EFFECT OF THE DRYING TECHNIQUE ON THE SORPTION PROPERTIES IN CEMENTITIOUS MATERIALS

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Abstract

A good understanding of the nano-pore structure gives insight in several concrete properties like compressive strength, permeability and durability aspects. Dynamic water vapour sorption tests may be used to study this porosity, but the technique is difficult to interpret as the microstructure is very sensitive to stress, drying and rehydration due to humidity exposure.

The removal of interlayer water held by gel pores in C-S-H or chemically bound water can also cause considerable microstructural shrinkage. As all drying techniques more or less dehydrate C-S-H and ettringite, they cause a restructuration of the C-S-H, changing the C-S-H in denser ones.

Several drying techniques were studied. These include: no-drying, freeze-drying, oven-drying at 40°C and 105°C, air-drying in the presence of silica gel (20±2°C), vacuum-drying (20±2°C), and the solvent-exchange-method in methanol and isopropanol followed by vacuum-drying (20±2°C). The effect of these various drying techniques on the sorption characteristics in cementitious materials was studied by means of dynamic water vapour sorption tests. To prevent carbonation, the samples were always stored together with soda lime. Thermo-gravimetric analysis was used to elucidate carbonation.

Freeze-drying changed the microstructure due to thermo-mechanical stress in the inner C-S-H. Oven-drying removed part of the non-evaporable water, dehydrated C-S-H, monosulfoaluminate (AFm) and ettringite (AFt) phases, and caused thermo-hydric stresses due to differential expansion. Capillary stresses due to receding water menisci may also induce a modification of the textural properties of the sample.

Oven-drying and air-drying proved to cause carbonation, which is unwanted to study the microstructure. Methanol reacted with C-S-H but isopropanol seemed to be inert with cementitious compounds.

The ideal drying technique, which can preserve the microstructure and can remove only the non-bound water, does unfortunately not exist. All drying techniques affect the microstructure in their own way. Only vacuum-drying and the solvent-exchange-method with isopropanol proved to be acceptable drying techniques to prepare specimens for water sorption analysis.

Introduction

There are three types of water. First, the pore water in the capillary pores, a few hundred nanometres in size. Second, the interlayer water held by the gel pores by capillary tension and strong hydrogen bonds to the C-S-H. The size is in the order of nanometres. Removal of this water by drying can cause considerable microstructural shrinkage. The third type of water is the chemically bound water, part of the chemical structure of the hydrated silicate phases, only to be removed by hydrate decomposition.

Moisture transport processes cannot be understood without the knowledge of the moisture fixation in the concrete pore system. Water vapour sorption is therefore a key parameter. While performing a water vapour sorption test, however, it is of great importance to know the extent and history of drying.

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 [1]. Drying causes restructuration of low-density C-S-H and a collapse below RH = 40% as well as conversion of loose-packed C-S-H to low-density C-S-H. Drying enhances the chemical ageing, which means that the degree of polymerization of the silicate chains is increased and the C-S-H is changed irreversibly in stiffer, stronger and denser ones [2]. 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 [3, 4]. During chemical aging, C-S-H tend to link with each other, causing a compression of the cement particles. A strong drying accelerates this reaction because the C-S-H are brought closer together [5].

Which drying technique to use is discussable. Zhang and Scherer [6] concluded 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 > freeze drying > solvent replacement*

In this study, the effects of different drying techniques on the microstructure were approached using a new and supplementary technique: water vapor adsorption isotherms.

Materials

A cement paste with a water-to-cement ratio of 0.5 was made and casted. The cement used was CEM I 52.5 N and the standard used as mixing procedure was EN 196-1. After one day of storage in a relative humidity of 95±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 complete hydration and 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 CO_2 and the effects of carbonation, the samples were stored in water, or in the presence of soda lime during drying. The soda lime was replaced every day.

Methods

Drying techniques

Several drying techniques were studied. These include: no-drying, freeze-drying, oven-drying at 40°C and 105°C, air-drying in the presence of silica gel (20±2°C), vacuum-drying (20±2°C), and the solvent-exchange-method in methanol and isopropanol followed by vacuum-drying (20±2°C). Also, ground specimens were stored for 6 months in water and 6 months in air to receive complete carbonation.

Water vapour sorption test

The Dynamic Vapour Sorption Apparatus used was from Surface Measurement Systems, London, UK. The temperature was set to 20°C, and the mass criterion was dm/dt<0.002 %/min. The RH levels at which samples (0.01–0.015 g) were subsequently equilibrated included 98-90-80-70-60-50-40-30-20-10-5-2-1-0% RH. Wet samples underwent two desorption-adsorption cycles. Dried cement pastes were first conditioned at 0% RH followed by two adsorption-desorption cycles.

Thermogravimetric analysis

The TGA instrument used in this investigation is a TGA Q50 Thermogravimetric Analyser. A sample was gradually heated with 10°C min^{-1} until 900°C under a controlled N_2 atmosphere.

Results

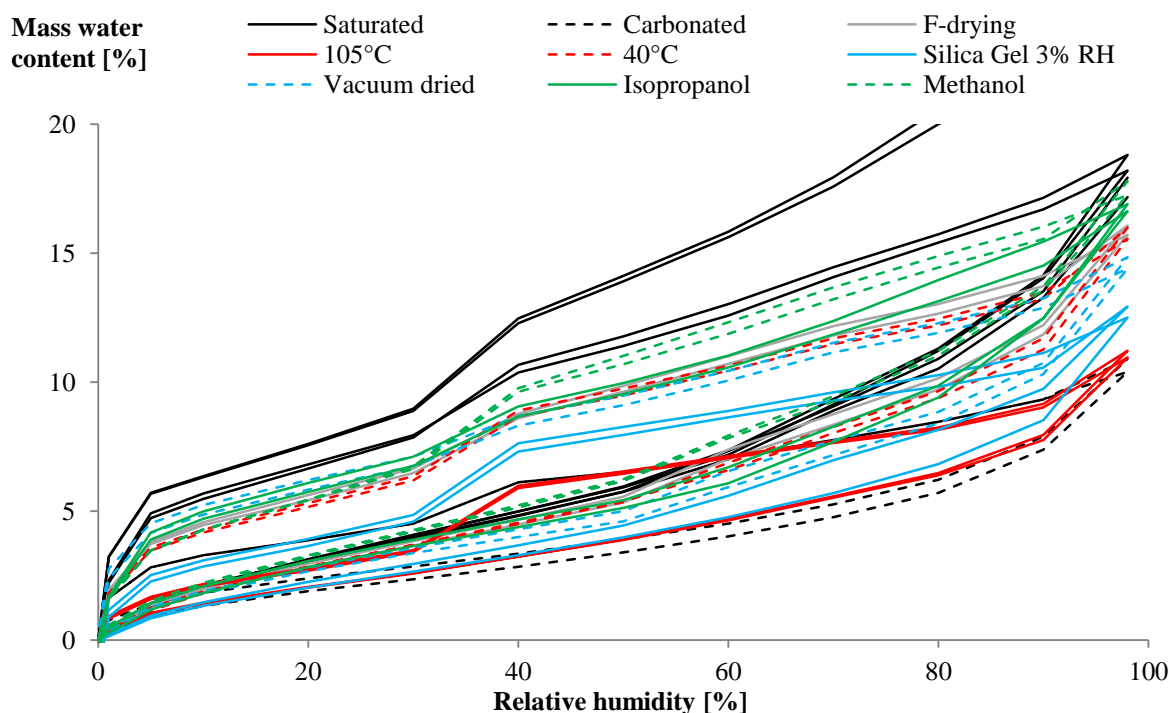The water vapour isotherms are shown in Fig. 1.

Fig. 1: Effect of drying techniques on the water vapour sorption isotherms

The water vapour sorption curves are in correspondence with the ones found by Baroghel-Bouny [7]. Each drying technique affects the water vapour sorption curves. The most prominent changes are found in a carbonated sample, followed by oven drying at 105°C and drying in air with silica gel. The difference between non-carbonated and carbonated specimens was also observed in literature [8].

The BJH (Barrett, Joyner and Halenda) method [9] allows the determination of the pore size distribution in the meso-pore range (2-50 nm) from experimental isotherms using the Kelvin model of pore filling. The results may differ from reality, but the method remains relevant and useful for comparative studies. The micro-pore volumes (< 2 nm) have been calculated by applying the Dubinin-Radushkevich equation [10]. The results, together with the specific surface area using the BET method, are shown in the Table 1.

Table 1. Summary of the results from BET and BJH calculations

	S_{BET} $m^2 \cdot g^{-1}$	V_{total} $mm^3 \cdot g^{-1}$	$V_{meso+macro}$ [*] $mm^3 \cdot g^{-1}$	V_{micro} [*] $mm^3 \cdot g^{-1}$
Saturated	131	199	165	34
Carbonated	77	118	95	23
F-drying	121	173	142	31
105°C	81	120	99	21
40°C	122	175	141	34
Silica Gel 3% RH	93	143	115	28
Vacuum dried	110	160	130	30
Isopropanol	122	184	151	33
Methanol	138	190	156	34

[*] IUPAC pore classification: micro pores (< 2 nm), meso pores (2-50 nm) and macro pores (> 50 nm)

Typically, the S_{BET}-values range from 80-140 m²/g. These values are in good correspondence with literature [7]. Several authors observed that the minimum surface area was found in oven-dried samples at high temperatures [11, 12]. This is also reflected in the S_{BET}-value for 105°C oven-drying. The lower values for carbonated specimens and drying in air can be explained by the degree of carbonation. In addition, methanol-calcium ion products have a high surface area which can affect the isotherm determination. The latter explains the highest value of S_{BET} for the solvent exchange method with methanol followed by vacuum drying.

The porosity is reduced the most with increasing degree of carbonation. Carbonation reduced the porosity among the outer C-S-H (10-100 nm), as already observed by other researchers [8].

F-drying causes thermo-mechanical stresses in the C-S-H. Oven-drying causes capillary hydrostatic stresses due to the surface tension of the receding water menisci. This results from dehydration and causes the collapse of monosulfoaluminate (AFm) and ettringite (AFt) phase at 60°C [13]. Generally, oven drying results in 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. Oven drying is thus an unsuitable drying technique to preserve the fragile microstructure of cement-based materials. Vacuum drying may lead to the structural and physical collapse of hydrates including AFm and AFt phases [13]. The solvent-exchange methods followed by vacuum drying causes the lowest change in microstructural properties.

The TGA curve of the samples stored in water only show a minor form of carbonation. Specimens dried with the solvent exchange method followed by vacuum drying also show almost no carbonation (isopropanol) and partial carbonation (methanol). As methanol, upon heating, will react with C-S-H to form CO_2, this is reflected in a higher carbonate peak. Vacuum drying does not show any significant carbonation. F-drying and oven-drying caused partial carbonation. Oven-drying in a ventilated oven and in air with silica gel caused significant carbonation, even though the soda lime was replaced regularly.

Conclusion

The ideal drying technique, which can preserve the microstructure and can remove only the non-bound water, does unfortunately not exist. All drying techniques affect the microstructure in their own way. Only vacuum-drying and the solvent-exchange-method with isopropanol proved to be acceptable drying techniques to prepare specimens for water sorption analysis.

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