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Contribution of the results of the CEBAMA project to decrease uncertainties in the Safety Case and Performance Assessment of radioactive waste repositories

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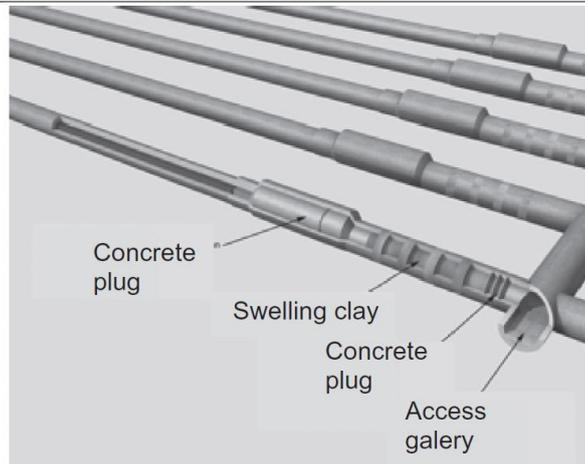
Abstract

Cement-based materials are key materials used in repositories of low, intermediate and high-level waste in any host-rock concept. These materials are used as waste forms, liners, seals as well as structural components. The CEBAMA project (2014-2019) has been an initiative granted by the European Commission under the Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM), focused on the study of cementitious materials. The project has addressed key issues of relevance for long-term safety and key scientific questions related to the use of cement-based materials in nuclear waste disposal applications. This publication presents the advances resulting from the research undertaken in the CEBAMA project, with special emphasis on their contribution to decrease uncertainties in the Safety Case and the Performance Assessment of radioactive waste repositories. The analysis is presented in three different axes, in coincidence with the lines of research of the project: degradation of cement-based materials and its impact on cement/clay interfaces; retention of safety relevant radionuclides and toxicants on cement-based materials and modelling advances in cementitious related systems. The research investigations have provided important new insights on process understanding and model developments which have significantly decreased the level of uncertainty.

1 Introduction

Cement-based materials are widely used in radioactive waste management. This type of materials conforms sections of the engineered barriers in the form of concrete plugs and backfill in repositories for High Level Waste (HLW) disposal (see Figure 1A). They are also used for stabilisation of the excavations comprising access tunnels to the deep geological repository as shotcrete applications (see

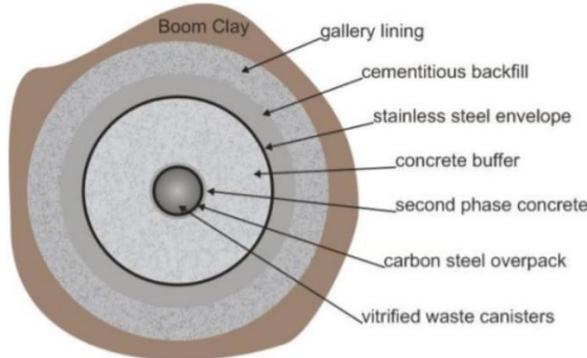
Figure 1B) and planned to be used in the design of the supercontainer for deep geological disposal of HLW in the case of Belgium (see Figure 1C). In Low and Intermediate Level Waste (LILW) management, cementitious materials are used for waste conditioning and immobilisation, for construction of waste containers, or for the construction of the deep or surface facilities where the waste is located (see Figure 1D), among other uses. It is a fact that cementitious materials are or will be present in large amounts in the radioactive waste repositories and their behaviour and long-term performance deserves special attention when assessing the future evolution of these type of facilities.



A)
*Disposal cells for ANDRA (France)
B-type wastes.*



B)
*Shotcreting of a gallery in
ONKALO (Finland). Photo ©
POSIVA*



C)
*Belgian supercontainer concept for
high-level waste.*



D)
View of the LILW facility of El Cabril (Spain). In the insert, a picture of one of the drums with waste conditioned with cement.

Figure 1. Illustrations showing some of the applications of cement-related materials in radioactive waste management.

Hydrated cement evolves in contact with groundwater and produces highly alkaline leachates that may induce changes in the surrounding environment. As it degrades, the composition of the leachates and the solid phase vary. Atkinson (1985) defined the evolution of cement in three stages: (i) stage of degradation I, producing very alkaline leachates (pH over 13) rich in alkaline metals (Na^+ , K^+); (ii) stage of degradation II, during which the pH of the leachates is dominated by the presence of portlandite ($\text{Ca}(\text{OH})_2(\text{s})$) and fixed at a pH around 12.5; (iii) stage of degradation III, dominated by Calcium-Silicate-Hydrates (C-S-H) decreasing their the Ca/Si ratio with continuous leaching over time. This last stage is characterised by pH around 11 until the cement paste is completely degraded and the system is generally dominated by carbonates and the pH reaches intermediate values around 8.5. Table 1 shows the results obtained by Kosakowski et al. (2014) on composition of the water and the main solid phases retained in concrete for each degradation stage.

The extent of cement degradation depends on the rate at which it interacts with water and changes its microstructure, potentially altering its properties of transport of water and physical stability. Cement degradation can also influence the performance of other components of the repository system, such as the (bentonite) buffer or the host-rock.

Performance of cementitious materials used in radioactive waste applications must be ensured for extremely long lifetimes (hundreds and even thousands of years), and alterations due to interactions with water must be considered. With the aim to minimize the possible impact of cement in the repositories, new "low-pH" cementitious material formulations based on replacing cement with alternative hydraulic binders such as silica fume, fly ash and/or blast furnace slag are being tested for nuclear waste applications. Low-pH concrete generates a lower alteration of the pH in contact with the surrounding environment and, therefore, also a potentially lower impact to the bentonite/clay buffer and the host-rock. Cement hydration is exothermic and in the hydration of low-pH concrete the temperature increase is generally lower. This fact is expected to positively impact the long-term durability of the material e.g. by reducing the formation of cracks in concrete (Cau-dit-Coumes et al., 2006; Codina et al., 2008).

Table 1. Composition of the water in contact with concrete and major solid phases in the composition of concrete at different degradation stages of concrete (I to III). Data from Kosakowski et al. (2014).

	Stage I	Stage II	Stage III
Porosity (%)	20	20	18
pH	13.1	12.54	11.07
Eh (mV)	-529.9	-198.1	-1809.7

Ionic strength (m)	0.168	0.0983	0.15
pCO ₂	-13.1	-13.1	-9.65
Solutes (mol/L)			
Na	$9.68 \cdot 10^{-2}$	$4.21 \cdot 10^{-2}$	0.104
K	$7.27 \cdot 10^{-2}$	$3.30 \cdot 10^{-3}$	$2.55 \cdot 10^{-2}$
Ca	$2.43 \cdot 10^{-3}$	$1.80 \cdot 10^{-2}$	$5.35 \cdot 10^{-3}$
Sulphate	$6.24 \cdot 10^{-4}$	$4.70 \cdot 10^{-5}$	$7.81 \cdot 10^{-3}$
Chloride	$2.46 \cdot 10^{-4}$	$3.74 \cdot 10^{-2}$	$1.23 \cdot 10^{-1}$
Carbonate	$4.46 \cdot 10^{-5}$	$8.04 \cdot 10^{-6}$	$1.67 \cdot 10^{-5}$
Si	$4.34 \cdot 10^{-5}$	$3.42 \cdot 10^{-5}$	$3.45 \cdot 10^{-4}$
Al	$2.61 \cdot 10^{-5}$	$6.89 \cdot 10^{-6}$	$1.15 \cdot 10^{-4}$
Fe	$2.11 \cdot 10^{-7}$	$5.58 \cdot 10^{-8}$	$3.86 \cdot 10^{-8}$
Major solid phases			
	C-S-H	C-S-H	C-S-H
	Portlandite	Portlandite	
	Ettringite(i)	Ettringite(i)	Ettringite(i)
	Monocarbonate(ii)	Monocarbonate(ii)	
	Calcite(iii)	Calcite(iii)	Calcite(iii)
	OH-hydrotalcite(iv)	OH-hydrotalcite(iv)	OH-hydrotalcite(iv)

i) Ettringite stands for aluminium ferric oxide containing three molecules of anhydrite (AFt) $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$; (ii) Monocarbonate stands for $\text{Ca}_3\text{Al} \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$; (ii) Calcite: $\text{CaCO}_3(\text{s})$; (iii) OH-Hydrotalcite: Al substituted brucite ($\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2$)

The CEBAMA project (2014-2019) has been an initiative granted by the European Commission under the Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM). The project has addressed key issues of relevance for long-term safety and key scientific questions related to the use of cement-based materials in nuclear waste disposal applications. The scientific quality and impact of the project builds on joining the best expertise available to tackle these problems and emphasising how the knowledge can be applied in Performance Assessment and the Safety Case. The project has involved 27 beneficiaries consisting of Research Institutes, Universities and SMEs from 9 EU members countries, Switzerland and Japan.

To ensure that the research of the project was properly directed towards application of the results, CEBAMA set up a group of End Users, formed by representatives of European radioactive waste management organisations from 9 countries: ANDRA (FR), COVRA (NL), ENRESA (ES), NAGRA (CH), ONDRAF/NIRAS (BE), POSIVA (FI), RMW (UK), SKB (SE), and SURAO (CZ). These organisations come from countries in very different stages of implementation, so that the implication that the results of CEBAMA have on their interests may vary from case to case.

The project was organised in three scientific and technical work-packages. The focus of the first work package has been the study of the cement evolution and of the interfaces between cementitious materials with natural host-rocks or engineered barrier components. The aim was to quantify relevant alteration processes and how they may impact the physical properties of the materials. The second work package focused on the study of the behaviour of several relevant radionuclides or toxic elements in the presence of cementitious materials under different degrees of alteration or under conditions imposed by the presence of these materials. Finally, the third work package developed, tested and benchmarked numerical models that were then used to quantify the evolution of the properties of cementitious materials under the conditions expected to prevail in experiments and in a radioactive waste repository. The publications of Altmaier et al. (2019); Vehmas et al. (2019);

Grambow et al. (2019) and Idiart et al. (2019) present an overview of the main scientific highlights of each one of the work packages and the interested reader is directed to those publications for a complete and more detailed description of the scientific advances of the project.

The research developed within CEBAMA has been published in 29 peer-reviewed publications, and 40 additional publications are submitted for publication or in preparation at the present moment. The intention of this manuscript is not to repeat what has been or is in process to be published, but to highlight the relevance that some of the research undertaken within CEBAMA has for the development of the Safety Cases and the Performance Assessment of the repositories of high, low and intermediate level wastes related with the use of cementitious materials.

According to IAEA (2012) the Safety Case is the collection of scientific, technical, administrative and managerial arguments and evidences in support of the safety of a disposal facility, covering the suitability of the site and the design, construction and operation of the facility, the quantitative assessment of short- and long-term risks, as well as more qualitative safety indicators and assurance of the adequacy and quality of all of the safety-related work associated with the disposal facility. Safety Assessment, an integral part of the Safety Case, is driven by a systematic assessment of radiation hazards.

CEBAMA has improved the knowledge base for the Safety Case via the following specific items: (i) Safety impact of microstructural and porosity changes of cementitious materials, (ii) Safety impact of cement degradation, (iii) Development and implementation of long-term models, (iv) Decrease of uncertainties in radionuclide retention processes, (v) Development of modelling expertise, benchmarking and methodologies, and (vi) Upscaling modelling in time and space. A specific focus was put on the investigation of low-pH concrete materials, and hence conclusions can be drawn from the work within CEBAMA on the potential use of this relatively new material in the Safety Case.

The state of the different waste management programmes represented in CEBAMA varies from case to case. While some countries, such as Finland, Sweden and France, are in an advanced state with construction license applications of Deep Geological Repositories for HLW in place or submitted, some others, such as the UK, Germany or the Netherlands are still in a stage where generic repository concepts are being considered. The case of repositories for LILW is different, as most of the countries have in place a final disposal solution either on the surface or at depth, for this type of wastes.

In the following sections, the main highlights of the project are described with special emphasis on their relevance for the Safety Case and Performance Assessment of repositories for radioactive waste disposal. The highlights are organised in three main sections, corresponding to the work packages of the project and to the input received from the waste management organisations participating in the Group of End Users of the project: 1. Advances on the study of cement interfaces. 2. Advances on radionuclide retention, and 3. Modelling advances.

2 Advances on the study of cement interfaces

Only limited public experimental data on laboratory and field scales were available for the low-pH concrete / bentonite system when the CEBAMA project started in 2015. In the last years the impact of low-pH concrete materials on surrounding clay host-rocks (e.g. Opalinus clay) has started to be investigated (Savage and Benbow, 2007, Dauzères et al. 2014, Jenni et al., 2014, Lerouge et al.

2017) and the impact that these degradation processes can have in radionuclide migration have never been studied before.

The Performance Assessment in the various countries taking part in the project vary from each other regarding the consideration of the clay/concrete interface and its impact on the transport and mechanical properties. In the case of SKB (SE) the concrete/clay interfaces found in the low and intermediate level waste repository (SFR) are those corresponding to concrete and bentonite, as the hosting rock is granite. In the analyses made by SKB, the properties of these materials are considered to vary over time with different values during different time periods (see e.g. Höglund, 2014, Table 9-1). SKB follows a conservative approach and neglects the possible beneficial properties of the interface such as a decrease in porosity which may prevent water transport or sorption properties. In its conservative approach, interfacial reactions are only considered as contributing to the degradation of the materials of the engineered barriers (concrete and bentonite). In the case of NIRAS/ONDRAF (BE), the evolution in time and space of the cement mineralogy is modelled to understand their consequences on the transport properties of these structures. Regarding the Belgian surface disposal for IL-LILW, although the interfaces between cement-based materials and the environment are taken into account, the processes occurring are not considered pertinent from the point of view of altering the performance of the repository, and the main process considered to alter cementitious properties is carbonation. NAGRA (CH) assumes an increase in the hydraulic conductivity of the liner between bentonite and the Opalinus Clay (OPA) host-rock in the HLW repository due to cracks forming at the interface between liner and host-rock. The bentonite adjacent to the liner is affected by the high pH-plume coming from the low-pH cement. This results in a slow local porosity increase in the bentonite adjacent to the liner. The calculations conducted to assess the impact of this interaction show no impact on dose estimation even after the potential degradation of 20 cm of bentonite (see Figure 6.2-2 in NAGRA, 2010). The transport/sorption parameters in the bentonite barrier are kept constant as the pH buffering capacity of clay is high. Only a small effect on sorption/solubility of some of the radionuclides is considered (see Table A3.4-4 in Wieland 2014) besides the loss of swelling capacity of the bentonite affected by its transformation from sodium to calcium bentonite due to cement degradation. The concrete and the host-rock interfaces are neglected because the interaction zone is much smaller compared to the OPA thickness. The same applies to the Swiss LILW repository: due to the diffusive regime imposed by the clay host-rock, the maximum extent of the concrete-clay interaction would be about 2 m into Opalinus Clay, which is considered negligible in comparison with the OPA thickness. COVRA (NL) considers the positive effect of the interface in the increase of containment in its Safety Case although no specific calculations accounting for this effect are implemented in the Performance Assessment. ANDRA (FR) considers the use of low-pH cementitious materials to give mechanical support for bentonite seals as they slowly hydrate, helping to isolate the sections of the repository system.

The studies within CEBAMA were, therefore, very relevant to feed conceptually the Safety Case and to guide calculations for the Performance Assessment of deep and surface repositories where concrete-clay interfaces are encountered. At this point, it is relevant to clarify that for some countries these concrete/clay interfaces occur only at the engineering barriers (concrete/bentonite) while for others, such as France, Belgium and Switzerland, the host-rock is mainly composed of clay so that the interfaces have relevance also when discussing about the effect on the host-rock.

From the revision of the Safety Cases and Performance Assessment exercises it is clear that, although in some of them the interfaces as considered (see previous paragraph), there are no clear indications on whether the use of low-pH cementitious blends can be more beneficial than a typical high pH Ordinary Portland Cement (OPC) alone. This is the reason why within CEBAMA low-pH cementitious blends were tested. A specific CEBAMA reference material was prepared to be used by

all partners interested. This facilitated comparison between results (see Vehmas et al., 2019 for details).

Vehmas et al. (2019) studied the effect of bentonite water on cement pastes through-diffusion experiments and observed that the Ca/Mg ratio was kept constant and equal to the initial one at 400 μm of the interface suggesting that the reactive front developed this depth (i.e. 400 μm) in 6 months. The same studies did not observe precipitation of calcite in the pore structure but only on the holes at the surface between cement and bentonite. The results indicate that the use of low-pH cement does not minimize the extent of reaction between bentonite and concrete and it does not represent any advantage regarding ionic transport across the boundary.

Bourbon et al. (2017) studied the evolution of two different low-pH concrete formulations under in-situ emplacement in the Bure underground research laboratory: i) T_{CV}, rich in fly-ash and ii) T_L, rich in slag. The materials were specifically designed to fulfil low physical and chemical impact in their surroundings: low temperature hydration and low-pH impact. Two walls, one with each one of the materials were built in the tunnel. One of the surfaces of each wall was exposed to the air ventilation of the tunnel and submitted to atmospheric carbonation while the other surface was in contact with the Callovo-Oxfordian (COx) claystone. In both cases, a small impact on the temperature evolution at the surface was observed, with a maximum of 12°C difference with the ambient temperature at the surface of the walls and 17°C with the bulk of the wall. Samples taken from the thin walls to perform chemical and physical analysis indicated no significant evolution/transformation of neither concrete at the interface with the COx argillite, with the absence of cracks at a large scale. No relevant chemical reactivity in the concrete was observed within the time frame of the experiments and very low deformation was observed after a few years of the emplacement of the walls (in the range 100/150 $\mu\text{m}/\text{m}$). These results are of high interest for the assessment of the adequacy of low-pH concrete materials performance in the repository. Additional analyses are on-going and for more details the reader is referred to the original reference in Bourbon et al. (2017).

Lalan et al. (2016, 2019) studied the influence of temperature on the behaviour of high pH-cement (CEM-I) and different low-pH concrete formulations in contact with argillite from Tournemire. Low-pH binder was initially designed to reduce the impact of cement matrix on the argillite. However, at 70°C, the results highlight an argillite degradation (clay-phase dissolution) not clearly observable with the CEM-I, certainly linked to the chemical transitory during the cement paste hydration. In addition, the cement alteration is clearly more important for the low-pH material (decalcification, M-S-H precipitation causing porosity opening) compare to the CEM I formulation.

Gaboreau et al. (2019) and Phung et al. (2018) studied the chemical degradation processes occurring at the interface between cementitious materials and Boom Clay (reference host-rock for the Belgian repository) with the focus on leaching and carbonation as the most dominant degradation processes. Interfaces between Concrete and Boom Clay materials, which have been in contact for 14 years in the underground Belgian research laboratory in clay (HADES), were investigated. The microtomography and autoradiography results on the alteration of porosity at the interface showed an increase in total porosity of the concrete interface due to Ca-leaching. This can be taken as an indication that clogging at the cementitious materials side might not occur, contrary to what is usually hypothesized. In contrast, the porosity in the clay side seems to decrease indicating some precipitations which may clog the clay pores in the long-term (see Figure 2).



Figure 2. In-situ interface between concrete and clay from the HADES laboratory. The materials have been in contact for 14 years (picture from Phung et al., 2018)

Liu et al. (2019) studied the interfaces between low-pH cement and bentonite. The results showed that the permeability of the interface sample is at the magnitude of 10^{-20}m^2 . This value is similar to the intrinsic permeability of the COx claystone and of high-performance concrete, what may be taken as an indication that the interface does not represent a weak zone of permeability.

Cuss et al. (2019) examined the temporal evolution of the host-rock/low-alkali cement interface in the French repository concept to changes in geochemistry, mineralogy and stress to assess their impact on the development of hydraulic permeability and strength (shear strength). Initial testing of fresh samples shows that the COx/TL interface has little strength, yet is an effective seal. One order of magnitude reduction in flow was seen through the re-hydration of the COx/TL interface.

The work of Bernard et al. (2019) represented a step ahead in the characterisation of magnesium silicate hydrate and the aged interfaces between cement pastes and OPA by micro-X-Ray diffraction.

Studies within CEBAMA of the interface between OPC and bentonite from the FEBEX experiment, after 14 years of interaction, and from lab tests of 10 years of duration allowed the identification of the main processes occurring at the interfaces (for details see Torres et al., 2018). The results were compared with short term alteration experiments (González-Santamaria et al., 2018) and the processes observed were alike, although occurring in much lesser extent in the case of the short-term experiments: Accumulation of Ca and Mg observed at the bentonite interface with concrete; penetration of Cl (up to 2-3 cm) and sulphates (up to 1-2 cm) was detected with a profile decreasing inside the concrete bulk. The kinetic of the process of Cl diffusion was modelled and the same effective diffusion coefficient was obtained from the long and the short-term experiments, what provides robustness to the value ($D_{\text{app}}=3\pm 0.8\cdot 10^{-12}\text{ m}^2/\text{s}$) for use in calculations supporting Performance Assessment and to the conceptual models feeding the Safety Case. The amount of ettringite is observed at the interface with simulated bentonite water also in both cases, the long-term and the short-term test. The comparison of granitic groundwater interacted with high and low-pH concrete indicate that, while in the first case an hyperalkaline water is generated starting at pH 13 and decreasing to values below 10 only after 1500 water exchange cycles, the pH in the second case is always kept below 9, showing the lower impact of the low-pH concrete on the groundwater pH.

Vasconcelos et al. (2018a,b) studied the evolution of the Nirex Reference Backfill (NRBV) concrete material and the CEBAMA low-pH reference material in contact with three different groundwater types representing the three concepts of host-rock for disposal of high level radioactive waste: granitic, clay and saline. NRVB is the backfill cementitious composition proposed by the British radioactive waste management agency (RWM, UK) to use in the repository. The results of the analyses of the solid after interaction with the groundwaters for one year (Thermo-Gravimetric

Analyses -TGA-, X-Ray Diffraction -XRD- , Nuclear Magnetic Resonance of ^{27}Al - NMR- , Scanning Electron Microscopy -SEM- and ^{29}Si NMR) indicated that the changes in the NRVB composition (and the expected impact in its solute transport properties) were minimised for the composition of the granitic groundwater (see Figure 3). This is an important conclusion as it sets the more adequate conditions to ensure the stability of the proposed material.

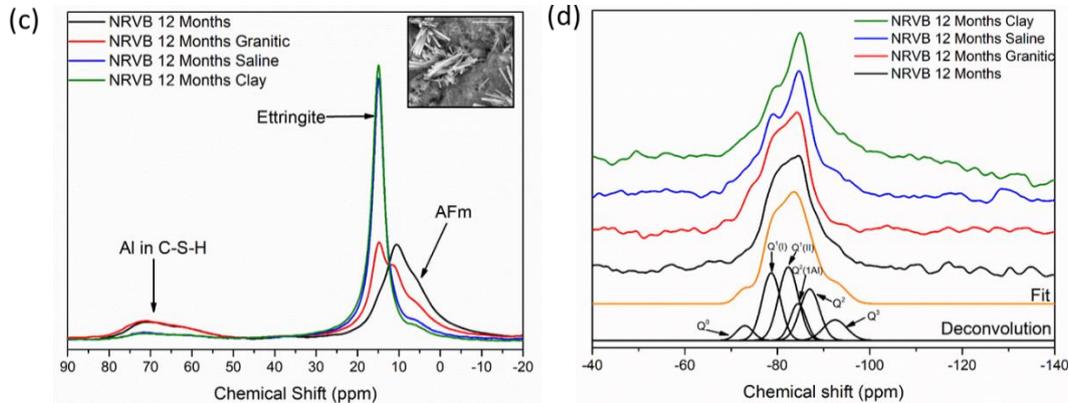


Figure 3. Comparison of NRVB samples exposed to three different groundwater solutions for 12 months, and comparison to blank (i.e. non-groundwater contacted) material: left: ^{27}Al NMR analysis; insert shows SEM images of ettringite needles; right: ^{29}Si NMR analysis and deconvolution.

Vehmas et al. (2017) studied the leaching of cementitious materials with Calcium to Silicon (Ca/Si) ratios from 0.2 to 3.1 when put in contact with deionized water, saline groundwater and saline bentonite porewater. The results indicated that the lower modification of the composition of the groundwater occurred for the saline waters, due to the common ion effect.

The methodological advances help underpinning robust scientific arguments to the Performance Assessment of repositories and the Safety Case. This must be put in context with the fact that several of the interfaces investigated in the project are aged, what can be taken as more representative of the processes of interest in the long-term assessment needed for radioactive waste management applications.

The main highlights can be summarised as follows:

- Concrete-clay interfaces can co-exist safely.
- The research of the project has provided a deeper understanding of impacts from material interface processes for more realistic description of the performance of the system.
- Although porosity changes with time have been observed and quantified at the interfaces, clogging effects on transport properties need further research.
- The use of low-pH cement contributes to preserving the properties of the clay as the lower release of calcium ions prevents massive transformation of the clay and dramatic loss of their swelling properties, although specific effects on transport of solutes are not yet clear.

3 Advances on quantifying and understanding radionuclide retention by cementitious phases.

The role that cement-based materials have on the retardation of radionuclides transport is especially interesting in the safety assessment of LILW repositories, where cement is ubiquitous and, as previously presented, used for waste stabilisation, mould and containers fabrication, and as backfill and construction material.

The Swedish waste management organisation, SKB, defines in its safety analyses the “Safety Functions” as “a role by means of which a repository component contributes to safety”. For the case of the repository of LILW in Sweden two safety functions are defined: limitation and retardation, on which the design of the SFR1 is based (SKB 2008). The main retarding material being the cementitious barriers.

In a similar way, in the LILW disposal systems of Switzerland, hydrated cement – or hardened cement paste (HCP) – is considered the main material that can retard the release of radionuclides in the case of water contact with the waste (Wieland, 2014). Aluminum-Ferric oxide phases ($\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ with one (AFm) and three (AFt) anhydrite molecules formed in the course of cement hydration) mainly control anion uptake in hard cement pastes, while the retention of metal cations is predominantly controlled by C-S-H phases.

Most of the current models accounting for radionuclides and toxicants retention on cement-related materials rely on the use of conditional distribution constants (Rd or Kd values) which are bulk values relating the concentration of contaminant in the solid phase with that in aqueous solution. Rd and Kd constants are lump parameters which include all the amount of sorbate which disappears from the solution after being contacted with a solid under a varying range of conditions (Gaona et al. 2012), independently on the actual retention process acting (sorption, precipitation, coprecipitation, occlusion, etc.). There are substantial amount of data in the literature compiled in reviews such as the ones of Wang et al. (2009) and Ochs et al. (2016), although the actual understanding of uptake mechanisms is limited by the scarcity of mechanistic sorption studies on safety-relevant radionuclides with support of spectroscopic investigations (see e.g. Pointeau 2000, Schlegel et al. 2004, Stumpf et al. 2004, Bonhoure et al. 2006, Vespa et al. 2006, Gaona et al. 2011, Tits et al. 2011, Gaona et al. 2013). The existence of these mechanistic models is important at the Safety Case and Performance Assessment level because they allow the justification of the selected Rd and Kd values.

CEBAMA has studied the interaction of different safety relevant elements with different cementitious solid phases by using synthesised cement phases such as AFm, AFt and C-S-H with different Ca/Si ratio, but also high pH cement pastes of different compositions (CEM I, CEM V).

The results obtained within CEBAMA have provided an increased understanding of the behaviour of several safety relevant radionuclides within cementitious materials in the repository environment, thus decreasing uncertainties with respect to relevant radionuclide retention processes. The results can be used to substantiate and justify assumptions made with respect to the radionuclide migration behaviour in safety assessments. How do specific radionuclides of interest behave in the presence of cement-based materials, or in media altered by the presence of these materials? CEBAMA addressed the behaviour of radionuclides or toxic elements which have high priority from the scientific and applied perspective in cement-driven environments: Be, C, Cl, Se, Mo, I, and Ra.

A large amount of data on the interaction of safety-relevant and toxicants elements with cementitious phases has been generated. This helps reducing uncertainties in the Safety Case and in Performance Assessment of repositories of radioactive waste.

3.1 Beryllium (Be)

Beryllium is a light element used as neutron reflector in nuclear reactors in order to use more efficiently the neutrons generated in the reactor. It is also used as neutron moderator which decreases the energy of the neutrons to better sustain the fission reaction (Tomberlin, 2004). Beryllium also represents a neutron source and protects metallic surfaces against corrosion. Beryllium in the waste comes from the dismantling of the nuclear reactors, mainly in metallic form. Beryllium is a toxic element which may represent a toxicological risk in Performance Assessment exercises. Publications on the discussion of the relevance of Beryllium in toxicological assessment of radioactive waste repositories (Thorne and Kautsky, 2016) concluded that although it may represent a toxicological hazard, the scarcity of thermodynamic data on solubility and speciation, as well as the lack of sorption parameters prevent an adequate assessment of its relevance. It has been considered as a toxic hazard for the UK repository as the dose calculations indicated concentration levels over the drinking water limit in the base case scenario (Thorne, 2007), while it has not been considered as relevant for other cases such as the Belgian concept of the repository.

Before, CEBAMA started, Beryllium has been assumed not to sorb onto cementitious-related materials. All the information contained in the supporting material to the Performance Assessment of repositories for low and intermediate level waste assumed no sorption (distribution coefficient $K_d=0$) of Be on concrete (Thorne, 2007; Wieland, 2014; SKB 2014; Wang et al., 2009). This assumption is based on the understanding that at high pH values, the speciation of Be is dominated by anionic species ($\text{Be}(\text{OH})_3^-$ and $\text{Be}(\text{OH})_4^{2-}$), as seen in Figure 4.

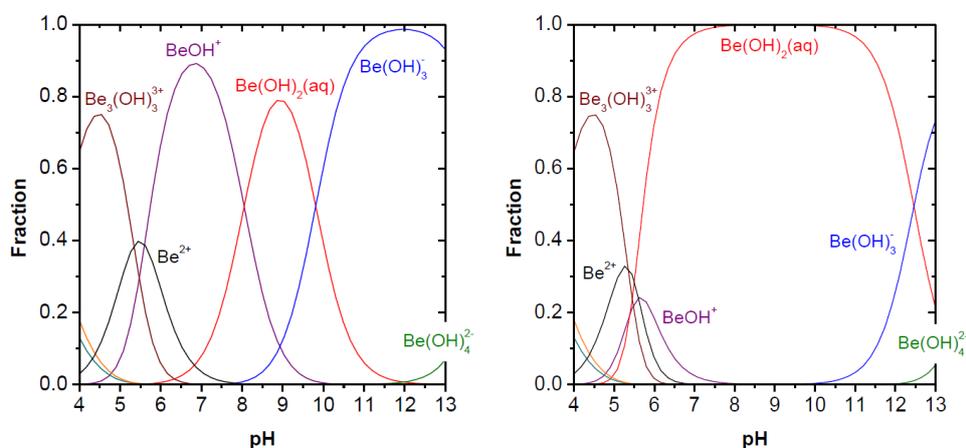


Figure 4. Fraction diagrams of Be(II) underlying the solubility curve of $\text{Be}(\text{OH})_2(\text{cr})$. Left diagram for the solubility proposed by Baes and Mesmer (1976). Right diagram calculated with the solubility proposed by Bruno (1987). All calculations performed at $I = 0$. For details the reader is referred to Gaona et al. (2019).

Work developed by (Gaona et al., 2019) within CEBAMA has determined the solubility of beryllium oxide and the associated aqueous speciation in the pH range 6-13 under different ionic media.

Within CEBAMA sorption studies of Beryllium on cement (CEMI type) in the three degradation stages, and on Calcium-Silicate-hydrates (C-S-H) phases with Ca/Si ratios of 0.6 and 1.2 has been investigated. These studies (Gaona et al., 2019) have provided the first set of sorption parameters for the Be-concrete system (Gaona et al., 2019) with K_d values between 1 and $1000 \text{ m}^3/\text{kg}$. This finding can be very relevant to support the Safety Case as it shows a strong uptake of Be(II) species at high

pH values in all investigated systems. This is undoubtedly a relevant result reducing unnecessary conservatism in transport calculations in support of Performance Assessment of repositories.

3.2 Selenium (Se)

Selenium is present in the waste as ^{79}Se , a fission product with a half-life of $3.3 \cdot 10^5$ years. Selenium presents four different oxidation states: selenide (Se(-II)), elemental selenium (Se(0)), selenite (Se(IV)) and selenate (Se(VI)). Selenium in oxidation states -II and 0 are poorly soluble whereas oxidation states IV and VI are considered to be soluble and mobile.

The retention of Se(IV) and Se(VI) was found to be mainly due to the uptake by AFm phases and to a lesser degree by AFt. The retention by C-S-H phases was lower than by AFm and/or AFt. It is then a conclusion that the high pH cement material, which presents higher content of alumininate phases, has a higher affinity for selenite and selenite sorption in comparison with the lower-pH cementitious material. Nedyalkova et al. (2019) studied the influence of the redox potential of the sorption of selenium onto cement phases. To this aim, the potentiality of Se and I to form binary AFm solid solutions was investigated in several types of solid solution series. The results indicated the formation of solid solutions between $\text{SeO}_3\text{-SO}_4$ AFm (see Figure 5), which is a very relevant indication contributing to process understanding. It was also relevant to study the behaviour of Se(-II) as there was no previous data in the literature on how this anion interacted with cement phases. The results suggested that $(\text{HS}^-)_2\text{-AFm}$ and $(\text{HSe}^-)_2\text{-AFm}$ phases may be stable under the reducing and alkaline conditions developed by the influence of cementitious environments.

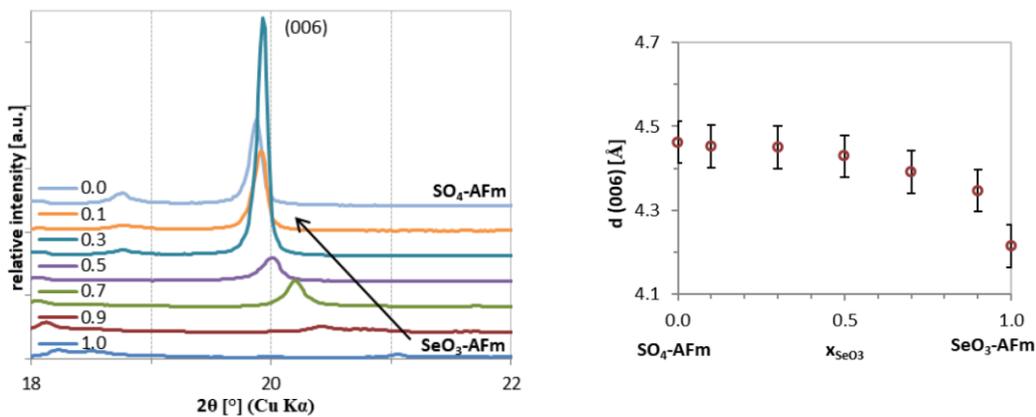


Figure 5. Evolution of the (hkl 006) reflexion (left) and the interlayer distance (right) in the $(\text{SeO}_3\text{-SO}_4)\text{-AFm}$ solid solution series ($\text{pH} \sim 13$) after 3 months equilibration time and drying over a saturated NaOH solution. The numbers 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0 indicate the mole fraction of the SeO_3 -end member (x_{SeO_3}). Figure from Nedyalkova et al., 2018.

3.3 Molybdenum (Mo)

Molybdenum isotopes in LILW are ^{99}Mo and ^{93}Mo . While the former has a half-life of 66 hours, the latter (^{93}Mo) in turn is a synthetic radioisotope with a half-life of 4000 years formed by irradiation with thermal neutrons and fast neutrons (Lindgren et al. 2007). Sources for ^{93}Mo are metallic materials (steels and zircaloy in the core region), and activation of molybdenum in dissolved form or as corrosion particles in the coolant. The release of activation products in the core components is controlled by the corrosion of steel and stainless steel. ^{93}Mo poses a threat to LILW disposal safety

as it is able to form highly mobile and thermodynamically stable molybdate anions in cementitious porewaters.

Under cementitious conditions, molybdenum may precipitate in the form of powellite ($\text{CaMoO}_4(\text{s})$) with its solubility dependent on the concentration of Ca available. Literature assessment of the concentration of Mo given by equilibrium with powellite under the different water compositions imposed by the degradation states of concrete, indicate that the concentrations of Mo would be in the range $2 \cdot 10^{-6}$ - $4 \cdot 10^{-4}$ M (Ochs et al., 2016; Grivé et al, 2012).

Given the large amounts of concrete-related materials in the repository, sorption processes are usually credited for reducing the concentration of molybdenum below its solubility limit. Data on Mo sorption on cementitious phases is scarce in the literature, and this has a direct consequence to the assessment of concentration limits supporting Performance Assessment calculations. Analogies have been sought for when assessing the sorption of Mo onto this type of solid phases. Selenium(VI) forms the oxyanion SeO_4^{2-} , which is similar in charge and size to the oxyanion formed by Molybdenum (MoO_4^{2-}) and this is why Se has been frequently taken as analogue for Mo sorption what, as recognized in Ochs et al. (2016), gives a conservative sorption assessment of Mo sorption in these environments.

In the assessment of the concentration limits supporting the Swiss Performance Assessment, no sorption of Mo onto cementitious materials is credited (Wieland, 2014). In the Swedish exercise a value of $0.003 \text{ m}^3/\text{kg}$ (with maximum and minimum values of $3.3 \cdot 10^{-2}$ and $3.3 \cdot 10^{-4}$) is considered for the K_d of Molybdenum under degradation states I and II of cement, while no sorption ($K_d = 0$) is considered in state III (pH = 10.5 and below). This approach is consistent with the selection in Ochs et al. (2016), who selects Mo sorption data by analogy to Se(VI) sorption. Belgium considers the same central value of $K_d = 0.003 \text{ m}^3/\text{kg}$ for fresh cement.

CEBAMA has produced a large amount of data on sorption of molybdenum onto different cementitious phases, which represents an important change to the existing state of the art regarding the start of the project.

The results have shown different modes of retention of molybdenum onto cementitious phases. Results of X-Ray diffraction of AFm- SO_4 phases after interaction with Mo in solution showed an increase in the basal spacing with the increase of the amount of Mo retained in the solid. This is an evidence of the structural substitution of SO_4^{2-} by MoO_4^{2-} , given the larger size of molybdate with respect to sulphate.

When studying the interaction between Mo and AFm-Cl, evidences of the replacement of two chloride anions by one molybdate (MoO_4^{2-}) in the interlayer were found (Marty et al., 2018). The presence of OH^- of the solution competed with MoO_4^{2-} for Cl^- substitution in the solid phase. The work of Marty et al. (2018) goes beyond the K_d model, as it proposes exchange reactions with associated selectivity coefficient based on the Gaines and Thomas convention, providing a more mechanistic understanding to the process of Mo interaction with AFm phases and increasing the level of scientific understanding supporting the Safety Case (Marty et al., 2018).

Ettringite, an AFt phase, has been credited in the literature as the main solid phase responsible for the sorption of Mo in cementitious environments. This phase is present in the stages I, II and III of concrete alteration, and the hypothesis is based on the analogy of the molybdate (MoO_4^{2-}) with the selenate (SeO_4^{2-}) anion. Investigation within CEBAMA performed by López et al. (2019) compared the sorption of Mo by AFt and mixtures of AFm and AFt phases where the ratio AFt/AFm varied

between 2.5 and 0.5. The results indicated negligible sorption for high ratios (high content of AFt) and very fast and high sorption extent of Mo for low AFt/AFm ratio, with K_d values of $1.2 \text{ m}^3/\text{kg}$ for AFt/AFm = 0.5 (see Figure 6). This finding has implications on the use of sorption analogies for Mo, as the results do not support the use of Se as analogue for Mo in sorption estimations, contrary to what has been done in previous compilations of K_d values for use in Performance Assessment.

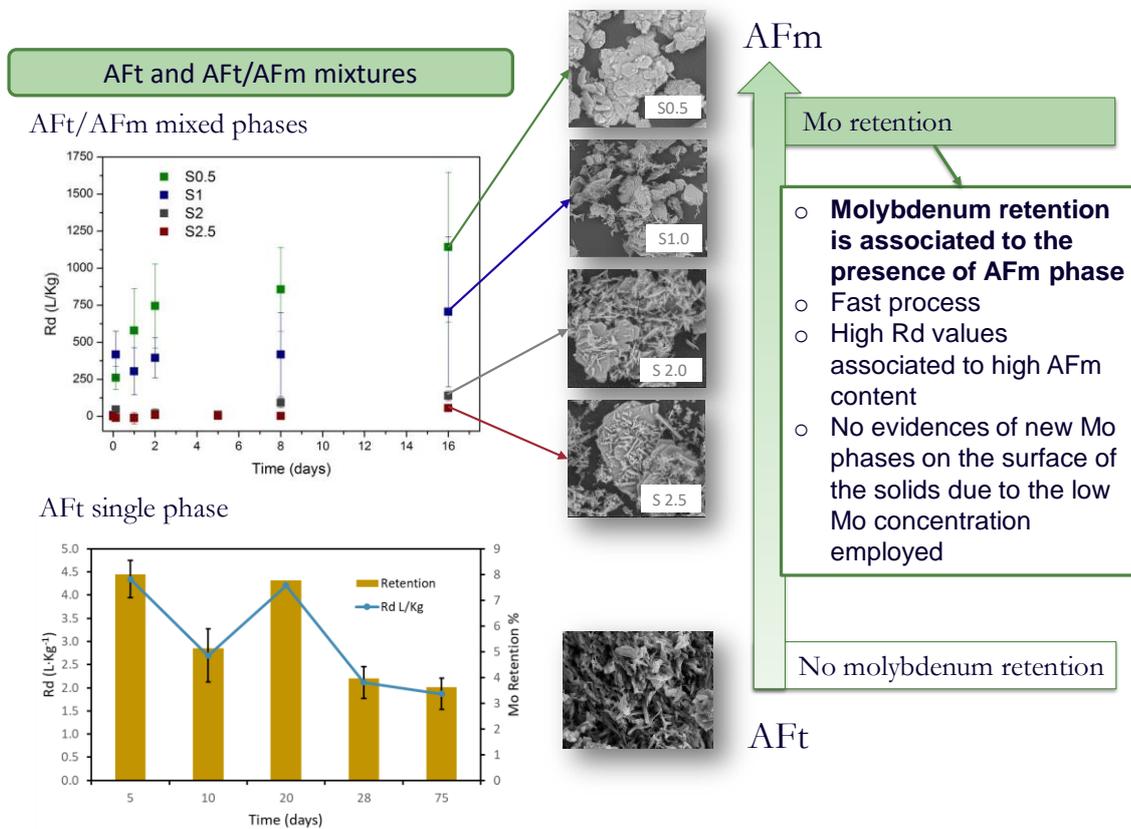


Figure 6. Distribution coefficients (R_d) measured for Mo onto single AFt phase (left lower) and mixtures of AFt and AFm phases at different AFt/AFm ratios (left upper). ESEM images of the solid phases (central images). Main findings and conclusions from the experimental results (right inserts). For a more detailed explanation the reader is referred to López et al. (2019).

These results represent a step forward in the mechanistic understanding of the sorption behaviour of Mo onto cement phases, which improves scientific grounds supporting Performance Assessment and the Safety Case.

3.4 Iodine (I)

^{129}I is an important radionuclide contributing to the dose in radioactive waste repositories. This is partially supported by the fact that being an anion its interaction with the cementitious phases at high pH values is considered very low. K_d values used in Performance Assessment exercises are in the order of $0.001 \text{ m}^3/\text{kg}$. Nevertheless, Iodine can undertake different retention processes by anion substitution in the different cement-related phases that can retard its movement and the extent of this retention is one of the studies developed within the CEBAMA project.

Uptake of iodine onto different cementitious phases was studied. The mechanism was found to depend on the redox speciation. I(-I) was found to be exchanged in the interlayer of AFm-SO₄ to a

larger extent than on AFm-CO₃. The uptake of iodate (IO₃⁻) by the same type of phases and by AFt occurred by anion exchange or phase transformation. It was also interesting to observe that the uptake of iodide by C-S-H phases was generally lower than on AFm and AFt phases and that it was inversely correlated with the Ca/Si ratio of the C-S-H phase. Therefore, the major contribution to iodine uptake can be attributed to the minor cement hydration phases like AFm/AFt that exhibit slightly higher R_d values for IO₃⁻ than for I⁻.

A detailed structural and thermodynamic understanding of I uptake by AFm phases was achieved by PSI which allow a quantitative justification of the K_d values selected in radionuclide sorption databases for application to Performance Assessment. Also, the thermodynamic studies allow an estimation of the effects of the degradation of cement on K_d values for iodine (see Nedyalkova et al. 2019 for details).

3.5 Radium (Ra)

²²⁶Ra is a daughter nuclide of ²³⁸U, the most abundant uranium isotope, as result of the 4n+2 decay chain. ²²⁶Ra decays with a half-life of 1600 years to ²²²Rn. ²²⁶Ra can be a main contributor to dose in the long term (i.e. after more than 100,000 years) due to the high concentrations of uranium present within some waste inventories (SKB, 2010). Radium is present in the waste in the ion exchange resins and scrap, and as release and ingrowth from the spent nuclear fuel alteration. Radium forms the divalent cation Ra²⁺ and, in solution can form aqueous carbonates and sulphates, and it can also precipitate from solution in the form of solid carbonates and sulphates. Radium forms solid solution with calcium and barium sulphates and this process is accounted for in several assessment of concentration limits of use in Performance Assessment under mild alkaline conditions.

Sr has been used as analogue for the sorption of Ra onto C-S-H phases. Kittnerová et al., (2018) showed a significantly higher retention of Ra than that of Sr onto C-S-H phases, in agreement with the specification by NAGRA (Wieland, 2014). This again, decreases uncertainty and conservatism, and leads to a recommendation to revise sorption analogies used in SC to date, as Sr seems not to be a meaningful analogue for the uptake of ²²⁶Ra in cementitious systems. As the carbonation of the solid proceeds, the ²²⁶Ra bound to C-S-H is released into the pore solution with some Ra still retained in the newly formed calcite. This process must be carefully considered, especially in the case of carbonate-rich groundwaters in the repository environment.

3.6 Carbon (C)

In literature, very few sorption data exist for ¹⁴C in fresh non-carbonated HCP (pH=13.5). Pointeau et al (2008) reported a distribution ratio (R_d) value of 600 L.kg⁻¹ for a CEM I HCP (pH=13.2). In cement-based materials, ¹⁴C may react by isotopic exchange with calcite which is considered as the main phase for ¹⁴C uptake in “real” materials (such as mortar or concrete). ¹⁴C may also react with Portlandite and C-S-H. For C-S-H, a fast sorption mechanism is suggested with rather low R_d values (40 L.kg⁻¹) (Henocq et al. 2018).

For inorganic ¹⁴C (carbonates), a new set of sorption/desorption data on fresh HCP has been produced in CEBAMA. For non-carbonated HCP, data are completely in line with the trend described in literature, For carbonated HCP, data close the gap between sorption data on calcite and more complex calcareous materials (mortar, concrete). Interpretation of kinetics data with a 1D solid diffusion model was rather successful. Finally, in-diffusion experiments gave a first idea on the upper limit of C-14 diffusion coefficient in non-carbonated and carbonated HCP.

4 Advances in modelling

Modelling of the evolution of the cementitious materials in the repository is a very difficult task due especially to the coupling of physico-chemical processes, the long-term nature of these, and the large scale of the systems that need to be modelled. The transport properties of concrete (permeability, pore diffusion coefficient, porosity) depend on the evolution of the pore structure and chemical composition during hydration and during long-term alteration. The different nuclear waste management organisations (NWMO) use various approaches to model the processes in the repository scale which generally imply an important level of simplification. These simplifications need a very sound scientific basis in order to allow for uncertainties to be assessed and quantified.

At the onset of the CEBAMA project, a review of how the different NWMO modelled the repository system processes was done. The main outcome was that, although clay-concrete alteration processes were usually conceptualised in the Safety Case, in several cases they are not explicitly considered in the modelling. Instead, overall effects of the different processes are considered when assigning data for the quantification. For example, it is considered that corrosion of metals may cause cracking of concrete surrounding them, and thus changing the transport properties of concrete. However, the process of metallic corrosion is not explicitly coupled with degradation of concrete in the models. Other examples are the use of different sorption parameters for radionuclides as concrete degrades: while K_d data is changed in some cases for different stages of cement degradation, this change is not coupled to the dissolution/precipitation of different solid phases of cementitious materials.

Development of modelling tools to support the Safety case decision-making process has been performed within CEBAMA. For example, Rohmen et al. (2017) developed a coupled code named *iPP* (interface Palabos PhreeqC) able to calculate reactive transport processes in porous media at the pore scale using the operator splitting technique (Sequential-Non-Iterative-Approach, SNIA) to distribute the task of transport to the dedicated advective-diffusive transport code, while a chemical simulator solves the chemical system. Promising benefits of using a Lattice Boltzmann based technique compared to finite element methods (FEM) are straightforward obtainable computational parallelization, due to localized calculation of transport properties and simple and flexible implementations for updating pore geometries.

Leroy et al (2019) has developed a modelling tool including the Poisson-Boltzmann equation to compute the electrochemical properties of highly charged micropores containing multivalent ions. Meeusen et al. (2019) and Hax Damiani et al. (2019) developed new and very efficient ways to implement multi-component diffusion, which implies taking into account species-dependent diffusion coefficients and the resulting interaction via charge and potential effects. This was implemented in the ORCHESTRA and FEniCS-Reaktoro modelling tool, used to perform safety assessment calculations for radioactive waste repositories.

Perko and Jacques (2019) developed a procedure to accelerate simulations of the dissolution process in cementitious materials at the pore scale, decreasing the number of time steps needed. This procedure is based on reducing the iterations of the calculation by bringing transport to the steady-state. The accelerated simulations can be transformed back to time-scales for the real system. Without acceleration, the calculation takes one month while the accelerated process solved the problem in hours (see Figure 7). This optimization allows for fast sensitivity and uncertainty analyses, helping decision-making processes needed for performance and safety assessment as per the long-time scales involved in this type of assessments.

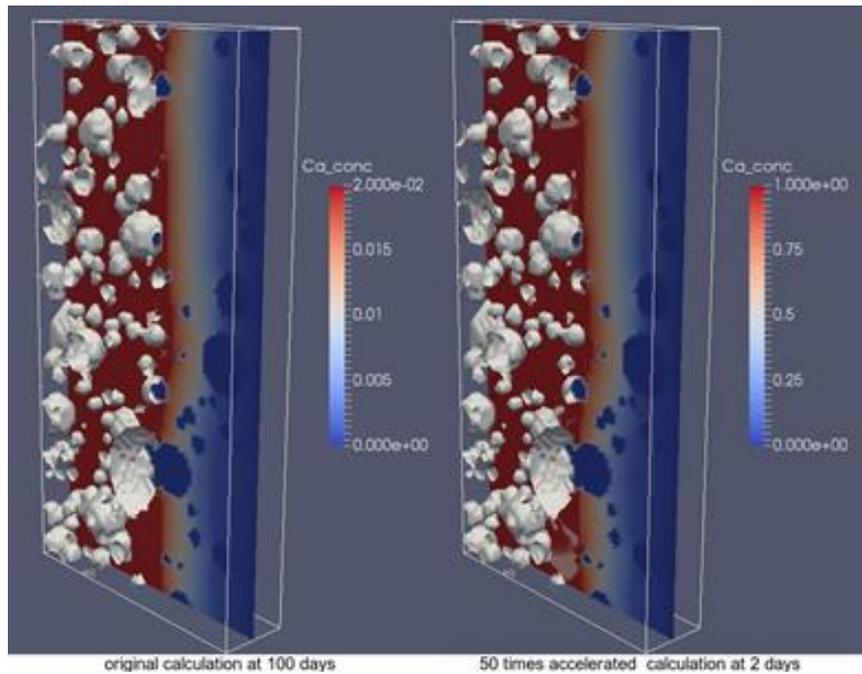


Figure 7. Calcium concentration in a dissolution front of mortar after 100 days. Left: non-accelerated solving at 100 days calculation; right: the same system after 2 days of accelerated calculation. For details see Perko and Jacques (2019).

Validation of the developed models have been possible by comparing of the modelling results with the experimental data generated in the laboratory and field scale (Montoya et al. 2018, Rosendorf et al. 2018, Samper et al. 2018, Vasconcelos et al. 2018b, Yang et al. 2017). Vehmas et al. (2019) compared data on low-pH concrete interaction with different types of groundwater compositions and obtained very interesting results highlighting the relevance of kinetics of precipitation/dissolution processes in the simulations of the evolution of cementitious materials in laboratory scale

The long term benchmark modelling exercise performed in Idiart et al. (2019) was undertaken to build confidence on the prediction of the long-term evolution of the interface between low-pH concrete and a clayey host-rock (CO_x claystone). The results obtained with different reactive transport codes used within CEBAMA, showed in general a very good agreement of the geochemical evolution of the system and pointed out that including kinetic reactions in that scales is not relevant. This is one of the future outlooks that will allow an improvement in the calculations supporting Performance Assessment.

All in all, the outcomes of modelling efforts within CEBAMA represent a significant step forward in the quantitative assessment of physical and chemical processes of cementitious materials and their interface to clayey host-rocks and the development of numerical tools. Results showed a high level of understanding of governing processes and the good agreement between reactive transport codes, which is essential for the use of these tools for the purposes of the Safety Case and Performance Assessment. The specific focus put on low-pH cement-based materials, allows drawing conclusions on their potential use for nuclear waste geological disposal. CEBAMA has improved the knowledge base for the Safety Case by improving the following modelling aspects: (i) impact of cement degradation, microstructural and porosity changes of cementitious materials, (ii) development and benchmark of long-term and upscaled models, (iii) development of modelling expertise and methodologies. CEBAMA clearly represents a step forward in modelling the behaviour of cementitious materials and cement-clay interfaces.

Some of the most relevant modelling results are detailed below:

- New model features developed and implemented include: coupling between porosity changes and diffusion coefficient, development of electro-chemical multi-component diffusion, homogenization schemes for mechanical and transport properties, development of more efficient pore-scale reactive transport tools, and extended membrane polarization models for porosity and pore size distribution.
- These models have been developed and used to quantify how chemical interaction of concrete with other materials affect the mechanical integrity of cement-based barriers (i.e. mechanical strength, stiffness, pore space).
- Thermo-hydro-mechanical models of clay-concrete interfaces, based on elasto-plasticity, have been developed that can now be used in future assessments of the behaviour and evolution of interfaces between concrete and different host-rocks.
- New insights on low-pH cement and concrete were derived, including: hydration modelling in low-pH systems; assessment of diffusion properties from microscopic considerations; pore structure (pore-scale reactive transport models, homogenization models and membrane polarization models); assessment of thermodynamic data in low-pH systems: C-S-H, C-(A)-S-H, Fe speciation, alkali uptake, etc.; and hydro-mechanical behaviour of clay/concrete interfaces.
- For the first time, reactive transport models have explicitly considered the hydration of low-pH cement and how water consumption during hydration impacts the final mineralogical composition. This information is essential in Safety Assessments to determine the initial state and the early evolution of low water-to-binder ratio low-pH cementitious materials in the post-closure period.
- The comparison between the results of the models obtained by using different reactive transport codes in benchmark study of the interaction between low-pH concrete and a clayey host-rock rendered a very good level of agreement. This is crucial for application purposes to the Performance Assessment supporting calculations. On the one hand, the uncertainty in the calculations was decreased and, the agreement provides confidence on the Safety Case and the decisions taken on materials and repository layouts. (see Idiart et al. 2019 for more details).

5 Summary and conclusions

The project CEBAMA has generated data and models helping to improve the understanding of the role and evolution of cementitious materials used in radioactive waste management applications. The evolution of the composition of concrete with time due to interaction with groundwater has been studied. The changes observed in chemical and physical properties have been related to the alteration of transport properties. The influence of the presence of cement and related materials in contact with clays, either used as engineered barriers or as host-rock, has been assessed. The results obtained have helped reducing very relevant uncertainties for performance and safety assessment of radioactive waste management. Comparisons of traditional cement formulations with the newly proposed “low-pH” cement blends have shown that the impact of the new materials is lower, as expected, in terms of pH and alteration of the contacting clays, due in part to the low calcium content of the low-pH materials. Several uncertainties remain, such as the extent to which clogging of pores is relevant for solute transport. The results, nevertheless, have shown that concrete and clay can safely co-exist.

A special contribution of the project relies on the use and experimental study of cement-clay interfaces where cement and clay have been in contact for long times, up to 14 years in some cases, and under conditions of underground research laboratories which resemble those expected in repositories. Methods of investigation of the surfaces have been developed that will be useful in the characterisation needed in support of Performance Assessment. This constitutes unique opportunities as the project has put together a large amount of resources and investigation techniques rarely found at a unique facility or country.

The investigation of the interaction of safety relevant radionuclides with cementitious phases, for which no previous data existed is an unquestionable value of the results of the project. CEBAMA has provided data unknown to date which reduces both qualitative and quantitative uncertainty. Qualitative uncertainty is reduced as the processes responsible for the retention of solutes onto cementitious phases have been investigated, including initial cement and concrete phases, as well as individual phases resulting from cement hydration and degradation. This type of investigations helps to build the conceptual model and arguments needed in any Safety Case. Quantitative uncertainty has been reduced as specific data on the strength of the interaction of radionuclides onto different cementitious phases has been generated. In this line, some of the achievements of the CEBAMA project for future Performance Assessment exercises are: the need of revising element analogies, reducing unnecessary conservatism in transport calculations and understanding the extent of alteration of cement-related materials under different groundwater compositions.

Finally, modelling developments in the project have been innovative and with large domain of application for performance and safety assessment. Coupling processes in a numerical model that considers long-term and large-scale simulations is fraught with difficulties. CEBAMA has provided a unique forum for discussions and joint model developments. Models upscaling the observations made at porous level to large scale have been developed, implemented and benchmarked. Optimization of the codes have shortened the time needed for calculations. This allows for more adequate decision-making procedures as the main features of the complete domain can be visualized and numerically considered in the model.

The formula used in the project, which consists of a combination of experimentalists, modellers and end users, has proven to be an excellent framework to ensure the focus of the investigations towards the application needs.

Nonetheless, many open issues remain, and further data is needed in particular for better understanding and modelling the impact of mineralogical alteration of cementitious materials on their transport properties, and to derive more consistent and realistic thermodynamic and kinetic data for key mineral reactions.

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