Influence of Sample Preparation and the Addition of BFS on Water Vapour Sorption Isotherms

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ABSTRACT

Blast-furnace slag (BFS), a by-product of the steel production, can be added to a concrete mix as cement replacing material. However, the presence of BFS has a significant influence on the microstructure of the matrix. To study the pore structure of pastes in the micro- and mesopore range, dynamic water vapour sorption experiments were performed. This method allows to determine the water vapour adsorption/desorption isotherms by continuously monitoring the weight change of a sample placed in an environment with controlled temperature (20°C) and relative humidity. To obtain complete adsorption/desorption cycles, the relative humidity was increased/decreased in steps by mixing dry and humid nitrogen gas. The tests were performed on pastes with water-to-binder ratios of 0.5 and BFS-to-binder ratios of 0 (CP0), 0.5 (CP50) and 0.85 (CP85).

First of all, the effect of the predrying method on the sorption isotherms was investigated. The test results indicate that the water removed by vacuum drying can probably re-enter at high relative humidity. At low relative humidities, specific interactions possibly occur by formation of hydrogen bonds. This topic will be investigated in more detail in the near future. Furthermore, the mass water content at 100% RH after a step-by-step desorption/adsorption cycle never reaches the mass water content of saturated test specimens. A step-by-step adsorption to 100% RH cannot fill all of the large meso and macro pores. Moreover, a decrease of the RH to 0% induces no irreversible changes to the pore structure.

Secondly, the sorption isotherms of CP0 were compared with those of CP50 and CP85. Although differences are noticed between BFS and OPC pastes, additional tests are necessary to draw conclusions.

KEYWORDS

Water vapour sorption, Isotherm, Predrying, Microstructure, Blast furnace slag.

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1 INTRODUCTION

Sorption experiments allow to characterize the pore structure of cement-based materials in the micro and meso porous range. The most common used gases are water vapour and nitrogen [Odler 2003] but it seems from literature review that the type of sorbate strongly influences the test results.

- Water penetrates the vacated interlayer spaces, which are inaccessible for nitrogen molecules but which should be excluded from surface area measurements [Garci Juenger & Jennings 2001]. However, not all researchers share this opinion. In Mikhail [1963], it is stated that the layer structure of tobermorite gel is not the cause of the difference between water and nitrogen adsorption.
- The ‘bottle-neck’ effect obstructs nitrogen to enter large pores with a small opening. Influencing parameters are the size of the nitrogen molecules, which are larger than water molecules, and the test temperature. Since water vapour sorption tests are performed at a higher temperature (ambient temperature in comparison to 77K for nitrogen adsorption [Odler 2003]), the permeability of water molecules is artificially increased by activated diffusion.
- Furthermore, the water molecules have a strong dipole moment, enabling the molecules to penetrate into the pore space [Mikhail et al. 1963].

Moreover, the drying process, preparatory to the gas adsorption tests, has a significant influence on the test results and complicates comparison between different research projects. Theoretically, the free and adsorbed water must be removed, while the interlayer water must remain behind. However, different drying techniques, as e.g. D-drying, P-drying, oven-drying, freeze drying remove different amounts of water and cause collapse of the CSH structure on nanometer scale to different extents [Odler 2003]. Therefore, water vapour sorption experiments sometimes start with a desorption instead of an adsorption process [Ahs 2008], [Rouquerol et al. 1999].

All the above-mentioned arguments clearly show that the sorption experiments are influenced by a lot of parameters. In this article, the difficulties associated with the technique of water vapour adsorption on cement based materials are discussed more in detail. Experiments were performed with water vapour since this is a natural adsorbate for building materials exposed to environments with changing relative humidities.

2 MATERIALS

Cement pastes with a water-to-binder ratio (w/b) of 0.5 and slag-to-binder ratios (s/b) of 0 (CP0), 0.5 (CP50) and 0.85 (CP85) were cast in cylindrical moulds, which rotated for 24 hours at a speed of 15 rotations per minute. Afterwards, the specimens were cured under water at a temperature of (20 ± 2)°C until the time of testing. The chemical composition of the used cement (CEM I 52.5N) and blast-furnace slag is tabulated in Table 1.

Table 1. Chemical composition of ordinary Portland cement (OPC) and blast-furnace slag (BFS).

<table>
<thead>
<tr>
<th></th>
<th>CaO [%]</th>
<th>SiO₂ [%]</th>
<th>Al₂O₃ [%]</th>
<th>Fe₂O₃ [%]</th>
<th>MgO [%]</th>
<th>K₂O [%]</th>
<th>Na₂O [%]</th>
<th>SO₃ [%]</th>
<th>S⁻ [%]</th>
<th>CO₂ [%]</th>
<th>IR [%]</th>
<th>LOI [%]</th>
<th>Blaine [m²/kg]</th>
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<tr>
<td>OPC</td>
<td>63.4</td>
<td>18.9</td>
<td>5.74</td>
<td>4.31</td>
<td>0.89</td>
<td>0.73</td>
<td>0.47</td>
<td>3.34</td>
<td>/</td>
<td>0.50</td>
<td>0.41</td>
<td>1.51</td>
<td>353</td>
</tr>
<tr>
<td>BFS</td>
<td>41.2</td>
<td>36.4</td>
<td>9.83</td>
<td>0.26</td>
<td>7.41</td>
<td>0.41</td>
<td>0.28</td>
<td>1.62</td>
<td>0.79</td>
<td>0.90</td>
<td>0.43</td>
<td>1.3(*)</td>
<td>394</td>
</tr>
</tbody>
</table>

(*) Correction for oxidation of sulfides has been taken into account

3 DYNAMIC WATER VAPOUR SORPTION (DVS)

3.1 DVS-apparatus

The test setup to perform dynamic vapour sorption (DVS) experiments is shown in Fig. 1 (DVS – SMS: Surface Measurement Systems, UK). This method allows to determine the water vapour
adsorption/desorption isotherms by continuously monitoring the mass change of a sample placed in an environment with controlled temperature and relative humidity. In this research, the temperature was maintained at 20°C and the RH was controlled by mixing dry and humid nitrogen gas. The RH varied between 100% and 0% and changed in steps of 10%. During each step the mass change was continuously recorded. When the software detected a change in mass lower than 0.002% per minute, the RH was changed automatically by 10%.

3.2 Influence of the sample preparation on the sorption isotherms

Since sample preparation seems to have a considerable effect on the sorption isotherms (see introduction), some preliminary tests were performed on cement pastes, which were differently treated before the sorption experiments started. Part of these results were published in [De Belie et al. 2010].

3.2.1 DVS experiment starting from an adsorption process on vacuum-dried test specimens

In a first phase of the research, vacuum dried test specimens (at 80°C) were subjected to a dynamic water vapour sorption experiment, starting with an adsorption process [De Belie et al. 2010] (Fig. 2 (a)). As can be seen, the first adsorption isotherm deviates from the subsequent ones, and, from the second cycle onwards, the adsorption – desorption curves overlay each other. The dry masses, obtained by both techniques, diverge from each other and indicate that more water is evacuated by vacuum drying than by a step-by-step desorption. Since CSH in hydrated cement pastes contains different types of water (chemically bound water, interlayer water, adsorbed surface water), it is not surprising that different drying techniques can remove different amounts of water. De Belie et al. [2010] refer to [Jennings 2008] and [Feldman 1973] to interpret the chemical formula of CSH. When no surface adsorbed water is included, the chemical formula of the CSH is C$_{1.7}$SH$_{1.8}$, containing 1.3 mol chemically bound water and 0.5 mol interlayer water. When adsorbed surface water is included, the formula is C$_{1.7}$SH$_{2.1}$. The 0.3 mol extra water is formed as an outer monolayer at a relative humidity higher than 11%. From literature review, it seems that a step-by-step desorption to 0% RH only removes the monolayer water and part of the interlayer water [De Belie et al. 2010], while severe drying techniques as e.g freeze-drying, D-drying and oven drying at 105°C, can completely remove interlayer water [Baroghel-Bouny 2007]. Moreover, extraction of interlayer water induces collapse of the CSH structure. Due to the compression of the cement gel, the open meso gel pores diminish and the volume of capillary pores increases [Espinosa & Franke 2006]. However, no consensus exist concerning the re-entry of water molecules into this collapsed structure [Korpa & Trettin 2006]. According to Feldman (cited by [Espinosa & Franke 2006]) interlayer water is taken up in the CSH phases at low relative humidities. However, in our experiments the first and second adsorption isotherms are parallel for a relative humidity below 50%, indicating that no more water enters the paste in this RH range after vacuum-drying than after a step-by-step desorption. Since the slopes of both adsorption curves deviate from each other at relative humidities between 50% and 80% and the mass water content at 90% RH remains the same, De Belie et al. [2010] assumed that interlayer water will re-enter at higher RH, and will not (completely) be extracted again in the step-by-step desorption. Although this statement is in contradiction with that of Feldman, the theory of Lodewyckx [2008], who assumed that specific interactions occur at low relative humidities (interaction between the active sites on the surface and H$_2$O (hydrogen bonds) and formation of water clusters (again by hydrogen
bonding)) while micro and meso pore filling takes places at higher relative humidities, can give a suitable explanation. This implicates that the suitability of the BJH theory, to calculate pore size distributions, the t-curves as obtained by Hagymassy [1969] and the BET theory, to determine the specific surface area, on this kind of curves is questioned. This subject will be investigated more in detail in the near future. Additionally, it is not sure that equilibrium is attained during the step-by-step desorption. If equilibrium is not attained, the adsorption curve also alters and deviates from the first one. From her literature review, Baroghel-Bouny [2007] concluded that moisture transport is slow and consequently establishment of equilibrium is retarded, especially in the mid-range RH. In our research, the measurements automatically changed to the next RH step when the mass change was lower than 0.002% per minute. Nevertheless, after the relatively fast initial adsorption, a subsequent significantly slower uptake of water can take place [Odler 2003]. Lodewyckx [2010] also noticed a second increase in water uptake at later ages and ascribed this phenomenon to the transformation of the cluster structure of H$_2$O into a more ordered chain-like structure so that water nanochains are able to enter a small opening (ultramicropores with a diameter < 0.7 nm) if sufficient time is given.

![Figure 2](image-url)

**Figure 2.** Dynamic water vapour sorption experiments: (a) starting from an adsorption process on vacuum dried cement paste (CP0) (age ~ 4M) [De Belie et al. 2010] and (b) starting from a desorption process on saturated test specimens (CP0) (age ~ 2M).

### 3.2.2 DVS experiment starting from a desorption process on saturated test specimens

In a second stage of this research, the experiments started with a desorption process of saturated test specimens. After all, in real building materials subjected to climate changes, the drying process is milder than freeze-drying, D-drying, vacuum-drying or oven drying and interlayer water, which is no pore water according to the definition of Feldman (cited by Espinosa [Espinosa & Franke 2006]), will not be (completely) extracted from the material in real circumstances. Moreover, this approach allows to preclude the complications associated with the different drying methods. An example of an isotherm, obtained in that way, is presented in Fig. 2 (b). Now, the first desorption isotherm deviates from the subsequent ones. To investigate whether this deviation would be caused by an irreversible process, test specimens were twice subjected to the same adsorption – desorption cycles. In between the two measurements, the sample was re-immersed in water. Since similar desorption isotherms are obtained in both dynamic sorption experiments as can be seen in Fig. 3 (a) and (b), the differences in mass water content between first and second desorption are probably due to a transition of hygroscopic water content into over-hygroscopic water content and filling of the macropores at RH above 90 - 95%. At these high RH, water layers can be formed on the pore walls of the larger meso and macro pores, however, no complete filling will be obtained by water vapour sorption. The saturation degree of these large pores after immersing in water will always be higher than after a step-by-step adsorption process.

Furthermore, literature review reveals that desorption processes below 10% RH would damage the pore structure [Ahs 2008], while other researchers claim that drying below 40% RH already induces collapse of low density CSH [Jennings 2000, Thomas & Jennings 2006]. Therefore, during the
preliminary experiments, the first desorption isotherm was limited to 30%, while the relative humidity was lowered to 0% RH during the second desorption. From Fig. 3, it seems that no remarkable influence could be detected between (i) the second and subsequent desorption isotherms and (ii) the mass water content at 100% RH obtained after drying to 30% and 0% RH. Based on these test results, it was decided to vary the relative humidity immediately between 0% and 100% in later experiments.

Moreover, it is worth mentioning that the shape of the isotherms of Fig. 2 (b) and Fig. 3 corresponds more with that of a hydrophobic material. However, this is unexpected. A possible reason can be that not all pore water was extracted from the test sample during desorption (due to a too short equilibration time – see section 3.2.1) probably especially at low RH. As a consequence, the pores were still (partly) covered. Furthermore, a more detailed study of the test results reveals that the mass and size of the samples subjected to dynamic water vapour sorption tests also plays an important role within this story. The shape of the sorption isotherms of specimens with a dry mass (mass at 0% RH) lower than ~50 – 60 mg (Fig. 4) slightly differs from those obtained for samples with a higher dry mass (up to 130 mg for CP0 – 2M as presented in Fig. 2 (b)). Since the dimensions of heavier test specimens are larger, diffusion of water is delayed and the time necessary to achieve equilibrium is prolonged. Taking into account these considerations, it is advised to perform dynamic water vapour sorption tests on very small test specimens (mass < 50 mg) to obtain reliable test results within a relatively short time period and to reduce experimental errors caused by equilibration.

In Fig. 4, the sorption isotherms of CP0 (4M), CP50 (18M) and CP85 (18M) obtained by DVS measurements after vacuum drying are presented. As can be seen, the first adsorption isotherms

**Figure 3.** (a) Sorption experiment starting from saturated test specimens (CP0 – 2M) and a desorption process. (b) Repetition of experiment (a) on the same test specimens (CP0 – in the meantime 3M old), which was immersed in water between the two experiments.

**Figure 4.** Sorption isotherms of CP85 – 7 days (dry mass at 0% RH = 21 mg).

### 3.3 Sorption isotherms of pastes containing different amounts of BFS

In Fig. 4, the sorption isotherms of CP0 (4M), CP50 (18M) and CP85 (18M) obtained by DVS measurements after vacuum drying are presented. As can be seen, the first adsorption isotherms
overlay each other between 0 and 10% RH. Between 10% and 50% there is a slight difference, while at RH above 50% the difference is more pronounced. Since the measurements above 90% are not reliable (see above), these will not be considered in the further discussion. Moreover, the dry masses of CP50 and CP85 at 0% RH after a step-by-step desorption do not deviate considerably from those obtained after vacuum drying (~ 0.16% for CP50 and CP85 ↔ 1.99% for CP0). According to De Belie et al. [2010], this is due to the firm binding of interlayer water in the CSH structure which is more polymerized and becomes stronger and denser at later ages. Therefore this interlayer water will be removed by vacuum drying for young samples, but not for older ones. The lower increase in mass water content for pastes containing slag will then not necessarily mean that less micropores are present, but it is also possible that both drying techniques do not allow to extract all of the micropore or interlayer water. Above a RH of 80% the increase in mass water content of BFS paste is higher than for the reference paste. In the near future, these preliminary test results will be verified by extra measurements. Moreover, other techniques like IR spectroscopy, XRD and nitrogen sorption will be applied to clarify the observations from dynamic vapour sorption experiments.

Figure 4. (a) Water vapour sorption isotherms of CP0, CP50 and CP85. (b) First adsorption isotherm of the vacuum dried test specimens [De Belie et al. 2010].

4 CONCLUSION

During this research, dynamic water vapour sorption experiments were performed on cement pastes to investigate the influence of sample preparation and measuring procedure on the isotherms. Although further research will be necessary, the first conclusions/recommendations can already be drawn.

- After a relatively fast initial adsorption, a subsequent significantly slower uptake of water can take place. Therefore, it is advised to verify if the specimens are in equilibrium at each RH step (also for the dynamic tests, which yield results much faster than the semi-equilibrium method, where samples are placed above saturated salt solutions). In some cases and depending on the settings (e.g. mass change < 0.002% per minute), the DVS equipment decides too fast to change the relative humidity.

- Use small specimens (mass < 50 mg) to avoid extra equilibration problems due to slow diffusion processes.

- A step-by-step desorption (to 0% RH) is less severe than vacuum drying (dry masses are different). However, it seems that interlayer water (micropore range) can re-enter the pore structure at higher RH (between 50% and 80%) and therefore this removal of interlayer water cannot be considered to be irreversible. With ageing of the CSH, this interlayer water becomes more firmly bound. At low RH, specific interactions (hydrogen bonds) probably occur. This subject will be investigated more in detail in the near future.

- In situ, the drying processes are less strong. Therefore, we opted to start the experiments from saturated test specimens and subject them first to a desorption process. The test results demonstrate that no complete filling of the large meso and macro pores can be obtained by water vapour sorption. By lowering the relative humidity to 0%, pores probably do not empty completely and the pore structure does not change irreversibly. After resaturation (by immersing in water) the same isotherms could be obtained.
The sorption isotherms of CP0, CP50 and CP85 slightly differ from each other. However, additional tests must be performed to draw conclusions.

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REFERENCES


