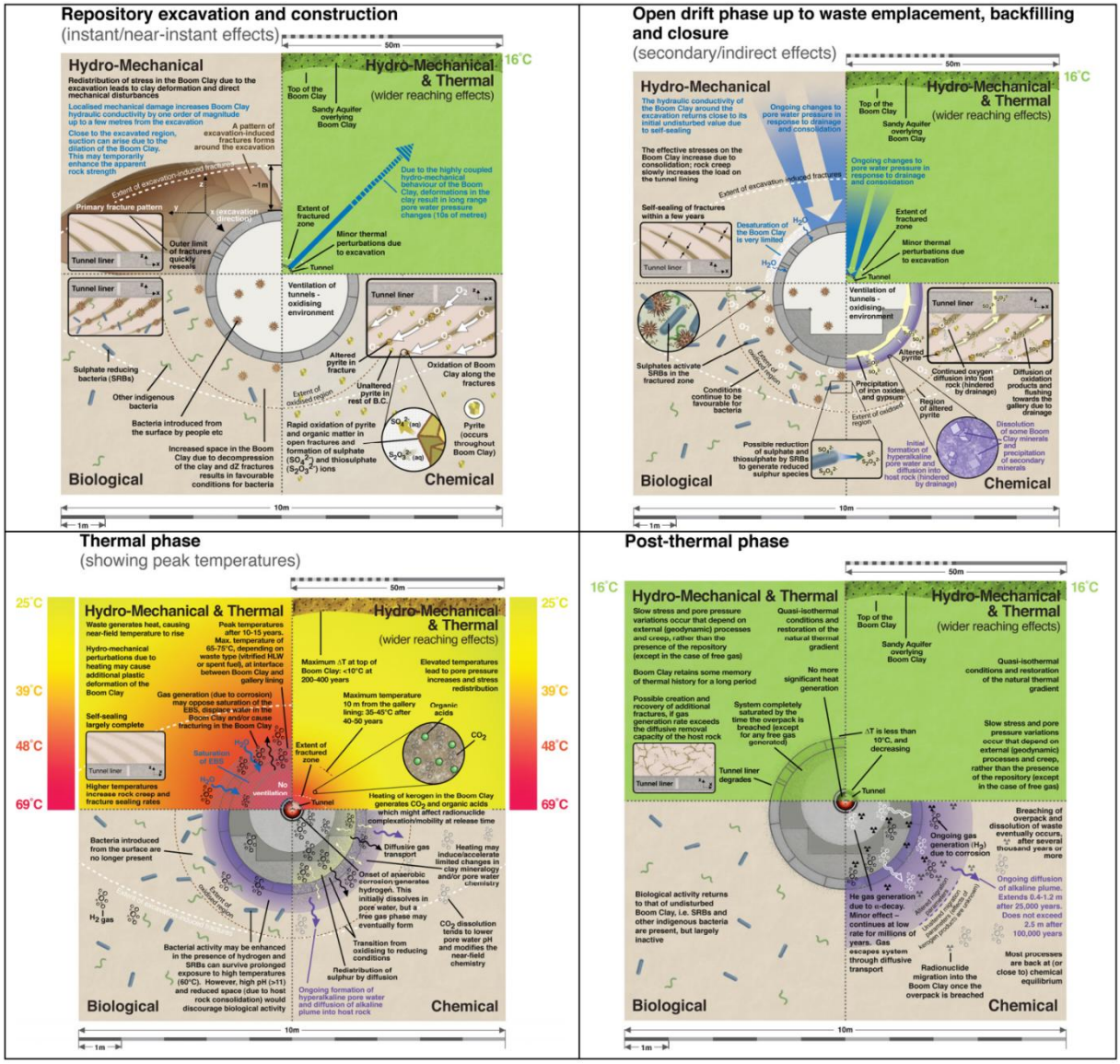

Figure 2: Storyboard diagrams used by ONDRAF/NIRAS illustrating the evolution of the disturbed zone during different phases of the repository lifetime. Here for category C waste in Boom Clay as potential host rock (Harvey et al., 2011, modified from Wickham S. (2008) Evolution of the Near-Field of the ONDRAF/NIRAS Repository concept for Category C wastes, NIROND-TR 2007-07E).

When looking at perturbations that may affect radionuclide retention and migration, there are a few that deserve further attention, and which are the focus of RAMPEC. The perturbations we are concentrating on are: i) temperature (T), because of presence of heat emitting waste and also higher T in deep underground; ii) partial desaturation as result of ventilation and gas production by metallic waste; iii) chemical perturbations as alkaline plume (cement from waste forms, engineered structures and the engineered barrier system – EBS -), ionic strength (nitrates and sulfates releases from “salt” bearing wastes) and small organic molecules (organic degradation products, complexing ligands,…) present in waste.

In the next paragraphs a brief description of the current understanding on the selected perturbations will be presented.

2.2 Temperature

Final disposal of heat emitting high level radioactive waste (HLW), and spent fuel (SF), will result in the creation of a zone in the HR with increased temperature (fading as function of distance) for a considerable long time (fading as function of time). This is called the “thermal period” and typically the GDF is designed in a way that the contact temperature between EBS and HR does not exceed 90°C. In case of an “early canister failure” scenario, causing accidental release of radionuclides during this period, it is needed to know how this would affect the retention and transport of radionuclides.

Furthermore, depending on the depth of the GDF, the temperature is different (geothermal gradient 25-30° $C \cdot km^{-1}$) compared to temperature used in majority of lab studies on speciation, retention and migration of radionuclides which are conducted at room temperature. With respect to parameter selection and uncertainties, it is desirable to understand this effect.

Chemical reactions are temperature dependent; hence the speciation of radionuclides depends on temperature, as well as solids solubility. Thermodynamic databases used for speciation calculations can account for temperature, but it depends on the availability of T-relationships in the thermodynamic databases.

Temperature will also influence the protonation/deprotonation reactions of the sorption sites in minerals. In analogy to oxide surfaces. Surface site protonation of clays is generally exothermic (Duc et al. 2008). Acid-base properties for clay minerals are available but are again often studied at room temperature and studies at temperatures above 25°C are rare (Tertre et al, 2005). Angove et al (1998) explained the sorption dependence of kaolinite by the increase of surface charge density; Duc et al. (2008) concluded that protonation-deprotonation of dissociable sites at the edges of clay platelets is not significantly temperature dependent (25-80°C).

Sorption studies with radionuclides on clays at temperatures above 25°C are scarce. Tertre et al. (2005) performed a highly relevant experimental sorption study of Ni^{2+}, Cs^{+} and Ln^{3+} onto montmorillonite up to 150°C. They also determined sorption enthalpies. They noticed a weak but measurable influence of temperature on sorption. K_d’s for Ni^{2+} and Ln^{3+} increase by factor 2-5 with temperature increase from 25 to 150°C. The effect seems higher at higher ionic strengths (IS). For Cs^{+}, a temperature effect was only noticed at low IS and neutral pH with a decrease by factor 3 in K_d. They conclude that T effect on sorption depends on the underlying sorption process. In the case of an ion exchange dominated reaction (low pH and low ionic strength), the temperature effect is negligible. In the case of surface complexation (high pH and high ionic strength), the observed increase of K_d with temperature reflects either an increase of the sorption equilibrium constant with temperature or an endothermic property for reactions describing the montmorillonite surface chemistry.

The effects of temperature on K_d were confirmed on clay-rocks. Chen et al., (2015) observed the reduction of the K_d isotherm for Cs^{+} onto the Callovo-Oxfordian clay-rocks and determined the sorption enthalpies. Results are in a good agreement with those obtained on montmorillonite. Montavon et al. (2022) studied the sorption of U(VI) on Callovo-Oxfordian clay-rock between 20 and 80°C. They highlighted an increase of the U sorption with temperature and suggested this is mainly due to the limitation of the uranium complexation by carbonates at high temperature.

Exposure of clays to high temperatures can also induce changes in the composition and, as such, influence RN transport. Thermally exposed bentonites can undergo alteration processes as cementation by precipitation of SiO_2 and illitisation (transformation of smectite to non-swelling illite). Wersin et al. (2007) concluded that for temperatures below 120°C, no significant changes occur. In natural host rocks containing organic matter (OM - kerogen), a thermal load can result in decomposition of the kerogen with the production of small organic acids and CO_2. This will trigger changes in the mineral/water equilibrium (CO_2/carbonates, pH) and composition (OM degradation products like small organic acids) invoking changes in the RN speciation with possible increased mobility (complexation to organic

ligands). This phenomenon is of particular interest for the Boom Clay (potential host rock in Belgium) and has been/is extensively studied (Honty et al., 2024).

Diffusion of tracers in solution is temperature dependent and can be described by the Stokes-Einstein relation, where diffusion is related to the temperature dependency of the viscosity of bulk water:

$$D_0 = \frac{k_B T}{6\pi\eta R_H}$$

where k_B is the Boltzmann constant (in J K^{-1}), T is the temperature (in K), η is the viscosity of water (in Pa s) and RH is the solute's hydrodynamic radius (in m). Knowing the value of D_0 at a reference temperature Tref, one can calculate the diffusion coefficient, D_0^i, at different temperatures, thanks to the following equation:

$$D_0^i = \frac{D_0^{\text{ref}} \cdot \eta_0}{T_{\text{ref}}} \cdot \frac{T_i}{\eta_i}.$$

Table 1 shows the temperature effects on D_0 values for some radionuclides, according to the Stokes-Einstein equation.

Table 1: Temperature effect on the D_0 values for some typical used radionuclides calculated using the Stokes-Einstein Relation (Savoye et al. (2011).

D_0 (x 10-9 m²/s)	At 21°C	At 80°C
HTO	2.008	6.646
$^{36}Cl^-$	1.771	5.862
$^{22}Na^+$	1.180	3.096
$^{137}Cs^+$	1.739	5.756

Besides this relationship, the T dependency of aqueous diffusion can also be described by the Arrhenius equation (Eisenberg and Kauzmann, 1969 in Van Loon et al. 2005):

$$D_w = A \cdot e^{-E_{A,w}/R \cdot T}$$

with: A, (empirical) Arrhenius parameter ($m^2\ s^{-1}$), also called a pre-exponential factor; $E_{A,w}$, activation energy (J mol-1) for diffusion in free water; R, gas constant 8.31451 (J mol^{-1} K^{-1}) and T, absolute temperature (K).

The latter expression seems to be the most suitable to explain the temperature dependent behaviour of diffusion. In general, the effect of T (up to 80°C) on the diffusion coefficient remains less than a factor of 10.

Studies on bentonite (Kozaki et al. 1997, 1998 a,b, Liu et al 2003, Suzuki et al. 2004) with HTO, Cl^-, Sr^{2+}, Na^+ and Cs^+ show that the activation energy depends on the degree of compaction. Sanchez et al. (2008) investigated the self-diffusion of water as function of T in compacted montmorillonite, illite and kaolinite and the Arrhenius' equation was successfully used to interpret the data. However, activation

energies obtained for one type of clay are not directly transferable to other clays, as it seems to depend on the way water is bound to the clay surfaces. Recently, Garcia-Gutiérrez et al. (2024) published a study combining the effect of dry density (1.20 - 1.65 g cm^{-3}) and temperature (25-80°C) on the diffusion of HTO, Cl^-, Sr^{2+} and Ba^{2+} in compacted bentonite. Da values increased with T and decreased with dry density. Activation energies of the diffusion process were successfully determined using the Arrhenius' law, while the Stokes-Einstein approximation only worked well for dry density < 1.4 g cm^{-3}.

Besides studies on pure clay minerals, several studies were made on clay host rock materials. Van Loon et al. (2005) used the Arrhenius law to interpret the self-diffusion of HTO, Na^+ and Cl^- in compacted Opalinus Clay for a temperature range of 0-70°C. The Stokes-Einstein relation was not applicable for HTO, indicating difference in structure of the pore water in OPA. Savoye et al. (2011) performed similar studies with HTO, Cl^-, Na^+ and Cs^+ on Callovo-Oxfordian clay. In the latter study, the effect of a thermal period (80°C) on the diffusion behaviour was investigated. As no difference in diffusion coefficients were obtained before and after the thermal load, it suggests that at laboratory scale, heating of Callovo-Oxfordian (COx) samples did not alter the claystone containment properties. Stokes-Einstein relation could be used for HTO and Cl^-, but not for Na^+ and Cs^+.

Another consequence of a temperature gradient is that it can promote the transport of solutes. This is called thermal diffusion (Onsager transport phenomena) or the Soret effect. Soret coefficients measured in the laboratory are usually positive, *i.e.*, they indicate solute transport down temperature gradients, and range between 10^{-3} and 10^{-1} K^{-1} for a wide range of concentrations and temperatures (Soler, 2001).

$$\text{Thermal diffusion} \qquad J_{TD} = -D_e s c_i \frac{\partial T}{\partial x}$$

Soler (2001) did an assessment of the implications of coupled transport phenomena (Onsager phenomena) on RN transport in Opalinus Clay. He concluded that even for large values of the Soret coefficient s (0.1 K^{-1}), the contribution to transport, on top of advection and chemical diffusion, is negligible. However, to the authors knowledge any experimental data to back up this statement is currently missing. Large scale studies in the context of radioactive waste disposal are however initiated to address this issue. In Tournemire underground laboratory, the DIGIT experiment (Diffusion under Thermal Gradient) was initiated (Desfeux et al., 2024), similarly in Mont Terri the DR-C (Nussbaum et al., 2023) experiment has been initiated.

In general, studies on the effect of temperature on species transport behaviour in clays are limited. The impact on diffusion has achieved most attention and can be reasonably explained using Arrhenius' law or Stokes-Einstein relationship but it deserves further attention. The transport under a T gradient is however only evaluated theoretically and needs experimental proof. With regards to sorption behaviour at elevated temperature, again there is limited data available, and more studies are needed. This goes however hand in hand with extending thermodynamic databases with temperature correction functions. Section 2.5 provides an overview of the studies planned in RAMPEC.

2.3 Chemical Perturbations

2.3.1 Alkaline plume

Cement type materials will be omnipresent in radioactive waste repositories as materials for structural support of galleries and drifts as well as part of the waste EBS (concrete super container, grouts/mortars of waste packages). These cementitious materials will be in contact with both host rock clay formation and bentonite barriers. Because of the contrasting chemical and mineralogical properties of cementitious materials and clays, there exist chemical gradients that will cause interactions at the cement-clay interface. Progressive degradation of the cement materials after resaturation of the repository leads to cement pore fluids that range over time from pH~13.5 (fresh Ordinary Portland Cement, OPC) to pH~10

(degraded cement) maintaining for a long time a pH gradient with the surrounding HR that typically has pH between 7-8.5.

Within the context of geological disposal of nuclear waste, cement/clay interactions have been investigated for more than three decades by means of laboratory and *in-situ* experiments, studies on natural and industrial analogues, and by using reactive transport modelling. Comprehensive reviews on various aspects of cement/clay interactions have been published and for a comprehensive overview of the available studies and knowledge related to the evolution of near field (NF) we refer to the report of Deissmann et al. (2021) as part of the EURAD ACED project. We furthermore refer to the EC CEBAMA project where studies on cement/interface interactions were performed (Duro et al., 2020).

From these studies it becomes evident that there is a strong coupling between fluid and solute transport, the dissolution of solids and precipitation of secondary phases, ion-exchange and sorption on clays, and the resulting changes in physical properties of the materials (porosity, permeability, swelling of clay). Depending on the mineralogical changes and consequently the porosity (e.g. pore clogging), changes in hydraulic conductivity may occur. The changes in mineralogy may also affect the sealing behaviour of the clay HR (smectite dissolution/alteration) and the sorption behaviour (degradation of clays, formation of new phases like calcium silicate hydrates, CSH, and/or zeolites).

Most of the attention of the studies was devoted to understanding the changes that are occurring in the HR (and cement barrier) to be able to describe as good as possible the chemical evolution of the NF using modelling tools, and to assess the impact on their functioning as barrier on the long term. Simulations show a narrow zone (mainly order of cm to dm) of perturbed zone (mineral and fluid) located close to the interface for time scales up to and beyond 100 000 years (Savage and Cloet, 2018, Bildstein et al., 2019).

The pH is one of the most important factors influencing the speciation of RN and affecting sorption. Quite extensive thermodynamic databases (e.g. ThermoChimie https://www.thermochimie-tdb.com/, OECD/NEA TDB https://www.oecd-nea.org/dbtdb/, NAGRA/PSI database https://www.psi.ch/en/les/database, THEREDA – Thermodynamic reference database for nuclear waste disposal in Germany https://www.thereda.de/de/,…) are currently available that are helpful to predict radionuclide speciation with high level of trust.

Sorption of radionuclides on clay minerals (and other minerals formed by pH alteration like CSH and zeolites) is well studied and numerous datasets are currently available, and new datasets are coming available on regular basis both for clay minerals as for the new formed species.

In sorption research it is common practice to measure sorption as a function of pH, so-called sorption edges. These datasets form a cornerstone to extract surface complexation values that can be used in geochemical and reactive transport modelling. The expanding availability of new sorption data helps a lot in feeding chemical databases and in refining reactive transport modelling leading to more trustworthy predictions.

Besides sorption there are also other retention mechanisms that can become triggered by an alkaline plume such as co-precipitation, solid-solution formation, etc. For more information on retention mechanisms in clays and datasets we refer to Maes et al. (2024).

Changes in the mineralogical composition induced by the alkaline environment will alter the pore structure and hence the transport behaviour of water and solutes. Most important changes will occur at the interface where the chemical gradients are the highest.

Studying transport in an alkaline plume disturbed clay is not straightforward. Passage of an alkaline plume trough compacted clay is very slow and the reactions taking place are slow. Even when experiments are conducted for long periods of time (several years) systems are still in “chemical transient”. Nevertheless, providing transport parameters characteristic for altered area are of great importance to improve the (predictive) simulations.

Experimental studies related to transport in an alkaline disturbed clay system are limited. Wang et al. (2010) report a study where Boom Clay cores have been percolated with “young” (Na/K rich, pH>13) and “evolved” (Ca dominated, pH 12.5) cement water for over 2 years. Transport parameters for HTO, I^-, and HCO_3^- were measured before and after alkaline perturbation. An increase in hydraulic conductivity was observed in case of young cement water (more aggressive) while the opposite was observed for evolved cement water (precipitation of calcite). Migration parameters (apparent diffusion coefficient, D_a and nR – porosity*retardation) for HTO were not affected by the alkaline perturbation. For HCO_3^- significant retardation was observed for evolved cement water, probably related to precipitation of calcite and porosity decrease.

To conclude, numerous studies have been made on the interface clay/cement which have led to a good understanding of the processes at hand that may influence the transport behaviour. Despite that, this can still be improved. In contrary to the number of studies at the interface, the number of transport studies on alkaline perturbed clays is very limited. However, based on the available knowledge coming from sorption studies, clay/cement interface studies and model developments, it is now possible to set-up well defined experiments and to achieve a better interpretation through modelling of the outcome of these experiments. Section 2.5 provides an overview of the studies planned in RAMPEC.

2.3.2 Ionic strength

Some types of waste are rich in salts, more specifically $NaNO_3$ (nitrates) and sulfates. As these salts are very soluble, they may leach out, up to molar concentrations, and disturb the pore water composition of the near field by increasing the ionic strength (IS). This may induce changes in the reactivity and migration of the radionuclides. High ionic strength has a strong influence on the electric double layer (EDL) properties of the clay which will have an impact on the migration of charged species by diminishing the effect of anion exclusion and EDL enhanced cation diffusion (“surface diffusion”). Additionally, the presence of high nitrate and sulfate concentrations may impact speciation of radionuclides by complexation and by increasing solubility. The highly concentrated (saturated) chloride-rich salt brines and related systems and processes potentially relevant for a repository in rock salt are not addressed within RAMPEC.

An increase in ionic strength has a negative effect on (cation) sorption because of the lowering of the potential for ion-exchange but has limited impact for sorption through surface complexation. This mainly affects sorption of alkaline and alkaline-earth elements. Anion adsorption can be affected by the presence of high nitrate or sulfate concentration, for their possible competitions for sorption sites.

Sorption of radionuclides on clay minerals is well studied, and numerous datasets are currently available, and new datasets are becoming available on regular basis. Common practice in sorption research is the measurement of sorption isotherms at different ionic strengths. These datasets form a cornerstone to extract surface complexation values that can be used in geochemical and reactive transport modelling. The expanding availability of new sorption data helps a lot in refining chemical databases and reactive transport modelling leading to more trustworthy predictions.

An increase in ionic strength in compacted clays will result in a lowering (collapse) of the electric double layers present at the negatively charged surfaces of the clays. It will diminish the anion exclusion (effective diffusion coefficients, D_e, values typically lower than D_e for neutral species). The diffusion accessible porosity for anions increases and will converge to the value for neutral and cationic species.

Cationic species are attracted by the negative surface of the clay by sorption phenomena and will enrich in the EDL which can create an extra diffusive flux near the surface in addition to the diffusive flux in the free pore water. This results typically in much higher D_e values compared to neutral species (so called surface diffusion effect). However, with an increase in IS and the collapse of the EDL, this effect tends to disappear. This has been extensively studied recent years partly within EC projects EC CATCLAY

and EC EURAD FUTURE. For more information on the effect of IS on the diffusion of RN we refer the reader to Altmann et al (2015) and Maes et al. (2024).

With respect to effect of a $NaNO_3$ plume (stemming from bitumen) on the transport properties of Boom Clay, we like to refer to the work of Bleyen et al. (2018) and Valcke et al. (2021). They report on long-term migration experiments with Boom Clay cores by percolating, in a successive manner, increasing concentrations of $NaNO_3$ and hereby investigating the changes in the transport parameters of HTO, I^- and HCO_3^- at the different IS. Transport of HTO is not affected, and as expected, the transport of anions was affected through the lowering of the anion exclusion effect.

The Mont Terri BN experiment is a long-running, *in-situ* study at the Mont Terri rock laboratory in Switzerland that investigates the interactions between bitumen, nitrate, and Opalinus Clay to understand how geochemical and microbial processes in clay formations can affect the long-term safety of radioactive waste repositories. Key aspects of the experiment include injecting nitrate to study microbial reduction, observing how electron donors from the clay influence this process, and performing recent tests with selenate to model the fate of redox-sensitive radionuclides. (Bleyen et al. 2017, 2021, Hendrix et al. 2023)

Dagnelie et al. (2017) also studied the perturbations caused by a $NaNO_3$ plume on the diffusion of solutes in large scale rock samples of the Callovo-Oxfordian clay. Similarly, they observed the diminishment of the anion exclusion effect and the decrease in D_e value for cations.

We can state that effect of ionic strength (not for extreme high IS) on sorption and diffusion in clays has reached a good level of understanding. However, when it comes to sulfate and nitrate plume, not only produces changes in IS, but it can also influence the geochemical behaviour of both the HR and the radionuclides. Transport studies on clay rocks that have undergone a sulfate or nitrate perturbation remain limited, thus more dedicated studies are needed to achieve a better understanding of the effect of this perturbation. Section 2.5 provides an overview of the studies planned in RAMPEC.

2.3.3 Organic complexing ligands

Organic substances will be part of any disposal concept, either originating from the waste (e.g. bitumen, organic degradation products in Intermediate Level Waste (ILW)), EBS (e.g. superplasticiser used in concrete) or organic matter present (e.g. humic substances, kerogen degradation products) in the host rock. The organic matter present in host rocks are by definition not considered as a perturbation, but their behaviour may be changed as an effect of perturbations and as a consequence may have an effect on the transport behaviour of RN: (i) Humic/fulvic/kerogen decomposition at elevated temperature into CO_2 and small organic molecules (Honty et al., 2024 and section on Temperature), (ii) changes in IS will change the structure and reactivity of humic/fulvic colloids with an effect on the interaction behaviour with RN and their colloidal transport behaviour, (iii) similar effects can occur with an alkaline plume...

These organic substances can have a dual effect on RN retention: on the one hand they can be complexed by the clay surface modifying its reactivity, and at the other hand they can complex the RN itself, changing its solubility and sorption. In case of large organics (humic colloids), the pore structure may also influence the transport by filtration processes.

Following organics are particularly studied (non-exhaustive list and related to clays): EDTA (complexing agent used in e.g. decontamination), ortho-phthalate (plastics degradation product), isosaccharinic acid (ISA) (cellulose degradation product), di-acids as oxalate and succinate (found in dissolved organic matter in HR pore waters) and humic/fulvic acids (HR pore waters). Hereafter we provide a limited set of references.

Dagnelie et al. (2015) investigated the perturbation induced by EDTA on HDO, Br^- and Eu(III) diffusion in large COx rock samples. Descostes et al. (2017) studied the adsorption and diffusion of Eu-EDTA- through COx. Darban et al. (2000) reported Zn and Pb-EDTA sorption on kaolinite, Missana and García-

Gutiérrez (2023) reported the effect of EDTA, citrate and phthalate on Cs(I), Sr(II), Eu(III) and U(VI) retention in montmorillonite.

Schott et al. (2012) studied the influence of temperature and small organic ligands (citrate, tartrate) on the sorption of Eu(III) on Opalinus Clay. Recently, an extensive study was published by Fralova et al. (2021) providing a large dataset related to the effect of organic compounds (EDTA, α-ISA, phthalate, oxalate, acetate) on the retention of Eu(III), Th(IV) and U(VI) in COx. This study further comprised a sorption modelling study for mechanistic modelling which allowed evaluation of robustness of surface complexation constants and the ThermoChimie database (v10a) that accounts for the speciation.

Particularly for Boom Clay, which contains a relative high content of dissolved organic matter, DOM, (humics and fulvics), the effects of DOM on RN transport have been studied intensively. Maes et al. (2011) developed a consistent phenomenological model that was able to describe the natural organic matter linked transport of a range of RN: Tc(IV), Cm(III), Np(IV), Pu(III/IV), Pa(V) in Boom Clay based on long-term migration experiments. No such studies have been done to see the effect of a “chemical plume” on their “combined (RN-OM)” transport behaviour. Experiments conducted on Boom Clay cores after subjection of a $NaNO_3$ and alkaline plume (previous sections) showed that it released quite some organics. But no detailed studies were done to further characterise them.

For the small organic molecules, there is a need to gather basic interaction data (complexation, sorption ternary systems) of the organic species with radionuclides and with solid surfaces to grow the database (complexation constants, surface complexation constants). For the natural organic matter (humics, fulvics, kerogen), there remains a need to understand its stability (degradation under influence of perturbations as temperature, saline plume, alkaline plume) and characteristics of the perturbed organic matter/degradation products, robust ways to describe radionuclide interaction and parametrisation (general complexation constants, Tipping model, Nica-Donnan). Also, the effect of saline plumes (nitrate / sulfate) on the radionuclide retention and diffusion in the presence of organics has not been investigated in depth. Section 2.5 provides an overview of the studies planned in RAMPEC.

2.4 Partially saturated conditions

In the event that clays as part of the EBS or host rock remain/become partially water-saturated (insufficient resaturation, desaturation by hydrogen production through anaerobic metal corrosion) (ANDRA, 2016; Marschall et al., 2005), understanding and parameterisation of the diffusion processes under these conditions is required to evaluate the performance of the clay system. Only a limited number of studies address this issue.

Nunn et al. (2018) presented a new method using X-ray radiography and iodide tracers for quantifying the degree of partial saturation of shale samples and measuring effective diffusion coefficients (D_e) of tracers in such conditions. They showed that the D_e of iodide value decreased by around 22% when saturation decreased from 100 wt% to 93 wt%.

Diffusion and advective transport of gaseous species and the effect of saturation on the diffusion of water and the cations have been investigated by molecular dynamics simulation. The simulations show that surface adsorbed water film provide an important contribution for the solute and water transport even at low partial water pressure (Churakov, 2013; Owusu et al., 2022, 2023).

Savoye et al. developed an original approach to perform diffusion experiments under partially water saturated conditions in illite-sand mixtures (Savoye et al., 2014) and in Callovo-Oxfordian claystones, (Savoye et al., 2010; Savoye et al. 2012a,c; Savoye et al., 2017). They observed in Callovo-Oxfordian claystones a sharp drop in the De values for HTO, ^{125}I and ^{22}Na by factors of 6, 50 and 17, respectively, under conditions of 81% water saturation compared to full saturation conditions. The strong decrease in D_e for iodide was explained by the anion exclusion phenomenon that restricted iodide to the largest pores where dehydration was more pronounced. Nevertheless, the distinct behaviour of D_e evolution for HTO and sodium was still speculative. Two different processes for which their relative contribution

requires further investigation were proposed. On the one hand, the extent of surface diffusion may be attenuated when dehydration occurs in claystones, reducing the enhanced diffusion phenomenon for cation species (Savoye et al., 2012a). On the other hand, in addition to HTO diffusing in the liquid phase, HTO diffusing in vapor form may contribute to the relatively high (compared to sodium) HTO diffusive rate, even at 81% water saturation (Savoye et al., 2017).

More recently, the same type of investigation was performed in compacted kaolinite, known to be a very weakly surface-charged clay mineral (Wang et al., 2022) in order to estimate the role played by vapor phase in water diffusion. Results indicated that from 100% down to 67% of degree of water saturation, the decrease of diffusive flux of water in kaolinite was also smaller than that observed for anionic and cationic tracers (iodide and sodium) that behaved in the same manner. Based on previous results, a conceptual and numerical model was developed for describing the macroscopic diffusion of water tracers in both liquid and gas phases to reproduce the decrease by a factor of 7 from 100% down to 67% of the diffusive flux. The diffusion of water through both liquid and vapor phases explains why water tracer diffuses faster than the ions which only move through the liquid phase.

However, for more complex systems made of surface charged clay minerals, even though molecular dynamics showed that surface effect can be enhanced when saturation decreases (Churakov, 2013; Le Crom et al., 2022), the evolution of enhanced diffusion phenomenon for cation species when dehydrating is still an open question. This requires addressing this issue using simpler clayey media than argillaceous rocks such as compacted illite or vermiculite.

Garcia-Gutierrez et al. (2023) used the Instant Planar Source method to study diffusion of HTO, ^{36}Cl and ^{75}Se in partial saturated recompacted COx and Spanish lutite. Upon decreasing water saturation level from 100 to 60% they noted a decrease in the apparent diffusion coefficient for the studied radionuclides showing that by lowering the saturation, transport becomes hindered.

Recently, Jacops et al. (2024) showed a preliminary study (conducted under EC EURAD GAS) on the impact of desaturation on the diffusion of gases in clay-based materials. Similarly to HTO, gases can migrate both in dissolved and in gas phase. For an artificial clay mixture of bentonite/sand/silt (60/20/20), only a minor impact on the diffusivity of He and Ar was observed for desaturation down to 70% indicating that net gas transport was still controlled by the diffusion in dissolved state.

Only a limited number of studies is available, which provide already interesting insights in the transport processes that may play, but we are just at the beginning. Datasets should be expanded towards different pore structures, other host rocks, other radionuclides, combined perturbations, etc.

Section 2.5 provides an overview of the studies planned in RAMPEC.

2.5 Workplan for EURAD2 RAMPEC for the clay systems

The aim of the work is to provide experimental data for clay systems (illite, bentonite, OPA, COx, Boda Claystone, Upper Toarcian, Lower Strength Sedimentary Rocks) to increase the understanding in the radionuclide (dissolved species) transport behaviour for the following perturbations: temperature (higher T in deep underground, heat emitting waste, up to 90°C), partial desaturation (as result of ventilation and gas production by metallic waste), and chemical perturbations: alkaline plume (cement from waste forms and EBS), ionic strength (nitrates and sulfates releases from “salt” bearing wastes), small organic molecules (organic degradation products, complexing ligands, etc, in waste). Data will be used to further develop macroscopic/mechanistic models (chapter 5).

The effect of temperature on sorption will be studied for a selection of radionuclides (anions and moderate to strongly sorbing transition metals, La/Ac) in model clay components (illite, bentonite,..) and host rocks (OPA, Boda claystone). Batch sorption studies will be complemented with transport studies at elevated temperature and supplementary the effect of a thermal gradient on transport of radionuclides (thermo osmosis and thermal diffusion/Soret effect) will be investigated.

Different aspects of the effect of partial saturation will be studied: (i) the relation between saturation state/sample composition and the effect on the transport of dissolved gases, (ii) the combined effect of temperature and saturation on transport of RN in compacted bentonite, (iii) the coupled effect of a chemical plume and saturation on water, anion and salt diffusion in compacted illite.

For the influence of chemical perturbations on RN behaviour (sorption and diffusion), different aspects will be studied: (i) the effect of an alkaline plume, (ii) disturbance in ionic strength (by chloride, sulfate, nitrate), (iii) the influence of small organic molecules and (iv) combined effect of sulfates/nitrates and small organic molecules. Table 2 summarises schematically the work matrix specifying the type of process (complexation, sorption, diffusion), type of perturbation, type of clay substrates and foreseen RN.

Table 2: Summary *of the work-matrix related to effects of perturbations on RN migration in clay systems.*

Process	Perturbation	Organics	IDP	bentonite	OPA	COX	BODA	upper toarcian	LSSR (Oxford Clay & MMC)
									UMAN,BGS,NNL,NWS
Complexation	*organics*	**ASNR** (U-TBP)/**HZDR** (Tc(IV)-acet)							**UK teams** (bioreduction U, Np, Se, Tc)
Sorption	*T*		**SCK CEN** (Cs&Am, diff salinity)/**HZDR** (Cm, diff salinity)/**KIT** (Cs or Ba or Co)	**CIEMAT** (HTO, Cl, SeIV, S, UVI)/**HUN-REN** (Ni, UO22+?, SeO32-, I-)	**KIT** (Ba, Co, Cs, Na)		**HUN-REN** (Ni, UO22+?, SeO32-,I-)		
	salinity (very high)							**ASNR** (U-TBP)	**UK teams** (U, Np, Se, Te, Ni)
	organics		**HZDR** (Tc(IV)-acetate	**CIEMAT** (HTO, Co, Eu, Pu + EDTA, cit, phtal & Na2SO4)					
	organics+salinity		**BRGM** (Co, SeVI? - tigific, phtalic)			**BRGM** (Co, SeVI? - tigific, phtalic)			
diffusion	*T static*		**PSI** (Co and HTO, Cl&Na?)	**HUN-REN** (Ni, UO22+?, SeO32-,I-)/**PSI** (Co and HTO, Cl&Na?)/**CIEMAT** (SeIV, S, UVI)	**KIT** (HTO, Na, Cl)		**HUN-REN** (Ni, UO22+?, SeO32-,I-)		
	T gradient		**PSI&KIT** (HTO, Na, Cl, + Co)						
	unsaturated		**SCK CEN** (He, CH4)	**CIEMAT** (HTO, Cl)					
	unsaturated + Salinity		**IC2MP** (saline plume diff by gradient HDO, NaCl, Na2SO4, NaNO3), **CEA** (fix salinity, HTO/Cl-/SO42- diffusion)					**ASNR** (U-TBP)	
	organics								
	organics + salinity			**CIEMAT** (HTO, Co, Eu, Pu + selection of EDTA, cit, phtal & Na2SO4)					
	Salinity		**IC2MP** (saline plume diff by gradient HDO, NaCl, Na2SO4, NaNO3), **CEA** (fix salinity, HTO/Cl-/SO42- diffusion)	**HUN-REN** (Ni, UO22+?, SeO32-,I-)			**HUN-REN** (Ni, UO22+?, SeO32-,I-)		**UK teams**
	pH plume			**HUN-REN** (Ni, UO22+?, SeO32-,I-)			**HUN-REN** (Ni, UO22+?, SeO32-,I-)		**UK teams**

2.6 References to Chapter 2

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3. Crystalline systems

3.1 Introduction

Crystalline rocks are internationally considered to be a potential host rock formation due to their mechanical stability, low permeability in intact formations, low solubility, high temperature resistance, and intermediate retention capacity. Countries such as Finland, Sweden, Switzerland, Germany, and the Czech Republic have advanced national programs exploring or implementing deep geological repositories (DGRs) in crystalline formations. Finland and Sweden are global leaders in the repository development, with the Onkalo repository in Finland and the Forsmark site in Sweden undergoing final construction and licensing stages, while e.g. the Czech Republic and Germany continue the site characterization, site selection, and feasibility studies (e.g. Zou and Cvetkovic (2023), Müller et al. (2025)).

Radionuclide migration in crystalline rocks is governed by advective flow through fractures, diffusion into the stagnant water zones, diffusion into the rock matrix, and sorption onto mineral surfaces (e.g. Brady et al. (2019), Crawford et al. (2006), Figure 3). Sorption and retardation mechanisms are crucial for limiting radionuclide mobility and, hence, transport of radionuclides (RNs) from a repository to the biosphere (e.g. Park and Baik, 2009). Besides thermal, hydraulic, and mechanical influences, these retardation processes are also affected by e.g. pore water chemistry (e.g. salinity, pH, groundwater composition etc.), which affects aqueous radionuclide speciation and the reactivity of mineral surfaces. In this context, the most studied mechanisms include surface complexation and ion exchange, while others such as redox reactions, incorporation, surface precipitation, and solid-solution formation, or reversibility of surface processes are less explored but potentially significant (Maes et al. (2024), Neumann et al. (2021), Britz (20218), Fricke (2023), Noseck et al. (2014, 2018)). As an example, experimental studies show that radionuclides such as Sr^{2+}, Cs^{+}, Ni^{2+}, Am^{3+}, Cm^{3+} exhibit varying degrees of sorption as a function of e.g. increasing pH-values, ionic strengths, and ligand concentrations, whereas different mineralogy such as adjacent minerals in crystalline formations (e.g. phyllosilicates) also play significant roles. Besides perturbations related to pore water chemistry affecting sorption and retardation efficiencies, RN migration is also influenced by parameters such as the porosity and permeability which govern diffusion and eventually advective pathways (e.g. Pakkanen et al. (2023), Figure 3*).*

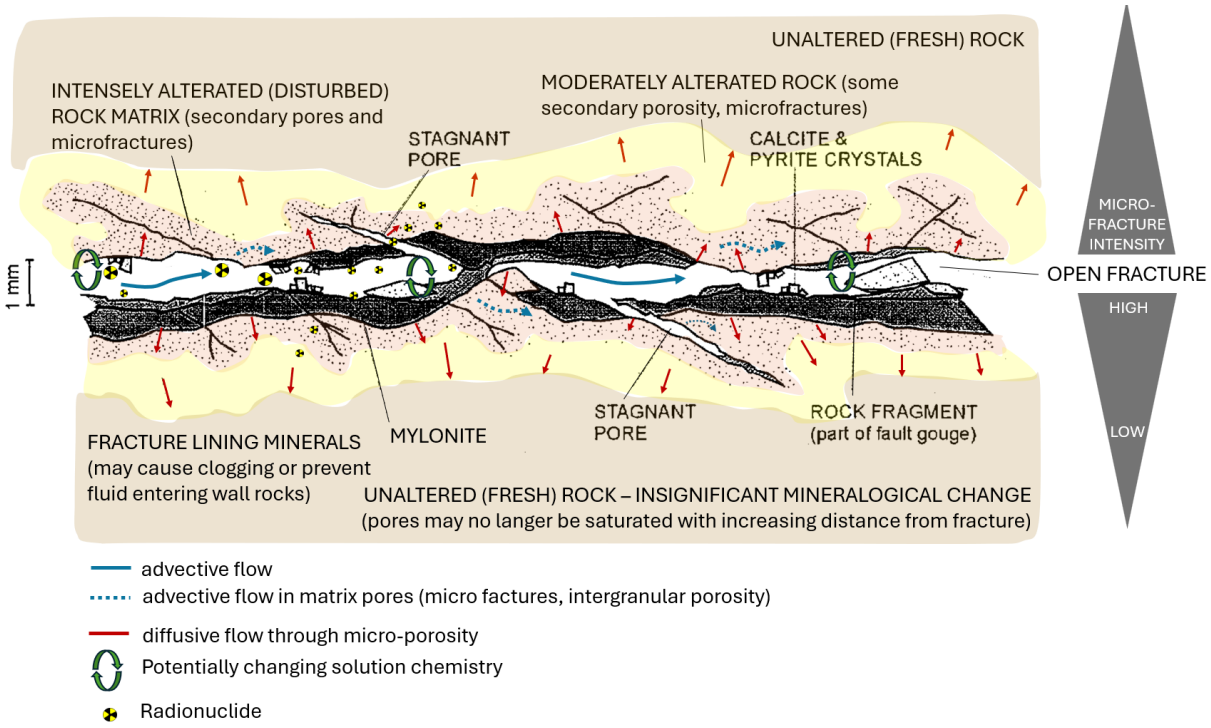

Figure 3: Scheme of advective and diffusive processes and typical features to be considered when dealing with sorption and transport processes in crystalline rock where decreasing diffusion coefficients may be expected with increasing distance from fracture networks. Figure adapted from Widestrand et al. (2007) and Metcalfe et al. (2021).

Main challenges in capturing RN transport in crystalline/granitic rocks lie in the understanding of coupled thermal, hydraulic, mechanical, chemical, and biological (THMCB) processes that interact in complex ways over geological timescales. Hence, sorption processes in crystalline formations are, besides solution chemistry, also influenced by fracture or fracture network permeability, and matrix porosity (Maes et al. (2024), Figure 3). Furthermore, to describe transport and retardation as close to nature as possible, one also has to consider and distinguish between unaltered and altered rock zone as well as fractures with and without mineralization (Maes et al., 2024a). Finally, upscaling experimental findings from lab to the repository scale remains challenging (Zhang et al., 2022).

In the next paragraphs the current understanding of relevant perturbations resulting from pore water composition, porosity, alteration of rock formations due to weathering and their effect on RN migration are further elaborated. Open questions are posed and a workplan is presented to address some of the missing answers.

3.2 Selection of perturbations relevant for the safe disposal of HLW in crystalline rock

3.2.1 Changes in pore water composition: ligands, ionic strength and pH influence

The efficiency of crystalline rock formations as natural transport barriers involves a series of complex physical and chemical processes. The factors affecting sorption capacity can be broadly categorized into two main aspects: (1) properties of the aqueous solution (e.g., pH, ionic strength, concentration, and complexing ligands), and (2) characteristics of the sorption phase (e.g., mineral composition, surface area, and sorption site density). Among these, the retardation effect is significantly influenced by the surface area in contact with groundwater (e.g. Crawford and Moreno (2003), Bodin et al. (2003), Zhang et al. (2022)).

The mobility and retention of RNs are governed by their speciation in pore water and interactions with solid phases under both intact in situ and altered conditions. Consequently, the transport rate of RNs in groundwater is strongly controlled by their retention on mineral surfaces, under specific geochemical boundary conditions. This includes interactions with engineered barrier materials, their alteration products, and diffusion into low-permeability rock matrices—commonly referred to as "rock matrix diffusion" (Zhang et al., 2022*,* Figure 3*).*

Extensive studies have been conducted over the past decades to characterize radionuclide (RN) retention and sorption processes in crystalline rock and relevant mineral phases (e.g. Noseck et al., 2018; Maes et al., 2024; Neumann et al., 2021; Havlová et al., 2020; Sabau, 2015; Heberling et al., 2011; Alexander et al., 2003; Winberg et al., 2000, Fabritius et al., 2024). A thorough understanding of evolving geochemical boundary conditions in deep geological repositories (DGRs) is essential for designing meaningful experimental studies. RN sorption is highly dependent on surface reactivity, which is in turn influenced by solution chemistry. For instance, competition for sorption sites between RNs and naturally occurring ions (e.g., Ca^{2+}, Fe^{2+}, Mn^{2+}, Cl^{-}, SO_4^{2-}) may reduce available sites for radionuclides and alter their speciation in solution, thereby affecting sorption affinities (Maes et al., 2024).

Brady et al. (2019) demonstrated through reaction path modelling that water fixation via zeolite and chlorite formation can increase the salinity and Ca/Na ratios of deep brines in contact with granitic rocks, reflecting rock-dominated brine chemistry. Therefore, sorption mechanisms—such as surface complexation—must be further characterized to improve coupled chemical-transport models across various rock types and salinities, including the reversibility of sorption (adsorption *vs.* incorporation) (Maes et al., 2024).

When interpreting results from batch sorption experiments, it is important to recognize that laboratory conditions often do not replicate the natural environment of the rock mass. Experimental setups may bias sorption data and fail to capture evolving geochemical boundary conditions. For example, Crawford et al. (2006) found that sorption capacity and particle size (or specific surface area) significantly affect sorption (Figure 4). Crushing and grinding of rock samples can artificially increase surface area and sorption capacity, potentially leading to overestimation of distribution coefficients (K_d) by up to an order of magnitude (Aromaa et al. (2019), Crawford et al. (2006)). Clearly, such experiments involve uncertainties that can only be mitigated by monitoring variables such as the specific BET surface area before and after experiments—data that are unfortunately rarely reported. One proposed solution is to report distribution coefficients normalized to BET surface area (K_a-values) rather than to sample weight (K_d-values) (Havlová et al., 2020). Thus, direct determination of K_d in intact rock is preferable, though experimentally challenging due to the complexity of coupled diffusion and sorption processes (Zhang et al., 2022).

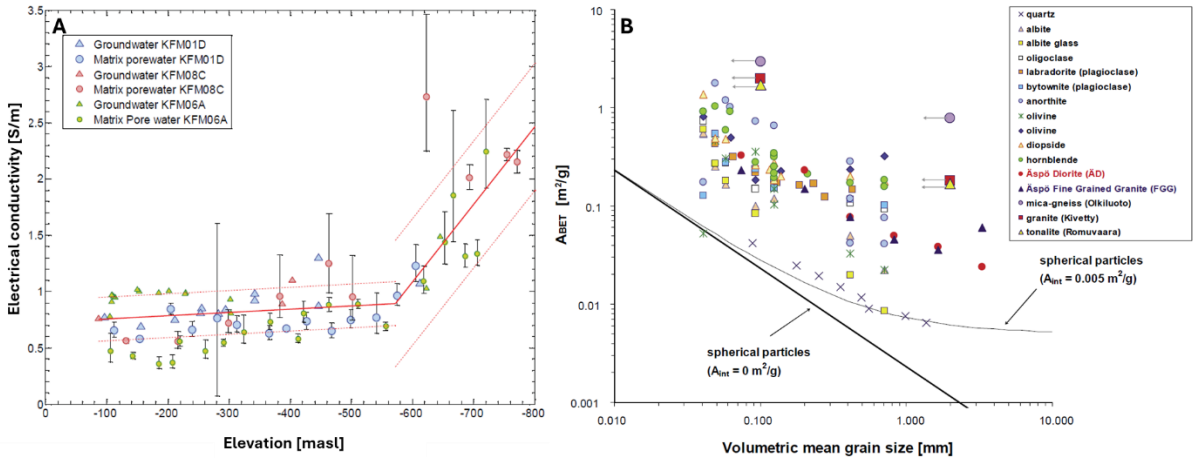

Figure 4: A) Increasing conductivity with increasing depth collected from the Forsmark site in Finland (Crawford, 2012), B) Relationship between BET specific surface area and grain size influencing RN uptake in lab experiments (Crawford et al., 2006).

Remaining uncertainties stem from the difficulty of replicating undisturbed in-situ conditions in the laboratory, particularly for non-preservable parameters such as pCO_2, pH, and E_h. Additionally, replicating the formation conditions of solid solutions of carbonate and sulfate phases is challenging, yet these phases may significantly influence RN migration in crystalline rock. The impact of perturbations - such as alkaline/cementitious plumes from DGR construction, secondary mineral formation, and bentonite interactions with granitic rock - on the chemical and mineralogical evolution of the system remains poorly understood.

3.2.2 Effect of pore structure

Besides water chemistry (e.g., pH, ionic strength, and water composition; see section 3.2.1), grain boundaries, porosity, water saturation, pore size variability, pore connectivity, and distribution (particularly at the nanometer scale, including mesopores and macropores) significantly influence radionuclide (RN) retardation processes (Maes et al., 2024).

Already in 1980, Neretnieks demonstrated that for a contact time of 100 years, a non-sorbing nuclide could penetrate tens of meters into rock, whereas a strongly sorbing nuclide with a distribution coefficient (K_d) greater than 10^4 mL·g^{-1} would only penetrate a few millimeters in non-fractured crystalline rock. Diffusion into the rock matrix can enhance retardation by several orders of magnitude compared to surface reactions alone. However, if the entire rock is accessible via diffusion and fractures, retardation may be significantly reduced, depending on fracture width and spacing. Neretnieks (1980) stated that if it can be conclusively demonstrated that transport in the selected crystalline host rock is governed solely by diffusion, then a few hundred meters of competent rock could serve as a highly effective barrier for most radionuclides of concern in spent nuclear fuel. However, validating diffusivity requires more than laboratory-scale experiments - it must also be supported by geological evidence of long-term ion migration.

Havlová et al. (2020) emphasized the challenges of measuring porosity in crystalline rocks with porosities below 1%. Common methods such as gravimetry, mercury porosimetry, and ^{14}C PMMA impregnation (Sammaljärvi et al., 2024; 2016) have great advantages but also some limitations. Therefore, combining porosity measurements with visualization techniques like scanning electron microscopy (SEM) is recommended (Voutilainen et al., 2019; Havlová et al., 2020). Experiments by

Havlová and Voutilainen showed that despite differences in rock type and origin, effective diffusion coefficients for various radionuclides fell within a narrow range: for ^{3}H (4 - 10)· 10^{-13} m^2 s^{-1}, for ^{36}Cl (1 - 10)·10^{-13} m^2 s^{-1} and for ^{125}I (1 - 4)·10^{-13} m^2 s^{-1} (Voutilainen et al., 2019; Havlová et al., 2020). Combining CT tomography with ^{14}C-PMMA and SEM-based mineralogical analysis enables 3D structural characterization of crystalline rock (Maes et al., 2024). In this context, Iraola et al. (2017) investigated cesium diffusion in fractured crystalline rock and found that sorbing radionuclides can penetrate much deeper into the rock matrix than predicted by homogeneous reactive transport models. Their grain-scale inter-granular network model, supported by micro-CT data, explained the observed anomalous diffusion patterns, showing that sparse distributions of reactive mineral grains strongly influence sorption behavior.

Kulenkampff et al. (2008, 2018) used positron emission tomography (PET) to study tracer propagation in fractured rock cores. Conservative tracers provided spatiotemporal images of transport, while reactive tracers revealed sorption sites during fluid–solid interactions. Widestrand et al. (2007) demonstrated that incorporating detailed porosity and heterogeneity data significantly improves the interpretation of diffusion experiments. Their integrated approach distinguished between bulk and altered rock retention properties, enhancing the understanding of in situ tracer test results.

In addition to diffusion, advective transport cannot be ruled out over geological timescales (e.g., 1 million years, as required by German regulations). While many studies focus on single-fracture systems, Zhang et al. (2022) emphasized the need to characterize complex fracture networks in natural systems. Maes et al. (2024) summarized that channeling can result from variable aperture, intersecting fractures, and offset displacements (Löfgren et al., 2007), all of which affect hydraulic and retention properties. High-resolution µCT (spatial resolution ~50 µm) is particularly useful for studying transport processes in large fractures, while optical microscopy can quantify surface roughness (Maes et al., 2024).

Finally, anion exclusion - electrostatic interactions that reduce anion mobility in nanopores - must also be considered when characterizing RN retention in crystalline rock: The electrostatic charge depending on interactions modifying ion mobility are dominant for pore sizes in the nanometre range. Though well-documented in argillaceous rocks, this effect is also significant in crystalline matrices. As a result, diffusion coefficients determined in diffusion experiments in crystalline rock matrices for anions are often lower than for cations or water (Smellie et al., 2014; Tachi et al., 2015; Voutilainen et al., 2019; Kuva et al., 2018; Havlová et al., 2020; Maes et al., 2024).

As previously discussed, characterizing crystalline porosity and fracture networks remains a significant challenge. Therefore, future research should focus on how dynamic and static distribution coefficients of radionuclides correlate with variations of flow velocity, mineralogy, and porosity in crystalline rock. A comprehensive understanding of the fracture system, including pore distribution and sorption properties in both fracture fillings and the surrounding host rock, is essential to accurately reflect the transport pathways. Moreover, evaluating system heterogeneity in relation to retention processes is indispensable. It is also not yet fully understood how non-equilibrium conditions - such as those arising from advective transport in fractures - may alter adsorption kinetics. These uncertainties highlight the need for integrated experimental and modeling approaches that can capture the complexity of radionuclide transport under realistic repository conditions.

3.2.3 Presence of secondary phases, fracture filling, alteration, and rock compositions

To describe transport processes in crystalline rock, it is essential to distinguish between unaltered and altered rock matrices, as well as between fractures with and without mineralization (see Figure 3). In high-strength crystalline rocks, groundwater flow and thus RN migration primarily occurs through interconnected fracture networks. Over time, these fractures may become filled with secondary minerals, depending on factors such as temperature, fluid composition, and reaction kinetics. This mineralization

can significantly influence porosity, permeability, surface coatings, microbial activity, and ultimately the sorption behaviour of long-lived radionuclides (Maes et al., 2024).

Newly formed secondary minerals and alteration products in fractures often exhibit crystal sizes down to the nanometer scale, in contrast to the millimeter to centimeter-scale crystals of primary crystalline rock. These secondary minerals also show a wide variability in pore diameter, volume, and porosity, which can significantly affect tortuosity and permeability (Svensson et al., 2019). As a result, complex flow fields develop due to surface heterogeneity and micro-scale fracture roughness, highlighting the strong influence of spatial surface variability. In fact, fracture geometry alone can cause retardation of solutes and colloids through hydrodynamic effects, even without invoking matrix diffusion, sorption, or redox processes (Maes et al., 2024).

Crystalline rocks like granite and gneiss are mainly composed of aluminosilicates and minor accessory minerals. Most radionuclides in groundwater are cationic or neutral, enabling surface complexation and cation exchange with the negatively charged mineral surfaces. Therefore, many radionuclides exhibit some degree of sorption, with exceptions like ^{36}Cl and ^{129}I, which are typically non-sorbing (Singhal & Gupta, 2010). Numerous studies have characterized surface charge and sorption behaviour of individual minerals and crystalline rocks (Britz (2018); Neumann et al. (2021); Fricke (2023); Fabritius et al. (2023); Alonso et al. (2009, 2014); Havlová et al., 2020; Heberling et al., 2011). In this context, Singhal and Gupta (2010) reported highly varying K_d values for Cs ranging from 1.35×10^{-2} to 9.52 $m^3 \cdot kg^{-1}$, and for Sr from 2×10^{-4} to 1.35×10^{-1} $m^3 \cdot kg^{-1}$ taking various (crystalline) rocks into account. Similarly, Zhang et al. (2022) confirmed that mica and chlorite are key sorbents in crystalline rocks for U(VI) in granite, based on sequential extraction and X-ray mapping. Havlová et al. (2020) found that Cs is strongly sorbed on Bukov rock, Sr shows weak sorption, and Se and U(VI) behave as non-sorbing. The presence of layered minerals (e.g., mica, kaolinite) was critical for cationic RN retention. Experiments with fracture fillings (chlorite, carbonates, kaolinite) and tracers like ^{125}I, ^{36}Cl, and Eu confirmed that Cs is retained most effectively, while Se, U, and Cl remain mobile due to their anionic speciation.

Studies on the desorption and incorporation of rare earth elements and yttrium (REEY), as well as Cs, Ba, Sr, Ni, Th, and U, from fracture mineralization, alteration halos, and host rock at the Bukov site (Czech Republic) indicate that REEY uptake is primarily governed by fluid composition, redox conditions, and temperature. The observed high distribution ratios emphasize the critical role of fracture mineralization on the retention of trace elements under evolving geochemical conditions (Müller et al, 2025). Poonoosamy et al. (2020) reported that solid solutions can form during the precipitation of mineral phases on fracture surfaces and in adjacent pore spaces, a finding also highlighted in Maes et al. (2024). These solid solutions typically involve sulfates (e.g., barite, celestite) or carbonates (e.g., calcite) and can serve as important retention mechanisms for certain radionuclides, such as radium (Ra). For instance, calcite precipitation may occur in carbonate-rich groundwater at elevated pH levels.

Curti (1999) demonstrated that actinides can form solid solutions with calcite under reducing conditions. In contrast, Ni(II) shows moderate incorporation, while U(VI), Cs(I), Sr(II), and Ra(II) are generally weakly incorporated into the calcite lattice. These findings underscore the importance of mineral precipitation and solid solution formation as complementary mechanisms to sorption in the long-term retention of radionuclides in fractured crystalline rock environments.

RN retention may also be influenced by mineral-induced redox reactions. For instance, Fuhrmann et al. (1998) showed that pyrite, biotite, and magnetite retain iodine via surface-mediated reduction of IO_3^- to I_2. In accordance with the latter study, Se(IV) may also be reduced to Se(0) or Se(-II) in the presence of Fe-bearing minerals like biotite as summarized in Maes et al. (2024a) from studies reported by Videnská et al. (2013, 2015), Stamberg et al. (2014), and Hakanen et al. (2014). According to Maes et al. (2024a) this abiotic reduction is slow, indicating that they are likely microbially mediated.

Finally, all alteration processes affect pore structure, particularly tortuosity and permeability, which are critical for RN migration. Katsube and Kamineni (1982) found that alteration reduces connected porosity and permeability while increasing tortuosity, due to mineral dissolution and secondary mineral deposition.

The limited understanding of coupled physical and chemical processes in multi-scale fractured systems remains a key challenge in accurately predicting radionuclide transport. Further research is needed to improve our knowledge of fracture geometry and transport mechanisms and to develop novel experimental and simulation techniques that integrate coupled thermal-hydraulic-mechanical-chemical (THMC) processes to predict long term behavior of RNs. Moreover, since most current studies are conducted at laboratory scale, larger-scale investigations are essential to bridge the gap between lab and field conditions (e.g. Zhang et al., 2022).

3.3 Workplan of EURAD-2 WP RAMPEC for granitic systems

Some of the challenges mentioned above are being addressed in Subtask 3.2 in the work package RAMPEC of EURAD-2. It will aim to advance our comprehension of reactive transport of safety-critical elements (e.g. Se, Ba, Ra, Cs, Na, Ni, Cl, I, HTO) via state-of-the-art experimental set ups applying unique combinations of spectroscopic and microscopic techniques (e.g. Raman spectroscopy, micro-X-ray fluorescence, X-ray tomography (µCT), scanning electron microscopy, SEM, ion beam (RBS and uPIXE), EXAFS or XANES, ^{14}C-PMMA digital autoradiography, confocal microscopy etc., Figure 5).

Diverse perturbed geochemical boundary conditions will be applied alongside with different crystalline rock samples from host rock formations or fracture fillings from Finland, Sweden and the Czech Republic. Studies comprise perturbations mainly focussing on the influence of secondary phases, changes in pore-water composition, and pore structure.

Figure 5 illustrates the envisioned workflow and interrelated activities in the subtask. The following aspect are planned to be addressed:

Characterization of natural (supplied by SURAO, POSIVA, SKB) intact and granulate rock samples (e.g. mineralogy, pore structure: connected porosity, fracture geometry; *Figure 5* yellow).

- Examination of radionuclide sorption/desorption processes with respect to characterized crushed rock samples (first bullet) or rock samples of comparable nature (fracture fillings, bulk granite) in close-to-nature systems (batch, flow through column and diffusion experiments, light green and orange in *Figure 5*).
- It is the aim that all partners work with similar if not the same rock samples, e.g. for experiments with crushed rock it is envisioned to partly work with homogenized rock samples for comparability reasons (*Figure 5* sample preparation).
- Analyses of sorption processes and radionuclide mobility in realistic systems using intact rock samples (e.g. cores); determination of effects such as diffusion, pore structure and possible anion exclusion effects on radionuclide retention (*Figure 5* light green and orange).
- Application of complex experimental geochemical boundary conditions: solution composition, pH and e.g. temperature to mimic as close-to-nature conditions as possible.
- Effects of perturbations: Influence of solution composition and pH (mimicking influence of e.g. cementitious waters or e.g. saline deep waters) sulfate concentration (imitate possible sulfate leaching from bentonite buffer material or the host rock itself) and/or porosity on the evolution of mineralogy, geochemistry, and radionuclide transport properties in granitic rocks.

Data and information generated/gathered in Subtask 3.2 will be used by Task 4 and potentially 5 to develop a model-based understanding of the experimentally examined processes (*Figure 5*).

Figure *5*

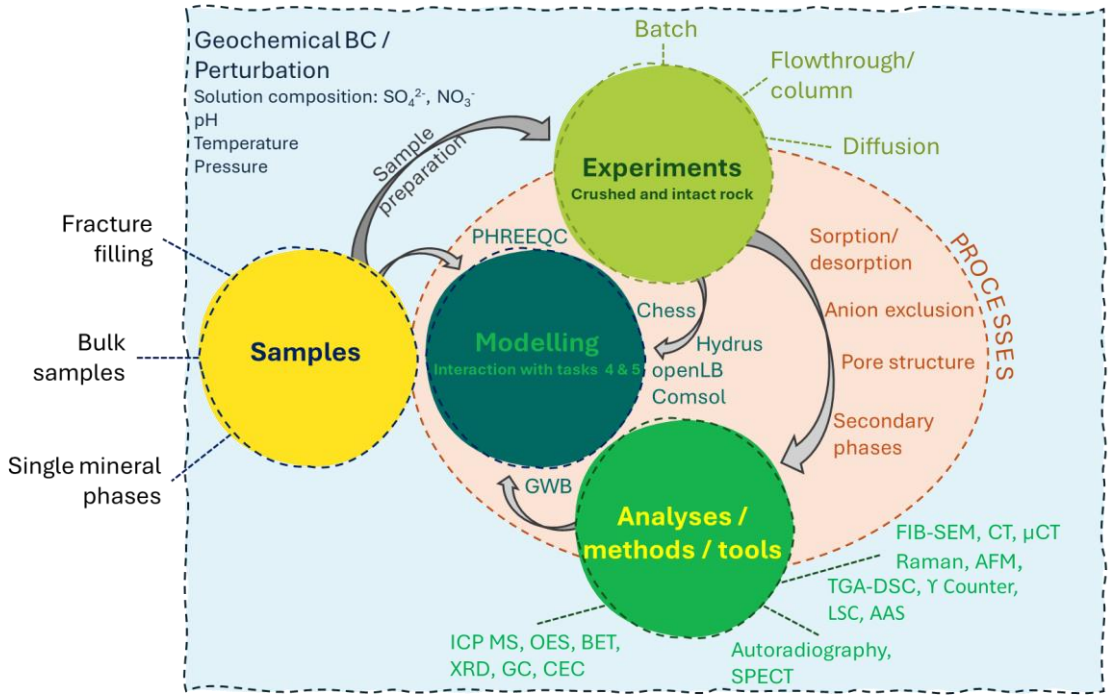

Figure 5: Schematic illustration of the workflow, interaction, and processes addressed in RAMPEC, Subtask 3.2. Yellow stands for the envisioned samples to be used; green indicates the workflow starting out from the experiments and involved analyses which offer information for the planned modelling approaches and therefore interaction with Task 4 and 5; orange indicates the processes the subtask wants to tackle.

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4. Cementitious systems

4.1 Introduction

The ubiquity of cement in the framework of radioactive waste disposal is no longer to be demonstrated. Cement is considered in all disposal scenarios as radioactive waste confinement or radioactive waste stabilization matrix and as part of the engineer barrier system (EBS) (see e.g. Atkins and Glasser (1992), Glasser and Atkins (1994) or Rahman et al. (2014)).

Ochs et al. (2016) described the influence of the presence of cement on the behavior of radioactive species, in terms of solubility and retention. They proposed reference values (expressed as distribution ratios, K_d values) of several radionuclides (RN) of interest as a function of pH, alteration state of the cement matrix and the nature of the cement. The retention properties of cementitious materials can be very strong for some RN such as actinides and lanthanides. This high affinity is often coupled with a very low solubility in alkaline media, such as in cementitious porewater. This leads to a very limited migration through the cement matrices. As reported in Ochs et al. (2016), most retention/diffusion experimental data are available for CEM I (Ordinary Portland Cement, OPC) cementitious systems. Some RN migration data can also be found for CEM V/A, and in a lower extent for CEM II, CEM III or low-pH cement (see e.g. Drtinová et al. (2023), Jo et al. (2024) or Shiner et al. (2022)).

Depending on the radioactive waste (i.e. those containing reactive metallic or highly irradiating residues) some specific cements are also studied as alternative binders for immobilization of toxic and radioactive wastes: calcium aluminate cements, calcium sulfoaluminate cements, phosphate cements and alkali-activated cements (see e.g. Navarro-Blasco et al. (2013), Pang et al. (2022) or Alonso et al. (2018)). Note that novel cement formulations are also emerging in the industry as alternative to OPC to reduce CO_2 such as CEM VI cement. For these new cement types, no data are currently available.

During the lifetime of a radioactive waste disposal facility, many external perturbations could impact the cement matrix of waste packages, which would affect its capacity of RN stabilisation, and the speciation of the RNs present in the waste. The external perturbations could also affect the EBS, which could impact RN migration. As shown in *Figure 6*, the main perturbations occurring between the radioactive waste, the EBS and the host-rock which can be considered in this context are:

- Cement degradation by leaching and production of an alkaline plume;
- Radiolysis and radiolytic gas production, due to the presence of specific radionuclides in the waste;
- The presence of complexing agents in the waste;
- Saline plume perturbation generated from waste;
- Temperature elevation due to the presence of specific exothermic wastes and also due to exothermic reactions of cement hydration;
- Chemical-mechanical perturbation due to the interaction of cement with groundwater;
- Desaturation and/or atmospheric carbonation of the cement barrier during the operating activities and early post-closure.

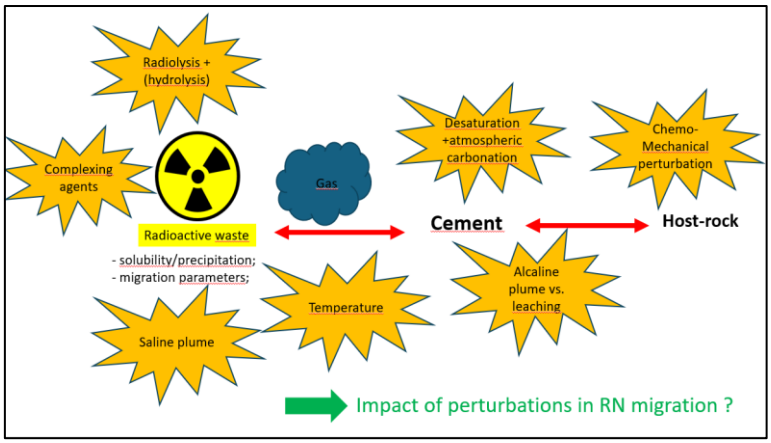

Figure 6: Simplified scheme for main perturbations occurring to the cement matrix in the context of a radioactive waste disposal facility.

The main objective of the present chapter dedicated to "cementitious systems" is to give a brief description of selected data focused on potential perturbations occurring to cement and to radionuclides migration, which are topics of interest to RAMPEC Subtask 3.3. This initial SOTA will therefore not cover in detail all available papers in the literature addressing cementitious systems, but will highlight some specific issues that are currently studied in RAMPEC Subtask 3.3. based on the corresponding relevant papers.

4.2 Potential perturbations occurring to cement and to radionuclide migration

The structure of this chapter proposes a short summary of the state of knowledge for the main identified potential perturbations occurring to cement (as cement matrix or EBS, see Figure 6) and to radionuclide migration in these perturbed cementitious systems.

4.2.1 Degradation of the cement by leaching and alkaline plume production

During its "normal" life, a cement matrix exposed to water is leached and this degradation leads to mineral phases coupled to porewater composition evolution [see e.g. Hewlett and Liska (2019) or Taylor (1997)]. For a more detailed description of the physical-chemistry of cement in the context of a radioactive waste disposal facility, one can also refer to the SOTA of the European CEBAMA (Cement-based materials) project (see Vehmas and Holt (2016)) and to those provided by EURAD-WP16-MAGIC (see Dauzères *et al.* (2024)) or EURAD-WP3-CORI (see Altmaier et al. (2024a)).

Radionuclide migration in degraded cement systems is poorly studied. Recently, EURAD-WP3-CORI experimental studies were mainly performed at Stage II, *i.e.* with a porewater buffered by portlandite (see Altmaier et al. (2024b)). From these studies performed at Stage II, the main observation that has been highlighted is the strong effect of dissolved calcium concentration on RN-organic chemical speciation.

The degradation of the cement matrix by water is well studied in literature, especially for CEM I type cement, where alteration states are buffered by alkalis (Stage I), portlandite (Stage II) and CSH (Stage III). Such a description for blended cements would reveal the presence of other mineral phases, such as CASH. Coupling the degradation of such cement by other types of perturbation (i.e. temperature, saline plume …) or studying RN migration through real old concrete specimens would be then

challenging. Section 4.3 provides an overview of the studies planned in RAMPEC addressing degradation by leaching, indicating which cementitious systems have been selected to complete the literature data on the effect of this perturbation on RN migration and provide inputs data for the RAMPEC Task 4, dedicated to the development of macroscopic mechanistic models.

4.2.2 Chemo-Mechanical perturbation onto RN migration

The main reactive processes controlling the chemical evolution of cementitious materials are well understood at the interface with the host rock or directly with the natural water (*cf.* Neeft *et al.* (2020)). In post-closure of the radioactive disposal facility, *i.e.* when fully saturated conditions of the cement matrix are achieved, the main processes identified as chemical-mechanical perturbation are water leaching (see section 4.2.1), carbonation, magnesium, sulfate or chloride attacks. To illustrate these types of perturbation, some examples are given in the following paragraphs.

Chemo-mechanical perturbation induced by carbonation

Depending on the composition of the groundwater coming from the host rock, carbonation is induced by the presence of high content of carbonate in solution, which in contact with a CEM I material leads to the decalcification of CSH and calcite precipitation (see. Ochs et al. (2016) and Berner (1992)). Olmeda et al. (2017) performed a modelling exercise to describe the chemical degradation of blended-cement based materials (CEM V/A) by several host-rock solution leaching cycles, containing ca. 3 mM of carbonate at pH 7.2 (solution in equilibrium with calcite and dolomite). The final Stage V of the blended-cement material is reached where the precipitation of calcite is favoured. Seigneur et al. (2017) described for a cementitious model system leaching using pure water and carbonation degradation using a multi-scale approach and reactive transport modelling. While the experimental leaching degradation is well-described by the models, the simulation of calcite clogging (linked to atmospheric carbonation *i.e.* a fast penetration of carbon dioxide in the porosity and calcite precipitation within the material without crust formation) failed. The precipitation of calcite is dependant of the microstructure, thus the pore size distribution. Except for the reaction kinetics, the degradation mechanism is well reproduced with proposed the 2D reactive model: carbonation initiated by an enriched carbonated solution leads to the formation of calcite crust at the surface, which limits diffusion. Sarott *et al.* (1992) compared the diffusion and retention of ^{36}Cl, ^{125}I and ^{134}Cs behaviours in HCP in non-carbonated and carbonated conditions (pCO_2 ~ $10^{-5.5}$ bar vs. $10^{-3.5}$ bar, respectively) in water-saturated conditions. Carbonation in HCP disc leads to $CaCO_3$ (calcite) precipitation in the near surface pore space causing a significantly reduction of the diffusion rate and hydraulic conductivities.

Chemo-mechanical perturbation induced by magnesium attack

Recent works presented in EURAD-WP16-MAGIC focused on the behaviour of the alteration of a cement paste (prepared by mixing CEM III/A with silica fume) in an aggressive solution containing 50 mM of $MgCl_2$. The Mg attack mainly consist in the leaching of calcium and sulfate (from CSH and ettringite dissolution) and the precipitation of Si-Mg phases (*e.g.* MSH see Bernard et al. (2017) and Bernard et al. (2019)). Considering the poor microstructural and mechanical properties of MSH compared to CSH, the mechanical property of the paste is significantly reduced from this chemical attack.

Chemo-mechanical perturbation induced by chloride attack

Chloride-induced corrosion of reinforced concrete is a well-studied damaged mechanism in saturated conditions, which leads to the initiation of cracks (Ali *et al.* (2024)), which could represent migration preferential and accelerated pathways. The elevated concentration of chloride ions can lead to chemical reactions with other substances, such as tri-calcium aluminate (C_3A), resulting in the formation of Friedel's salt (Balonis *et al.* (2010)), which, depending on the considered RN, could play as a migration barrier at the surface of the sample.

Chemo-mechanical perturbation induced by sulfate attack

Concerning the "sulfate attack", the type of cement formulation can limit the effect, i.e. using manufactured sulfate resistant cements. The interaction between sulfate and calcium aluminate phases produces ettringite and its expansion in the cement porosity leads to micro-cracks formation. Recently, Pouya *et al*. (2024) observed that cracking was initiated in the gypsum formation zone, leading to significant loss of mechanical properties and increase of diffusion. This was explained by the hydrolysis process and the opening of the porosity by portlandite leaching.

The type of perturbation is depending on the environment. Studies performed recently in EURAD-WP16-MAGIC, (see e.g. Dauzères *et al*. (2024)), have contributed to a better understanding of chemo-mechanical ageing of cementitious materials in geological disposal conditions. In EURAD-2, the work-package SUDOKU will provide new insights on the transport properties of mobile radionuclides (such as ^{14}C, ^{36}Cl, ^{129}I, ^{93}Mo or ^{99}Tc) in cementitious barriers damaged by chemo-mechanical perturbation. That is the reason why studies in RAMPEC Subtask3.3 will not take directly into consideration such perturbations.

4.2.3 Radiolysis (and hydrolysis) effects

Depending on the irradiation conditions and on their initial composition, concrete or cementitious matrices will undergo various degree of radiation damage (see e.g. Bouniol and Thouvenot (1997), Bouniol and Bjergbakke (2008) or Pomaro (2016)). The irradiation of the high alkaline porewater in concrete could lead to internal gas overpressure (mainly hydrogen and oxygen) until micro-cracking the matrix. The formation of oxidizing products by radiolysis can induce the corrosion of steel bars of the concrete. In particular, cement paste, and aggregates can react differently under radiation. The cement paste shrinks under drying conditions associated to the radiation heat, while the volume of aggregate is expanded under irradiation. The association of both effects could explain the damage in irradiated cementitious materials and the impact onto RN migration. Note that the recent results provided by Hoarau Belkhiri *et al.* (2025) give new insights to moderate literature observations on gamma radiation damages. As temperature, drying and carbonation are not systematically controlled in the majority of published studies, the impact onto the cement matrix cannot completely be attributed to radiolysis. For a large variety of investigated cementitious samples (C_3S, CEM I, CEM III/A and CEM III/C pastes), the gamma exposure up to a few MGy represents no significant effect. Only some pore size distribution modifications and redox potential in pore solution could be attributed to irradiation and may affect RN migration.

Another aspect to be considered for radiolysis effect in the framework of radioactive waste disposal is the fact that in LILW-LL waste, organic materials are present. The organic materials can be found in various forms (cellulosic mater such as paper-tissue, plastic such as gloves, ion exchange resins, etc.) and can also be part of the cementitious matrices, as superplasticizer used as admixture to increase the workability or to decrease the water content of the prepared cement materials. It is necessary to consider the coupled effect of radiolysis and hydrolysis to describe the degradation processes. In the framework of EURAD-WP3-CORI, the degradation by radiolysis and hydrolysis of cellulose, polyvinyl chloride (PVC), ion exchange resins (IER) and superplasticizers (SP) were investigated. The results obtained allowed to increase the knowledge about the degradation of organic materials and the identification of degradation products for the selected organic materials.

Legand (2023) proposed schematic view of the potential radiolysis-hydrolysis effects onto radionuclide migration in cement matrix containing SP (see *Figure 7*).

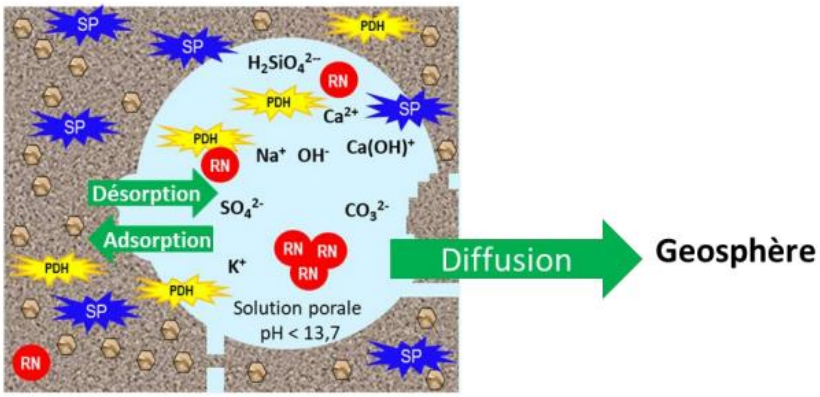

Figure 7: Schematic view of the potential radiolysis-hydrolysis effects onto radionuclide migration in cement matrix containing superplasticizer in the context of radioactive waste (extracted from Legand (2023) SP: superplasticizer, PDH: degradation product, RN: radionuclide. In French).

As shown by Legand *et al.* (2023) experimental results, the direct addition of SP in alkaline solution leads to increase the Eu(III) solubility with the dose of irradiation. However, in extracted pore solution (from a grout prepared with SP), no significant impact of coupled effect of radiolysis for doses lower than 250 kGy, and alkaline hydrolysis (pH 12.9) of SPs on Eu(III) solubility was observed. The small amount of SP degraded molecules leached in pore solution has a weak effect on Eu(III) solubility.

In EURAD-CORI, the real leachates generated from organic material degradation by radiolysis and (very long-term) hydrolysis have been used in RN migration experiments. *Figure 8* represents the quite strong effect of cellulose degradation products (CDP) onto ^{63}Ni sorption, for both fresh and HCP Stage III. The CDP effect is much stronger in comparison to pure α-ISA with a decrease of log(R_d) of more than 2 log units for $1 \cdot 10^{-2}$ M of α-ISA. This result could suggest the involvement of cellulose degradation products other than α-ISA in the ^{63}Ni sorption reduction.

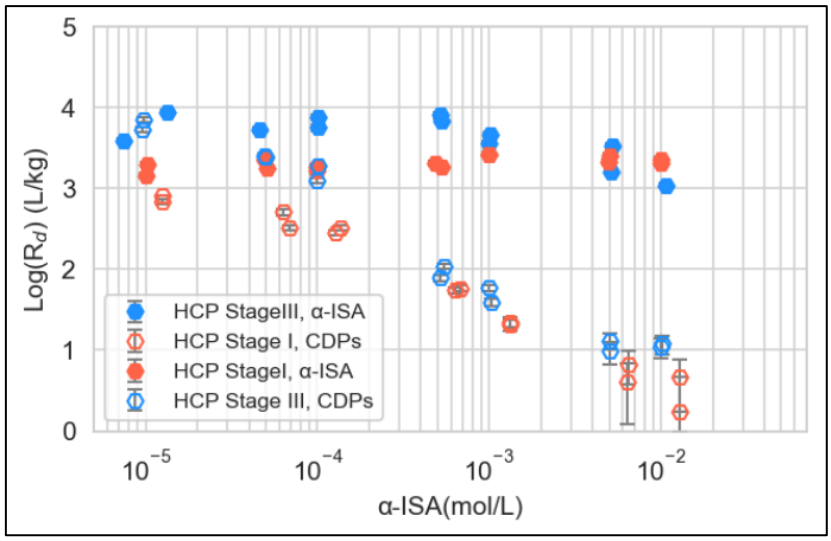

Figure 8: Sorption isotherms of ^{63}Ni (C_{ini} = 3x10^{-9} M) in presence of pure α-ISA and cellulose degradation products on HCP at different degradation stages. The data are here plotted as a function of α-ISA concentration through the cellulose degradation products contains also other organics. Sorption isotherms of ^{63}Ni as a function of α-ISA concentration (extracted from Altmaier et al. (2024b) and published by Durce et al. (2025)).

From literature review, it can be highlighted that radiolysis coupled to hydrolysis could have two main effects: (i) generating cracks into cement matrices and (ii) producing complexing organic degradation products. As presented in Section 4.3, the effect of radiolysis coupled with hydrolysis will not be specifically studied in RAMPEC. A few studies in RAMPEC are planned to be performed in the presence of complexing ligands or carbonate.

4.2.4 Presence of complexing ligands

The main results obtained in EURAD-WP3 CORI have extended knowledge beyond the already published data and state-of-the-art documented in the literature of the presence of complexing ligand onto the RN migration in cement matrices. From CORI results, it was clearly confirmed that interactions between organic molecules (ORGA) and RN in a cementitious environment can significantly influence RN retention. In many investigated cases, the effect of organic species on the solubility of RNs was zero or minor. 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 the RN-ORGA retention behaviour, especially by the effect of dissolved calcium on the chemical speciation. Detailed experimental results and perspectives can be found in the final deliverable of EURAD-WP3-CORI (Altmaier *et al.* (2024b)).

As mentioned in Section 4.3, a few studies in RAMPEC are planned to be performed in the presence of complexing ligands (either cement additives or isosaccharinate, ISA or organic plume) so as to better document some specific cases of high interest in terms of potential changes in orders of magnitude in retention, that were not investigated in EURAD-WP3-CORI. The studied systems were thus selected to emphasis their potential impact onto RN migration.

4.2.5 Desaturation and atmospheric carbonation

During the operating and early post closure period of the disposal facility, cementitious materials are desaturated due to the continuously renewing atmosphere. In this context, the main identified chemical process under unsaturated conditions is atmospheric carbonation. Drouet et al. (2019) investigated the effect of atmospheric carbonation coupled to temperature up to 80°C and relative humidity (26% and 76%). For both studied cements (CEM I and CEM V/A), it appears that cracking is a combined result of desiccation and carbonation shrinkage (*see Figure 9).*

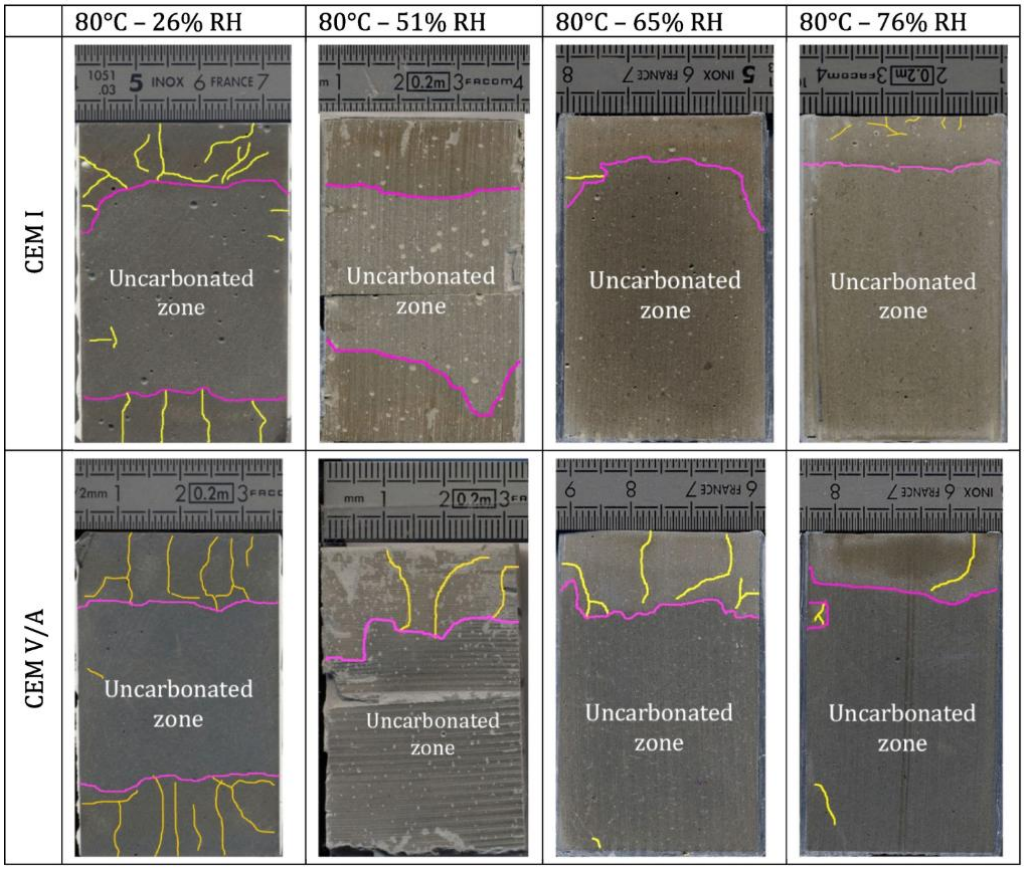

Figure 9: Images published by Drouet et al. (2019) corresponding to cracks zones (yellow lines) in carbonated zones at 80°C for CEM I and CEM V/A HCP specimen. The pink link corresponds to the frontier observed between the carbonated and the intact core sample.

The atmospheric carbonation leads to chemo-mechanical evolution of the cement, which have been studied and modelled from nanoscale to macroscale in EURAD-MAGIC (see e.g. Dauzères *et al*. (2024)). The impact of carbonation is mainly the formation of calcite by the reaction between $CO_2(g)$ with portlandite and CSH. The carbonation rate of the C_3S paste is much lower than that of the CSH paste, due to the protective presence of portlandite. The presence of portlandite in the cementitious materials is a key with respect to carbonation intensity. This explains why low-pH concretes are more susceptible to carbonation than Portland cement-based concretes. The results specifically acquired in EURAD-WP16-MAGIC provide a clearer picture of the effect of carbonation on water retention in cementitious materials.

Water saturation is a key parameter to be studied to understand gas diffusion in the porous network of a cement matrix: vapour water diffusion is linked to drying process when $CO_{2(g)}$ leads to carbonation. Savoye et al. (2018a, 2018b and 2018c) studied the effect of water saturation degree of the cementitious materials on reference RN migration, *Figure 10*. Main conclusions are an extent increase of irreversible HTO uptake on cement-based materials with desaturation and a decrease of diffusivity rate of ^{36}Cl with desaturation, which is similar to the trend observed by Mercado-Mendoza *et al*. (2014) for OPC samples. Sercombe et al. (2007) measured the diffusion of $H_2(g)$ in non-saturated cement materials. Due to its low solubility in water, dihydrogen mainly diffuses under gaseous form. Since desaturation of the porosity is low enough, the contribution of $H_2(g)$ diffusion in gas phase increases, resulting to an increase of the D_e value. HTO exhibits an intermediate diffusive behaviour between dihydrogen and chloride, because of its ability to diffuse both under vapour and liquid forms.

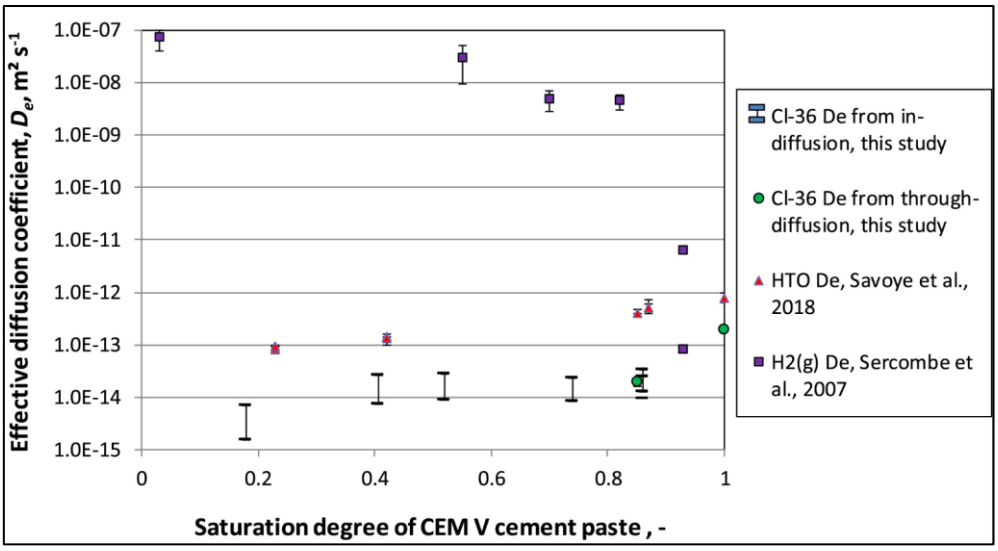

Figure 10: Values of the effective diffusion coefficient values (D_e) for ^{36}Cl determined on CEM V-hardened cement pastes (HCP) as a function of their saturation degree. Comparison with the effective diffusion coefficient values for dihydrogen obtained by Sercombe et al. (2007) and for tritiated water obtained by Savoye et al. (2018a) through the same type of cement-based materials. Graphs extracted from Savoye et al. 2018b.

Concerning perturbation occurring by desaturation or atmospheric carbonation, it is well described in literature that these perturbations could lead to cracks into the cement matrix, thus increasing diffusive paths in the porous media. When only desaturation is occurring, the effective diffusive coefficient value for non-reactive species is lower. These results are not confirmed for all RN of interest, all types of cement matrix and the evolution with cement degradation is unknown. As mentioned in Section 4.3 some studies in RAMPEC are planned to be performed as a function of humidity in the presence of highly sorbed species (Se) and in different type of cement matrix (HCP, mortar and concrete).

4.2.6 Temperature effects

In the lifetime of a radioactive waste disposal facility, the modification of the temperature could occur from different reasons:

- ⇨ due to the exothermic reactions occurring during the cement hydration.
- ⇨ due to the exothermic properties of specific radioactive waste.
- ⇨ due to climate changes.

The last consideration is part of a strategic study of EURAD-2 dedicated to the study of the impact of the climate changes on nuclear waste management (WP11-CLIMATE) and will not be detailed here.

A maximum increase in temperature up to 70-80°C resulting from exothermic hydration reactions and heat generation by the radioactive waste is expected depending on the considered scenario. This transient of temperature would then lead to important changes in the mineralogy of the cement matrix (changes in the apparent density of CSH (Gallucci et al. 2013) or ettringite dissolution for instance (cf. Zhou & Glasser (2001)) or delayed ettringite formation (*cf.* Taylor *et al*. (2001)) and then could affect its confinement properties. Generally, the increase of temperature is studied to access the modification of the porewater composition and the mineralogical phase composition of the cementitious matrices [e.g. Lothenbach et al. (2008)]. Additional studies investigated the temperature impact onto the migration parameters (e.g. Macé (2006) and Macé *et al.* (2007)), which could be explained by considering enthalpy reactions, described by the van't Hoff equation coupled with mineralogical changes (cf. *Figure 11*).

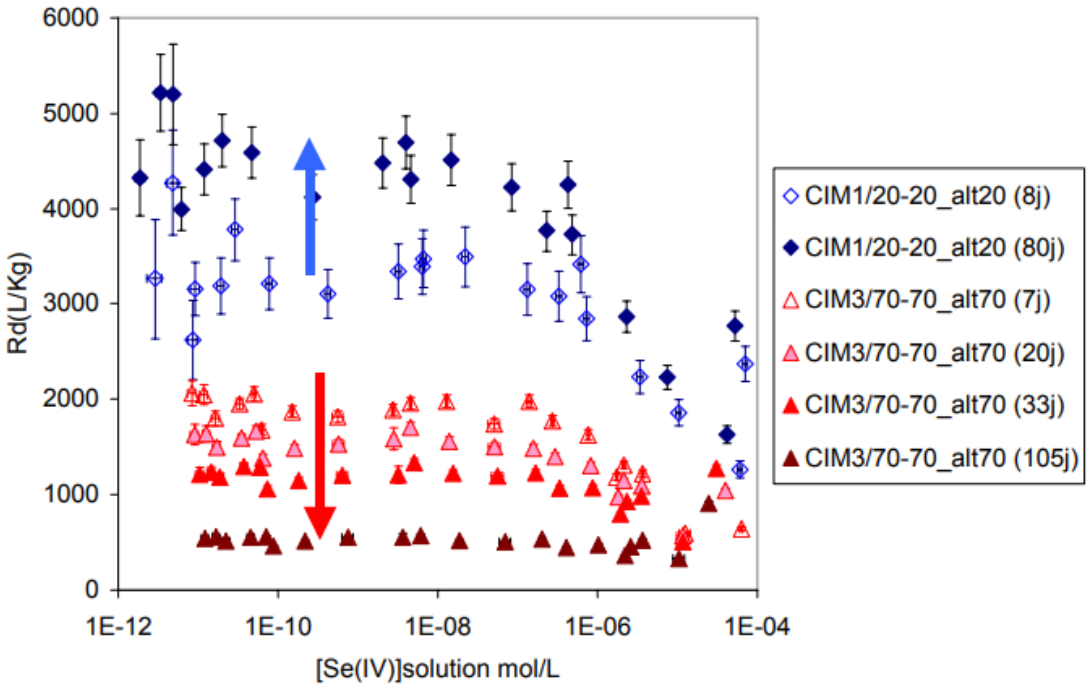

Figure 11: Kinetic evolution of the retention for Se(IV) at 20°C and 70°C by thermally altered HCP (figure extracted from Macé (2006)).

Temperature has a great importance for water transport in cementitious materials. Drouet *et al.* (2015) showed by dedicated water retention experiments that an increase in temperature from 20°C to 80°C leads to increase significantly the intrinsic permeability of the HCP, but without following the Arrhenius activation law. The data was consistent with an increase in the transport properties associated to porosity opening, which could be explained by the formation of micro-cracks in the solid.

Experimental results obtained by Caré (2008) showed the effect of temperature upon the chloride diffusive properties and the microstructural features of cementitious materials. It has been observed by MIP technique measurements, that the capillary porosity is affected by temperature. The chloride ingress increases with the water to cement (W/C) ratio (thus the total porosity) and with heating temperature. The presence of non-well-connected macroscopic cracks induced by thermal treatment could also explain in some extend the modification of chloride transport properties. This result is supported by the study of Takiya *et al.* (2015), where the diffusion of HTO and $H_2{}^{18}O$ is investigated as a function of W/C ratios and temperature. From the model, the dominant diffusion pathway of water in HCP was that capillary pores and Arrhenius' law can describe the evolution of the apparent diffusion coefficients of HTO in HCP at W/C ratios of 0.36, 0.45, and 0.60, where the log D_a values are decreasing with increasing temperature.

Concerning perturbation occurring by temperature increasing onto RN migration in cementitious media, several cases can be drawn: (i) temperature affects the RN mobility by changing thermodynamic constants (solubility, sorption or diffusion), (ii) temperature affects the stability of the cement matrix, and (iii) a more complex case arises in case of combination of both. A problematic issue is the lack of a predictive model able to describe all cases, owing to a lack of data. As mentioned in Section 4.3, one study in RAMPEC is planned to be performed as a function of temperature. The results will feed to Task 4 and help the development of macroscopic mechanistic models.

4.2.7 Saline plume

Depending on the radioactive waste to be stabilized in cement matrices (grout, cement paste or mortar), particularly high levels of soluble salts, mainly composed of sodium sulfate (Na_2SO_4) or sodium nitrate ($NaNO_3$), can be present in the alkaline porewater (see *e.g.* Reynolds et al. (2013)) and thus, inducing potential RN speciation and mobility changes.

A significant degradation is observed at high ionic strengths in the mineralogical assembly and chemical equilibria of the cement matrix. Note that for ionic strengths higher than 4 mol/kg_{water}, thermodynamic databases require specific developments considering the Pitzer model for activity coefficient correction [Pitzer (1991)], which can limit the calculations due to the lack of data. Johnston & Grove (1931) observed that the solubility of portlandite in cement mineralogical assembly was increasing by a factor of 1.35 – 2.8 compared to its solubility in pure water, independently of the salt used to fix the ionic strength, including sodium chloride, potassium chloride, lithium chloride, caesium chloride, and sodium nitrate, but not calcium chloride.

The use of ammonium nitrate (NH_4NO_3) solution is a laboratory practical way to rapidly reach a degraded state of the cement paste (see e.g. Gallé *et al*. (2004) or Carde et al. (1997)). The difficulty comes then for migration experiments to reach an enough degradation state without cracks in the matrix. With respect to access the effect of saline plume stemming from bitumen waste, sodium nitrate ($NaNO_3$) is highly soluble also in alkaline media and it is largely used in migration experiments to increase significantly the ionic strength of the solution without initiating cracks in the solid. After dissolution of ettringite in contact with an aggressive solution containing high amount of $NaNO_3$, sulfate is released from the OPC matrix and darapskite phase ($Na_3(NO_3)(SO_4)(H_2O)$ can precipitate (see e.g. Malone *et a*l. (1997), Toghiani *et al.* (2008) or Macé *et al*. (2023)) on the surface and eventually decrease the RN mobility.

Concerning the behaviour of CSH phases in saline solution, results depend on the nature of the soluble salt. When CSH phases are in contact with high $NaNO_3$ content solution (100 $g{\cdot}L^{-1}$ and 500 $g{\cdot}L^{-1}$) results show their decalcification by Ca^{2+} leaching and the silica gel polymerization (Zheng *et al.* (2020a)). From these first observations, Zheng *et al.* (2020b) proposed to investigate the behaviour of the simulated cemented waste prepared from a solution containing high amount of $NaNO_3$ and Sr^{2+} mixed with OPC. Similar effect of the increase of $NaNO_3$ content is observed onto leaching behaviour of Sr^{2+}. The presence of sodium nitrate degraded the pore structure and the average pore diameter as well as the porosity increased obviously. It was also observed that nitrate ions limit the length chain of CSH and thus, increase the Ca/Si ratio in the cement paste.

For saline solution with high content of NaCl, another behaviour is observed for CSH and CASH. After 90 d of contact in artificial seawater (pH = 8.2 and a mixture of soluble salts mainly NaCl, $MgCl_2{,}6H_2O$ and Na_2SO_4 according to ASTM D1141), Borno *et al*. (2023) observed a significant increase of crystallinity of CSH and CASH pure phases (cf. *Figure 12*). The formation of tobermorite phase at ambient temperature is possible depending on the pH and Al content. The change of the crystallinity of major sorbent phases may then affect their migration in the complex cement matrix. Note that chloride penetration test in cementitious monolith is part of a normalized procedure in civil engineer domain (Nordtest NT Build 443. 1995). In that protocol, the matrix is exposed over a 5-week period to a very high NaCl content solution (165 $g{\cdot}L^{-1}$ = 2.8 $mol{\cdot}L^{-1}$). The solution is renewed at the end of each period. At the end of the diffusion experiment, the chloride profile is determined by grinding the concrete along the diffusion path. Under these conditions, the model interpretation should consider ionic strength correction and reaction between the chloride and the solid matrix; which is never the case.

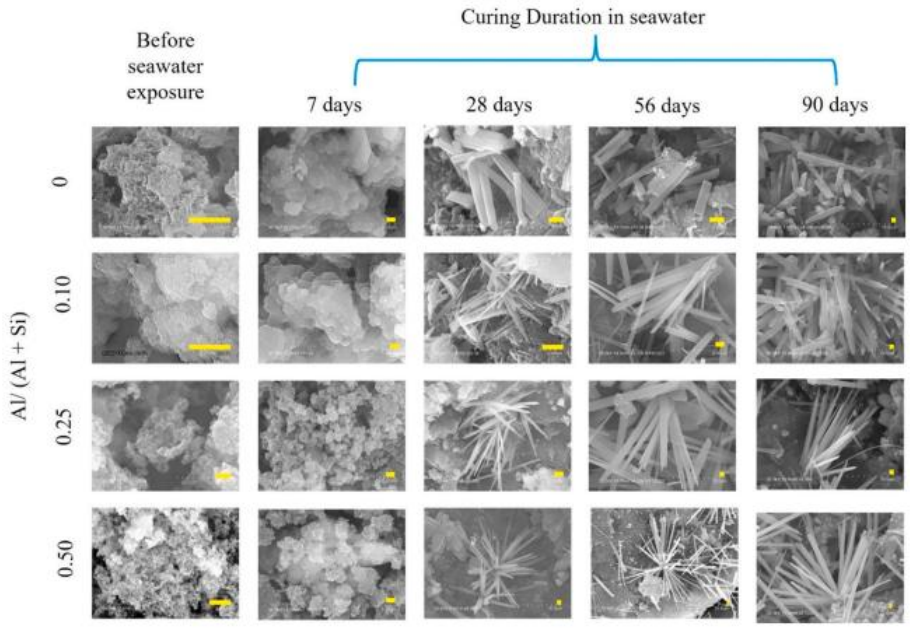

Figure 12: Scanning electron micrograph (SEM) images showing the evolution as a function of contact time in artificial seawater: from CSH and CASH gels initially to higher crystallinity after 90 days of contact. (Figure extracted from Borno et al. (2023)).

De Weerdt *et al*. (2023) studied the long-term changes of mineral phase assembly of a Portland cement-based material in contact with different type of saline solutions, where the driving force of the degradation mechanism is leaching. As already observed in literature, this study confirms by calculation that portlandite is firstly destabilized, then AFm/AFt phases followed by the decomposition of C(A)SH. Depending on the composition of the aggressive solution, new mineral phases aim at precipitating, such as calcite for carbonate-rich solution or NASH phase, when Na-rich composition is involved. These long-term changes may therefore destabilize the immobilisation of RN in the OPC.

Altmaier *et al.* (2017) proposed a solubility study for U(VI) in diluted and concentrated NaCl solution (from 0.03–5.61 mol·kg_w^{-1}). The main output of this work is to provide chemical, thermodynamic and SIT activity models for the system U^{VI}–Na^+–H^+–Cl^-–OH^-–H_2O(l). This study was then completed by the work of Çevirim-Papaioannou *et al.* (2018) considering the effect of the presence of alkaline KCl solution on the U(VI) solubility and by Endrizzi *et al*. (2019), in which the effect of temperature (up to 80°C) is studied. Depending on the physicochemical conditions, these thermodynamic data allow to calculate the U(VI) speciation in chloride perturbed alkaline media.
Very recently, the study proposed by Almendros-Ginestà *et al.* (2025) shows an even more perturbed system by adding organic complexing agent (citrate) in a solubility study of Ni(II) in alkaline media and a presence of NaCl. The formation of quaternary complexes Ca–Ni(II)–OH-citrate was observed and, in all cases, the β-$Ni(OH)_2$ is the solid phase controlling the solubility, even in the presence of citrate.

Considering RN migration properties in presence of high saline and alkaline conditions, one can address the study presented by Landesman *et al*. (2018). The authors investigated the effect of the presence of $NaNO_3$, Na_2SO_4 and a $NaNO_3$/Na_2SO_4 mixture (to reach ionic strength from 0.2 to 4.3 mol/$kg_{solution}$) onto HTO and ^{137}Cs transport in a CEM V/A hardened cement paste. The result shows a moderate effect of ionic strength on the effective diffusion coefficient (D_e) and the factor capacity (α) for HTO through the HCP sample. For all the experiments, HTO steady-state diffusive flux is reached after around 200 days and a mean value of D_a(HTO) = (8.6 ± 2.7)·10^{-13} m^2·s^{-1} is calculated. ^{137}Cs species show an even lower diffusivity compared to HTO. For this CEM V/A cement, no significant effect of salt could have been evidenced on HTO and Cs diffusion parameters. Considering now an HCP prepared from CEM I in

contact with similar amount of $NaNO_3$ (up to 2.8 $mol/kg_{solution}$), Macé et al. (2023) investigated the operational solubility (which corresponds to the determination of the highest RN concentration in the studied conditions bellow precipitation) and the retention of U(VI). The R_d values decreased by a factor of approximately four, with a decrease by a factor of three from the operational solubility limit measured at high ionic strength compared to the reference cementitious condition. Even if the sorption of U(VI) appears to be reversible, the affinity of this species for the cement matrix is very high, which may significantly limit the migration of this RN in concrete.

Saline perturbation in cementitious media is one of the main perturbations described in literature. Portland-type cement degradation by nitrate plume can lead to damage the mineralogy assembly and modify the porosity (clogging or opening). The effect of very high saline plumes on other cement systems is less reported in literature. RN solubility and sorption at high ionic strength is also well published in NaCl-content systems. Diffusion data are present for reference species (HTO, chloride or caesium). Due to the need of long-term experiments to obtain diffusion parameters, these are scarce. The aim of RAMPEC is to preferentially feed the gap of knowledge on saline plume effect – mainly sulfate and nitrate plumes - on RN migration data. As mentioned in Section 4.3 all studies in RAMPEC Subtask 3.3 will be performed as a function of saline plume, using different types of soluble salts and at varying ionic strength. The target is to support the development of a macroscopic mechanistic models in collaboration with Task 4 of RAMPEC.

4.3 Workplan of EURAD2-RAMPEC for the cement systems

Due to the large variety of cements currently used worldwide and due to the difficulty to access by modelling the RN behaviour in high-perturbed systems, new experimental data acquisition for RN migration in controlled perturbed conditions is mandatory to better understand and improve the predictions by thermodynamic models, the main objective of the Subtask3.3 in the work package EURAD-2 RAMPEC. As shown in *Figure 13*, the RAMPEC Subtask3.3 covers a large variety of radionuclides of interest, of cement types, and of composition of the saline plume. This allows to provide new experimental data as input for the retention database developed in Task 2 of EURAD-2 RAMPEC but also to feed the Task 4 for the development and validation of thermodynamic models (see Chapter 5).

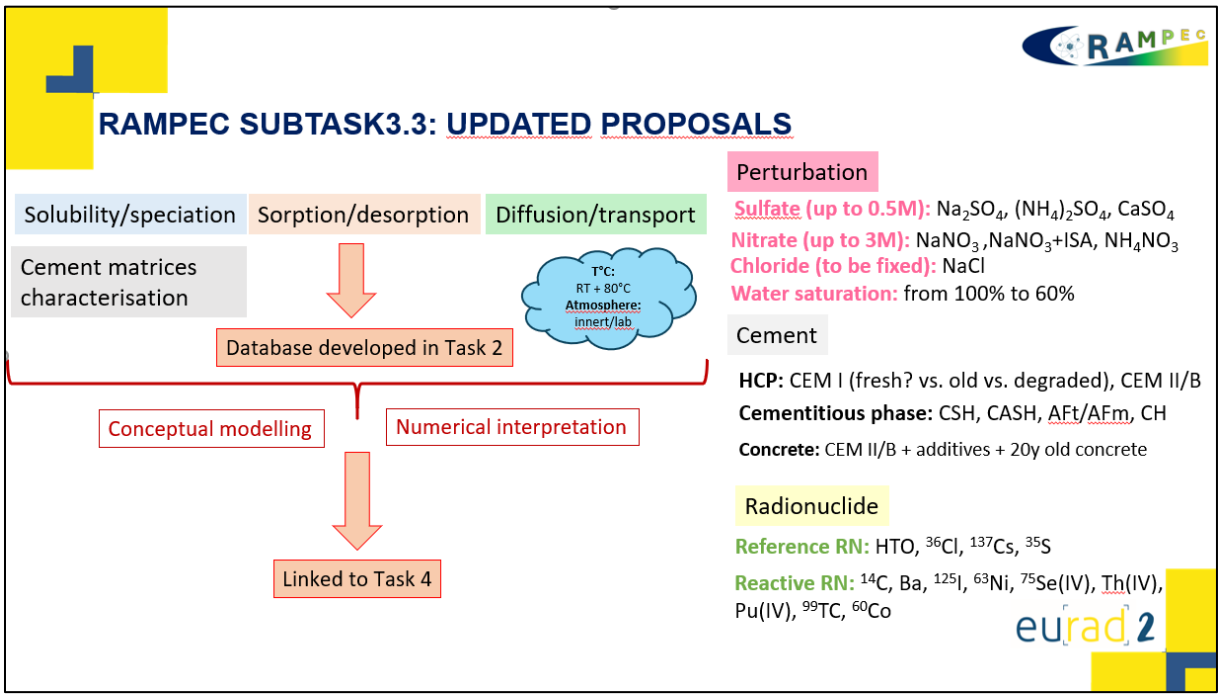

Figure 13: Simplified scheme of the workplan in subtask 3.3 of RAMPEC.

Table 3 describes in more detail the experimental investigations performed by partners in RAMPEC. This table gives a general overview of the systems of interest in RAMPEC and highlights the common thread of the experimental investigations, i.e. the effect of a saline plume especially from soluble sulfate and nitrate rich salts.

Table 3: Experimental investigations performed in RAMPEC – Subtask 3.3

		AMPHOS[21]	CEA	CIEMAT	UJV, CTU SURAO	HUN-REN EK	HZDR	EMPA	PSI	KIT
Solid characterization		X	x	x	x	x	x	x	x	x
Speciation/sorption		X	x	x	x	x	x	x	x	x
Diffusion			x	x	x	x				
Cement	**HCP**		x	x	x	x	x			x
	mortar, concrete					x	x			
	CH, CSH, CASH, …	X	x				x	x	x	
RN	**Neutral (HTO)**		x	x		x				
	Ref. RN			^{35}S, ^{36}Cl, ^{137}Cs	Cs	^{36}Cl			^{35}S	Cs
	other	Th	^{75}Se(IV-VI)	^{75}Se, ^{60}Co	Ba, C, I and mixture	^{125}I, ^{75}Se, ^{99}Tc	^{75}Se		^{75}Se, ^{125}I	Ni(II), Pu(IV), $^{14}CO_3^{2-}$
Effect of saline plume	**$NaNO_3$ (or NH_4NO_3)**	X	x		x	x				
	Na_2SO_4 (or $(NH_4)_2SO_4$ or $CaSO_4$)		(x)	x	x	x	x	x	x	x
	other		(mixture)			NaCl				
Other perturbations		Organic plume (ISA)		RH effect	Groundwater interaction	BCF porewater	RH effect			Effect of temperature +presence of Fe(0)

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5. Development of macroscopic mechanistic models

RAMPEC Task 4 focuses on the development of macroscopic mechanistic models that describe retention and transport of radionuclides in complex geochemical systems under perturbed conditions. This work will be carried out in close collaboration with the experimental work as described in chapters 2, 3 and 4 for clay, crystalline and cementitious systems. The discussion in this section is intended to complement the information presented in those chapters from a modelling perspective.

Model development may involve developing new chemical and/or reactive transport model codes, and/or use experimental work to derive new parameters for existing model codes. Within RAMPEC the focus will be on deriving new chemical / physical reactive transport parameters for use in existing codes.

Although the main focus of the model development is aimed at a selected group of radionuclides, and a specific set of perturbations, the mechanistic, thermodynamic approaches followed are aimed to be generic, and thus the models developed to describe these processes can in principle be extended with additional substances or processes. For the same reason, the model development efforts within RAMPEC for the different systems will technically partly overlap. That means that the same codes can be used with input parameters that are specific for clay rock, crystalline rock and cementitious materials.

Such an overlap also makes it technically possible to model migration processes under variable chemical and physical conditions, and at boundaries between different systems, which can be useful to model radionuclide behaviour at the boundaries between waste repository and host rock zones.

The model development work within RAMPEC significantly builds further on previous work conducted in this area within the European context, e.g. within the EURAD FUTURE, DONUT, and CEBAMA projects.

The RAMPEC model development also makes use of the results of extensive work already carried out in this area which is available in the form of different widely used codes and thermodynamic databases. In general, these codes include reactive-transport equations (Steefel and Lasaga, 1994) for solute transport and chemical reactions, e.g. PHREEQC, PHREEQC-PHAST, HPx, CHESS, Geochemist's Workbench, HYTEC, CRUNCHFLOW, ORCHESTRA, PFLOTRAN, OpenGeoSys, TOUGHREACT, GEM2MT, (Steefel et al., 2014).

Regarding existing thermodynamic databases that will be used as starting point for the RAMPEC model development the most relevant examples are; ThermoChimie https://www.thermochimie-tdb.com/, Cemdata2018, https://www.empa.ch/web/s308/thermodynamic-data, OECD/NEA TDB https://www.oecd-nea.org/dbtdb/, THEREDA – Thermodynamic reference database for nuclear waste disposal in Germany https://www.thereda.de/de/, and https://www.oecd-nea.org/dbtdb/, NAGRA/PSI database https://www.psi.ch/en/les/database.

The German Thermodynamic Reference Database (THEREDA) is designed for geo-chemical models in the context of a radioactive waste repository. THEREDA especially addresses high-salinity aqueous solutions (brines) and therefore supports the Pitzer ion-interaction approach. Great effort has been made to ensure the internal consistency of the data. The primary focus is on the correct calculation of the solubilities of radionuclides, fission products and matrix elements (construction materials and mineral phases of the surrounding host rock).

The ThermoChimie database (Giffaut et al., 2014) is managed by the French, Belgian and British waste management agencies; Andra, Ondraf-Niras and RWM, respectively. Since its initial creation by Andra in 1996, ThermoChimie has been based on (i) previous thermodynamic database compilations; (ii) open scientific literature; (iii) data obtained by means of specific experimental programs on actinides and fission products carried out under the auspices of Andra or other reputable experimental programs endorsed by Nuclear Waste Management organizations and research institutions; (iv) estimations (Giffaut et al., 2014).

The thermodynamic databases mentioned above predominantly contain thermodynamic data on pure phases and aqueous complexation reactions. Data specifically on sorption reactions is much more sparsely reported in scientific literature, for example sorption data on illite, bentonite, and argillaceous rocks (Bradbury and Baeyens, 1997), as well on bentonite (Bradbury and Baeyens, 2003), illite (Bradbury and Baeyens, 2017), and Opalinus Clay and related formations (Baeyens et al., 2014)

New information, e,g. chemical adsorption reactions and reactions constants, obtained from experimental work within RAMPEC project, as discussed in chapter 2-4, will be made available in the form of thermodynamic data that can be used in combination with different codes.

5.1 Clay rock

As described in chapter 2, migration behaviour of radionuclides in clay rocks or clay materials is strongly dominated by a combination of physical diffusion of ions through small sized, charged pores in combination with adsorption of ions to charged clay particle surfaces.

Numerical models to describe migration in such systems therefore require a description of physical diffusion combined with a description of retention or sorption behaviour.

The physical diffusion process is complex because it is dominated by diffusion of charged ions through a medium with charged particle surfaces and double layers. There is a strong interaction between chemical and physical processes.

Many studies have been undertaken to investigate the sorption behaviour of charged clay surfaces for a wide range of radionuclides under variable macro chemistry conditions. An up-to-date comprehensive overview of the latest developments in this area and remaining research questions is given in Maes et al. (2024).

This overview also highlights that specifically in the areas of changing temperature, changing water saturation, changing alkalinity (alkaline plume), changing ionic strength (salt intrusion), effect of organic molecules, understanding and model data is lacking.

This was a main motivation for the focus within RAMPEC on the effects of these perturbations as also explained in chapter 2.

Regarding the code aspects of model development this implies that to be consistent with the planned experimental work codes will be required to be able to describe:

- temperature dependent chemical reactions in solution for adsorption and parameters for temperature dependence.
- salt dependent chemical reactions (PITZER, SIT) and parameters
- salt dependent behaviour of clay surfaces
- temperature dependent diffusion coefficients
- transport and chemical properties of small organic molecules

5.1.1 Temperature perturbations

Several studies have coupled experimental and modelling approaches to the assessment of temperature effects on sorption in clay minerals. There are mixed results among these studies, with some identifying little or no effect of temperature, while others have used temperature-dependent data to fit Arrhenius-type laws and extract activation energies for the sorption of different cations. The modelling approaches used have generally been more empirical than based on underlying thermodynamic mechanisms. Modelling is often complicated by the fact that the temperature-dependent effects observed experimentally (see e.g. the Cs sorption data of Chen et al. (2014) at 22 and 80°C) are

small, and in some cases within the charted experimental uncertainty bounds. On this basis, Chen et al. (2014) chose to exclude temperature changes (on a 10^5 year timescale) from the development of their formation-scale model. However, they did identify from their temperature- and concentration-dependent parameters that there are different ΔH parameters for the different sorption sites described in a Bradbury-Baeyens type model for the clay.

Other workers, e.g. Savoye et al. (2011) also reached similar findings in fitting activation energies to their temperature-dependent transport experiments, using HTO, ^{36}Cl, ^{22}Na, and ^{137}Cs tracers. The behaviour of their HTO and ^{36}Cl tracers could be explained using the Stokes-Einstein relationship and the temperature dependence of fluid viscosity, but the cationic tracers also showed some temperature effects that could not be directly captured by this simple model.

The review of Kale and Ravi (2021) addressing the effects of thermal history on the physicochemical and engineering properties of compacted bentonites also concluded that significant advances in modelling would be important in advancing this topic; in particular the coupled time-temperature effects were highlighted as an area requiring attention.

5.1.2 Chemical perturbations

The pH is one of the most important factors influencing the speciation of RN. As already explained in chapter 2.3.1 there is a strong coupling between fluid and solute transport, the dissolution of solids and precipitation of secondary phases, ion-exchange and sorption on clays, and the resulting changes in physical properties of the materials (porosity, permeability, swelling of clay). Most of the attention of the studies was devoted to understanding the changes that are occurring in the HR (and cement barrier) in order to be able to describe as good as possible the chemical evolution of the NF using modelling tools, in order to assess the impact on their functioning as barrier on the long term. Simulations show a narrow perturbed zone (mainly on the order of cm to dm for mineralogical changes, and on the order of meters for pore water composition changes) close to the interface for time scales up to and beyond 100 000 years (Savage and Cloet, 2018, Bildstein et al., 2019).

Geochemical approaches coupled with reactive transport models have been used extensively to study the influence of an alkaline plume (e.g. from concrete or cement pore water) on the properties of clays (Gaucher et al. 2004, Idiart et al. 2020). A large number of the available models to describe this phenomenon have been compiled and summarized by Sun et al. (2022), and it is clear that the more effective models are those which are able to efficiently couple each of the thermo-hydro-chemo-mechanical aspects of this complex and multiscale process without incurring excessive penalties in computational cost or duration.

Ionic strength effects on clay sorption processes are largely observed as competitive processes which can displace relatively dilute radionuclides through the imposition of a pulse of high ionic strength fluid. These have been modelled (using PHREEQC and the ThermoChimie database, and an edge-surface electrostatic term derived from the Poisson-Boltzmann equation) by Orucoglu et al. (2022), as shown in *Figure 14*, where the effect of ionic strength on the sorption of Pb^{2+} on montmorillonite is seen to be accurately described by this model across a range of Pb^{2+} and NaCl concentrations.

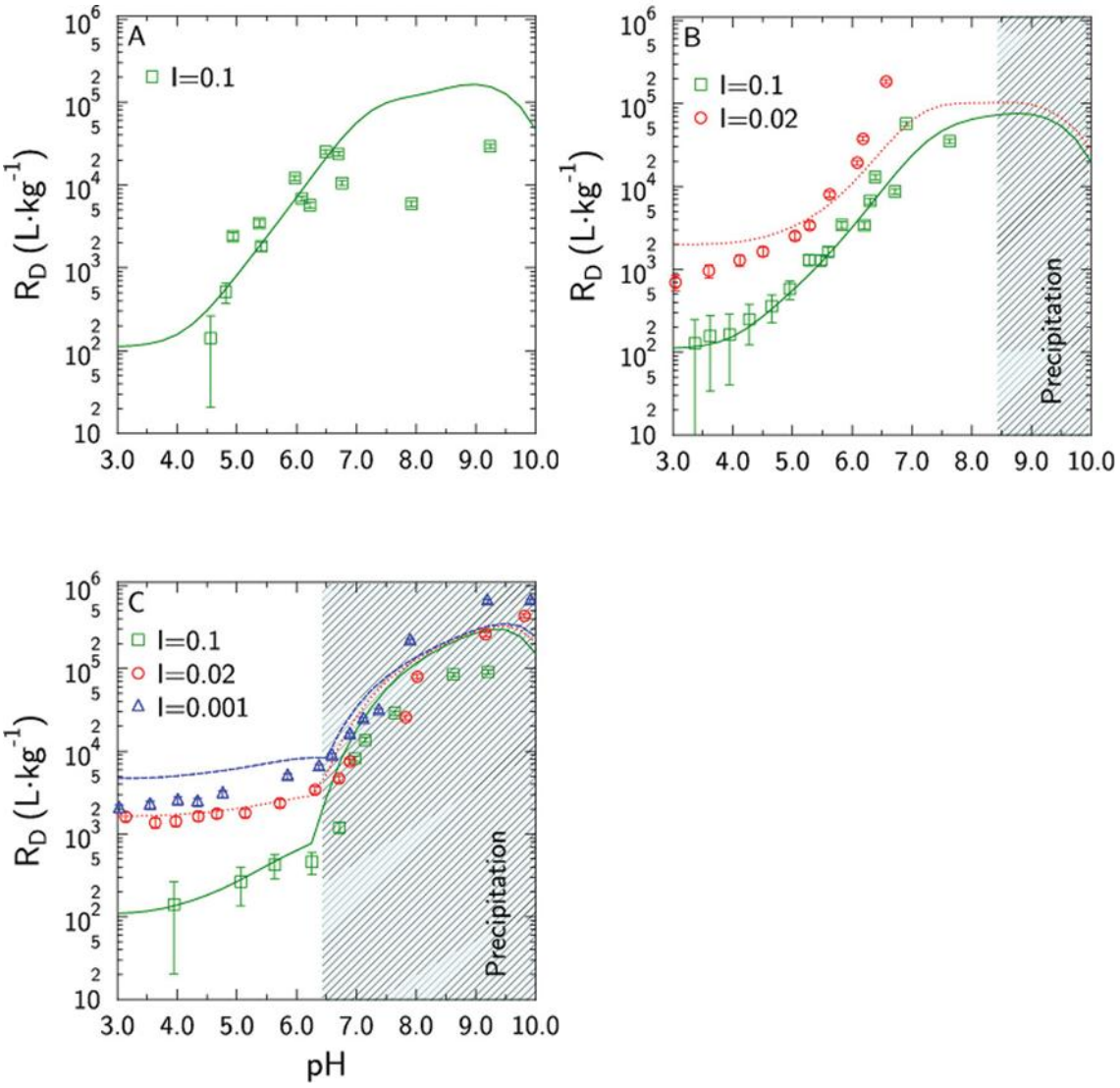


Figure 14: Modelling by Orucoglu et al. (2022), using PHREEQC and ThermoChimie, of Pb^{2+} adsorption data on SWy-2 montmorillonite. Data (from Akafia et al. (2011)) are shown as symbols, and model calculations are shown as lines. Pb^{2+} total concentrations are (A) 0.5 µmol·L^{-1}, (B) 5 µmol·L^{-1}, and (C) 50 µmol·L^{-1}; ionic environments are 0.1 mol·L^{-1} NaCl (green); 0.02 mol·L^{-1} NaCl (red); 0.001 mol·L^{-1} NaCl (red). Published under a Creative Commons Licence.

Atomistic simulations have also been used to provide information about the response of clays to changes in salinity and other environmental perturbations (Zhou et al., 2025), driving new insight into swelling behaviour which may be important in a GDF context (Shen and Bourg, 2022), and also to their behaviour under drying (unsaturated) conditions (Underwood and Bourg, 2020).

Modelling radionuclide sorption processes in the presence of organic ligands or natural organic matter (NOM) is challenging because these substances can strongly influence radionuclide mobility and retention. Organic matter may act as a sorbent or as a ligand that forms complexes with radionuclides, thereby modifying their sorption behavior on natural or engineered barriers.

Radionuclide retention is typically represented by using sorption distribution coefficients (K_d) or, more mechanistically, through surface complexation models (SCMs) that describe interactions with mineral surfaces. When organics or NOM are present, several additional mechanisms must be considered:

- Complexation: Organic ligands can form aqueous complexes with radionuclides, often increasing their solubility and mobility.
- Competitive sorption: Organic molecules may compete with radionuclides for sorption sites on mineral surfaces or colloids, displacing them or inhibiting their sorption.
- Direct sorption: NOM itself can sorb radionuclides, introducing an additional partitioning pathway.

Redox effects: Organic matter can mediate redox reactions that modify radionuclide speciation, thereby influencing mobility and sorption behavior. Modelling frameworks are available to address this complexity: e.g. the Tipping Humic Ion-Binding Model V and Model VI, and the NICA-Donnan approach which are specifically designed to describe metal–NOM interactions.

Geochemical speciation models can incorporate equilibrium assumptions for systems containing multiple organic and inorganic components. Surface complexation models (SCMs) remain central for representing interactions with mineral surfaces, though they often require extensions to explicitly account for ternary systems (mineral–radionuclide–organic).

5.1.3 Planned model developments within RAMPEC

Within this Task, work will be undertaken to derive new sorption parameters (complexation constants or selectivity coefficients) at different types of clay surfaces and under different perturbed conditions. Also, work is planned to experimentally investigate effects of the presence of different types of organic molecules and to translate experimental results into model parameters. At the pore scale, molecular dynamics will be used to simulate the diffusion of surface complexing ions as function of T and IS, furthermore, mechanistic pores scale type models (e.g. Lattice Boltzmann) will be used to simulate the transport of surface complexing radionuclides in the illite pore structure in a T gradient. In terms of model framework development, no completely new code developments are foreseen. However, in order to describe the full combination of chemical and physical perturbations, extensions of existing codes are planned. For example, the implementation of the PITZER ion interaction model in the ORCHESTRA framework which will make it possible to develop adsorption models for clay and organic particle surface at high salt levels. Furthermore, to combine the newly developed chemical model descriptions with advanced transport mechanisms, work is planned to combine existing chemical solver codes (e.g. PHREEQC and or ORCHESTRA) to the versatile open-source transport framework OPEN FOAM. Also stand-alone reactive transport frameworks (e.g. Crunchflow) will be used by RAMPEC partners to implement advanced combined models for transport of ions under high salt conditions in unsaturated pores as affected by local electric potentials and charges.

5.2 Crystalline rock

As explained in Chapter 3 the migration behaviour of nuclides in granitic systems is dominated by coupled hydrogeological, hydrodynamical, and chemical processes in multi-scale fractured systems. Therefore, in comparison to clay systems, not only diffusion and the chemical retention behaviour of the rock matrix itself is important in determining radionuclide migration behaviour, but additionally there are advective and dispersive flow processes that determine transport rates and processes. Grain boundaries, porosity, water saturation, pore size variability, pore connectivity, and distribution (particularly at the nanometre scale) may significantly influence radionuclide retardation in addition to water chemistry (e.g., pH, ionic strength, and water composition; see Sec. 3.2.1, Maes et al. (2024)).

These heterogeneous geophysical properties of the matrix have a strong effect on flow patterns and may cause heterogeneous flow fields which have a strong effect on migration rates. Additional complexity is formed by possible feed-back between chemical and hydrodynamical processes, such as

filling in fractures with newly precipitated material. Therefore, it is crucial to differentiate between unaltered and altered rock matrices, as well as between fractures with and without mineralization (see Figure 3.1). Neretnieks (1980) demonstrated that over 100 years, non-sorbing nuclides can migrate tens of meters into crystalline rock, whereas strongly sorbing nuclides (K_d >10^4 mL·g^{-1}) might only penetrate a few millimetres. Matrix diffusion greatly enhances retardation. However, if the entire rock is accessible via diffusion and fractures, retardation may be significantly reduced, depending on the fracture and pore network. As stated, in crystalline rock environments flow and radionuclide migration primarily occurs through interconnected fracture networks (e.g. fracture and pores). Over time, these pathways may become filled with secondary minerals, depending on factors such as temperature, fluid composition, and reaction kinetics causing mineralization processes that can significantly influence porosity, permeability, surface coatings, microbial activity, and ultimately the sorption behaviour of long-lived radionuclides (Maes et al., 2024).

Characterization of this fracture flow, how diffuse flow processes could be affected by pore space distribution, and its relevance for performance assessments at a field scale is a continuing modelling and experimental issue (Wersin, 2017). The fractal nature and partial self-similarity of rough fracture surfaces have been studied for their effects on the geometric constraints of transport models (Cardona et al., 2021; Wang et al., 2022). This topic has recently been discussed in a general review on transport mechanisms (Gao et al., 2023) and with a focus on RN transport (Zhang et al., 2022b).

The combination of chemical and hydrodynamic “feed-back loops”, effects of pore space distribution, and e.g. fracture surface structure are the reasons why the development of mechanistic understanding, quantitative description and prediction of reactive transport processes in crystalline systems is still very challenging. A further description of the state of the art on research in the field of radionuclide migration in crystalline systems can be found in the recently completed work within the EURAD Future project, Jankovský (2024).

5.2.1 Effect of temperature and fractures

Medved’ and Černý (2019) provided a detailed review of modelling approaches to radionuclide transport in porous media, particularly fractured rocks, and identified the need for improvements in parameter value determination, and uncertainty quantification, to support further progress in this field. This coupling between experimental and modelling approaches is evidently central to further advancements, because validated sorption and diffusion parameters are needed to support model development, to identify controlling mechanisms, and to enable new theoretical approaches to be tested and implemented. Those authors specifically noted that temperature and concentration dependence of diffusion coefficients will sometimes be dominant effects and need much more detailed evaluation. The work in RAMPEC on perturbed systems will go a significant way toward meeting this identified need.

Holgersson and Kumar (2023) provided a specific assessment of modelling approaches to radionuclide sorption on granitic rocks, with a focus on identifying knowledge gaps related to interactions of different species with specific mineral constituents of common granites (sheet-silicates and feldspars).

The use of an inverse modelling approach to define the mechanisms responsible for radionuclide (Np, U) transport in fractured tuffaceous rock has been demonstrated by Dai et al. (2012), who used this methodology to develop and fit a set of models including or excluding different potential rate-controlling steps. The best-fit models were found to involve sorption of radionuclides on both matrix and fracture sites, and kinetic control of sorption under flow conditions which agrees well with findings presented in Section 3. Evolution of fractures, particularly by partial filling through mineral precipitation, has been shown to be an essential aspect of models validated against data from scenarios such as the Maqarin natural analogue site (Watson et al., 2016). Transport of plutonium in fractured granite has also been shown via application of several candidate model formulations to be under significant influence from kinetic control and defined in terms of a dual porosity scaled network (Zhang et al., 2022a). To model problems on longer timescales and/or length scales that are relevant to GDF conditions, the role of

dispersivity in transport equations also becomes important (Jia et al. 2023). The potential value of an approach with time-varying K_d values has also been discussed (Trinchero et al. 2015).

5.2.2 Planned model developments

Within this Task, work is planned to derive surface complexation, or sorption parameters for the adsorption of several nuclides for crystalline rock materials, at different salt levels and different temperatures. Additionally, work is planned to measure and improve the models for ion diffusion in fractured rock material. This includes measurements under variable saturated conditions and at different temperatures and time scales. The results of this work will contribute to improve model descriptions of radionuclide migration rates through fractured rock under physically and chemically perturbed systems.

In comparison with the planned modelling work for clay systems, the focus for crystalline rock will be less on purely the chemical behaviour but more on physical processes, such as the effects of mechanical stress on radionuclide transport, and the challenge of scaling of transport properties with particle size and the aperture of fractures.

5.3 Cementitious systems

Many of the considerations raised in the preceding sections, relevant to perturbations in clay and crystalline rock systems, apply also to the modelling of cementitious systems under perturbation effects. Both chemical and thermal perturbations can cause important changes in the physicochemical properties, and thus key performance metrics (radionuclide retention/sorption, and other material properties), of cements in a repository context.

Modelling of perturbations in cementitious systems is usually conducted in close conjunction with experimental research, and so the information presented for Task 3.3 (see preceding sections) is an essential support to the details given here, which focus specifically on modelling approaches. The State-of-the-Art Reports produced by the CEBAMA project (Vehmas & Holt, 2016; Idiart, 2019) provide essential background and detail, and it is not the intention of the current report to repeat what has been presented in those and other key reference documents. The assessment here is designed to be brief and focused on topics central to RAMPEC Task 4.3. Much of the available information related to the broader material and performance characteristics of cementitious materials has been developed and framed in the context of concrete for civil engineering construction and so needs to some degree to be translated and adapted for use by those with an interest in repository design and performance. Conventional concrete serves mainly at ambient temperature and humidity, often with short-term (hours to years) cyclic exposure to humidity/moisture and chemically aggressive agents, and for a design life usually measured in decades. None of these factors are entirely accurate in describing a deep geological repository, and so the information available from conventional engineering sources needs to be carefully reconsidered if it is to be used to assess repository performance.

5.3.1 Chemical perturbations

The most important chemical perturbations that are likely to influence cementitious materials and their performance in a repository are related to interactions with groundwater. This has been described in several conceptual frameworks, but the model developed by Berner (1992), describing three main stages of degradation, has proven to be powerful in characterising and predicting cementitious environments under this perturbation (Tits & Wieland, 2023):

- Stage 1: undamaged cement, high pH controlled by alkali hydroxides,
- Stage 2: partially leached cement, high pH controlled by portlandite,

- Stage 3: significantly degraded cement, pH buffered by incongruent (and then later congruent) C-S-H dissolution.

The dissolution of cementitious phases under groundwater attack has been discussed extensively, for different types of groundwater and different cement formulations; the CEBAMA project deliverables provide very detailed analysis of important issues in this regard (Vehmas et al., 2020), and there remains ample scope for these findings to be incorporated into ongoing and future modelling (Deissmann et al., 2025). The available tools and approaches have recently been assessed by Claret et al. (2024) in the context of a EURAD State of the Art report (DONUT), and the advantages of the use of surrogate modelling to greatly accelerate the (otherwise potentially time-consuming) computation of thermodynamic equilibria have particularly been highlighted in the context of cement evolution (Laloy & Jacques, 2022).

In assessing water leaching of cements, two main types of modelling approaches are applied: either a coupled reaction-diffusion scheme (often, although not always, based on simplified or surrogate descriptions of the complex chemistry of the cement), or a two-stage (temporally decoupled) model whereby reaction kinetics are directly imposed by, for example, using a kinetic expression to specify the input species into a thermodynamic model which calculates a pseudo-equilibrium state on this basis. Essentially, the first option brings a very rigorous description of transport together with sufficiently detailed chemistry to give useful outcomes, while conversely the second links simplified kinetics to a detailed chemical computation. The choice of which pathway (or combination of pathways) to take depends to a significant extent on the final aim of a particular study, and the importance of validation of the model and its underlying databases using high quality experimental data must be highlighted (Lothenbach et al., 2010; Savage et al., 2011).

Intuitively, it may be argued that the “gold standard” would be to couple rigorous chemistry with detailed transport and kinetic descriptions; the computational cost of such an approach is unfortunately very high, and limits its use to either geometrically small units, short simulation times, or both. The fundamental problems in modelling cementitious materials do often relate to the need to span length scales; cements have important structural (mineralogical and pore network) features on length scales down to the order of nanometres, and the material characteristics at this scale are influential when discussing performance in structures that are tens or hundreds of metres in size. Similarly, chemical reaction processes – for example, re-equilibration related to cement mineral alteration by groundwater, or the chemical reaction steps in cement hydration – can take place on timescales of minutes to hours, but repository performance needs to be predicted on timescales of millennia or more. The concentrations of the important dissolved species in cementitious pore fluids also span many orders of magnitude; the overall ionic strength can exceed 1 mol/L with high concentrations of hydroxide and alkali metal cations, but key species such as magnesium may be present at sub-millimolar concentrations. The numerical challenges involved in spanning these length, time, and concentration scales are significant (Lothenbach, 2010; Prasianakis et al., 2020; Laloy & Jacques, 2022), and require specialist expertise in mathematical approaches to upscaling and solving “stiff” systems of equations to render the computations in some way tractable (Leal et al., 2020; De Lucia & Kühn, 2021; Ladd et al., 2021).

5.3.2 Sulfate perturbations

The assessment of cementitious materials under sulfate-induced perturbations is usually focused on the prediction (and understanding) of sulfate-induced expansion in structural concretes. The chemical evolution of cement under sulfate attack has been a very successful case study for “titration-type” thermodynamic models, where the evolution of the perturbed cement is presented as a function of the quantity of sulfate-containing solution with which it has been brought into contact; *Figure 15* provides an example of this, from Huang et al. (2024). The power of this approach was demonstrated by Lothenbach et al. (2010), in which results from titration-type thermodynamic simulations (obtained with a simulation time of 1 minute) were directly compared to a fully coupled reactive transport simulation taking 1-5 days

to compute. The titration-type simulation has the advantage of chemical precision and speed but is more difficult to map directly onto experimental (or real-world) time and length scales, as it does not include an explicit description of kinetics or transport rates (Lothenbach et al., 2010).

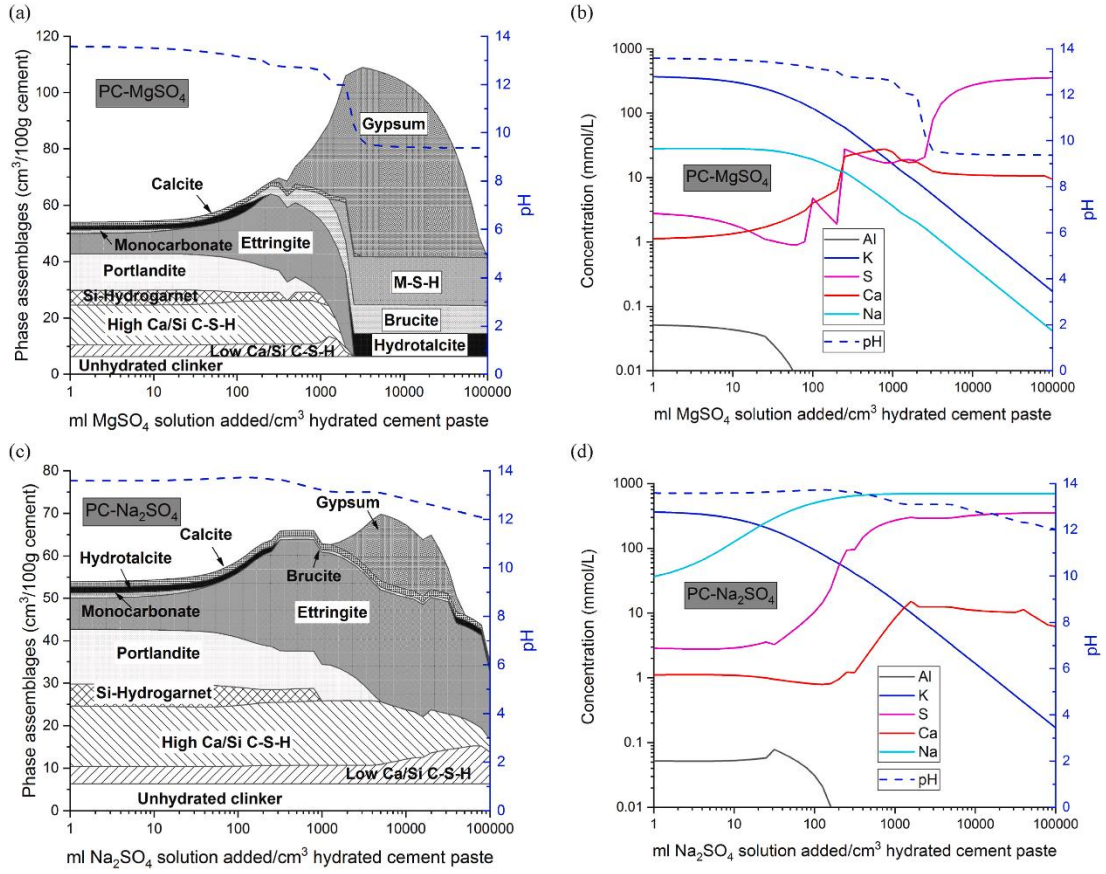


Figure 15: Calculated phase assemblages of CEM I mortars under simulated contact with (a,b) $MgSO_4$ solutions and (c,d) Na_2SO_4 solutions, each with 352 mmol/L sulfate, calculated using a titration-based approach, the GEM-Selektor software, and the CEMDATA18 database. Reproduced from Huang et al. (2024) under a Creative Commons CC-BY licence.

In the context of sulfate-induced perturbation of cementitious repository chemistry, in addition to the mineralogical alteration of the cement itself, it is important to consider the possibility of competitive sorption/desorption processes involving the incoming sulfate ions displacing sorbed radionuclide species. It has been concluded that the competitive effect of sulfate on sorption of cationic radionuclides is unlikely to be significant (Tits & Wieland, 2023), so the key species for which competitive effects need to be considered are the radiologically relevant anions. There is limited information yet available for the specific competitive sorption processes of interest here, and this forms a significant focus of the planned activities of the RAMPEC WP. In a degraded cement (stage III according to the classification mentioned above), the aluminate phases which would be expected to bind sulfate in an undamaged cement have already been decomposed, and so C-S-H is the most relevant phase to consider in this discussion when predicting repository performance in the medium to long term. Anion sorption on C-S-H, as well as other potentially relevant phases such as alkali-silica reaction products, relies on co-adsorption with divalent cations (Krattinger et al., 2021) and so must be considered and modelled in the context of a realistic (perturbed) pore fluid environment rather than in isolation.

5.3.3 Chloride perturbations

The influence of chloride on fundamental cement mineralogy is relatively limited (by comparison to sulfate, or other potentially damaging species such as magnesium); its role in the context of a perturbed repository system will mainly be in changing the ionic strength and pore fluid chemistry environment with which the cement is in contact. The monovalent chloride has a relatively weaker effect in competitive sorption than divalent sulfate (or carbonate) and must also compete with relatively high concentrations of hydroxide, particularly at early age (Wilson et al., 2022). and is observed to itself bind relatively weakly to C-S-H (Tits & Wieland, 2023). Nonetheless, the potential competition between groundwater-derived chloride and important radionuclide species (which may actually include $^{36}Cl^-$ as a waste constituent) needs to be considered – and as was noted above, the cooperative effects of divalent cation sorption on C-S-H and their influence on anion uptake are likely to be important in assessing this process. This is a key point for the RAMPEC WP to consider when modelling cement behaviour under chloride perturbations.

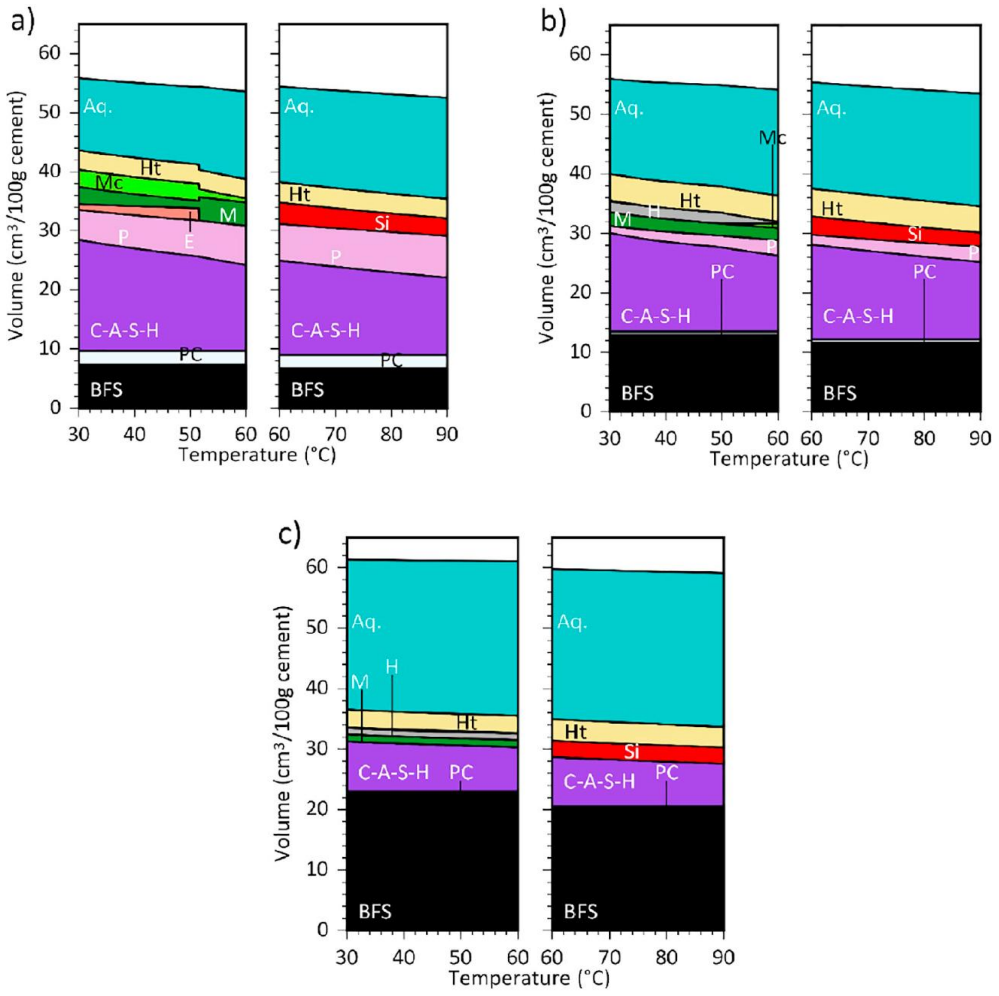
5.3.4 Temperature perturbations

The temperature environment that is likely to prevail within a repository is an important factor defining cement mineralogy (Poller et al., 2011), and will potentially involve several perturbations prior to repository closure:

- The naturally elevated temperature deep underground may perturb cements during construction – for example if pre-cast elements are fabricated on the surface and moved underground.
- The thermal output from high-level waste may reach cementitious components in the short or long term, depending on the design and implementation of any backfill that separates the waste from cementitious structures.
- If a cementitious backfill is used, the heat of hydration of this cement will also contribute to the overall thermal profile of the repository materials – potentially including also the high-performance concrete waste containers which are implemented in some countries.

The performance and characteristics of cement and concrete under extended high-temperature exposure are not yet well-constrained experimentally (Komendant et al., 1976), although important recent advances have been made in this regard (Abdo et al., 2025). When considering radionuclide retention in a repository, the ability of the cement or concrete to remain physically intact (i.e. not crushed or fractured (Mattigod et al., 2009; Perko et al., 2015)) is important, and thus the evolution of mechanical properties over a very extended period of time needs to be better described in a modelling sense; it does not appear that this work has yet been carried out in detail when considering the newest understanding of material properties evolution over timeframes of multiple years, and seeking to extend this to millennia or more. It is likely that rather than developing an explicitly time-dependent model, a more generalisable approach to the description of the effect of thermal perturbations on cement or concrete is to assess the relationship between time, thermal history, and the pore structure of cementitious materials (Vodák et al, 2004; Abdo et al., 2025), and then relate mechanical properties to pore structure via a validated model (Bahafid et al., 2018; Hou et al., 2019).

An example of the first part of this – intended to provide some of the basic information needed to replicate the evolution of a blast furnace slag-Portland cement during a representative thermal history for a conceptual design for a UK ILW repository – is shown in Figure 16 (Prentice et al., 2019). In this model, kinetic limitations on the formation of siliceous hydrogarnet at early age were implemented manually, by suppressing this phase at temperatures below 60°C, which was relevant to the particular context under investigation in that study. More recent updates to the CEMDATA database have altered the relative stabilities of some of the aluminate hydrate phases (Lothenbach et al., 2019), and very long-term repository simulations would not need these kinetic restrictions (which appear valid when considering timescales up to several months, but not beyond that), so there is scope for further advancement to refine these simulations.



d)

Phase of completion		Timescale (years)	Temperature (maximum - °C)
I	Emplacement	50	30–40
II	Care and maintenance	50	30–40
III	Short-term backfill	5	80
IV	Long-term backfill	25	50
V	Post-closure of GDF	–	35–45

Figure 16. *Phase assemblages of a) 1:1, b) 3:1 and c) 9:1 blast furnace slag-Portland cement blends as a function of temperature, determined using the thermodynamic modelling software GEM-Selektor v3 with the CEMDATA14 database; and d) the expected temperature profile during the operational and post-closure phase of the geological disposal facility (GDF) lifespan for an ILW facility. Siliceous hydrogarnet was only allowed to form above 60 °C, and each graphic shows a break at this point to reflect the change in model assumptions. The phase notations are: BFS – Blast furnace slag, PC – Portland cement, C – C-A-S-H, P – portlandite, E – ettringite, M – monosulfate, H – hemicarbonate, Mc – monocarbonate, Ht – hydrotalcite, and Si – siliceous hydrogarnet. From Prentice et al., (2019), published under a Creative Commons CC-BY licence.*

5.3.5 Additional modelling aspects that may be relevant, within or beyond RAMPEC

The process of describing and modelling the clay-cement interface, and resulting perturbations in both materials, has been covered in recent deliverables from the CEBAMA project (Idiart, 2019) and will not be repeated here. The partial conversion of C-S-H to M-S-H is relevant in this context (Dauzeres et al, 2016); this and other processes can lead to pore clogging (Wilson et al., 2019) and consequent hindrance of mass transport, in the cement and/or the material with which it is in contact, depending on the specific nature of each of these.

Corrosion processes of steel in a repository – whether it is present as part of the repository structure, as a canister material, or as part of the disposed waste – can also perturb the chemical (and redox) environment within the repository (Wittebroodt et al., 2024). The application of thermodynamic modelling to corrosion problems in cementitious contexts has recently been assessed by Furcas et al. (2025) and identified as an area ripe for future (and valuable) development in the future.

The influence of organics in causing chemical perturbations within a cementitious repository – assessed in detail in the CORI project (Altmaier et al., 2024) - is also an important future target for modelling. Many of the principles mentioned above related to competitive sorption are likely to come into play in this context also, and the formation of organic-radionuclide complexes will also alter their interactions with cementitious phases (Hummel, 1993; Androniuk, 2017). It will be valuable to improve the existing databases to describe complexation in this context (Pointeau et al., 2008), to enable the full range of potential species to be properly taken into account in models for sorption and transport processes. The same is likely to be true for carbonate and other potential complexant species which may be introduced from either groundwater, repository construction, or waste constituent sources (von Schenck & Källström, 2014).

5.4 References to Chapter 5

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6. Upscaling and cell disposal scale modelling

This section reviews current capabilities of models and case studies aiming at representing organic, saline, and/or alkaline perturbations, and the effects of these on radionuclide migration at the disposal cell scale (meter to decameter scale). Like Neeft et al. (2025), the disposal scale is defined between repository scale and detailed scale, in which the waste packages, the gallery and a few or several meters of the host rock around the gallery are represented. This scale is characterized by several different types of materials with different geochemical properties. Perturbations can increase the mobility of radionuclides (and toxic chemicals) and in turn influence the dose potentially received by human or non-human biota. Therefore, the goal of these models is to support Performance and Safety Assessment calculations.

Post-closure Safety and Performance evaluations of radionuclide migration require the development of modelling tools and techniques that can simultaneously consider the following features:

- Geometries of the waste cell and waste packaging.
- Realistic material properties of the near field (e.g., liner, waste packages, etc.) and the host-rock in terms of transport and retention processes and their evolution over time due to spatiotemporal perturbations.
- The properties of the waste (type of salts, type of organics) and inventory (total mass of salt, alkaline reserve, etc.).
- Typically, many radionuclides and toxic chemicals need to be assessed.

Today, the effects of perturbations on radionuclide migration over such large scales remain poorly considered and/or documented as shown in this review.

This review does not cover the fundamentals of transport processes in porous media, already included in the EURAD project deliverables of the FUTURE Work Package (Maes et al., 2024), nor the numerical methods for reactive transport modelling in the field of radioactive waste management, recently reviewed in EURAD by Claret et al. (2024).

6.1 Upscaling radionuclide migration processes in porous media

Upscaling refers to the use of methods to accurately assess mass transport behaviours at large scales based on an understanding of parameter variations at smaller scales with affordable computational cost (Soltanian et al., 2018). In practical terms, upscaling involves replacing a heterogeneous domain with a homogeneous one, such that both produce the same response when subject to the same boundary conditions (Rubin, 2003). In this review, upscaling is also referred to as the methods that can be used to define and analyse the appropriate simplifications that are needed to handle large scale modelling without losing fundamental information from lower-level scales and processes. This includes how heterogeneities and natural variability are treated, how the role of interfaces between materials can be effectively assessed, how long-time scales can be considered in agreement with the spreading of perturbations in the rock, and how consistency and complementarity between geochemical and transport models can be achieved.

The crucial scale of the up-scaling approach is the macroscopic scale (mm to dm scale), where integrated parameters can be acquired experimentally, although for rather short time scales (from months to few years), and transferred to models able to represent large scale (m to tens of m). To validate the transferability of the parameters and the application of models, two experimental approaches are usually used (Altmann et al., 2012):

- Mock-up experiments which are operated in surface laboratories and operated with dm^3 volume under well-controlled conditions.

- *In-situ* experiments in Underground Research Laboratories (URLs) with systems involving the injection of tracers from boreholes.

The following description of such experimental approaches can be complemented with Section 3.2.4 of Maes et al. (2024) on "Experimental approaches to upscaling". The study of the effects of perturbations on radionuclide migration using mock-up experiments has been given little attention in the literature. The work of Dagnelie et al. (2012) and Dagnelie et al. (2015) perfectly illustrates the potential of this approach to study a nitrates perturbation and an organic perturbation, respectively (see Figure 17). The benefits of such experiments result mainly from the interpretation of the diffusion profiles and monitoring of the tracer concentrations in the injection zone to derive K_d and diffusion coefficient values. The evolution of these migration parameters can then be compared to those acquired under unperturbed conditions.

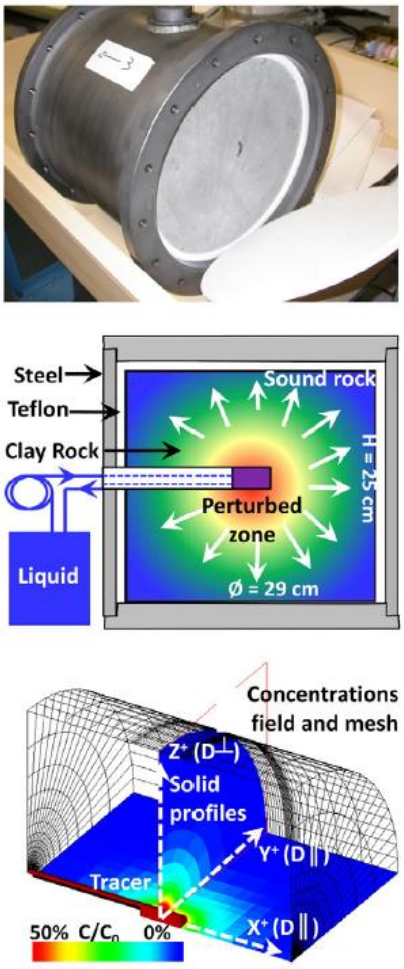

Figure 17: Illustration of a mock-up experiment dedicated on the effect of organic perturbation on the radionuclide mobility (From Dagnelie et al., 2015). Top: Picture of the clay rock in its stainless-steel cell. Middle: Scheme of the experimental setup. Bottom: Mesh and geometry of the solid profiles.

Even if several in-situ experiments deal with the diffusion of radionuclides (see e.g. Leupin et al., 2017 for a historical summary of diffusion and sorption experiments at Mont Terri URL or Dewonck, 2007, Delay et al., 2007 for experiments in Bure URL), and the recent publications summarizing the large scale diffusion tests in HADES URL in Belgium (Van Geet et al., 2023, Aertsens et al., 2023, Govaerts et al., 2023, Nussbaum et al., 2023), few of these integrate the effect of perturbation on radionuclide migration. Several experiments at the Mont Terri URL are on-going, such as:

- The Bitumen-Nitrate-Clay experiment, which studies the behaviour of selenium in the presence of nitrates (Hendrix et al., 2023). In this experiment, microbiological mediated processes rule the reactivity of nitrates and selenium with redox state evolution having in turn an effect on their mobility.
- The CI-D experiment is also in progress and aims at characterizing the diffusion of HTO and $^{36}Cl^-$ in the altered skin present at the interface between cement and clay (Maes et al., 2024; Sarsenbayeb et al., 2025), to assess porosity changes (i.e. the possible clogging of the pores at the interface).
- DR-C, a new diffusion experiment that investigates the diffusion of radioactive tracers and stable isotopes in a thermal gradient (Pochet et al., 2024).

Other experiments dealing with only the perturbations themselves have also been reported, with a monitoring of the chemistry, for example the EPT experiment (Lundy et al., 2013) for a thermal perturbation and the DRO experiment (Dagnelie et al., 2023) for an organic perturbation, both in Bure URL in France, or the Long-Term Cement Studies, LCS, in Grimsel Test Site in Switzerland (Soler et al., 2006; Soler et al., 2020; Wilson et al., 2018) for a hyperalkaline perturbation. Particularly for alkaline plumes, there is a vast knowledge and understanding of key processes based on years of experiments and modelling (e.g. Wang et al., 2010; Deissmann et al., 2025).

6.2 Modelling radionuclide migration at the disposal cell scale under perturbed conditions

This section compiles repository-scale modelling studies for high-pH (alkaline), organic-ligand, nitrate and sulfate plumes released from low and intermediate level radioactive waste (L/ILW) repositories into different surrounding host rocks. It is intended to give an overview on how national waste-management organisations (WMOs) and regulators assess their development and effects on host rock properties.

6.2.1 Alkaline plumes

Repository-scale (or cell scale) modelling attempts are available in the literature for alkaline plumes in the host rock, which are driven by national WMOs. However, of these, very few consider the simultaneous impact on radionuclide migration.

For fractured crystalline rocks, SKB undertook several modelling studies to simulate cement-grout degradation and a hyper-alkaline plume advancing tens of metres into Forsmark's fracture network over 10 kyr (Sidborn et al., 2014; Molinero et al., 2016). In the same line, Posiva also assessed the extent of an alkaline plume due to grout degradation at Onkalo via modelling (e.g. Soler et al., 2011). In turn, Posiva assessed the potential migration of an alkaline plume from the LILW repository at mid-depth towards the spent fuel repository at full depth via the fractured granite host rock using advanced models (Höglund et al. 2018). Finally, Trinchero et al. (2020) proposed a smart K_d approach and used the code iFM (interface to MARFA) and a large-scale reactive transport model implemented in PFLOTRAN (millions of cells) to study the effect of an hyperalkaline plume in Forsmark site, generated by cement grout degradation in the fractures, on cesium migration. They included a model for caesium sorption onto magnetite from (Granizo and Missana, 2006). The results of caesium transport clearly showed the effect of the spreading of the high pH plume on caesium sorption, when comparing the resulting breakthrough curve to that computed using a constant K_d value.

For argillaceous formations, Nagra assessed the impact of an alkaline plume on the retention capacity of several radionuclides in Opalinus clay (Bradbury and Baeyens, 2004), coupling a pH plume with evolving K_d values for Performance Assessment. This, in combination with the quantification of the alkaline plume extent (estimated in 1-2 m range at 100 kyr in Leupin et al. 2016) can be used to estimate the effect of an alkaline plume on radionuclide migration over the cell scale. An example of such study

combining reactive transport and radionuclide migration at a cement-claystone interface was presented by De Windt et al. (2004) using 1D simulations.

6.2.2 Organic plumes

Disposal-scale organic plume modelling has also been addressed in the literature, although to a much lesser extent than alkaline plume development. A summary of published work by WMOs and from scientific collaboration is given here, with focus on isosaccharinate (ISA), EDTA, NTA, and gluconate.

For fractured crystalline rocks, SKB assessed the initial content and evolution of ISA, gluconate, and NTA in the LILW SFR repository (Keith-Roach et al., 2014) and then studied the spread of organic complexing agents around the repository using reactive transport modelling (von Schenck and Källström, 2014). Höglund et al. (2018) also quantified the potential migration of ISA from within the LILW repository towards the SNF repository and concluded that dilution along the downstream flow path of the host rock would be sufficient to decrease the ISA concentrations to negligible values at SNF repository depth.

In clayey rocks, Nagra does not consider any sorption reduction factor for the potential impact of organics on radionuclides mobility in Opalinus clay or the Callovo Oxfordian claystone, respectively, in performance assessments, given the low concentration of organic matter in Opalinus porewater (Bradbury and Baeyens, 2003). On the contrary, for the case of Boom clay in Belgium and the Callovo Oxfordian claystone in France, ONDRAF/NIRAS and Andra, respectively, consider the impact of organics on the transport and retention parameters of some radionuclides (Bruggeman and Maes, 2017; Andra, 2025).

6.2.3 Saline plumes: NO_3^- / SO_4^{2-}

In clayey rocks, ONDRAF/NIRAS studied the geochemical perturbation of Boom Clay resulting from the release of a $NaNO_3$ plume from Eurobitum waste (Bleyen et al., 2018). They showed, by means of reactive transport modelling using HYTEC and Phreeqc, that the nitrate concentration falls below 10 mM within 8 m from the interface with the gallery, while the sulfate concentration front is buffered by gypsum saturation. Previously, Weetjens et al. (2006) determined using 1D axisymmetric simulations of diffusion of nitrates in the Boom clay that the maximum concentrations close to the gallery are around 1 M and would decrease to 0.1 M and 0.01 M at 10 and 30 metres from the gallery, respectively. They also stated that these high concentrations could persist more than 10 kyr. No attempts to couple the saline plume to radionuclide migration was included in those studies.

Höglund et al. (2018) simulated the release of salt concentrates in the waste for Posiva considering the composition from the SFR repository given that specific data for the VLJ Finnish repository was unavailable. However, their modelled domain did not consider the far-field and only reactions with the concrete barriers were included.

Grivé et al. (2014) simulated the long-term (10 kyr) geochemical interaction of highly saline radioactive waste from a LILW repository in claystone with the surrounding near-field materials and host rock, including concrete from waste packages, backfill, vault walls, and the Callovo-Oxfordian (Figure 18). They considered a set of batches, 1D and 2D reactive transport simulations aimed to estimate the extent of claystone affected by the high ionic strength released from the waste. They considered explicitly how salinity conditions affect solute transport and the mobility of uranium in the entire system.

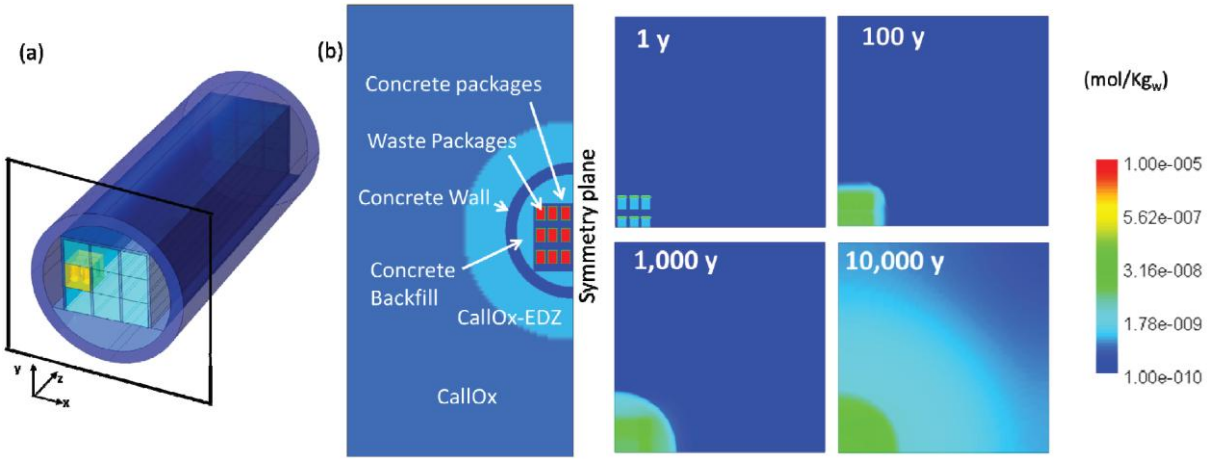

Figure 18: *Schematic representation of the vault studied by Grivé et al. (2014): 3D view (a), half the 2D cross-section analysed (b), and aqueous uranium concentrations up to 10 kyr (right).*

As part of the development process of repository concepts for radium-bearing waste (from REE purification and treatment) on a shallow underground repository in clay-rich geological formation (Tégulines clays), Grivé et al. (2017) assessed the fate of Ra in combination with a nitrates plume over a 10 kyr period. A 2D transversal section including the clay cover and backfill and the host rock was used in the reactive transport simulations with iCP. The waste porewater chemistry considered a high ionic strength (1.5 M) caused by the release of nitrate and ammonium from the NH_4NO_3 salt. The key outcome was that Ra release is highly buffered by the clays, decreasing the radium plume in the clay-rock formation and cover by almost 3 orders of magnitude from the initial activity.

6.2.4 Thermal perturbations

Modelling thermal perturbations in the near field of radioactive waste repositories has been studied extensively and it is not intended here to address the effects of temperature on the hydromechanical (HM) response nor on the reactivity of the near field materials. Bildstein et al. (2019) briefly reviews the role of TH couplings on the reactivity of steel-bentonite-concrete interfaces and as part of the EURAD project there are several overviews on the subject (Neeft et al., 2025; Deissmann et al., 2025).

Pekala et al. (2015) and Silva et al. (2017) studied the thermal perturbation effects on radionuclide mobility around a high-level waste cell in the Callovo Oxfordian claystone using reactive transport modelling in 2D implemented in iCP. They considered cation exchange and surface complexation reactions for radionuclide retention and assessed the long-term (100 kyr) migration of radionuclides (U, Th, Sr, Cs, Pu, Ni, Tc and Se) using mechanistic mineral-specific retardation models defined separately for each radionuclide, considering retardation competition effects from the major background dissolved elements (e.g. Ca, Mg, K and Sr).

Sookhak Lari and Mallants (2022) studied the effect of a heat pulse generated by radioactive decay on radionuclide migration in a fully saturated porous medium to determine the role of buoyancy (thermally driven fluid flow) on transport. The buoyancy effect was shown to have limited impact on radionuclide transport, suggesting that simpler models can be used without loss of accuracy.

6.3 Links with the Safety Case

For crystalline rocks, SKB and Posiva seem to base their assessments of radionuclide transport on a two-step process, in which based on reactive transport modelling of perturbations (e.g. Molinero et al., 2016, Keith-Roach et al., 2014; von Schenck and Källström, 2014; Höglund et al., 2018), the properties used for radionuclide transport simulations (e.g. K_d values that are constant in time) are then adapted (SKB, 2014; SKB, 2015). For saline plumes, no impact on radionuclide transport seems to be considered.

In clayey host rocks, Nagra predicts a limited alkaline plume in the LILW repository (Leupin et al., 2016), so that radionuclide transport parameters are largely unaffected in the host rock. In the same way, modifications of K_d values due to other types of plumes (saline, organics) are ruled out or deemed to be of limited importance.

Andra also uses a simplified approach to model the effect of perturbations on radionuclide mobility to support the safety assessment (Andra, 2016). Processes are decoupled with first the modelling of the spatial and temporal extent of the perturbation and then modelling of radionuclide migration directly integrating the effect of the perturbation on the governing parameters (e.g., solubility, K_d, or diffusion coefficient). This approach requires establishing laws defining how parameters are affected by the perturbations. For instance, these laws define how the K_d of radionuclides decrease according to the concentration of ISA or the ionic strength, which must be determined from experimental data. This type of approach is particularly adapted to deal with a large number of situations (with several radionuclides, organic compounds, waste inventory…). However, the decoupling of the processes leads to several limitations such as the extension of the perturbation fixed to model the migration of radionuclides or the impossibility of dealing with cumulative perturbations.

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7. Conclusions

This state-of-the-art document summarizes key information pertaining to the technical work performed in the RAMPEC work package of EURAD-2. The aim of the present SOTA is to provide general information on the topics addressed in RAMPEC. In addition, context is provided on the present technical knowledge base which the presently ongoing studies in RAMPEC are dedicated to improving. The topics covered in this SOTA reflect the structure of RAMPEC and include chapters on relevant issues for clay, crystalline and cement systems and sub-systems. This is complemented by a discussion on the modelling of radionuclide migration in perturbed systems as well as aspects related to upscaling and disposal cell modelling.

It is important to consider that the present initial SOTA will be updated at towards the end of the 5-year duration of RAMPEC. The updated, final SOTA version will highlight the new technical results generated in the experimental and modelling Tasks in RAMPEC and indicate the main results and impact in an integrated way.

The following paragraphs summarize the principal conclusions and key insights derived from this initial SOTA report on the relevant topics for RAMPEC.

Radionuclide migration processes in **clay host rocks** have been extensively studied and are generally well understood under undisturbed conditions. However, most of the existing knowledge and supporting data relate to such undisturbed states. In simplified and often conservative approaches, the disturbed zone of the host rock is commonly assumed to provide no retention capacity. As scientific understanding advances, there is increasing interest in moving beyond this conservative assumption by explicitly considering radionuclide retention and migration processes within the disturbed region. This allows safety margins to be quantified more realistically and increases confidence in the overall performance of the disposal system through a more advanced process understanding. Within RAMPEC, the focus is on perturbations induced by temperature, chemical plumes (e.g. alkaline plumes, variations in ionic strength, and organic complexants), and partially saturated conditions.

Studies investigating the effect of temperature on species transport behaviour in clay materials remain limited. Most attention has been devoted to the impact of temperature on diffusion processes, which can generally be described using Arrhenius-type relationships or the Stokes–Einstein equation, although further investigation is still warranted. In contrast, transport processes occurring under a temperature gradient have so far mainly been assessed theoretically and require experimental validation. With regard to sorption behaviour at elevated temperatures, the available experimental data remain scarce, highlighting the need for additional studies. This is closely linked to the further development and extension of thermodynamic databases, including the implementation of temperature-dependent correction functions.

The interface clay/cement has been studied in detail which led to a good understanding of the processes at hand that may influence the transport behaviour. In contrary to the studies at the interface, studies on radionuclide transport in alkaline perturbed clays are scarce. However, based on the available knowledge coming from sorption studies, clay/cement interface studies and model developments, it is now possible to set-up well defined experiments and to achieve a better interpretation through modelling of the outcome of these experiments.

The effect of ionic strength (not including extremely high ionic strength) on sorption and diffusion in clays has reached a good level of understanding. However, when it comes to sulfate and nitrate plumes, not only the ionic strength changes, it also influences the geochemical behaviour of both the host rock and

the radionuclides. Transport studies on clay rocks that have undergone a sulfate or nitrate perturbation remain limited and require further attention.

For the small organic molecules, there is a need to gather basic interaction data (complexation, sorption ternary systems) of the organic species with radionuclides and with solid surfaces to grow the database (complexation constants, surface complexation constants). For the natural organic matter (humics, fulvics, kerogen), there remains a need to understand its stability (degradation under influence of perturbations as temperature, saline plume, alkaline plume) and characteristics of the perturbed organic matter/degradation products, robust ways to describe radionuclide interaction and parametrisation (general complexation constants, Tipping model, Nica-Donnan).

Studies evaluating the effects of saline plumes (e.g., nitrate- and sulfate-rich groundwater) on sorption behavior in **crystalline rocks**, together with normalization of sorption coefficients to BET-measured surface areas, provide more realistic assessments. The pore structure of crystalline rocks - characterized by extremely low matrix porosity, heterogeneous pore-size distributions, variable connectivity, and the presence of both microfractures and macrofractures - strongly influences radionuclide mobility. Diffusion into the rock matrix can significantly enhance retardation of sorbing species, but heterogeneous fracture apertures, channelling, and large-scale connectivity can accelerate transport, sometimes can reduce the overall retardation capacity. Anion exclusion in nanometer-scale pores further diminishes the mobility of anionic species relative to neutral or cationic tracers.

Fracture fillings and secondary mineral phases exert an additional level of control on radionuclide migration in crystalline systems. Over geological timescales, fractures may develop coatings or infillings of clays, carbonates, zeolites, or sulate and carbonate solid solutions whose crystal sizes and porosity distributions differ significantly from those of the unaltered host rock. These changes can both enhance and diminish transport pathways by modifying permeability, tortuosity, and sorption capacity. Solid solution formation with minerals such as barite, celestite, or calcite can effectively immobilize certain radionuclides - especially radium or actinides under reducing conditions - while redoxactive minerals including pyrite, biotite, and magnetite may transform iodine or selenium into less mobile oxidation states, sometimes mediated by microbial processes. The complexity of these multi-scale, dynamic processes underscore the main challenge in crystalline environments: the necessity to capture heterogeneous fracture networks, evolving geochemical boundary conditions and coupled thermal-hydraulic-mechanical-chemical processes in models and codes.

Since more realistic modelling approaches require data that reflect close to natural conditions, the RAMPEC programme has established a coordinated experimental and analytical workplan to address major knowledge gaps concerning radionuclide retention and migration in argillaceous, granitic, and cementitious systems under perturbed conditions. For crystalline systems, this includes systematic characterization of intact and crushed rock samples from several European crystalline host formations, controlled sorption and desorption experiments, flowthrough and diffusion studies, and detailed micro and nanoscale imaging of mineralogical and pore structural features using advanced spectroscopic and microscopic methods. Perturbations addressed in these studies include changes in porewater chemistry (such as variations in pH, ionic strength and ligand concentrations), the presence and evolution of secondary minerals in fractures, and the effects of pore structure variability on transport. The investigations focus on radionuclides of high safety relevance - including Se, Ba, Ra, Cs, Na, Ni, Cl, I, and HTO - and aim to generate data that feed directly into mechanistic reactive transport models developed in subsequent tasks. These integrated efforts are intended to reduce uncertainties in safety assessments, improve the robustness of predictive models, and enhance scientific understanding of long-term radionuclide behaviour in crystalline rock repositories.

As **cement** is considered in all disposal scenarios as radioactive waste confinement or radioactive waste stabilization matrix or as part of the engineer barrier system, a good understanding of radionuclide

behaviour in cementitious systems under equilibrium conditions has been derived from past experimental studies in simplified reference systems. The degradation of the cement matrix by water is well studied in literature, especially for CEM I type cement. Coupling the degradation of cement by other types of perturbation (i.e. temperature, saline plume, organic plume, carbonation…) or predicting radionuclide migration through real old concrete specimens remain challenging. From the initial literature review, specific studies in RAMPEC were selected in order to feed migration experimental databases and to help the development of macroscopic mechanistic models. The studied systems were selected to emphasise their potential impact onto radionuclide migration. For example, studies in RAMPEC are to be performed in the presence of organics (either cement additives or isosaccharinate, ISA, as complexing ligands).

Concerning perturbations occurring by desaturation or atmospheric carbonation, it is well described in literature that these perturbations can lead to cracks into the cement matrix, thus increasing transport paths in the porous media. When only desaturation is occurring, the effective diffusive coefficient value for non-reactive species is lower. These results are not confirmed for all radionuclides of interest, all types of cement matrix and the evolution with cement degradation is unknown. In the experimental programme of RAMPEC, studies are planned to be performed as a function of humidity in the presence of highly sorbed species and in different types of cement matrix (hardened cement paste, mortar and concrete).

Temperature increase may also affect radionuclide migration in cementitious media. Several cases can be drawn: (i) temperature affects the radionuclide mobility by changing thermodynamic and physical constants (solubility, sorption or diffusion), (ii) temperature affects the stability of the cement matrix, and (iii) a more complex case arises from the combination of both cases. A predictive model able to describe all cases is lacking due to a lack of data. The proposed studies in RAMPEC performed as a function of temperature will provide novel experimental data to feed into database on radionuclide migration.

Saline perturbation in cementitious media is one of the main perturbations described in literature. Portland-type cement degradation by a nitrate plume can damage the mineralogy assembly and modify the porosity (clogging or opening). The effect of such a very high saline plume on other cement systems is less reported in literature. Radionuclide solubility and sorption at high ionic strength is also well published in NaCl-content systems. Diffusion data are present for reference species (HTO, chloride or caesium). Due to the need of long-term experiments to obtain diffusion parameters, these are scarce. The aim of RAMPEC is to preferentially feed the gap of knowledge on saline plume effect on radionuclide migration data. In the experimental programme of RAMPEC, all proposed studies will be performed as a function of salinity using different types of soluble salts and at varying ionic strength. The target is to support the development of a macroscopic mechanistic model.

In addition to the experimental laboratory work performed in RAMPEC, significant activities are dedicated to performing **modelling** of the investigated systems. The ability to model perturbations in clay, fractured rock, and clay systems depends fundamentally on the development and validation of suitable codes and databases. Existing modelling approaches are generally designed and implemented for specific domains of validity and must be appropriately extended (and benchmarked) to ensure that representative results are obtained outside these conditions – particularly when considering temperature perturbations, where temperature-dependent parameterisations of key database entries are not universally available. Modelling in RAMPEC is conducted in close partnership with experimental studies to strengthen the validation, but the true value of model application to perturbed systems is gained from simulating scenarios that are not directly accessible in an experimental sense. By treating a suitably validated model as a platform for computational experiments that simulate relevant physical scenarios, important additional insight can be unlocked.

Modelling approaches for organic, saline and alkaline perturbations, and their impact on radionuclide migration at the disposal cell scale (from meters to decameters), are critical for assessing the safety and

performance of radioactive waste repositories. Modelling at this scale involves scaling issues from both the perspective of experimental data and models.

- Lab-based (mock-up) and in situ experiments in underground research laboratories demonstrate that perturbations can alter the mobility of radionuclides, but the effects of combined perturbations and migration remain understudied.
- Upscaling techniques aim to simplify complex models by integrating homogenized parameters while preserving essential information about small-scale processes, thus enabling predictions about the behavior of radionuclides over large spatial and temporal scales. However, in the context of perturbations, up-scale approaches remain underdeveloped.

Simplified approaches are used to incorporate perturbations into integrated level performance assessments. However, these methods have limitations, such as process decoupling and difficulty in addressing cumulative perturbations. Comparisons of such simplified approaches with reactive transport modelling that incorporates geochemical processes are still lacking but will be implemented in Task 5 of RAMPEC.