

Degradation of Cement Pastes Subjected to Combined Carbonation and Leaching

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Abstract. *Carbonation and leaching are likely to be the primary concrete degradation mechanisms for concrete utilized in geological repositories when the concrete is fully saturated and in contact with host rock pore water containing increased CO₂ content. This work describes the changes in the microstructure and transport properties of cement pastes caused by coupled chemical degradation processes that occur at the cement paste-clay interface. In the laboratory, an experimental program was designed to accelerate the interface interaction under carbonation and leaching by bringing highly porous cement pastes (to mimic backfill materials used in geological disposal) and Boom Clay into contact in either accelerated percolation or batch-type experiments. Mercury intrusion porosimetry (MIP) was used to investigate the microstructural alteration. Inductively coupled plasma optical emission spectrometer (ICP-OES) and permeability, diffusion measurements were used to determine the evolution of chemical and transport properties, respectively. The results of the porosity change at the interface demonstrate an increase in porosity of the cement paste interface due to Ca leaching, which overwhelms the carbonation. As a result, the transport properties increase. This suggests that clogging of the cementitious material side is unlikely.*

Keywords: *Carbonation, Leaching, Cement Pastes, Boom Clay, Interface.*

1 Introduction

In both near-surface repositories for low/intermediate active waste and geological/deep repositories for high level long-lived radioactive waste, concrete materials have been widely used to encapsulate radioactive waste and as engineered barriers for disposal (Jacques et al. 2021). The role of cement-based materials in these applications is not only focused on the retention of radionuclides but also in helping creating beneficial conditions for the waste package integrity (limiting/inhibiting steel corrosion) and limiting the solubility of many hazardous elements because of its high-pH buffering capacity for a very long period. These concrete structures interact chemically in intricate ways with the geological matrix (such as clay and granite) while they are in use. Although the interaction processes are extremely slow, they are crucial for the assessment of long-term durability (> 1000 years).

Chemical reactions are projected to lead to changes in the chemical and physical properties of both host rock materials and cement, affecting the long-term durability of an engineered structure, due to the major geochemical variations between the host rock materials and cement. The interaction disrupts the equilibrium between the cementitious materials' pore solution and the solid phases of the cement matrix, resulting in mineral dissolution and/or precipitation. The change is significantly typically more noticeable on the host rock side. The interaction usually causes changes in mineralogy and microstructure, which are followed by changes in transport

properties and influence the long-term stability of an engineered structure. For example, (Lerouge et al. 2017) documented an increase in concrete porosity after 5 years of interaction with Opalinus Clay in the case of low pH concrete (including CEM III/B), although the alteration thickness was restricted to only 1 mm. The primary phases generated in those alteration areas were Mg-rich phases, which contributed up to 25% of the cementitious matrix. Opalinus Clay's mineralogy, on the other hand, remained substantially unchanged. Within a few millimeters of the interface, Mg-containing phases were also identified in bentonite that had been in touch with shotcrete for 13 years at the subterranean research facility in Grimsel (Switzerland). The calcite precipitation demonstrated heterogeneous carbonation on the concrete side.

Boom Clay has been researched in Belgium as a viable host rock for low, moderate, and high level radioactive waste. Concrete and boom clay components have been in close proximity at the 225-meter-deep underground research laboratory (HADES) in Mol since 2003, which is an accurate approximation of disposal conditions. However, a 14-year study on concrete-clay interfaces (Phung et al. 2017) revealed a limit change, up to a few hundred millimeters at the concrete side, making it difficult to fully understand the interaction process. In order to induce interface interaction under carbonation and leaching, backfill cementitious material (high porosity) and Boom Clay were brought into contact in either batch-type studies or accelerated percolation experiments. The goal of this research is to look into the changes in the microstructure of such artificial interfaces and how they affect the transport properties.

2 Materials and Test Setup

With the purpose of accelerating the interaction processes, cement pastes were made with a target high porosity for the laboratory experiments. The mixture compositions are mimicking backfill materials, but without superplasticizer (**Table 1**). Note that the backfill compositions for Belgian radioactive waste facilities have not yet fixed. The typical composition is composed of water, Portland cement, limestone filler, hydrated lime and to improve the workability some superplasticizer. Type I ordinary Portland cement (CEM I 52.5 N) was used, which creates a favourable geochemical environment to prevent the corrosion of steel overpack in Belgian Supper container concept. It is worth noting that the backfill materials are not the cementitious materials which are directly in contact with Boom Clay, but the concrete gallery liner which was made by a high strength concrete. The Boom Clay concrete liner interaction has been reported in (Phung et al. 2019).

Table 1. Mix compositions of cement pastes for laboratory experiments.

Cement	Limestone filler/cement	Lime/cement	Water/cement
CEM I 52.5 N	3/1	0.377	1.5

The main minerals in Boom clay are quartz and clays, in different proportions. **Table 2** presents the Boom clay mineralogical compositions (min – max ranges) at the Mol site (Honty et al. 2009). Note that the same minerals are present over the whole Boom Clay formation although the proportions of the various minerals vary in the vertical profiles. The reference composition of Boom clay pore water at the Mol site in Belgium is also described in **Table 2**. The carbonate concentration in pore solution is quite high (~ 0.014 mol/l NaHCO_3) which may

accelerate the carbonation of the concrete side.

Cement pastes were poured into and allowed to cure in a cylindrical PVC tube with an inner diameter of 78 mm in a temperature-controlled room (21 °C) to create the lab-made interface. Following curing, the cement pastes were sawed into 45 mm-thick slices. In a percolation cell, which was a modified design of a permeability cell (Phung et al. 2013), Boom Clay plugs and hardened backfill paste were brought into contact to establish the interface. The chemical environment can be precisely regulated in these studies. Chemical compositions and advective flow of Boom Clay pore solution were used to simulate the conditions of the HADES subterranean research facility. A syringe pump was used to feed clay pore water solution into the percolation cell from the clay side, bubbling 0.4% CO₂ gas (in an argon background) into the solution to imitate partial CO₂ pressure at the subsurface level (**Figure 1**). The Syringe pump also makes it possible to record the flow rate and total amount of injected pore water. The cell was subjected to a 3 bar pressure gradient, which quickens the interaction. To track changes in the pore solution's chemical composition, the outflow was also routinely sampled.

Table 2. Mineralogical and chemical properties of Boom clay and its pore water.

Mineralogical composition Boom clay, %		Boom clay pore water	
Quartz	22 – 66	Na	359 mg/l
Na-plagioclase	0 – 6.3	K	7.2 mg/l
K-Feldspar	0.4 - 8	Ca	2.0 mg/l
Siderite	0 – 1.5	Mg	1.6 mg/l
Calcite	0 – 4.6	Fe	0.2 mg/l
Dolomite	0 - 1	Cl	26 mg/l
Apatite	0 -0.9	SO ₄	2.2 mg/l
Pyrite	0.3 - 5	HCO ₃	879 mg/l
Illite/muscovite	5 - 37	DOC	115 mg/l
Kaolinite	2 - 14	pCO ₂ (atm)	10 ^{-2.62} atm
Chlorite	0.5- 4	pH	8.5

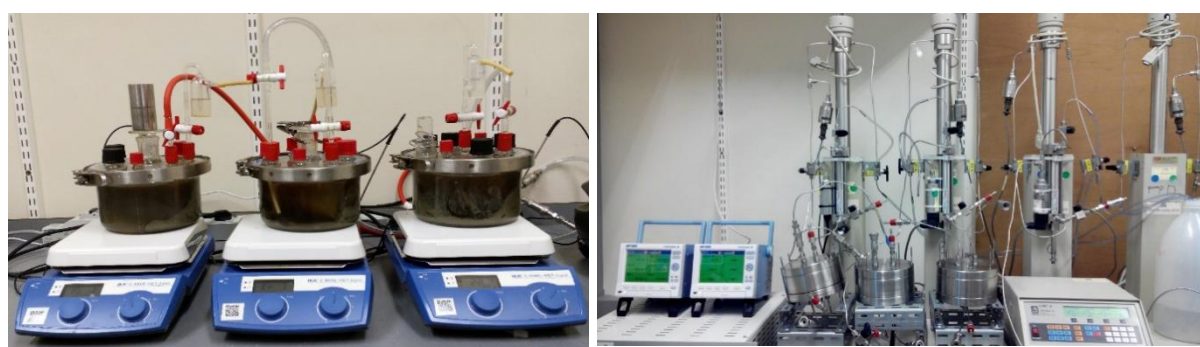


Figure 1. Test setups for batch (left) and percolation (right) experiment.

Batch type experiments were also performed in which a backfill material disc was immersed into a Boom clay slurry. The experiments were conducted in closed chambers which was modified from leaching tests (Phung et al. 2015). CO₂ 0.4% was also bubbled to the chambers to mimic in-situ CO₂ concentration. The chemical composition of the slurry was followed regularly.

3 Quantification of Transport Properties and Characterization of Microstructure and Mineralogy

3.1 Permeability

The percolation cell was built in such a way that the composite permeability of clay and concrete, as well as the permeability of individual materials, may be determined by removing a concrete or clay element from the assembly. The permeability of cement paste and clay samples was measured independently prior to the percolation experiments using a controlled constant flow approach as reported in (Phung et al. 2013). The method relies on a constant flow rather than a constant pressure, as in traditional methods, to address the challenge of sensing extremely low flow rates. After applying a constant pressure gradient until the flow nearly achieved steady state, the constant pressure mode was switched to the constant flow mode. The pressure was then measured until it reached a steady state, which is significantly more precise than monitoring flow rate. Syringe pumps precisely controlled the pressure and flow of water. At any point throughout the percolation experiments, the composite permeability of clay and cement paste samples can be computed. The percolation cell will be decoupled (separate clay and cement paste samples) at a particular contact time to determine the permeability of each material.

3.2 Diffusivity

The diffusion coefficients of initial materials were determined before and after a given time of interaction, similar to permeability. As presented in (Jacops et al. 2021), a through-diffusion methodology was used to determine the diffusivities of two dissolved gases (He and CH₄) in a single experiment. It is worth noting that the permeability/percolation cell can be readily detached and then rejoined to the diffusion setup due to its compatibility. A 1-D diffusive transport model was used to analyse the experimental data, taking into account the drop in gas pressure during sampling.

3.3 Microstructure

Mercury injection porosimetry was used to assess the change in microstructure due to interface interaction. The materials were sawn by a diamond saw to obtain a subsample of 3mm from the exposed surface and freeze-dried prior to the mercury injection porosimetry study. An AutoPore IV 9500 mercury porosimeter was used to assess MIP at KU Leuven, Belgium. Mercury was injected to a pressure of 200 MPa, and the pressure versus mercury infused volume was measured. Mercury is a non-wetting fluid that does not enter pores through capillary action. It only entered the pore after the resistive force was overcome. To overcome the resistance force in a pore of a specific diameter, a certain pressure must be applied. The Washburn equation (Washburn 1921)(Washburn 1921)(Washburn 1921) describes the relationship between pressure and pore diameter. By measuring the pressure versus the intruded volume and applying the Washburn equation, the pore size distribution may be computed.

3.4 Chemical Analysis

Throughout the testing, percolated solution at the outlet and the surrounding solution of batch

experiments were regularly collected. The pH of solutions was measured using a pH meter (Mettler Toledo). Ion chromatography (IC) and an inductively coupled plasma optical emission spectrometer (ICP-OES) were used to measure the amount of elements in the solutions. The measurements were performed using ThermoScientific ICP-MS Element 2.

4 Results and Discussion

4.1 Chemical Evolution

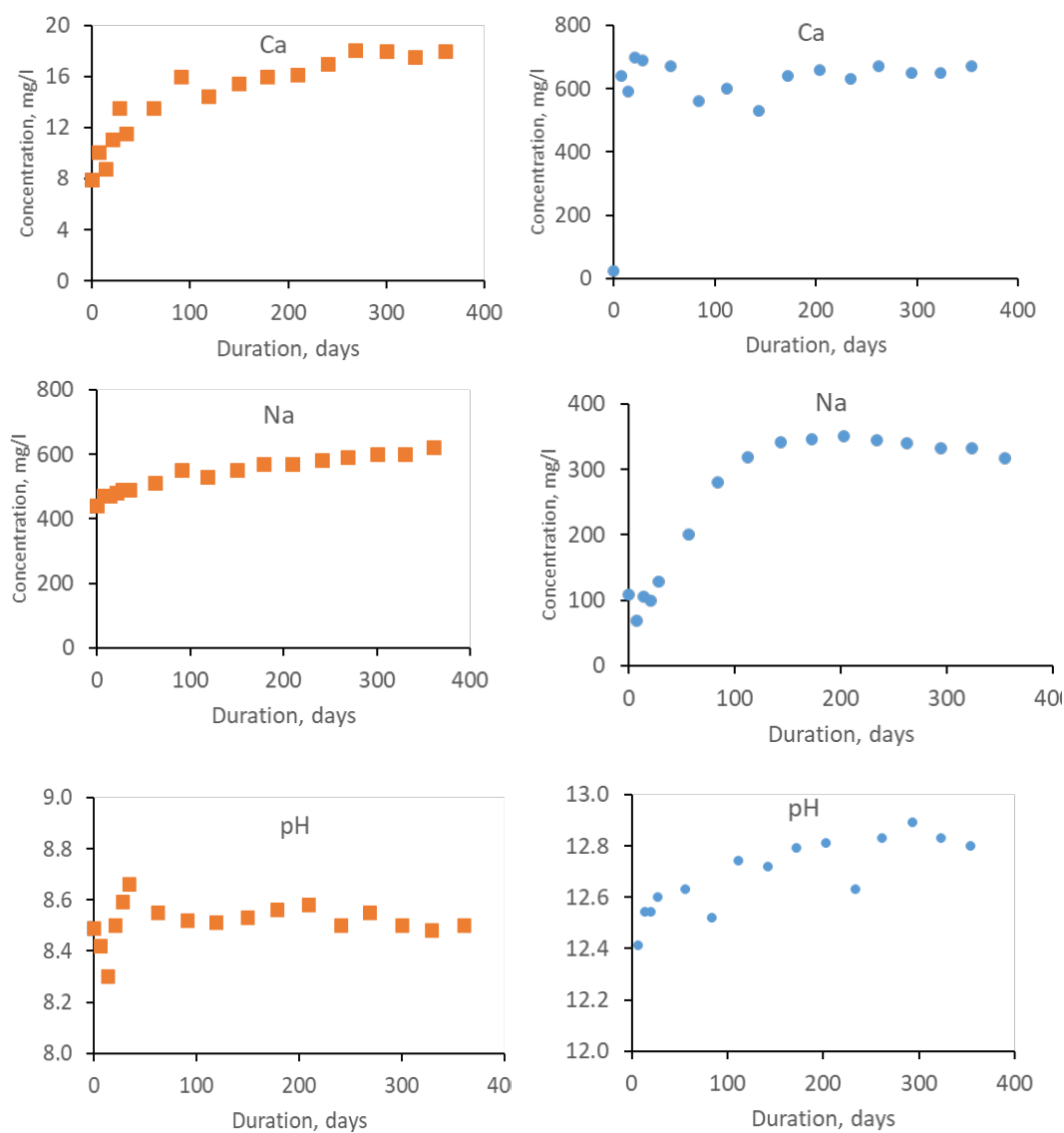


Figure 2. Evolution of Ca, Na and pH during batch (left) and percolation (right) experiments.

Figure 2 displays the main element (Ca, Na, others are minor) concentrations determined in the percolation experiment's solution collected at the experiment's outlet and in the batch experiment. Due to the diluting effect, the Ca content in the batch experiment was significantly lower than in the percolation experiment. The pore volume of the backfill material was substantially smaller than the volume of clay suspension. In both batch and percolation experiments, it is thought that the Ca from various hydrated phases of backfill material—primarily portlandite and C-S-H—is continually leached out. The Ca concentration, however, for the percolation experiment, only rose during the first month. It then fell and leveled off. The leached solution originally consisted of the highly concentrated pore solution of the backfill material. The Ca concentration decreases and the incoming water dilutes the Ca content dissolved from hydrated phases after several pore volume replacements by clay water (with low Ca content). After some time, there will be an equilibrium between the components that are dissolving and the pore water that is entering the system.

Both sets of experiments showed a rise in Na concentration as a function of time, showing that Na was being leached from the backfill material. However, due to the increased Na concentration in clay water, the Na content in the batch experiment was higher. The pH ranged from 8.5 to 8.6, which was very similar to the pH of the pore water in Boom clay, and was stable for a batch experiment (balanced by the clay in suspension + CO₂ bubbling). When the percolation experiment started, the pH went from 12.4 to 12.8, which is about where normal OPC cementitious materials fall on the pH scale. The leaching of Na (or/and K) that accumulated at the exit initially is responsible for this small pH increase. The fact that the pH of the leached solution is close to the pH of the backfill material suggests that, as long as the hydrated phases are not completely dissolved, the backfill material's pore solution regulates the pH of the leached solution.

4.2 Microstructural Alteration

Figure 3 shows the cumulative volume and pore size distribution of sound and degraded backfill materials determined by MIP. It is clear that the cumulative pore volume of the backfill material was significantly increased for both batch and percolation experiments. However, the intensity of the pore volume increase was more pronounced for the percolation experiment compared to the batch experiment. The longer the experimental duration, the higher the pore volume increase for the percolation experiment. For batch experiments, though a higher cumulative pore volume was observed after a 6-month experiment than that of a 3-month experiment, the pore size distribution was slightly refined if the testing duration increased from 3 to 6 months. It is interesting to observe that the sound backfill materials exhibited two pore size peaks, which became only one after either percolation or batch experiments. The first peak (smaller pore size) disappeared, whereas the second peak was amplified, which could be a consequence of leaching as reported in (Phung et al. 2015).

4.3 Changes in Transport Properties

Backfill material and Boom Clay have permeabilities (given as hydraulic conductivity) of 5.9×10^{-9} and 2.4×10^{-12} m/s, respectively. Since the permeability of the backfill sample is around three orders of magnitude greater than that of the clay sample, the permeability of clay should predominate in the flux moving through the percolation cell, which contains both samples. As

a result, it may be said that the composite permeability (for both clay and backfill) is quite similar to the permeability of clay. **Figure 4** shows the progression of the composite permeability throughout the course of one-year percolation experiment. The permeability of the composite slightly decreased. However, given the uncertainty of the permeability measurement in the percolation experiment, the difference from the reference permeability of clay may be insignificant. At the interface, precipitation and dissolution might both happen at once. The clay side may see some calcium carbonate precipitation as a result of carbonation, which will cause the porosity to decrease. However, some phases in clay may dissolve due to flow, which induces a porosity increase. As a result, no discernible difference in permeability was found. The backfill side can see a similar situation. These changes in microstructure might not, however, be significant enough to affect permeability.

Changes in diffusivity and permeability of backfill materials were measured after batch experiments (**Figure 4** (right)). Even in a CO₂-enriched environment (CO₂-equilibrated bicarbonate type pore water), the diffusivity of dissolved gases He and CH₄ and permeability of backfill materials were somewhat increased after a half-year interaction as a result of porosity increase owing to leaching.

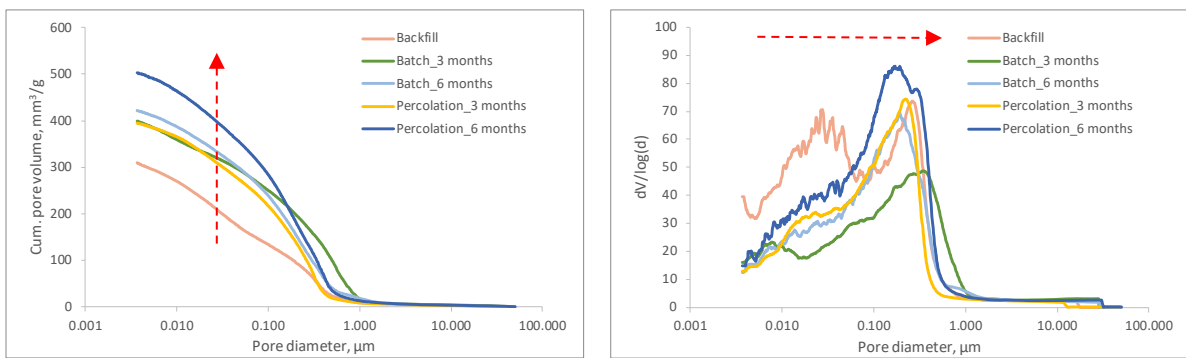


Figure 3. Alteration in cumulative pore volume (left) and pore size distribution (right).

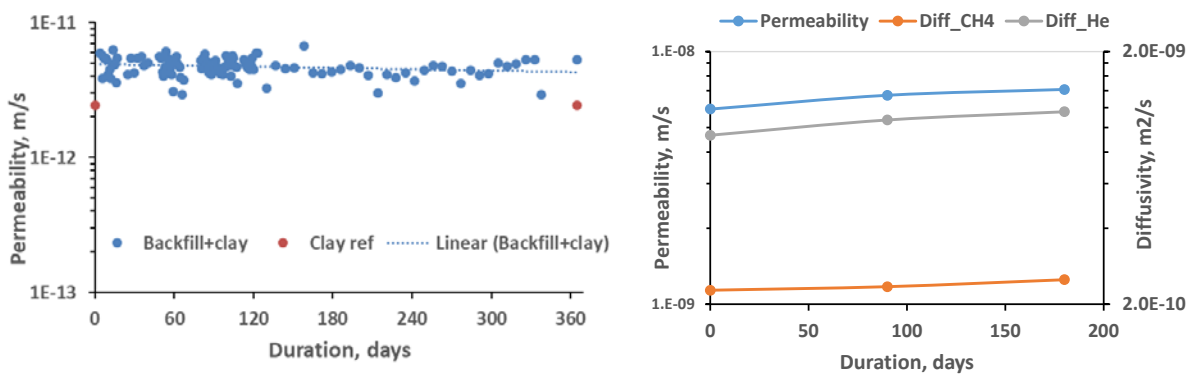


Figure 4. Alteration in diffusivity and permeability during percolation (left) and batch (right) experiments.

5 Conclusions

This paper presents preliminary findings from an investigation on the interface interactions between backfill material and Boom Clay under accelerated environments. The first results of the porosity change at the interface suggest that the total porosity of the concrete interface has increased. This suggests that clogging on the backfill side is unlikely. The increase in porosity of the backfill interface might be understood as Ca-leaching dominating over carbonation (resulting in decreased porosity) at the interface, resulting in an increase in permeability and diffusion. The chemical evolution also indicated the leaching of Ca and Na as the main leachable elements. More results in microstructural, mineralogical, and transport property modifications will help to clarify these concerns and address the remaining uncertainties, allowing this study to achieve its purpose.

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