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Investigation of the changes in microstructure and transport properties of leached cement pastes accounting for mix composition

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ABSTRACT

Ca-leaching of cement-based materials induces detrimental effects on properties related to long-term durability. A better understanding of leaching degradation in terms of alterations in mineralogy, microstructure, and transport properties is important for long-term assessments of concrete and reinforced concrete structures used in nuclear waste disposal systems or in hydro structures. However, the decalcification process is not easy to study because it is extremely slow. In this study, an ammonium nitrate (NH_4NO_3) solution of 6 mol/l was used to accelerate the leaching kinetics. The experiments were performed on cement paste samples with different water/powder (w/p) and limestone filler (LS) replacement ratios. Both the change of sample mass over time and the amount of calcium ion leached out were monitored during the test. Different post-analysis techniques including SEM/SEM-EDX, XRD/QXRD, MIP, ion chromatography, and N_2-adsorption were used to characterize the microstructural and mineralogical changes. The effect of accelerated leaching on transport properties was studied by measuring the changes in water permeability and diffusivity of dissolved gases. Results showed that the square-root-time law of degradation was applicable under accelerated conditions. Both higher w/p ratios and LS replacements increased the rate of leaching propagation; the former had a more significant effect. The accelerated leaching significantly altered the microstructure of the cement paste to a material with a higher specific surface area, increased total porosity and a shift to larger pore sizes. Those changes led to a significant increase in water permeability (one to two orders of magnitude) and diffusivity (less than one order) depending on degradation state.

1. Introduction

Ca-leaching in cement matrices is a dissolution–diffusion driven process when the cement is in contact with a low pH or low alkaline solution. The typical pH of a cement pore water solution is about 12.5–13. Therefore, in almost any environmental condition, surrounding waters (e.g., rain water, soil water, and ground water) could be considered as aggressive environments leading to Ca-leaching (e.g. [1]). Although an extremely slow process under natural conditions (few mm leaching front in a few hundreds of years [2]), Ca-leaching could be an important degradation process for reinforced concrete structures if a long service life is required (e.g. nuclear waste disposal system, or in hydro structures (dam, bridge, water tank)).

To study experimentally the long-term durability of concrete subjected to a slow degradation process, imposing accelerated leaching conditions is a relevant approach to quantify the effects of leaching on the alteration in microstructure and transport properties. A variety of accelerated methods have been proposed such as applying an electrical field [3], using deionized water [4,5], using low pH solutions [6,7], applying flow-through conditions [8], or using high concentration ammonium nitrate (NH_4NO_3) solutions [9,10]. The latter is one of the most popular methods. Leaching in a NH_4NO_3 solution leads to faster degradation compared to the other methods under diffusive-transport conditions while it gives the same end-products. For example, Carde et al. [9] compared leaching of CEM I cement paste with a water/cement (w/c) ratio of 0.5 using deionized water and ammonium nitrate solution. In both setups, leaching leads to complete portlandite dissolution in the degraded zone and to a progressive decalcification of C-S-H, but degradation rates are about two orders of magnitude faster with ammonium nitrate. Importantly, porosity changes are identical at the same leaching degree for both conditions. Besides being a low pH solution, NH_4NO_3 increases the solubility of the leachable phases in cementitious matrix (e.g. portlandite, calcium silicate hydrate (C-S-H), monosulphate (AFm), ettringite (AFt)) by forming the very soluble salt calcium nitrate ($Ca(NO_3)_2$). Therefore, the concentration of Ca ions in pore solution is

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much higher than in a portlandite-controlled system (e.g. 20 mM vs. 2730 mM [11]).

Most studies on Ca-leaching quantify the propagation of degraded depth and the consequences for the mechanical behavior [12,13]. However, only a few studies discuss microstructural alterations after leaching [14,15], typically leading to a material with coarser microstructure in case of accelerated leaching in ammonium nitrate solution, and the effects of leaching on transport properties [16,17]. However, to what extent the microstructure and transport properties are modified is still questionable. Alterations depend, beside on cement type and portlandite content, strongly on pozzolanic activity and other additives which may eventually even lead to porosity decrease by secondary precipitation [18–20]. Generally, additives such as fly ash and blast furnace slag or glass powder and silica fume [5] improve the resistance against leaching. From a mineralogical point of view, Ca-leaching mainly affects portlandite, but several studies show also important decalcification of the C-S-H phases, especially in long-lasting leaching experiments [5, 21]. As fillers in general, and also limestone fillers, specifically influence processes as carbonation [22], microstructure [23], hydration [24,25], and mechanical properties [26,27], it is expected that they also have an effect on Ca-leaching of cementitious materials. However, information is still missing in the literature.

A fundamental question raised in this study is how these microstructural and mineralogical changes during Ca-leaching alter effective transport properties as diffusivity and permeability. Alterations observed in reported experiments are in most studies in line with the expectations, which is an increase with increasing degradation [16,17,28], but the link with the underlying micro-scale changes is mostly not studied. A study of Bernard et al. [51] showed the importance of mineralogical changes on the interpretation of measured HTO diffusivity on degraded CEM I cement paste and mortar samples. The effective diffusivity increases from a 31-time increase, when only portlandite is completely dissolved, to a 118-time increase, when also hydrated aluminates and sulfoaluminates are dissolved.

As cement additives and fillers are expected to have consequences on Ca-leaching, this study presents an in-depth investigation of mineralogical and microstructural alterations and changes in diffusivity and permeability after Ca-leaching of cement pastes with limestone filler within a factorial design with limestone filler replacement and water/powder ratio as experimental variables. The extensive experimental flow chart consists of leaching cement pastes in aggressive environment (NH_4NO_3), during which Ca-leaching was followed up by ion chromatography (IC), followed by a series of quantitative and qualitative analyses (scanning electron microscopy (SEM) in combination with energy dispersive X-ray microanalysis (SEM-EDX), mercury intrusion porosimetry (MIP), (quantitative) X-ray diffraction (XRD/QXRD), N_2-adsorption, phenolphthalein spraying. Recent developed experimental setups were used to measure water permeability [29] and diffusivity [30] of dissolved gases in reference and leached samples.

2. Accelerated Ca-leaching in ammonium nitrate solution

2.1. Materials

Experiments were performed on cement pastes made from cement Type I ordinary Portland cement (CEM I 52.5 N, Table 1), tap water, and limestone filler. The limestone filler (Calcitec 2001S) has a Blaine specific surface of 3500 cm^2/g and a $CaCO_3$ content of 98.30% (see Table 2 for some other properties). Superplasticizer Glenium 27 was added to the mix with content of 0.5% with respect to mass of cement.

Cement paste compositions were made on the basis of a factorial experimental design with 2^2 factorial points and 1 center point along the experimental variables water/(limestone filler + cement) ratio (w/p) and the cement replacement by limestone (ls/p = limestone filler/(limestone filler + cement)). w/p ratio and ls/p ratio varied, respectively, from 0.325 to 0.425 and from 0 to 20% (Table 3). The material compositions used in this study simulate (but without coarse aggregates) the composition for the Belgian Supercontainer in the new reference design for disposal of high-level waste and spent fuel [31], in which limestone has been used as filler and aggregates because it contains low reactive constituents (silicon, aluminium, magnesium), which limits the alkali-aggregate reaction resulting in expansion and cracking [32]. S1 to S5 and S1L to S5L are herein referred to the reference and leached samples, respectively. The run order was randomly generated to eliminate bias. Note that in cement industry, Portland limestone cements have been produced by inter-grinding clinker and limestone (and gypsum) in which different limestone/(limestone + clinker) ratios are initially chosen. Therefore, the "water/cementitious material" ratio for Portland limestone cement is actually the "water/powder" ratio. For consistency, w/p ratio rather than w/c ratio was chosen as one of the experimental variables. However, dilution effects due to limestone filler addition can be easily obtained by converting w/p ratio to w/c ratio.

2.2. Experimental procedure and test setup

Cement pastes were poured and cured in a cylindrical PVC tube with an inner diameter of 97.5 mm. The samples were then rotated during 24 hours to prevent segregation [29] and subsequently cured for 28 days under sealed conditions in a temperature-controlled room (21 ± 1 °C). The cured cement pastes were sawn into 25 mm thick slices. To impose only one-dimensional leaching at the bottom and top of the slice, the PVC cover in the axial direction was not removed and any gap between the PVC cover and cement paste was filled with epoxy resin (Fig. 1a).

In order to avoid initial leaching, the cement slices were saturated in a saturated lime solution following the procedure described in [29]. The saturated cement slices were immersed in ammonium nitrate solution 6 M chambers. The water-contact surface area ratio was 8 cm^3/cm^2. This factor ensured that the pH of the solution remained below 9.25 because this pH is critical to maintain leaching acceleration [33]. As such, solution renewal was avoided which facilitated quantitative analysis of the Ca-leached amounts.

A picture of the test setup is given in Fig. 1b. Nitrogen was bubbled through the system to prevent carbonation during leaching and to remove the formed NH_3 gas via the bubbler (water lock). The solution was homogenized by a magnetic stirrer. There was an extraction line to extract solution for further analysis and follow up the pH. The setup consisted of three NH_4NO_3 chambers which allowed simultaneously leaching of three samples. Reference samples were prepared from the same batch of cement paste and kept under the same conditions except for immersion in ammonium nitrate solution.

Table 1
Chemical properties (wt. %) of the cement (from manufacture fact sheet).

CaO	63.0%	Chromium(VI)	$<2.10^{-4}$%
SiO_2	20.0%	Cl^-	0.06%
Fe_2O_3	3.0%	Na_2O eq.	0.85%
Al_2O_3	5.0%	Loss on ignition	1.60%
Sulphate SO_3	2.9%	Insoluble residue	0.50%

Table 2
Chemical and physical properties of limestone filler (from manufacture fact sheet).

Density	2.7 g/cm^3	$CaCO_3$	98.30%
Blaine-specific surface	3500 cm^2/g	MgO	0.36%
Particle size distribution:		SiO_2	0.75%
Passing 2 mm	100.0%	Al_2O_3	0.25%
Passing 500 µm	99.9%	Fe_2O_3	0.10%
Passing 125 µm	97.0%	Na_2O eq.	0.05%
Passing 63 µm	77.0%	pH	9.5
D_{50} (50% passing)	10.1 µm		