



The influence of different drying techniques on the water sorption properties of cement-based materials



D. Snoeck^{a,b}, L.F. Velasco^c, A. Mignon^{a,b}, S. Van Vlierberghe^b, P. Dubruel^b, P. Lodewyckx^c, N. De Belie^{a,*}

^a Magel Laboratory for Concrete Research, Department of Structural Engineering, Faculty of Engineering, Ghent University, Technologiepark Zwijnaarde 904, B-9052 Ghent, Belgium

^b Polymer Chemistry and Biomaterials Group, Department of Organic Chemistry, Faculty of Sciences, Ghent University, Krijgslaan 281, B-9000 Ghent, Belgium

^c Department of Chemistry, Royal Military Academy, Renaissanceaan 30, B-1000 Brussels, Belgium

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ABSTRACT

Dynamic water vapor sorption (DVS) may be used to characterize the pore structure of cementitious materials, but the technique is difficult to interpret as the microstructure is very sensitive to drying and rehydration due to humidity exposure. The removal of interlayer water or chemically bound water can cause microstructural shrinkage. As all drying techniques more or less dehydrate C–S–H and ettringite, they cause a restructuration of the C–S–H.

In the present paper, DVS measurements were performed to characterize the changes induced by different drying techniques in the textural and sorption properties of the material, while thermogravimetric analysis was used to elucidate carbonation.

The ideal drying technique, which can preserve the microstructure and can remove only the non-bound water, does unfortunately not exist. All drying techniques separately affect the microstructure to some extent. However, these changes are minimized when using vacuum-drying and the solvent-exchange-method with isopropanol as drying techniques.

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1. Introduction

At some level, the behavior of every material is related to its microstructure. One of the most important properties of a cement paste is thus the developing pore structure. Other cementitious material characteristics (e.g. strength and permeability) can be derived based on the knowledge of the total pore volume, the pore size distribution, the specific surface area and the pore connectivity [1,2].

Besides the differentiation between pores, there also exist three types of water related to the different pore sizes. First, there is the pore water in the capillary pores, which are a few hundred nanometres in size. Secondly, the interlayer water which is held by the gel pores by capillary tension and strong hydrogen bonds to the C–S–H. The size of the gel pores is in the order of nanometres. The gel is a three-dimensional build-up of C–S–H layers with physically adsorbed water molecules and interlayer water between the sheet structure [5]. Removal of this water by drying can cause considerable microstructural shrinkage. The third type of water is the chemically bound water, which is part of the chemical structure of the hydrated phases, and can only be removed by hydrate decomposition. Besides capillary and gel pores, voids are also a classification of pores. In this paper, however, a

classification was made according to *micro* < 2 nm, *meso* 2–50 nm and *macro* > 50 nm pores (originally proposed by Dubinin [3] and subsequently officially adopted by the IUPAC [4]).

Moisture transport processes cannot be understood without the knowledge of the moisture fixation in the concrete pore system. Water vapor sorption (i.e. the relation between moisture content and relative humidity) is therefore a key parameter. But, the moisture sorption isotherm is a function of the age, the moisture history, the temperature, etc. So, it is of great importance to know the extent and history of the drying process while performing a water vapor sorption test.

Also and comparatively with other sorption techniques, the use of water adsorption has some advantages, among them are: *i*) it can be performed at room temperature, *ii*) water has a small kinetic diameter (i.e. 0.28 nm) which allows it to enter pores even smaller than the ones accessible to CO₂ and N₂, and *iii*) for some kind of materials it is sensitive to surface chemistry. Moreover, it is not necessary to submit the sample to a degassing protocol prior to the measurement, thus avoiding the partial removal of the ettringite phase.

Generally, all drying techniques more or less dehydrate C–S–H and ettringite. A strong drying method may remove interlayer water from C–S–H which re-enters when the RH increases again [6]. Drying causes the restructuration of low-density C–S–H and a collapse below 40% RH as well as the conversion of loosely-packed C–S–H to a denser C–S–H. Drying enhances the chemical aging, meaning that the degree of

* Corresponding author. Tel.: +32 92645522; fax: +32 92645845.
E-mail address: nele.debelie@UGent.be (N. De Belie).

polymerization of the silicate chains has increased and the C–S–H has changed irreversibly towards stiffer, stronger and denser ones [7]. Incomplete water removal likely leaves plugs or residual water in the narrowest choke points, resulting in a complete pore blockage in some areas of the paste [8,9]. During chemical aging, C–S–H tends to link with each other, causing a compression of the hydrates. A strong drying step accelerates this reaction because the C–S–H are brought closer together [5].

The four main drying techniques described in literature to dry cementitious materials are discussed hereafter.

1.1. Freeze-drying

In freeze-drying (F-drying), the ice sublimates, causing less capillary stresses. Some investigations even showed a preservation of the pores in the fine pore region ($r < 5$ nm) [10,11]. For that reason, this drying technique is used frequently for MIP and TGA measurements [12] as it also stops hydration. However, F-drying may also change the microstructure [13]. It causes limited significant damage, due to thermo-mechanical stress in the inner C–S–H porosity [10,12,14]. So overall, the literature is not conclusive on the effects of F-drying.

1.2. Oven-drying

Oven-drying is widely used because it is a fast drying technique. Oven-drying, however, damages and alters the microstructure significantly, even to a greater extent than freeze-drying [14]. For example, oven-drying at 105 °C removes unbound water but the capillary hydrostatic stresses due to surface tension of the receding water menisci generate a collapse of the fine pores [11,14–16] as C–S–H is partly dehydrated at 105 °C [1,171]. Oven-drying also leads to the decomposition of monosulfoaluminate AFm and ettringite AFt phase at 60 °C ([18] as cited by [13]). It thus causes ettringite and C–S–H to lose a significant amount of non-evaporable water [14]. Drying at 50 °C coarsens the pore structure due to the polymerization of silicate anion chains and the development of a cohesive structure in C–S–H [19]. Generally, oven-drying thus results in large capillary porosity due to capillary stresses, cement hydrates (ettringite, AFm and C–S–H) desiccation, and micro-crack generation due to thermo-hydric stresses and the differential thermal expansion of the composition.

1.3. Vacuum-drying

Vacuum-drying is a slow technique and Zhang and Glasser ([18] as cited by [13,14]) already observed that ettringite and monosulfoaluminate may degrade (structural and physical collapse of hydrates like AFm and AFt phases), causing damage to the pore structure and increasing the pore volume ([18], as quoted by [12]).

1.4. Solvent-exchange-method

Solvent-exchange-methods replace the water by a solvent during submersion of a sample in the solvent. The solvent is afterwards removed by ambient drying or vacuum-drying. The solvent-exchange-methods show the best results in preserving the microstructure as they stress the microstructure less [10,12,20] and they are therefore used to stop the hydration and to study the microstructure. However, it remains possible that a solvent replacement creates chemical artifacts in the specimens by reaction with hydration products or through strong adsorption. Upon heating, methanol for example will react with C–S–H to form CO₂ and this is reflected in a higher carbonate peak [20–22]. It binds with hydrating and mature cement paste. Some researchers stated that there might be a possible reaction of isopropanol with calcium hydroxide [23], but in general, it is accepted that isopropanol does not react with cement [20] as does methanol.

Which drying technique is the optimal is feed for discussion. Zhang and Scherer [13] have summarized pros and cons of the various drying techniques available as follows:

To preserve microstructure:	solvent-replacement > vacuum-drying > F-drying > oven-drying
To preserve composition:	F-drying > oven-drying > solvent-replacement
To save time:	oven-drying > F-drying > solvent-replacement

In the present study, the effects of different drying techniques on the microstructure were approached using a supplementary technique, namely water vapor adsorption isotherms. In this way, knowledge is gained on the effects of the drying techniques on the sorption properties, namely the formed microstructure of cementitious materials. In addition, thermogravimetric analysis was used to elucidate carbonation.

2. Materials and methods

2.1. Materials

A cement paste with a water-to-cement ratio of 0.5 was made and cast. The cement used was CEM I 52.5 N (chemical and phase composition in Table 1) and the standard used for the mixing procedure was EN 196-1. After one day of storage in a relative humidity of $95 \pm 5\%$ and a temperature of 20 ± 2 °C, the samples were stored in water at 20 ± 2 °C for a minimum period of 6 months to ensure a stable formation of the cementitious matrix. Prior to testing, the samples were ground and sieved (500–1000 μm). To exclude the effect of contact with CO₂ and the effects of carbonation, the samples were stored in water or in the presence of soda lime during drying (Fig. 1b). The soda lime was replaced every day.

2.2. Methods

2.2.1. Drying techniques

Several drying techniques were studied. These include:

- *no-drying* (20 ± 2 °C): specimens are stored in water;
- *freeze-drying*: specimens are dried in liquid nitrogen and placed in a freeze-dryer instantaneously for two weeks;
- *oven-drying at 40 °C*: for two weeks (ventilated oven);
- *oven-drying 105 °C*: for two weeks (non-ventilated oven);
- *air-drying in the presence of silica gel* (20 ± 2 °C): for one month;
- *vacuum-drying* (20 ± 2 °C): for two weeks at 0.1 bar;
- *the solvent-exchange-method in methanol and isopropanol followed by vacuum-drying* (20 ± 2 °C): stored in the solvent (solution:sample volume ratio more than 100:1) for one week and subsequently vacuum-dried for two weeks.

Table 1

Chemical and phase composition of CEM I 52.5 N. The phase composition is calculated based on the formulas of Bogue, corrected with the amount of SO₃ for C₃S.

	CEM I 52.5 N mass-%	Phase composition mass-%
CaO	63.12	
SiO ₂	18.73	
Al ₂ O ₃	4.94	
Fe ₂ O ₃	3.99	
SO ₃	3.07	
MgO	1.02	
K ₂ O	0.77	
Na ₂ O	0.41	
C ₃ S		66.9
C ₂ S		3.3
C ₃ A		6.3
C ₄ AF		12.1

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