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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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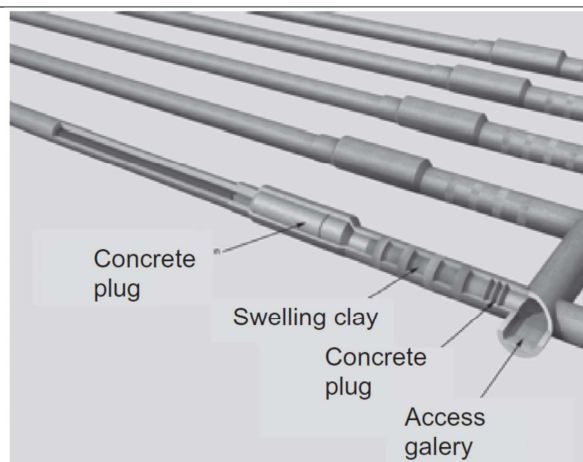
Abstract

Cement-based materials are key materials used in repositories of low, intermediate and high-level radioactive waste in any host-rock concept. These materials are used for waste conditioning, liners, seals as well as structural components. The CEBAMA (CEment-BAsed MAterials, properties, evolution, barrier functions) project (2015-2019) 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.

Keywords: low-pH concrete, radioactive waste, safety case, cement, clay-concrete interactions, radionuclide sorption, radionuclide-cement interaction.

1 Introduction

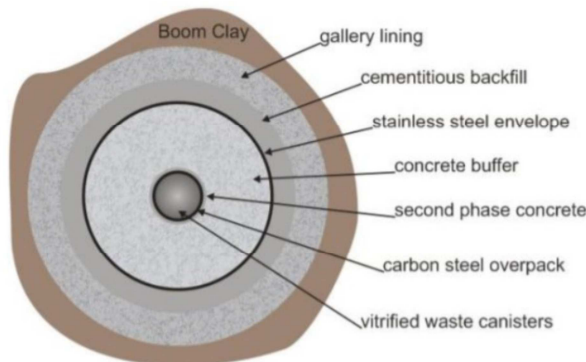
Cement-based materials are widely used in radioactive waste management. This type of materials conforms sections of the engineered barriers in the form of concrete plugs and backfill in repositories for High Level Waste (HLW) disposal (see Figure 1A). They are also used for stabilisation of the excavations 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, as backfill materials, or for the construction of the deep or surface facilities where the waste is located (see Figure 1D). It is a fact that cementitious materials are or will be present in large amounts in radioactive waste repositories. Thus, 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 (www.posiva.fi)*



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.
Picture by Lara Duro

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

Hydrated cement composition 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 hydrated cement in three stages of degradation: (I) a first stage producing highly alkaline leachates ($\text{pH} > 13$) rich in alkaline metals (Na^+ , K^+); (II) a second stage during which the pH of the leachates is governed by the presence of portlandite ($\text{Ca}(\text{OH})_2(\text{s})$) and fixed at a $\text{pH} \sim 12.5$; and (III) a third stage dominated by Calcium-Silicate-Hydrates (C-S-H) decreasing their Ca/Si ratio with continuous leaching over time. This last stage is characterised by a $\text{pH} \sim 11$ until the hardened cement paste is completely degraded and the system is generally dominated by carbonates, reaching intermediate pH values around 8.5. Table 1 shows the data calculated by Kosakowski et al. (2014) and reported in Wieland (2014) on the composition of the water and the main solid phases retained in Hardened Cement Paste (HCP) 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 negative impact of cement on the clayey barriers, alternative "low-pH" cementitious material formulations are being tested for nuclear waste applications (Codina et al. 2008). These formulations are based on replacing cement with alternative hydraulic binders such as silica fume, fly ash and/or blast furnace slag. Low-pH concrete induces a lower alteration of the pH in 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 than that of Ordinary Portland Cement (OPC). 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), as well as reducing the impact on the contacting clays (García Calvo et al. 2010). The kinetics of dissolution of clayey minerals increase substantially with pH in alkaline conditions (e.g. Bildstein and Claret, 2015), which is another potentially negative effect of high pH on clays.

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

	Stage I	Stage II	Stage III
Porosity (%)	20	20	18
pH	13.1	12.54	11.07
E _h (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 (2015-2019) 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 nuclear waste management organisations (NWMO) 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 one country to another.

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 work package 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 one country to another. 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 the degradation of cement materials and impact on interfaces with clay

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 clay/concrete interface and its impact on the transport and mechanical properties is considered in different ways in the Performance Assessment of the various countries taking part in the project. 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 host-rock is granite (Andersson et al. 1998). 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 concrete-bentonite interface such as a decrease in porosity which may prevent water transport or sorption properties. Instead, interfacial reactions are only considered as contributing to the degradation of the materials of the engineered barriers (concrete and bentonite). In the case of ONDRAF/NIRAS (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, being the transport of radionuclides diffusion-controlled (see Cool et al. 2013 and references therein). 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 the concrete liner and the host-rock (NAGRA, 2014). The bentonite adjacent to the liner is affected by the alkaline plume from the low-pH concrete. This results in a slow local porosity increase in the bentonite adjacent to the liner. The calculations conducted to assess the effect 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), as well as a loss of swelling capacity of bentonite affected by its transformation from sodium to calcium form 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 underground 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 (Seetharam and Jacques, 2015). 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). 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.

Although in some of the Safety Assessment exercises, the evolution of the concrete-clay interfaces is considered (see previous paragraph), there are no clear indications on whether the use of low-pH cementitious blends can be more beneficial than a traditional high pH OPC alone. This is the reason why within CEBAMA low-pH cementitious blends were tested, as well as OPC mixes. A specific CEBAMA low-pH reference material was developed to be used by all interested partners. This facilitated comparison between results of low-pH cementitious systems (see Vehmas et al. 2019 for details).

Vehmas et al. (2019) studied the effect of bentonite water on cement pastes in through-diffusion experiments and observed that the Ca/Mg ratio was kept constant and equal to the initial value at 400 μm from 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 or gaps at the surface between cement and bentonite. The experimental results indicate that, within short time scales, 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 conditions in the Bure underground research laboratory in France: 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 with two main features: low heat of hydration and low-pH of the pore solution. 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 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 deformations were measured 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 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, France. Low-pH binder was initially designed to reduce the chemical and thermal 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, precipitation of Magnesium-Silicate-Hydrates, or M-S-H, leading to an increase in porosity) compared 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).

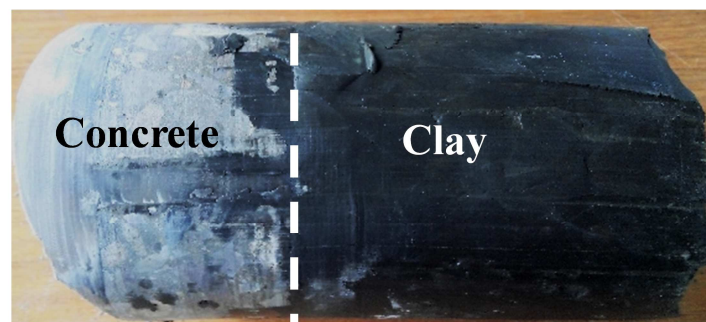


Figure 2. In-situ interface between concrete and clay from the HADES laboratory. The materials have been in contact for 14 years (picture adapted from Gaboreau et al. 2018)

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/T_L interface has little strength, although it is an effective seal for water flow. One order of magnitude reduction in flow was seen through the re-hydration of the COx/T_L interface.

The work of Bernard et al. (2019) represented a step ahead in the characterisation of Magnesium-Silicate-Hydrates (M-S-H) 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 apparent 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. 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 pore volumes, the pH of the interacting water in the second case is always kept below 9, showing the lower impact of the low-pH concrete on the groundwater pH (see Figure 11 in CIEMAT, 2019).

Vasconcelos et al. (2018a,b) studied the evolution of the Nirex Reference Backfill (NRBV) concrete material and other cementitious formulations, including the CEBAMA low-pH reference material, in contact with three different groundwater types: granitic, clay and saline. NRBV is the backfill cementitious composition proposed by the British radioactive waste management agency (RWM, UK) to use in the repository. The pH of the groundwaters increased due to the interaction with the cementitious materials. While the pH of those groundwaters in contact with the NRBV or with ordinary CEM I increased to 12.5-13 and was kept constant at these levels for more than 250 days, that of the groundwaters in contact with the CEBAMA low-pH reference material and other low-pH formulations, reached a maximum of 11 (Claret et al. 2019). The results of the investigation of the CEBAMA reference material showed a layer of Ca on the surfaces of cement pellets contacted with granite and saline waters, but not with clay. Precipitation of Mg-bearing phases was evidenced on the cement surface in contact with saline and clay groundwater solutions. The results of the analyses of the NRBV 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 NRBV 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. Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) formation was favoured in contact with the saline and clay groundwaters due to their higher sulphate concentration. Ettringite can be detrimental to the durability of concrete due to its expansive nature, potentially leading to cracks in concrete.

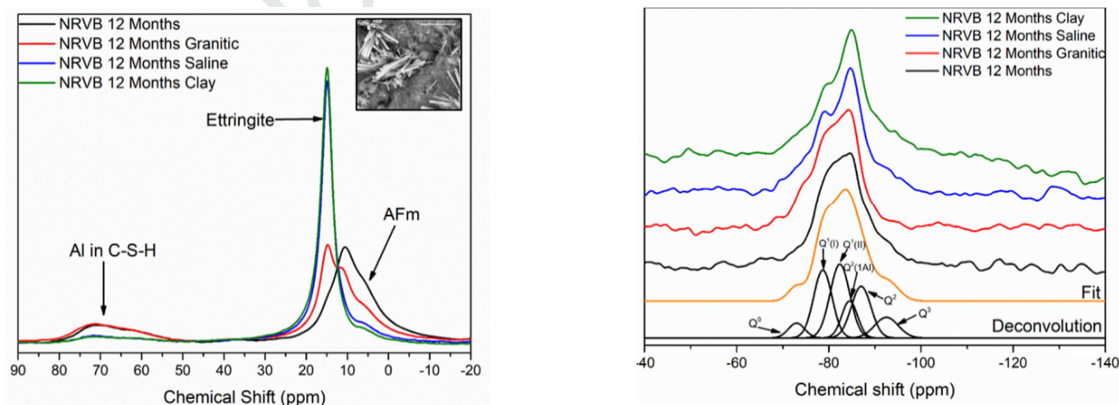


Figure 3. Comparison of NRBV samples exposed to three different groundwater solutions for 12 months, and comparison to blank (i.e. non-groundwater contacted) material: left: ^{27}Al NMR analysis; insert shows SEM images of ettringite needles; right: ^{29}Si NMR analysis and deconvolution. For details the reader is referred to Vasconcelos et al. (2018a,b).

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 summarized as follows:

- Concrete and clay can co-exist safely.
- A deeper understanding of impacts from material interface processes for more realistic description of the performance of the system has been achieved.
- 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 alkaline ions prevents massive transformation of the clay and dramatic loss of their swelling properties (Karnland et al. 2007), 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 as 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 (R_d or K_d values) which are bulk values relating the concentration of contaminant in the solid phase with that in aqueous solution. R_d and K_d 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 support the selected R_d and K_d 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, mainly in metallic form, comes from the dismantling of the nuclear reactors.. 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.

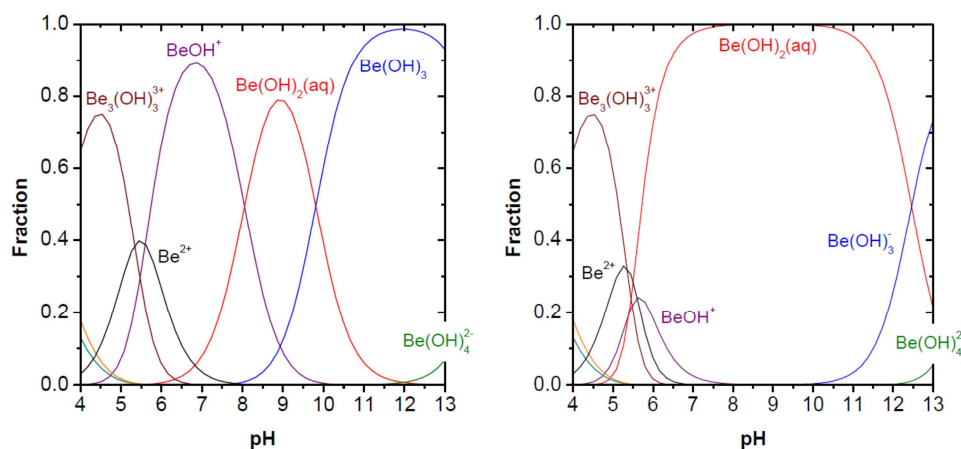


Figure 4. Fraction diagrams of Be(II) underlying the solubility curve of $\text{Be}(\text{OH})_2(\text{cr})$. Left diagram for the solubility proposed by Baes and Mesmer (1976). Right diagram calculated with the solubility proposed by Bruno (1987). All calculations performed at $I = 0$. For details the 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 in different ionic media.

Within CEBAMA sorption studies of beryllium on cement (CEM I 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 m^3/kg , increasing for the lower pH system, i.e., the more degraded cement material, with maximum sorption obtained with C-S-H phases with low Ca/Si ratios. For details the reader is referred to Grambow (2019). 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 ($\text{Se}(-\text{II})$), elemental selenium ($\text{Se}(0)$), selenite ($\text{Se}(\text{IV})$) and selenate ($\text{Se}(\text{VI})$). 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 $\text{Se}(\text{IV})$ and $\text{Se}(\text{VI})$ 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 aluminate phases, has a higher affinity for selenite and selenate 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 SeO_3 - 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 $(\text{HS}^-)_2$ -AFm and $(\text{HSe}^-)_2$ -AFm phases may be stable under the reducing and alkaline conditions developed by the influence of cementitious environments.

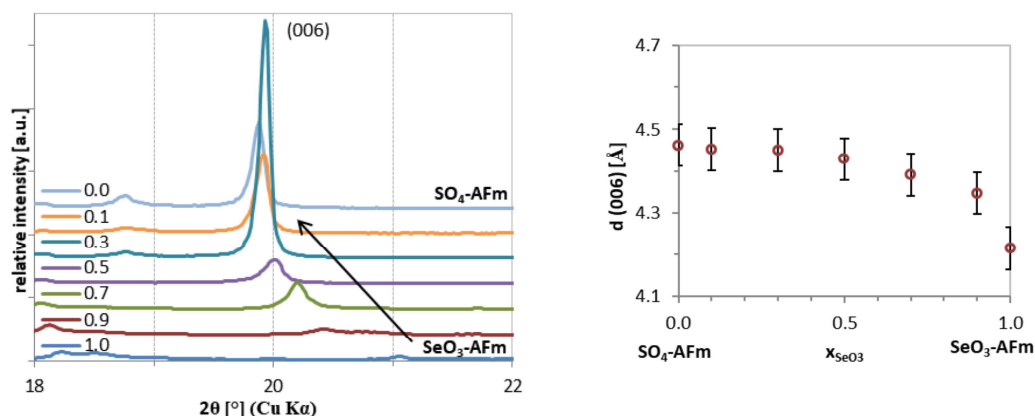


Figure 5. Evolution of the (hkl 006) reflexion (left) and the interlayer distance (right) in the $(\text{SeO}_3\text{-SO}_4)$ -AFm solid solution series (pH ~ 13) after 3 months equilibration time and drying over a saturated NaOH solution. The numbers 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0 indicate the 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-}). 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. In the Belgian calculations supporting performance assessment, the same central value of $K_d = 0.003 \text{ m}^3/\text{kg}$ for Mo on fresh cement is considered.

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-SO₄ 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 SO₄²⁻ by MoO₄²⁻, 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 (MoO₄²⁻) in the interlayer were found (Marty et al. 2018). The presence of OH⁻ of the solution competed with MoO₄²⁻ 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 (MoO₄²⁻) with the selenate (SeO₄²⁻) anion. Investigation within CEBAMA performed by Amphos 21 (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.

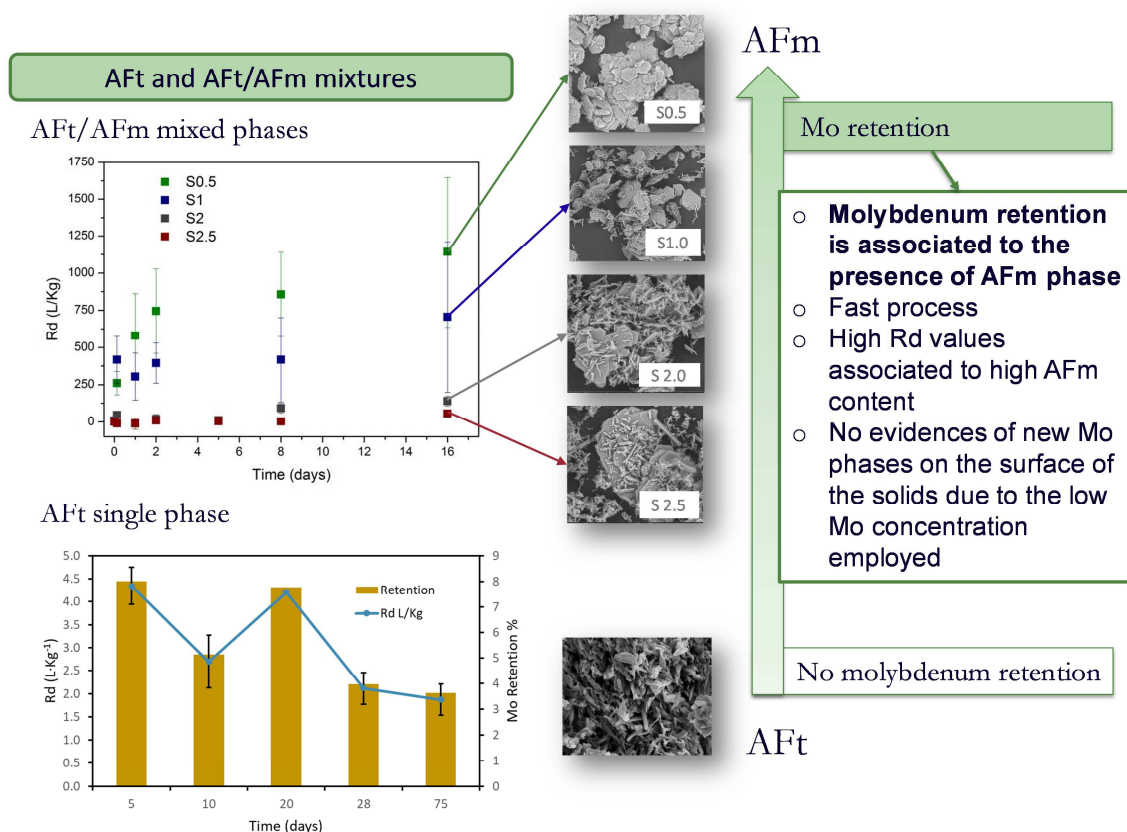


Figure 6. Distribution coefficients (R_d) measured for Mo onto single AFt phase (ettringite, left lower) and mixtures of tri- and mono- sulfate ferroaluminate phases (AFt and AFm) at different AFt/AFm ratios (left upper). The pH of the AFt experiments was 10.4; the pH of the AFt/AFm experiments varied between 11.0 and 11.8. 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 Amphos 21 (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 $0.001 \text{ m}^3/\text{kg}$ (Wieland, 2014). Nevertheless, iodine can undertake different retention processes (Ochs et al. 2016 and references therein) 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. $\text{I}(-\text{I})$ was found to be exchanged in the interlayer of AFm-SO_4 to a larger extent than on AFm-CO_3 . The uptake of iodate (IO_3^-) by the same type of phases and by AFt occurred by anion exchange or phase transformation. 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 IO_3^- than for I^- .

A detailed structural and thermodynamic understanding of I uptake by AFm phases was achieved 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)

^{226}Ra is a daughter nuclide of ^{238}U , the most abundant uranium isotope, as result of the $4n+2$ decay chain. ^{226}Ra decays with a half-life of 1600 years to ^{222}Rn . ^{226}Ra 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 Ra^{2+} 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 Safety Case to date, as Sr seems not to be a meaningful analogue for the uptake of ^{226}Ra in cementitious systems. As the carbonation of the solid proceeds, the ^{226}Ra 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 inorganic ^{14}C in fresh non-carbonated HCP (pH=13.5). Pointeau et al. (2008) reported a distribution ratio (R_d) value of 600 L/kg for a CEM I HCP (pH=13.2). In cement-based materials, ^{14}C may react by isotopic exchange with calcite which is considered as the main phase for ^{14}C uptake in “real” materials (such as mortar or concrete). ^{14}C 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) (Henocq et al. 2018).

For inorganic ^{14}C (carbonates), a new set of sorption/desorption data on fresh HCP has been produced in CEBAMA (see RATEN, 2019 and Armines/Subatech, 2019). 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 (Armines/Subatech, 2019).

The complete set of K_d values obtained in CEBAMA for the different radionuclides and materials tested is compiled in Grambow 2019. The comparison between the K_d s used in different performance assessment exercises and the K_d values obtained by the different groups working in CEBAMA is shown in Figure 7. Only data obtained with CSH and CEM materials have been included. For details on the obtention of the data in the experiments, the reader is referred to Grambow (2019).

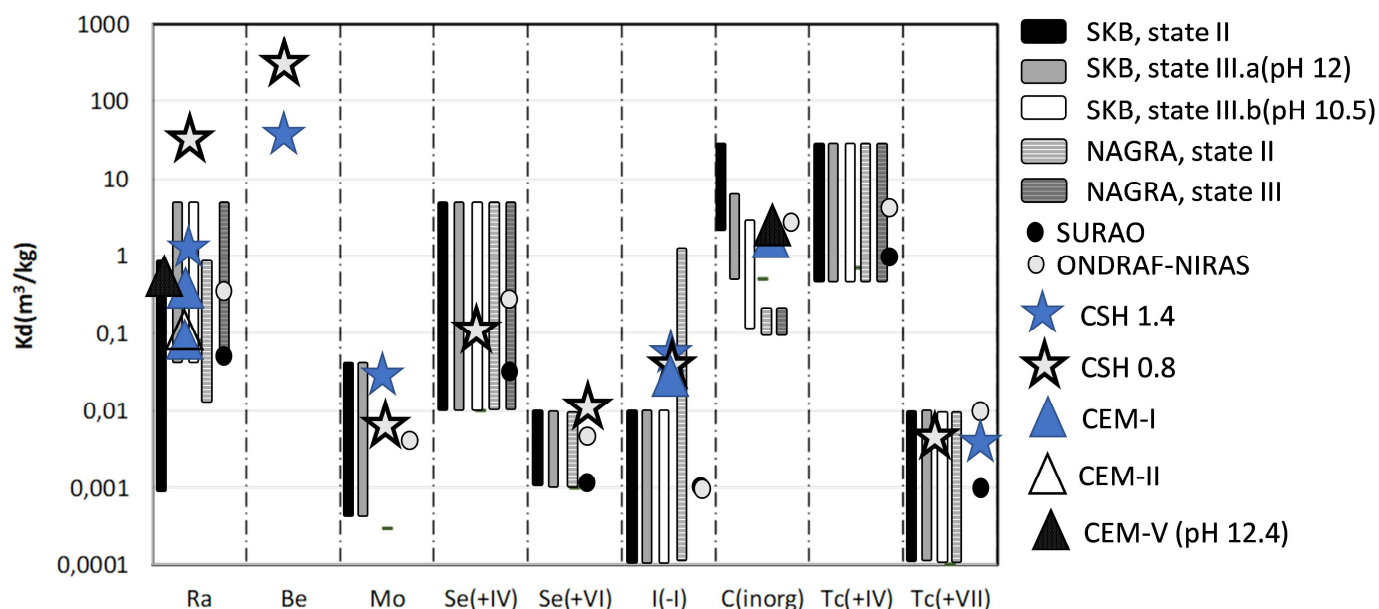


Figure 7. Comparison between K_d values experimentally obtained in CEBAMA for sorption onto Hard Cement Pastes and CHS phases and the K_d values used in different Performance Assessment exercises. SKB data reported in Tables 7-8, 7-9 and 7-10 of SKB (2014); NAGRA data reported in Table 6.1 of Wieland (2014); SURAO data reported by A. Vokal, pers.com; ONDRAF-NIRAS data from Ben Hadj Hassines pers.comm relates to K_d selected onto fresh cement pastes for the Belgian Surface Disposal Repository safety case.

Experimental data is within the range of K_d data used in performance assessment exercises for state II and III of the degradation of cement, except very high sorption obtained for radium, most likely responding to a precipitation process in the experiments with CSH 0,8. In general, the experimental K_d values obtained are in the upper range of the ones used in performance assessment, implying the conservatism implemented in the evaluation of the performance of facilities for radioactive waste disposal.

4 Advances in modelling

Modelling of the evolution of the cementitious materials in the repository is a very difficult task especially due to the coupling of physico-chemical processes, their long-term nature, and the large scale of the systems that need to be evaluated. 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 NWMO use various approaches to model the processes at 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 models. 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. (2017a,b) 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) comprise straightforward obtainable computational parallelization, due to localized calculation of transport properties and simple and flexible implementations for updating pore geometries as a function of chemical alteration.

Leroy et al. (2019) 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 (Nernst-Planck equations), 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 tools, 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 8). 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.

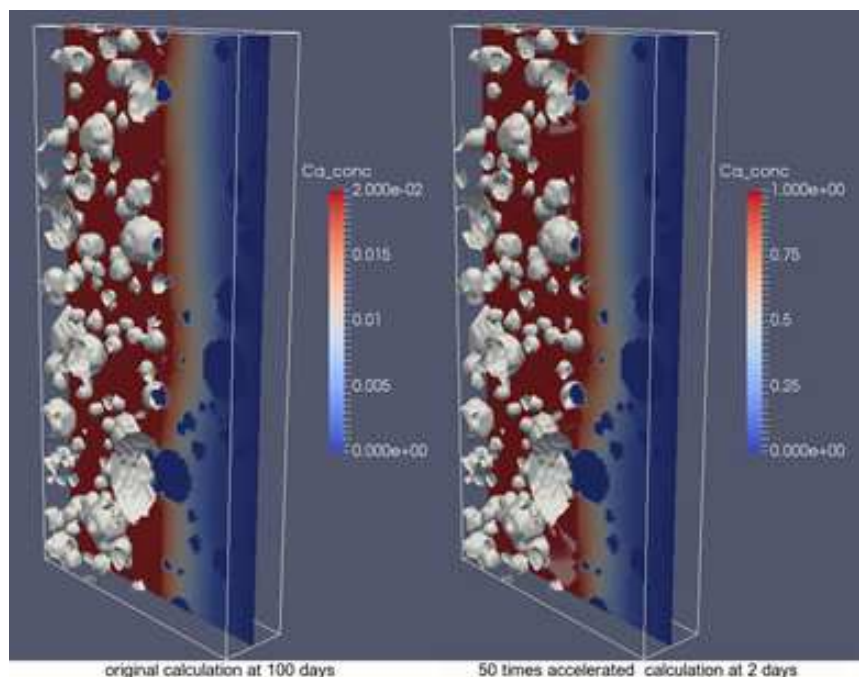


Figure 8. Calcium concentration in a dissolution front of mortar after 100 days. Left: non-accelerated solving at 100 days calculation; right: the same system after 2 days of accelerated calculation. For details see Perko and Jacques (2019).

Validation of the developed models consisted in comparing the modelling results with the experimental data generated within CEBAMA at the laboratory and field scales (Montoya et al., 2018; Rosendorf et al., 2018; Samper et al., 2018; Vasconcelos et al., 2018b; Yang et al., 2017). Vehmas et al. (2017) compared data on low-pH concrete interaction with different types of groundwater compositions and concluded that the role of kinetics of mineral precipitation/dissolution is essential when simulating the evolution of cementitious materials at laboratory time-scales.

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 (COx 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. They also suggest that including kinetic reactions in that time scale is not an essential feature for the studied system due to the low-pH nature of the cementitious system and the relatively small concrete/claystone volume ratio.

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 cementitious materials with time due to interaction with groundwater and clayey materials 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 cementitious 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 between the performance of traditional OPC mixes and the newly developed “low-pH” cement blends have shown the benefit of the latter materials in terms of lowering the pH and the extent of alteration of the contacting clays. This benefit is in part due to the more favourable chemistry of low-pH concrete (low alkalis and calcium contents) and the improved physical properties of the hydrated concrete (low permeability and diffusivity).

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 periods of time, 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 certainly 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 single facility or country.

Results obtained in the project from the investigation of the interaction of safety-relevant radionuclides with cementitious phases, for which no previous data existed is of an unquestionable value. CEBAMA has provided data unknown to date which reduces both qualitative and quantitative the level of uncertainty. Qualitative uncertainty is reduced as the processes responsible for the retention of solutes onto cementitious phases have been investigated,. 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 solute and radionuclide 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 the pore-scale to the 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 (e.g. extent to which clogging of pores is relevant for solute transport), and to derive more consistent and realistic thermodynamic and kinetic data for key mineral reactions. The results, nevertheless, have shown that concrete and clay can safely co-exist.

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Highlights

- Concrete and clay can co-exist safely in radioactive waste repositories
- Low-pH cement contributes to preserving the properties of the clay barrier
- Experimental sorption values are in general in the upper range of the K_d s used in performance assessment exercises. Sorption analogies considered in Safety Cases for anionic radionuclides should be revised.
- Reactive transport models developed a ver for the first time considered hydration of low-pH cement and how wter consumption during hydration impacts the final mineralogical composition of cement.
- Good level of agreement in a long-term reactive transport modelling benchmark has provided confidence on the Safety Case and the decisions taken on cementitious materials and repository layouts

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: