Microstructure and moisture transport in carbonated cement-based materials incorporating cellulose nanofibrils

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Microstructure and moisture transport in carbonated cement-based materials incorporating cellulose nanofibrils

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ABSTRACT

Carbonation of cement-based materials may lead to durability problems, so that it is necessary to find a way to reduce the effect of carbonation on concrete durability. This study investigated the effects of cellulose nanofibrils (CNFs) on the durability of carbonated cement-based materials. Two dosages of CNFs were used to prepare cement pastes and mortars. Before and after accelerated carbonation (4 % CO₂ concentration and 57 % relative humidity), their microstructure, mineralogical composition, moisture retention capacity, drying kinetics, and water absorption were measured. Results show that the contents of hydration products (CH, C-S-H, and ettringite) slightly decrease with the increase of CNFs dosage. After carbonation, the carbonation ratios of hydration products decrease with CNFs dosage so that more hydration products remain in the carbonated materials. The calcite content was found to increase with the dosage of CNFs which may help the transformation of other metastable calcium carbonates to calcite. The coarsening effect of carbonation on pore structure was clearly observed in measured pore size distribution for all materials, while our results show that this effect is weakened by CNFs. Moisture transport is clearly accelerated by carbonation, but the acceleration rate is diminished with the increasing dosage of CNFs, suggesting that CNFs are able to reduce the microstructural damage by carbonation.

1. Introduction

During the service life of concrete structures, carbonation of concrete commonly happens. In this process, CO₂ reacts with hydration products, mainly calcium hydroxide (CH) but also calcium silicate hydrate (C-S-H) and ettringite, depending on the carbonation stage. With the decrease of CH content, pH in the carbonated concretes decreases as well, which may thus destroy the passive layer on the steel surface and initiate steel corrosion. Meanwhile, the reactions of CO₂ with hydration products produce new phases, resulting in the precipitation of carbonation products (mainly calcium carbonate) in the pore network. The increase of the volume of new solids then reduces the total pore volume in the material. Measured porosity of carbonated materials has shown the reduction of total porosity for the Ordinary Portland cement-based (OPC) materials [1–8]. Based on the literature data, the porosity reduction depends on many factors, such as aggregate content, clinker content, and carbonation condition. For hardened Portland cement pastes (HCP) with water-to-cement (w/c) ratios of 0.4 and 0.5 and carbonated in an environment with 1 % CO₂ concentration [5], the measured total water porosity was 6 % to 12 % lower than that before carbonation [2]. Concretes made of composite cement with slag and limestone showed a reduction of 5 % to 12 % of the water-accessible porosity after the complete carbonation with 100 % CO₂ concentration [6]. A study compared HCP made of CEM I, CEM V/A, and low-pH mix and reported the porosity reduction was directly related to clinker substitution by pozzolanic additions; that is, the higher content of portlandite, the higher decrease of porosity [3]. The drop of porosity is commonly explained by pore clogging, implying that the precipitation of calcium carbonate is able to block some pores and of course alter the pore size distribution (PSD).

The alteration of the pore structure may depend on the location where the calcium carbonate precipitates. Carbonation is generally performed at relative humidity (RH) between 55 % and 76 %. At equilibrium state, these RHs correspond to water-filled pores with diameters...
between 3.5 and 7.4 nm according to the Kelvin equation. The precipitation of calcium carbonate can only happen in pores smaller than these sizes, which thus reduces the volume of these small pores and causes the main peak of the PSD to shift towards the large pore size, resulting in the increase of the volumetric ratio of large pores as commonly reported in the literature [1,2,5,9,10]. With prolonged exposure to CO₂, the coarsening effect can be further enhanced as the increase of solid volume may create pressure to small pores and finally cause microcracks [11]. Meanwhile, the prolonged exposure leads to carbonation of C-S-H gels which decompose to silica gel [9] so more large pores are formed.

As a result of the changes of porosity and PSD, the moisture retention and transport properties of the carbonated cementitious materials become different from the non-carbonated (NC) ones. Carbonation leads to a drop of water content over all the RH range because of the decrease of porosity [2,3,5,7]. Despite porosity clogging, carbonation induces an increase in the oxygen diffusion coefficient for most of the tested hardened cement pastes with different binders at all relative humidity (RH) levels [2]. Carbonation of OPC pastes has an effect on their oxygen diffusion coefficient by an increase of one order of magnitude, and a more significant effect was found for the blended pastes [9].

The increase of oxygen permeability for supercritically carbonated specimens was reported in the literature [12]. The water permeability determined by the cup test showed a decrease in the permeability of OPC pastes carbonated at 3 % CO₂, while a significant increase of permeability was found for the blended cements carbonated at the same condition [3]. Possibly, the occurrence of microcracks is conducive to transport of liquids and gasses through carbonated cementitious materials. For blended cement paste specimens (with 75–90 % Blast Furnace Slag), extensive cracking occurred as a consequence of carbonation, which significantly increases the oxygen permeability [13]. Nevertheless, it was also found that water permeability decreased by a factor of six and three after carbonation of OPC and blended cement paste with limestone powders, respectively [14]. Therefore, the influence of carbonation on the gas and liquid water permeabilities still needs more research work to have a clear overview [5].

In recent decades, studies found that adding nanofibers into concrete can improve mechanical properties, such as compressive strength and ductility [15]. Nanocelluloses, including cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs), have now become a good alternative reinforcing agent for concrete due to its remarkable mechanical properties, as well as owing to their comparable low price, hydrophilic nature, low health risk, environmental friendliness, and biodegradability [16]. CNFs show the internal curing capability [17], which thus is able to enhance cement hydration as shown by isothermal calorimetry and thermogravimetric analysis [18]. Nevertheless, measured chemical shrinkage curves revealed that the main hydration peak was delayed by 1–2 h for cement paste with 0.5 w/c and 0.75 wt% CNFs of cement mass, while the total chemical shrinkage showed no difference after one day [19]. The delay effect may be caused by absorption of CNFs on the surface of cement grains (thus slowing down cement dissolution) and cations (e.g., K⁺, Na⁺) bound with the hydroxyl group of CNFs which can reduce the reaction activity of cement hydration. As a consequence of hydration alteration, CNFs were reported to have the ability to improve the microstructure of cement hydrates. Data measured by mercury intrusion porosimetry (MIP) showed that the mean pore size of cement paste decreases with the addition of CNFs [18]. By adding a certain amount of cellulose fibers (e.g., 1–1.5 wt%), the measured autogenous shrinkage and cracking induced by drying shrinkage were significantly reduced [20,21]. The yield stress measured by a nanoindentor for cement pasted with 0.3 vol% of CNFs is at the same level as the plain cement. With a further increase of CNCs content, the yield stress increased significantly and surpassed the plain cement paste [22]. The cement mortar reinforced by CNFs shows a similar toughness to that with fine sand, but significantly greater flexural modulus and flexural resistance than those prepared with conventional pulps [23]. In addition, results of three-point bending tests for mortar with 3.3 wt% of CNFs showed a clear improvement of both the flexural modulus and strength, because the nanofibrils have higher intrinsic strength and stiffness [24]. Therefore, an excessively strong bonding is expected to form between the cellulose fibers and the matrix because of the presence of free hydroxyl groups, which can be chemically bound with hydration products [25]. Furthermore, CNFs have the potential to slow down water transport in cementitious materials. It was reported that fiber reinforcement reduces the permeability of concrete with 0.1, 0.3, and 0.5 vol% of cellulose fibers [24].

The use of (nano)celluloses may have certain benefits in improving the durability of cement-based materials. However, it is still not clear how nanocellulose can affect carbonation of cementitious materials. In the present study, cement pastes and mortars with two dosages of NCFs were prepared and their microstructural and moisture transport properties, as two important indicators of durability of porous materials, with and without carbonation were investigated. Liquid water permeability was also inversely determined by a moisture transport model based on the results of drying tests and water absorption tests.

2. Experiments

The aim of this study is to characterize the microstructure and measure moisture transport properties of carbonated and non-carbonated cement-based materials incorporating CNFs. There is no doubt that the microstructure of a material is closely related to its durability. Recent studies showed that the moisture condition inside carbonated concrete is the controlling factor to the corrosion of steel rebar [26,27]. Therefore, various measurement methods and techniques were chosen to obtain the necessary information of microstructure and moisture transport properties. Thermogravimetric analysis (TGA) was used to understand the carbonation effects on chemical composition. Nitrogen adsorption (NAD) and scanning electron microscopy (SEM) can provide quantitative and visual information of the microstructure. Water vapor sorption isotherms (WVSIs) indicate the capacity of a material retaining moisture at given relative humidities. Drying and water absorption measurements directly reflect how fast moisture can move inside materials and are used to determine moisture transport coefficients.

2.1. Materials

The cellulose nanofibrils (CNFs), also known as nanocellulose fibers (NCFs) and nanofibrillated cellulose (NFC), were supplied by the Cellulose and Wood Materials Laboratory at EMPA, Switzerland. The CNFs suspension was prepared from Eucalyptus pulp by chopping, swelling in water, and mechanical grinding [28]. The width of CNFs is from nm to μm and the length is generally a few hundred μm (see Fig. 1 for SEM images of CNFs). The nitrogen specific surface area, determined by the BET model, of the supercritically dried CNFs, is around 200 m²/g [28]. Two CNFs dosages were chosen in this study, 0.3 wt% and 0.8 wt% of cement mass, which are in the range of commonly studied CNFs dosages in the literature [29]. The CNFs slurry was diluted in water to reach the designed CNFs contents and then mixed with a high-speed mixer for 3 min. The mixture was stored in a bottle and stirred by a magnetic stirrer until the preparation of cement-based materials [19]. Cement paste and mortar specimens were prepared with CEM II/B-LL cement with <75 % Portland cement clinker and about 25 % limestone, from Vigier Ciment (see Table 1 for the chemical composition of cement). They both have a water-to-cement ratio of 0.6. For mortar, the sand-to-cement ratio was 3 with the maximum river sand size of 2 mm. The dry materials (cement or cement and sand) were mixed in a mixer with a low speed (approximately 140 RPM) for 30 s and then the liquid mixture with CNFs was slowly added while the mixer continued with the low speed for 60 s. After cleaning the mixing bowl to avoid dry materials settling at the bottom, the mixing continued for 60 s at a high speed (about 580 RPM) [30]. After mixing, materials were cast in plastic bottles (33 mm diameter for mortar and 31 mm for paste), which were slowly rotated for
one night to avoid solids separation and then sealed for curing. At the age of six months, plastic bottles were removed and cylinders (mortars and pastes) were cut into 2 cm long short cylinders. These short cylinders were preconditioned in a chamber with 57 % RH for about 2 weeks. Then, they were divided into two groups. One group was moved into a carbonation chamber with 57 % RH and CO\textsubscript{2} concentration of 4 %. Several specimens without CNFs (mortars and pastes) were broken to check the carbonation process by spraying phenolphthalein on the split surface. When there was no color change on the surface, the carbonation process was stopped. Meanwhile, specimens in the other group were still kept in the drying chamber with 57 % RH but without additional CO\textsubscript{2} supply. When carbonation procedure was completed, all cylindrical specimens, including carbonated and non-carbonated, were vacuum saturated with water and then kept in a 97 % RH desiccator until mass equilibrium. Cylinders were subjected to drying kinetics measurements and then water absorption tests.

When preparing short cylindrical specimens, a number of 2 mm thick paste disks were also cut from the cylindrical materials. They were carbonated in the same chamber as the cylindrical specimens and phenolphthalein was used to monitor the carbonation depth. For both carbonated and non-carbonated paste materials, disks for each type were crushed and sieved to select particles in range of 0.6–1.2 mm, which were then used for TGA and NAD measurements. This size is the generally used in the literature [31–34] as it was already proved as the optimal size for the NAD measurements [35].

### 2.2 Thermogravimetric analysis (TGA)

The TGA tests were performed with a PerkinElmer® instrument in an environment purged by ultra-pure nitrogen gas. About 30 mg samples, particles for the NAD measurements, were heated to 105 °C at 10 °C/min from room temperature and held at 105 °C for 30 min to remove all evaporable water, and then temperature increased to 1000 °C at a rate of 5 °C/min. Experimental details can be found elsewhere [19].

### 2.3 Nitrogen adsorption (NAD)

The NAD measurements were conducted using a Micromeritics TriStar II 3020 apparatus. About 1 g sieved samples were exchanged with isopropanol for about 12 h and then dried at 40 °C in a tube purged with nitrogen gas. Then, about 0.5 g samples were degassed at 5 μm Hg pressure at 40 °C for 12 h. The measurement started from relative pressure p/p\textsubscript{0} = 0.01 and increased to p/p\textsubscript{0} = 0.99 to measure the adsorption curve and then decreased to p/p\textsubscript{0} = 0.01 step wisely to obtain the desorption curve.

### 2.4 Scanning electron microscopy (SEM)

A few large crushed pieces were impregnated by a low-viscosity epoxy resin in a vacuum chamber. After about 24 h, when the epoxy resin had hardened, the embedded specimen was subjected to grinding and polishing, following the protocol reported in [30]. After grinding and polishing, the specimen was imaged as soon as possible to avoid damage during the storage. The specimens were coated with a thin layer of carbon (<10 nm thick). A FEI Quanta 600 environmental SEM with a BSE detector was used to image the polished surface under the high vacuum mode.

### 2.5 Water vapor sorption isotherms (WVSIs)

Water vapor sorption isotherms were measured by a Dynamic Vapor Sorption analyzer (DVS Advantage ET85, Surface Measurement Systems Ltd.). The DVS only needs very small amount of samples (generally <100 mg) which takes a much shorter time to reach the equilibrium state therefore, only paste samples were used in this study. The saturated paste disk was crushed and a small piece was put in the DVS analyzer. The controlled RH in the DVS started at 97 % and then decreased stepwise to 11 % to obtain the desorption curve. The piece was transferred to a tube that was constantly flushed with nitrogen gas for one week, to achieve the dry state. It was then put back to the DVA analyzer and RH started at 11 % and increased to 97 % to obtain the adsorption curve. The equilibrium criterion at each RH level was defined when a mass change (dm/dt) was <0.0005 %/min over 10 min or a maximal time of 1000 min for each step was reached. More information about

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**Table 1**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Weight ratio %</th>
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<tbody>
<tr>
<td>CaO</td>
<td>60.78</td>
</tr>
<tr>
<td>SiO₂</td>
<td>17.82</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.29</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.55</td>
</tr>
<tr>
<td>MgO</td>
<td>1.61</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.52</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.28</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.16</td>
</tr>
<tr>
<td>LOI</td>
<td>1.4</td>
</tr>
</tbody>
</table>

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**Fig. 1.** SEM images at different magnification of dry CNFs, after mechanical fibrillation using an ultra-fine friction grinder [28].
DVS measurements can be found elsewhere [36].

Even though the stop criterion is strict, the measured mass curves still show a very slow increase at the end of measurements; thus, the “real” final mass is expected to be different from the measured mass. To minimize the effect, a moisture transport model (i.e., Fick’s diffusion equation) can be used to fit the measured mass change curve and the “real” final mass (at equilibrium) can be estimated [37]. However, the geometry of crushed specimens in the DVS analyzer is generally irregular, so that a measured mass change curve cannot be simulated by the traditional moisture transport models which require the known geometry. This problem can be overcome by using some empirical equations, such as the Weibull function or the dual-Weibull function, which do not depend on the geometry of specimens [36]. In this study, the dual-Weibull function was used to correct the measured WVSIs.

2.6. Drying kinetics

After preconditioning at 97 % RH, the lateral surfaces of the cylindrical specimens were sealed with adhesive aluminum sheets. Two ends of the cylindrical specimen were uncovered to allow moisture exchange with the ambient environment. These cylinders were stored in desiccators with different RHs, namely, 44 %, 53 %, 75 %, and 85 %. The masses of these specimens were measured periodically to obtain the drying kinetics (mass change vs. time).

2.7. Water absorption

Drying kinetics measurements stopped at 128 days and then cylindrical specimens were subjected to water absorption tests. One end of a cylindrical specimen was in contact with liquid water and the other end was loosely covered with a plastic film to minimize moisture exchange. The mass of a specimen was periodically measured for about 250 h. During the measurements, each time when the specimen was taken out, water on the surface was wiped away by a damping cloth. After the water absorption tests, specimens were dried in an oven of 65 °C until the mass equilibrium. With knowing the measured volume of a specimen and saturated mass before drying kinetics measurements, we can calculate the total porosity (accessible-to-water porosity).

2.8. Naming rules

In the experiments, different materials with different treatment and CNFs dosages were studied at different RHs. To distinguish them, the abbreviations are summarized in Table 2 which are used in the following sections of this paper, in particular for figures.

3. Results

3.1. Mineralogical change after carbonation

Cement hydration and carbonation were investigated by the means of TGA results, which were obtained on paste materials that did not contain aggregates. Results in Fig. 2a show that carbonated specimens have much higher mass losses than non-carbonated materials, which is caused by the thermal decomposition of carbonate phases. No matter for carbonated or NC materials, the final mass change slightly changes with the dosage of CNFs. The decomposition of CNFs may contribute to this tendency. According to the TGA test on the pure CNFs [19], CNFs thermally decompose at around 360 °C, which is shown as a small peak at this temperature in Fig. 2b. In addition to this peak, a few large peaks can be identified in Fig. 2b. The first peak is between 105 and 200 °C, due to the emission of water from the decomposition of C-S-H and a small amount of ettringite [38]. It is clear that the carbonated materials have slightly smaller peaks than the non-carbonated materials. This may result from the low contents of C-S-H and/or ettringite that were partially carbonated during the process of carbonation. Upon carbonation, ettringite generally decomposes to gypsum, calcium carbonate, alumina gel, and water [39]. The main product - gypsum loses its two water molecules at temperature below 100 °C and becomes anhydrite II & III [40] so that this peak cannot be seen in the presented figure (which only shows curves above 105 °C). The thermal decomposition of alumina gel happens at 300 °C [41], while this peak is not obvious in Fig. 2b, indicating that the amount of decomposed ettringite is insignificant. The following peak is found at 440 °C, corresponding to the emission of water from the decomposition of one main hydration product – CH.

![Fig. 2. TG (a) and DTG (b) curves of different paste materials heated from 105 °C to 1000 °C.]

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<tbody>
<tr>
<td>P</td>
<td>Paste</td>
<td>CNF3</td>
<td>0.3 wt% CNFs dosage</td>
<td>NC</td>
<td>Non-carbonated</td>
</tr>
<tr>
<td>M</td>
<td>Mortar</td>
<td>CNF8</td>
<td>0.8 wt% CNFs dosage</td>
<td>C</td>
<td>Carbonated</td>
</tr>
<tr>
<td>RHxx</td>
<td>Drying at xx RH</td>
<td></td>
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Clearly, the carbonated specimens have a much smaller CH peak because most CH was carbonated. Peaks in the temperature range higher than the CH peaks are from the decomposition of calcium carbonates, which release CO₂. The NC materials only have one peak at around 720 °C from the decomposition of limestone (calcite). However, the carbonated materials show two peaks, at 550 and 740 °C. The peak at the lower temperature results from the decomposition of a metastable calcium carbonate formed at the early stage of carbonation of calcium hydroxides [42], which is believed to be vaterite. Depending on the availability of moisture and temperature, vaterite may transform to aragonite (with high temperature) and poorly crystallized calcite (when sufficient moisture supply) [43,44]. The thermodynamic stability of the polymorphs increases in the order vaterite → aragonite → calcite and their solubility decreases in the same order [45]. Therefore, the peak at the higher temperature is from the decomposition of calcite.

With the increase of CNFs dosage, the peak for vaterite becomes smaller, while the calcite peak becomes higher. Clearly, the presence of CNFs helps vaterite transform into calcite. Our hypothesis is that this is probably caused by the presence of CNFs which can in principle reduce the amount of Ca²⁺ in pore solution.

Based on the above description, a TG curve can be divided into three sections, the temperature range of the CH peak with two additional temperature ranges, below the CH peak and above the CH peak, corresponding to the decomposition of C-S-H & ettringite and calcium carbonates, respectively. Note that the temperature range of the CH peak should be identified individually for each DTG curve. By analyzing the mass losses in different temperature ranges, we can compare the contents of different phases in different materials. Mass losses from the decomposition of different phases are provided in Fig. 3. In these curves, the mass ratio of each phase was corrected by removing the CNFs-related mass loss at different temperature (from the thermal decomposition curve of CNFs). The presented mass ratio is the ratio of measured mass loss to the dried mass of material at 1000 °C (already subtracted the dried mass of CNFs). Note that mass losses were caused by releasing different gases in the decomposition of different phases, such as water for C-S-H & ettringite and CH, and CO₂ for carbonates. Therefore, values reported in Fig. 3 are not used to indicate the mass ratios in the actual materials. Instead, curves only compare the effects of CNFs on different phases.

Fig. 3a shows that, in the NC materials, both CH and C-S-H & ettringite contents decrease with the increasing CNFs dosage, indicating that the degree of cement hydration was reduced by CNFs. In the literature, the heat evolution measured with an isothermal calorimeter showed that CNFs delayed and increased the main hydration peak compared with specimens without CNFs [17], while a recent study reported that the measured chemical shrinkage curves for cement pastes with CNFs do not show an increase in the main hydration peak [19]. These results indicate that CNFs may slightly influence cement hydration at early ages (<3 days). For the long term, to a certain degree, CNFs may still work as a retarder to prevent the formation of hydration products.

After carbonation, the contents of CH and C-S-H & ettringite decrease as they are partially carbonated; meanwhile, the amount of carbonate phases become very high, comparing Fig. 3b with Fig. 3a. The uncarbonated hydration products are higher for the high dosage of CNFs and the amount of carbonates in pastes with CNFs is lower than that in the neat cement paste. These results imply that CNFs are able to help hydration products resist carbonation and preserve slightly more hydration products.

Assuming that the mass reduction of CH and C-S-H & ettringite after carbonation is only caused by the carbonation reactions, the carbonation ratios of hydration products \( \alpha_{i, C} \) can be determined by the mass difference of this phase in NC and carbonated materials to its mass in the NC material, which is written as

\[
\alpha_{i, C} = \frac{m_{i, NC} - m_{i, C}}{m_{i, NC}}
\]

where \( i = \text{CH or C-S-H & ettringite} \) and \( m_{i, NC} \) and \( m_{i, C} \) are measured mass losses for the phase \( i \) in NC and carbonated specimens, respectively.

Results in Table 3 display that the carbonation ratios for all phases decrease with the content of CNFs. After carbonation, only about 28.5 % CH remains in the neat cement paste, while about 40 % CH still can be found in the paste with 0.8 wt% CNFs. For all types of pastes, C-S-H and/or ettringite are partially carbonated. About 33 % C-S-H & ettringite in the neat paste are carbonated, while this value is halved for the paste with 0.8 wt% CNFs. These results indicate that all hydration products

<table>
<thead>
<tr>
<th>Materials</th>
<th>CH carbonation</th>
<th>C-S-H &amp; ettringite carbonation</th>
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<tbody>
<tr>
<td>P C</td>
<td>0.715</td>
<td>0.328</td>
</tr>
<tr>
<td>P CNF3 C</td>
<td>0.658</td>
<td>0.281</td>
</tr>
<tr>
<td>P CNF8 C</td>
<td>0.600</td>
<td>0.167</td>
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</table>
begin to be carbonated when exposed to CO₂ but CH is apparently carbonated faster than other phases as it is generally agreed that CH is more soluble and much easier to react with CO₂ than C-S-H. Moreover, the presence of CNFs seems to inhibit carbonation of these pastes.

### 3.2. Microstructure

The SEM images can provide visual information about the microstructure. Fig. 4 compares SEM images of NC and carbonated pastes with 0.8 wt% CNF. The NC specimen on the left-hand side shows a very heterogeneous microstructure and diverse phases. The needle-like C-S-H and ettringite/CH with long rod shapes are clearly visible. The wide CNF fibers are also seen and few hydration products are on the surface of CNFs. In terms of the carbonated specimen, the wide CNFs are clear, while the other regions seem more homogeneous than the NC materials. There no needles or rods of hydration products can be seen, which are believed to transform into carbonate products (as confirmed by EDX results in Fig. 4b), showing in many bright small clusters.

To have overall structure information of the cementitious materials, NAD data are useful. The nitrogen adsorption curves in Fig. 5a depict very different curve shapes between carbonated and NC cement pastes. The NC materials have much higher total absorption volume and more obvious hysteresis between adsorption and desorption curves. Amongst the NC pastes, the neat paste and the 0.3 wt% CNFs paste have both higher total absorption volume and larger hysteresis than the 0.8 wt% CNFs paste. This implies that the microstructure of these materials is more heterogeneous than the paste with 0.8 wt% CNFs. In other words, the differences in pore size between the large pores and the connected small pores are higher. On the contrary, the carbonated pastes have flat sorption curves and low hysteresis, indicating that pores become more uniform in terms of size and well connected so that the irregularity is low. In addition, we see a jump from p/p₀ = 0, which corresponds to the volume of the micro-pores. Clearly, the NC pastes have larger micro-pore volume than the carbonated pastes.

The pore size distributions (PSD) in Fig. 5b were calculated by the Barrett-Joyner-Halenda (BJH) method by assuming cylindrical pores. This method can provide reliable PSD for pore size between 2 and 50 nm for cementitious materials [46]. We clearly see that the NC pastes have higher pore volume for the whole range of measured pore size. The NC paste with 0.3 wt% CNFs shows slightly a higher PSD curve than the NC neat cement for pores smaller than 15 nm and the tendency is reversed for the larger pores. The NC paste with 0.8 wt% CNFs always has lower PSD curves than the other two NC pastes. The main peaks for the NC pastes appear at around 2 nm. For the carbonated pastes, the PSD curves are much lower than the NC materials. The insert in Fig. 5b shows that the peaks of carbonated pastes shift to the right to 3-4 nm compared with the NC ones, resulting from the coarsening effect of carbonation. The peak increases with the dosage of CNFs, indicating a more significant reduction in the volume of small pores in the neat cement paste than other materials.

The BET surface area was calculated based on data from the adsorption curve in the range 0.05 ≤ p/p₀ ≤ 0.3. The NC pastes always have much higher BET surface areas than the carbonated pastes (see Fig. 6), indicating that carbonation may induce damages to the microstructure. From the SEM images in Fig. 4, it seems that the carbonates occupy the volume of some pores, which are smaller pores as shown by the decrease of micro-pore volume in measured PSDs in Fig. 5.

It is generally accepted that the higher fraction of small pores leads to a higher BET surface area. Nevertheless, adding 0.3 wt% CNFs does not increase BET surface area for NC pastes even though Fig. 5b shows that this paste has a higher volume of small pores. This may be because the lower volume of large pores cancels out the increase of BET area due to the higher volume of small pores. Consequently, two pastes have very similar BET surface areas. With the further increase of CNFs content to 0.8 wt%, the measured BET surface decreases by about 15%. This may be due to the fact that fewer hydration products in the material if the content of CNFs is high as already shown in Fig. 3a that the amount of CH and C-S-H & ettringite decreases with the increase of CNFs content. After carbonation, BET surface area slightly increases with the CNFs content, which is in agreement with the observation in Fig. 3b and calculated carbonation ratios in Table 3 that less CH and C-S-H & ettringite are carbonated for the high content of CNFs. These results indicate that the presence of CNFs is able to reduce the degree of carbonation.

### 3.3. Water vapor sorption isotherms

WVSIs are commonly described in a function of the degree of saturation, S, vs. RH as shown in Fig. 7, in which black lines are from NC pastes and red lines represent results for carbonated materials. Clearly, the results vary with the CNFs dosage, measurement methods, RH level, and carbonation status. Considering the NC materials, the decrease rate
of the desorption curve at extremely high RHs (e.g., from 100 % to 83 %) becomes higher with the increase of CNFs dosage. It has been reported that CNFs have a strongly hydrophilic nature, so they can absorb much water when there is enough liquid water [17], while the absorbed water can be easily lost when the RH is lower than 100 %. However, with the decrease of RH, WVSIs with celluloses sharply decrease, resulting in low water content at the moderate RHs [47]. After carbonation, WVSIs for the neat pastes and mortars, shift down, which agrees with the common observations in the literature [3], resulting from the pores coarsening effect of carbonation. In other words, the carbonated materials are less sensitive to the change of RH than NC materials for the moderate RHs [7]. If a material has more large pores, it cannot hold more water at the moderate and low RHs, meaning low moisture retention capacity. Pastes with 0.3 wt% CNFs show the similar results to the neat cement pastes, but the differences between NC and carbonated materials are less obvious. The further increase of CNFs content completely changes the relation between NC and carbonated materials as shown in Fig. 7c. For the desorption curves, the NC materials are still higher at high RHs, while at low RHs, the carbonated materials are able to hold slightly more moisture than the NC ones, which is most likely caused by the fact that the moisture retention capacity of CNFs is less sensitive to carbonation than the hydration products. For the adsorption curves, the tendency is reversed, different from pastes with low and without CNFs.

Fig. 7 clearly displays that carbonation can markedly reduce the moisture retention capacity. This effect decreases with the increasing content of CNFs. The carbonation effect on moisture retention capacity can be quantified by a water content ratio [42],

$$R_w = 1 - \frac{w_C}{w_{NC}}$$

where $w_C$ and $w_{NC}$ are measured water contents of carbonated and NC materials at a given RH. $R_w$ shows the relative change of the moisture retention capacity due to carbonation. Results in Fig. 8 are calculated $R_w$ based on measured desorption isotherms. The general trend is that the values of $R_w$ at the moderate RHs are higher than those at low and high RHs. The $R_w$ is about 0.6 for the paste without CNFs, meaning that the moisture retention capacity is reduced by about 60 % compared with the NC paste. With the increase of CNFs content, the curve shifts down, indicating that the carbonation effect becomes weaker. The curve shapes of pastes without and with 0.3 wt% CNFs are very similar, while for the paste with 0.8 wt% CNFs, the carbonation effect on moisture retention capacity is much lower and the $R_w$ even become negative at low RHs. Therefore, we can say that the higher CNFs content is able to better reduce the carbonation effect on the microstructure so that CNFs can help cementitious materials retain moisture.

### 3.4. Drying kinetics

The measured drying kinetics for mortars and cement pastes with different dosages of CNFs are shown as symbols in Fig. 9 and Fig. 10, respectively. It can be seen that the total amount of mass loss increases with the drying RH, regardless of carbonated or non-carbonated materials. The lower environmental RH is able to remove more water from the porous media. For a given RH, the measured mass loss is higher for cement pastes than mortars with the same content of CNFs because cement pastes contain higher HCP per unit of volume than mortars which have a much lower ability to retain moisture than HCP. After carbonation, the drying mass loss at a given RH is much lower than the NC specimens dried at the same RH. As aforementioned, the moisture retention capacity of carbonated materials is lower at the moderate RH because of the increase of volume fraction of large pores. During preconditioning, in which the saturated specimens were dried at

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**Fig. 5.** Measured nitrogen adsorption curves (a) and pore size distributions calculated by BJH method (b). The enlarged PSDs for carbonated pastes are shown in the insert in figure (b).
97% RH, more water has been removed from the carbonated materials. Therefore, in the subsequent drying, less water remains in the materials for drying.

With the change of the dosage of CNFs, the mass loss at different RH conditions varies. In general, the moisture loss slightly decreases at the CNFs content of 0.3 wt%, while it slightly increases at 0.8 wt% CNFs. This trend is less pronounced for carbonated materials than the NC ones. The reason behind this is that the PSDs are altered by the additional CNFs, which further affects the moisture retention capacity of these materials. As shown in Fig. 5, the NC materials with 0.3 wt% CNFs have the highest measured pore volume (for pores smaller than 50 nm) and the NC materials with 0.8 wt% CNFs have the lowest measured pore volume. This would help to understand the drying mass loss curves in Fig. 9 and Fig. 10. For the carbonated materials, the nitrogen adsorption curves are very similar as shown in Fig. 5, so there is no significant difference in the drying mass loss in Fig. 9 and Fig. 10.

### 3.5. Water absorption

After the drying kinetics measurements, water absorption tests were performed on the same specimens. Water penetration into the porous materials is driven by capillary pressure. The measured water absorption data are shown in Fig. 11 and Fig. 12 for mortars and cement pastes, respectively. In these figures, the x-axis is shown in the square root of time, because traditionally the amount of cumulative absorbed water in the first stage (in the short term) linearly increases with the square root of time ($t^{1/2}$) for most porous media [48,49]. The slope of the linear region represents the ability of a material to absorb and transmit water by capillarity. Therefore, the amount of cumulative absorbed water $I$ can be written as a linear relation with $t^{1/2}$.

$$I = S_p t^{1/2} + A$$

where $S_p$ is the slope of the linear curve, called sorptivity, and $A$ is a parameter associated with the end effect (such as buoyancy, lateral invasion) [50]. By fitting the linear region of water absorption curves, the sorptivity of studied materials is determined and provided in Table 5 and Table 6 for mortars and cement pastes, respectively. 

Fig. 11 and Fig. 12 show that most measured water absorption curves have a linear relation with $t^{1/2}$, except for some cement pastes. The linear regions end at about 9 h for the fast absorption (higher $S_p$) and about 64 h for the slow absorption (lower $S_p$). For mortars, the carbonated ones and these NC mortars previously dried at low RHs (e.g., 44% and 53%) have steeper slopes (or higher $S_p$) than the other.

![Fig. 7. Water vapor sorption isotherms (S vs. RH) for materials without CNFs (a), with 0.3 wt% CNFs (b), and with 0.8 wt% CNFs.](image.png)

![Fig. 8. Carbonation effect on moisture retention capacity of cement pastes with different contents of CNFs.](image.png)
Fig. 9. Drying kinetics for mortars with different dosages of CNFs: a) without CNFs, b) with 0.3 wt% CNFs, and c) with 0.8 wt% CNFs. Symbols are measured data and lines are simulated results.

Fig. 10. Drying kinetics for cement pastes with different dosages of CNFs: a) without CNFs, b) with 0.3 wt% CNFs, and c) with 0.8 wt% CNFs. Symbols are measured data and lines are simulated results.
Fig. 11. Water absorption of mortars with different dosages of CNF. Symbols are measured data and lines are simulated results.

Fig. 12. Water absorption of cement pastes with different dosages of CNF. Symbols are measured data and lines are simulated results.
materials. The sorptivity $S_p$ is related to two main factors, the fraction of capillary pores and the capillary pore size distribution. The former determines the final amount of absorbed water and the latter controls the speed of absorption. If a porous material has more large capillary pores, it has a higher $S_p$. Specimens that were previously dried at low RHs have been removed more water (see Fig. 9) so that they have more large capillary pore space available for water absorption. On the contrary, specimens dried at high RHs (e.g., 75 % and 85 %) show slower water absorption because they have less large capillary pore volume for water penetration. After carbonation, the differences in water absorption curves between different RHs are smaller than the NC ones. This is because that the desorption WVSIs of carbonated materials are flatter than the NC ones as shown in Fig. 7. Therefore, the water retention capacity at the studied RHs is not significantly different.

After the first stage of water absorption, curves do not show a clear transition region and rapidly enter another almost linear region, in which water absorption does not change too much. The two linear stages of water absorption for cementitious materials have been reported in the literature and the second linear stage is considered as the secondary water absorption [51,52]. The slow increase of the second linear region is presumably caused by microstructural alteration [51,53,54], gas dissipation [52], and water redistribution [55]. Different from most studies in the literature, the specimens used in the present study are only 2 cm high, so at the end of the first stage, water has reached the top side of a specimen and the further increase of the curves only results from the secondary water absorption.

The final amount of absorbed water depends on the total available capillary pores in the mortar specimen, which clearly decreases with the
increase of previous drying RHs. According to the Kelvin equation, 44%, 53%, 75%, and 85% RH can remove water from pores with diameters larger than 2.6, 3.3, 7.4, and 13.2 nm, respectively. The cumulative absorbed water at the end in Fig. 11 shows that the NC specimens with 0.3 wt% CNFs have more pores larger than 2.6 and 3.3 nm than mortars without CNFs and with 0.8 wt% CNFs, agreeing with PSDs shown in Fig. 5. However, the NC specimens with 0.3 wt% CNFs have fewer pores larger than 7.4 and 13.2 nm than the other NC mortars. After carbonation, the differences in different pore sizes become smaller than for the NC materials. The carbonated specimens with 0.3 wt% CNFs have a slightly higher amount of pores larger than 2.6 and 13.2 nm than the other carbonated materials.

Regarding water absorption results for cement pastes, the NC specimens without CNFs show very gentle water absorption curves, while after carbonation, the water absorption curves sharply increase once they contact liquid water. Their water absorption are much faster and higher than other carbonated and NC specimens. Checking the specimen surfaces after water absorption experiments (see images in Fig. 13), we found that cracks have been formed in some carbonated specimens, which are most likely caused by drying. These cracks are able to significantly accelerate water uptake. Such damages were not so obvious for other specimens with CNFs, presumably because CNFs act as bridges to increase the bonds between hydration products and thus avoid cracking [20,21]. However, the carbonated cement pastes clearly show faster water absorption than the NC ones, while this tendency gradually disappears with the increasing dosage of CNFs. For cement pastes with 0.8 wt% CNFs, the effect of drying RH surpasses the effect of carbonation as shown in Fig. 12c that water absorption of the NC paste dried at 44% RH is the fastest one.

The effects of CNFs, drying RH, and carbonation on water absorption can be quantified by $S_p$ reported in Table 5 and Table 6. Either for mortars or cement pastes, if they are not carbonated, the calculated $S_p$ decreases with the drying RH, while after carbonation, this tendency is not so clear anymore. Before carbonation, the average $S_p$ increases with the dosage of CNFs, meaning that the presence of CNFs leads to more large capillary pores in the materials. However, after carbonation, the average $S_p$ decreases with the dosage of CNFs, which implies that CNFs are able to reduce the effect of carbonation on the volume of capillary pores. By calculating the ratio of average $S_p$ before and after carbonation, we have 2.4 for mortars without CNFs, 2.0 for mortars with 0.3 wt% CNFs, and 1.7 for mortars with 0.8 wt% CNFs. These ratios are 18.7, 2.0 and 1.3 for cement pastes with different dosages of CNFs. These data further suggest that the impact of carbonation on the microstructure is less significant for the materials with CNFs than the neat cement pastes and mortars.

### 3.6. Porosity and density

The saturated mass of a specimen was measured prior to the drying kinetic measurement and the dried mass at 65 °C was measured after water absorption measurement. With knowing the volume of the specimen, assuming no change of the volume, the saturated density $\rho_{sat}$, the dry density $\rho_{dry}$, and total porosity $\phi$ can be determined. Results for mortars and cement pastes are compared in Fig. 14. As generally known, mortars have higher $\rho_{sat}$ and $\rho_{dry}$ and lower $\phi$ than cement pastes because mortars contain sand. For the neat cement paste without carbonation, its total porosity is two times higher than the neat mortar, well agreeing with the calculation result based on the mix design. However, with additional CNFs in the cement paste and mortars, this relation is not valid anymore.

For cement pastes, with the increase of CNFs dosage, $\rho_{sat}$ and $\rho_{dry}$ linearly decrease and $\phi$ increases. A clear reason is that CNFs have a lower density than cement, but this effect is much smaller than the observed differences in Fig. 14. For instance, the calculated differences between neat cement pastes and those with 0.8 wt% CNFs according to the mix design are 0.006 g/l for $\rho_{sat}$ and 0.008 for $\phi$, while Fig. 14 shows differences of 137 g/l and 0.064, respectively. Another possible reason is that CNFs delay hydration [17,19], which is in favor of the formation of more high-density C-S-H as confirmed by the results of nanoindentation [25]. As a consequence, there are more empty spaces between hydration products. This is partially confirmed by the average $S_p$ (see Table 6) which increases with the dosage of CNFs for the NC cement pastes. After carbonation, the $\rho_{sat}$ and $\rho_{dry}$ curves shift up and the $\phi$ curve moves down because of the increase of precipitated calcium carbonate which occupies some pores.

For mortars, $\rho_{sat}$ and $\rho_{dry}$ are almost constant for different dosages of CNFs, while $\phi$ slightly increases. It is clear that the compaction of hydration products in mortars is higher than these in cement pastes. The formed more high-density C-S-H due to the presence of CNFs should contribute to this difference. After carbonation, however, $\rho_{sat}$, $\rho_{dry}$, and $\phi$ all slightly decrease from neat cement to 0.3 wt% CNFs and no further change for the higher CNFs dosage. In addition to the fact that the precipitation of calcium carbonate leads to the increase of specimen mass and reduction of total pore volume, it may be possible that the density of calcium carbonate formed in neat cement mortar is higher than that in mortars with CNFs.

Presumably, evaporable water in dried specimens is completely removed, so that the increase of $\rho_{dry}$ after carbonation is purely from CO$_2$ that is captured by reaction with hydration products. Hence, the amount of CO$_2$ absorbed by materials can be determined by calculating the differences in $\rho_{dry}$ before and after carbonation and multiplied by a
factor of 44/26 as the carbonation process generates water that is removed by drying when measuring $\rho_{dry}$. The calculated results are provided in Table 4 (mean values of four specimens). For cement pastes, adding 0.8 wt% CNFs is able to slightly decrease the amount of CO$_2$. In general, mortars capture less CO$_2$ than cement pastes. Results show that the amount of CO$_2$ varies with the CNFs dosage. Specifically, it clearly decreases for mortars, while for cement pastes, the amount of absorbed CO$_2$ increases for 0.3 wt% CNFs but sharply decreases for 0.8 wt% CNFs. Therefore, the additional CNFs show an ability to reduce carbonation reaction in this study, in particular for mortars. This result agrees with the calculated carbonation ratios in Table 3.

4. Discussion

4.1. Inverse analysis on water permeability

The above experimental results indicate that the moisture transport speed is markedly increased by carbonation, by the dosage of CNFs, and by cracks induced by drying. To quantify their effects on transport coefficients, the liquid permeability by cracks induced by drying. To quantify their effects on transport coefficients, the liquid permeability

\[
dS = \nabla[D_1(S)\nabla S] \tag{4}
\]

where $D_1(S)$ is an apparent diffusivity, which is a function of $S$.

It was reported that a two-phase model is necessary to simulate moisture transport in the whole range of RH [50]. The apparent diffusivity $D_2(S)$ has contributions from liquid water and water vapor,

\[
D_2(S) = D_1(S) + D_3(S) \tag{5}
\]

with

\[
D_3(S) = -k_l \frac{K_l}{\eta_l} \frac{dP_c}{dS} \tag{6}
\]

\[
D_3(S) = -\frac{M_w}{\rho_iRT \phi_0^2} \frac{1}{\phi S} \frac{dP_i}{dS} \tag{7}
\]

where $\eta_l$ is the dynamic viscosity of liquid water, $M_w$ is the molar mass of water molecule, $\rho_i$ is liquid water density, $\phi_0$ is a resistant parameter to consider the microstructural effect on vapor diffusion (taking as 2.74 for cement-based materials [61]), and $P_s$ is the saturated vapor pressure in air. The term $\frac{dP}{dS}$ represents the moisture retention capacity, which should be calculated from a WVSI. A measured WVSI is fitted by the van Genuchten equation [62]. The relative permeability $k_r$ is expressed as a function of $S$ by using the van Genuchten - Mualem model [62,63]. These equations can be found elsewhere [56,60].

Permeability in this model is expressed as $k_l = k_0k_r$, in which the intrinsic permeability $K_0$ is the only unknown; therefore, $K_0$ can be inversely determined by fitting a measured mass change curve of a specimen subjecting to drying or a water absorption curve. For simulating drying kinetics, a desorption WVSI is used to calculate $\frac{dP}{dS}$ because water content in a specimen decreases from high RH. After drying when performing water absorption measurements, however, specimens start at different initial $S$, which corresponds to 44%, 53%, 75%, or 85% RH. From these points to let specimens absorb water, the $S$ - $RH$ relation does not follow either the main desorption or main adsorption curves. Instead, because of the existing sorption hysteresis, the $S$ - $RH$ relation follows a scanning curve of WVSIs between two main sorption curves. Therefore, a sorption hysteresis model is necessary to correctly predict the path of the scanning curve. By comparing available sorption hysteresis models in the literature, previous studies have shown that the revised Mualem II model provides the best results well matching experimental data [60]. An example of scanning curves calculated by the revised Mualem II model with different starting points is illustrated in Fig. 15, which shows that the scanning curves gradually approach the main adsorption curve with the increasing RH.

The simulated drying mass loss and water absorption curves (solids for NC materials and dashes for carbonated ones) are compared with measured data in Fig. 9 and Fig. 10 for drying kinetics and Fig. 11 and Fig. 12 for water absorption. The inversely determined intrinsic permeability $K_l$ by using measured drying kinetics and water absorption data is provided in Table 5 and Table 6 for mortars and cement pastes, respectively. Figures show that most simulated drying mass loss curves can match well the measured data with only adjusting $K_l$ except for a few cement paste specimens. For water absorption, we only tried to fit the first linear region as this region reflects water transport in capillary pores. The slow moisture absorption in the later region, caused by the complex microstructure of cement-based materials [51-54,64,65], is not included in the present moisture transport model.

For NC mortars, $K_l$ determined from drying kinetics is in the order of $10^{-21}$ m$^2$, in the same range with data measured by various experimental methods in the literature [57,66,67]. Regardless of the carbonation conditions, $K_l$ determined from water absorption data is about 5–500 times (50 on average) higher than that from drying kinetics. It has been reported that the sorptivity method provides permeability about two orders of magnitudes higher than these determined by the Beam Bending method and inverse analysis [50]. The main reason is that specimens used for water absorption must be pre-dried in an environment with low RHs to remove a certain amount of water. As well known,
any drying methods can induce damage to the microstructure [32],
generally creating more capillary pores. Nevertheless, the sorptivity
method does not consider the drying damage, so the determined $K_l$ is
higher.

The drying effect on the pore structure of mortars is well shown in $K_l$
data in Table 5. No matter which methods are used to calculate $K_l$, the
clear tendency is that $K_l$ values decrease with the increase of drying RH.
It clearly demonstrates that the degree of drying damage decreases with
the increasing RH. So, it is reasonable to say that the inversely
determined $K_l$ at high RH is much closer to the “real” $K_l$ due to the least
damage to the microstructure [50]; that is drying at 85 % RH in this
study.

After carbonation, $K_l$ values in Table 5 are higher than NC specimens
at the same experimental conditions. Only looking at average $K_l$ values or
drying at 85 % RH (less drying damage to the microstructure), we see
that $K_l$ slightly increases for NC specimens with the CNFs dosage which
has the same trend to the total porosity as shown in Fig. 14, but after
carbonation, $K_l$ decreases with CNFs dosage. By calculating the ratio of
average $K_l$ based on drying kinetics before and after carbonation, we have
147.9 for mortars without CNFs, 25.5 for mortars with 0.3 wt% CNFs, and 5.0 for mortars with 0.8 wt% CNFs. The ratios become 7.6, 9.8, and 2.7 for water absorption results. This clearly proves that the presence of CNFs is able to reduce the enlarging effect of carbonation on moisture transport.

For cement pastes, drying kinetics or water absorption data of a few
specimens cannot be simulated by the moisture transport model because either the measured transport is too fast or
the measured data are less stable.
4.2. Effects of CNFs on durability of cement-based materials

As for non-carbonated cement-based materials, TGA data reveal that the formation of hydration products is hindered by the presence of CNFs (see Fig. 3a). Theoretically, nanomaterials have the steric stabilization ability to create a uniform distribution of cement particles in the fresh cement slurry and also enhance nucleation of the hydrated products because of the large surface area of CNFs; consequently, the early degree of cement hydration is improved [68]. However, the delay of the main hydration peak was reported in the previous studies [17,19,69]. The cause to this delay is still not clear yet, but the higher w/c, the more significant delay was found [19]. Considering that the deceleration period of cement hydration is controlled by factors including the diffusion process of dissolved ions, the availability of water and space [70], cementitious materials with high w/c are expected to have a high long-term degree of hydration [71]. Nevertheless, when CNFs are present, these fibers act as physical barriers and can absorb some ions; thus, ion diffusion is slowed down. This effect may be more significant for the higher w/c cementitious materials. Therefore, less hydration products were observed in cementitious materials with CNFs.

In terms of the microstructure, PSDs calculated from the nitrogen adsorption curves show fewer small pores in cement pastes with CNFs than the neat cement paste (see Fig. 5b). Together with the fact of the increasing total porosity with the dosage of CNFs (see Fig. 14), we can infer that the presence of CNFs results in more large capillary pores. This is confirmed by the calculated sorptivity and inversely determined permeability for NC materials, as both of them increase with the CNFs content (see Table 5 and Table 6). These results do not show promising benefits of CNFs in improving the durability of NC cement-based materials. Nevertheless, the use of CNFs is able to reduce shrinkage and cracking, which was reported in the literature [20,21] and also confirmed in this study (see Fig. 13).

However, after carbonation, the above-mentioned tendencies are completely reversed. TGA data show that the amount of remaining hydration products in carbonated pastes increases with the dosage of CNFs (see Fig. 3b) and the carbonation ratios for all hydration products decrease with the CNFs dosage (see Table 3). The nitrogen adsorption results show that BET surface area slightly increases with the CNFs content and the pore coarsening effect of carbonation is weakened by CNFs (see Fig. 5 and Fig. 6). The measured water vapor sorption isotherms further suggest that the carbonation effect on the microstructure is reduced by CNFs. After carbonation, both the calculated sorptivity and inversely determined permeability decrease with the CNFs content (see Table 5 and Table 6). The comparison of dry densities before and after carbonation implies that the amount of CO₂ reacting with cement-based materials decreases with the dosage of CNFs (see Table 4). All these results clearly show the benefits of CNFs in reducing the effects of carbonation on the durability of the studied cementitious materials. As the transport coefficients are lower in carbonated materials with CNFs, the penetration of moisture and oxygen, two essential factors for steel corrosion, are expected to be much slower than that in carbonated materials without CNFs. Therefore, we expect that the risk of steel corrosion is lower after carbonation if CNFs are used in cementitious materials.

5. Conclusions and outlook

Cellulose nanofibrils (CNFs) were used to prepare cement pastes and mortars and their microstructure, mineralogical composition, moisture retention capacity, drying kinetics, and water absorption were investigated in this study. Results indicate that the use of CNFs can reduce drying cracks but may not have other promising benefits to non-carbonated materials as CNFs can retard cement hydration, coarsen the microstructure, increase moisture transport and porosity. However, after carbonation, the durability benefits of CNFs are clear:

- Mineralogy. The presence of CNFs can help the material resist carbonation. The carbonation ratios of hydration products are lower for materials containing CNFs so that more hydration products remain in the carbonated materials. In the carbonation regime of this study, there are about 72 % CH being carbonated if no CNFs were added, but this value drops to 60 % with 0.8 wt% CNFs. The amount of carbonate C-S-H and ettringite is halved comparing materials with 0.8 wt% CNFs with no CNFs. The amount of CO₂ captured by the fully materials decreases with the increasing CNFs dosage.

- Microstructure. The measured PSDs for noncarbonated pastes indicate that the higher fractions of small pores are found in pastes with CNFs than the neat cement paste. After carbonation, BET surface area as well as the amount of small pores (<10 nm) slightly increases with the CNFs content. WVSIs also confirm that the higher CNFs content is able to better weaken the carbonation effect on the microstructure.

- Moisture transport. For the noncarbonated materials, water sorptivity and liquid permeability slightly increase with the dosage of CNFs. After carbonation, both water sorptivity and water permeability became higher than before, but they decrease with the CNFs dosage. CNFs are able to reduce carbonation effects (coarsening) on pore structure, in particular creating fewer large capillary pores than materials without CNFs.

In addition to these benefits, other conclusions drawn in this study are:

- The content of vaterite decreases with the increasing dosage of CNFs after the accelerated carbonation. Nanofibers seem to help the transformation of vaterite to a more stable polymorph of calcium carbonates - calcite.

- The TGA results show that the content of hydration products (CH, C-S-H, and ettringite) slightly decreases with the increase of CNFs dosage. Therefore, the retardation effect (via absorption on cement grain surface or chemically bound with cations) not only can delay cement hydration at early ages but also last longer than expected.

- The inversely determined permeability decreases with the increasing drying RH. The most like reason is that low RHs can induce more serious drying damage to the microstructure so permeability increases accordingly, while high RHs have lower effects on the microstructure so permeability is lower.

- The reliability of experimental data for cement pastes is slightly lower than mortars, because, during the drying tests, the drying cracks can be clearly seen on cement pastes, which thus changes the microstructure of cement pastes.

The present study only focused on paste and mortar made from one type of cement which were carbonated at six months. To represent the real situations of concrete structure, concrete with more types of cements and long-term experiments will be carried out to study the effects of CNFs and other nanomaterials on the durability of cementitious materials.
CRediT authorship contribution statement

Zhidong Zhang: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Funding acquisition. Ueli Angst: Funding acquisition, Methodology, Conceptualization, Writing - review & editing.

Declaration of competing interest
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.

Data availability
No data was used for the research described in the article.

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