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X-ray dark-field contrast imaging of water transport during hydration and drying of early-age cement-based materials

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ABSTRACT

In this study, we investigated by X-ray dark-field contrast imaging the internal displacements of water in early-age cement-based materials due to their spatial microstructural heterogeneities. We performed time-lapse multi-contrast X-ray radiography measurements with a laboratory-scale Talbot-Lau X-ray interferometer during drying and hardening of a model system. Such system consisted of two mortar layers with distinct pore size distribution and local porosities. With these measurements we propose a new approach to imaging water transport in such materials at early hardening ages.

The results show that such approach provides higher sensitivity to local water content changes and higher temporal and spatial resolutions as compared to standard X-ray attenuation contrast imaging. In this work, we assessed both qualitatively and quantitatively the roles of key drivers of such water displacements in the evolving microstructure: capillary force gradients created by the spatial heterogeneity in the pore size distribution and by evaporative drying. This was accomplished by correlating the dark-field contrast imaging results with information about the system's pore space features, obtained by attenuation contrast X-ray microtomography and respective 3D image analysis. Such correlative analysis provides new evidence of the existence of strong couplings between pore-scale water displacements and the microstructure formation in cement-based materials at early ages.

1. Introduction

Water transport occurs inside cement-based materials at early ages immediately since casting time. That is because of a highly heterogeneous spatial distribution of capillary forces inside the pore space. On one side, such heterogeneous distribution is caused by (1) the spatial heterogeneity and temporal evolution of the pore size distribution and (2) by evaporative drying [1,2]. On the other side, such transport significantly influences the microstructure evolution, thus the macroscopic poro-mechanical and fluid transport properties of the hardened materials. The influencing is not uni-directional. Rather, couplings and feedback loops exist between how the microstructure evolves and how consequently water moves through the evolving pore space [3].

The availability of methods for imaging early age water transport has a significant practical impact on developing approaches for improving the long-term durability properties of cement-based materials. Examples of such approaches include the mitigation of early-age shrinkage processes, e.g., plastic [4] and drying shrinkage [5]. Another important example is the achievement by internal curing [6–8] of higher degrees of hydration in low water-to-cement ratio (w/c), i.e., high and ultra-high performance, concretes. A final example is related with the optimal design of repair materials [9,10].

Evaporative drying leads to the formation of water menisci inside the pore space, typically starting from the surface(s) exposed to the environment, then progressing inside the bulk of the specimen. The heterogeneous spatial-temporal distribution of such menisci leads in turn to the development of very heterogeneous capillary force field gradients, responsible, at different early-age stages, of plastic shrinkage and drying shrinkage, respectively. Understanding the couplings between the microstructure formation, including the shrinkage-induced micro-cracks, and the evaporative drying progression inside the specimen is functional to the development of shrinkage reduction approaches based, e.g., upon shrinkage reducing admixtures [4] or internal curing water-saturated particles [8].

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Internal curing particles, e.g., light weight aggregates (LWAs) or super absorbent polymers (SAPs), have been used as internal reservoirs and suppliers of water. They are saturated before or directly during the mixing and uniformly dispersed in the cast volume, thus providing a spatially homogeneous supply of curing water [8]. Such supply to the hydrating cement matrix is thought of being driven by local capillary force gradients, which are dependent upon the local microstructure formation [11]. The optimization of internal curing methods requires a complete understanding of how and how far is water displaced from the more porous LWAs or from the SAP particles to the less porous cement matrix [12].

Cement-based composites for repair of already hardened concrete structures also rely upon an accurate understanding of how water is displaced by capillary force gradients generated by the spatial heterogeneities in the pore system. As hypothesized by Bentz et al., when the repair layer is designed to achieve a pore size distribution with a prevalence of the larger pores, compared with the substrate, the adhesion between the repair layer and the substrate could be increased by water capillary suction towards the substrate [1,2].

In their work, Bentz et al. were among the first to use model systems for investigating the role played by capillary force gradients in water transport at early ages. They did so by spatially mapping the temporal evolution of a proxy variable of local water content. The model systems they used consisted of different combinations of two layers of distinct cement pastes, one cast on top of the other in sealed or open molds. The cement pastes differed either in w/c value [1,2] or in cement particle size distribution [1]. In either case the overall effect was that of creating different pore size distributions for the two distinct layers. Independently of the position of the two distinct pastes, either at the bottom or at the top of the mold, and independently of sealing the top or not, a relative increase in local water content was observed for the layer with finer pores. On the contrary, a relative decrease was observed for the layer with coarser ones.

These results provided the first systematic evidence, for cement-based materials, of the movement of water from the "coarser pores layer" to the "finer pores" one. Even in the case of an open mold and the layer with finer pores on top of the other one, thus exposed to a lower relative humidity (RH) environment and subjected to evaporative drying, the bottom layer, not directly exposed to the lower RH, was observed to lose water. Moreover, the bottom layer started losing water earlier than the top one. This likely occurred by water displacements from the larger pores of the bottom layer to the smaller ones in the above layer. This observed loss in the "sealed" bottom layer suggests that water can be displaced not only by capillary force gradients created by evaporative drying, as it is well known from the poro-mechanics of drying [13,14], but also by capillary force gradients produced by intrinsic spatial gradients in pore size range and pore size distribution.

The experiments of Bentz et al. [1,2] were among the first results with broad impact on the understanding of water movement at early ages during the simultaneous and coupled microstructure formation and evaporative drying.

One consequence of such experimental observations was the description of drying mechanisms in computational models of hydrating cement-based materials [1]. In addition, these were the first measurements consisting of imaging, by X-ray attenuation measurements, the spatial-temporal distribution of water at early ages, even though only 1D spatial profiles could be obtained.

Since those first studies [1,2], the visualization of water transport in early age cement-based materials has been achieved by different imaging techniques.

Three of the most commonly used techniques have been neutron imaging (NI), magnetic resonance imaging (MRI) and X-ray attenuation-contrast imaging (XACI).

NI has been widely used for both visualizing and quantitatively characterizing a large variety of water transport processes in cement-based materials [15]. This is because of the large total interaction cross section of a neutron with hydrogen, leading to high contrast to spatial differences in local water content and to their changes.

Examples of NI applications, related with water displacements at early ages, include visualizing the release of internal curing water provided by saturated LWAs and the water movement across the surrounding cement [16,17] or mortar matrix [18]. Another example is related with the visualization of the release and movement of internal curing water provided by saturated SAP particles [19,20]. The last example regards locating the redistribution of water in fresh mortars exposed to external drying, leading to their plastic shrinkage and cracking [21].

Despite these applications (along with many others) to hardening cement-based materials show the usefulness and potential of NI, this technique has two main limitations. The first one is its limited accessibility, due to the small number of neutron facilities world-wide and to the time constraints in using them. The second main limitation is the maximum spatial and temporal resolutions, currently not sufficient for pore-scale investigations. The spatial resolution does not exceed yet the length scale of 10–20 μm at state-of-the-art facilities [22], even though current developments may reduce these limits to the scale of a few μm [23,24]. The maximal temporal resolution does not allow yet investigating in 3D such fast displacements driven by large capillary force gradients, e.g., the capillary suction of water from a more porous region or from a porous internal curing particle to a less porous one [17,21].

MRI has the advantage of allowing mapping quantitatively the local water content and, simultaneously, the local pore size distribution, the latter by nuclear magnetic resonance relaxometry, all feasible at the laboratory-scale [25,26]. In addition, different types of in-pore water can be distinguished and spatially mapped, still by NMR relaxometry. Thus, the two types of mapping have been successfully used for the investigation of the couplings between the microstructure evolution and the water displacements induced by evaporative drying [27]. However, compared to neutron imaging, this technique achieves even lower spatial and temporal resolutions [28]. Also the high cost of a scanning MRI instrument makes it less affordable by any laboratory.

X-ray attenuation contrast imaging (XACI) has so far achieved both high spatial (down to a few hundreds of nm) and high temporal (down to a few hundreds of ms, for tomography) resolutions in studying, in general, water transport in porous materials. Such achievements have been obtained not only at synchrotron radiation facilities [29,30] but also with more accessible and widespread laboratory-scale setups [31], whose availability is typically higher than MRI instruments', due to much lower costs.

XACI is based on measuring the attenuation of an X-ray beam transmitted through the specimen. The pixel value in single 2D projection images (radiographs) reflects the accumulated projection of the specimen's attenuation coefficient μ along the ray traced from the X-ray source to the detector's pixel (Beer-Lambert law). μ is related to the imaginary part, β, of the complex index of refraction n of the specimen,

$$n = 1 - \delta + i\beta, \tag{1}$$

where δ is the real part of such index (decrement thereof, respect to the unity) and i is the imaginary unit.

β is linearly proportional to n_e, to $Z^n$and to E^{-m}. n_e is the electron density, Z is the atomic number of a predominant composing element, with $n \cong 4 - 5$, and E is the photon energy, with $m \cong 3 - 3.5$ [32]. The contrast to local changes in water content strongly depends on the relative differences between water, air and the solid substrate, in terms of n_e and/or Z. For the majority of porous building materials, such differences are typically very small, leading to low contrast to local water content changes. Despite the low contrast, previous studies have shown that XACI can still allow visualizing water transport in porous materials when either the pore size ranges from hundreds of μm to tens of mm [33] and/or the water content change involves large volumes of water relatively to, e.g., the voxel size of the X-ray tomogram [34]. The last condition may be for example achieved when only 2D radiographs are