

Hygric properties of porous building materials (IV): semi-permeable membrane and psychrometer methods for measuring moisture storage curves

Chi Feng^{*}, Hans Janssen

KU Leuven, Department of Civil Engineering, Building Physics Section, 3001 Leuven, Belgium

Abstract: The moisture storage curve is an important hygric property of porous building materials. It describes the moisture storage characteristic of a material via the relation between the moisture content and the moisture potential. Current experimental protocols for measuring moisture storage curves are not satisfactory, as they often require extensive facilities while still lacking the capability to handle the adsorption process in most of the over-hygroscopic range. This paper proposes two novel and simple methods – the semi-permeable membrane method and the psychrometer method – to solve these issues. Measurements on calcium silicate, autoclaved aerated concrete and ceramic brick are performed and validated by comparing the experimental outcomes obtained from these two novel methods and from other existing protocols. It is proven that the semi-permeable membrane method and the psychrometer method are applicable for both adsorption and desorption processes, the latter both from saturated and capillary moisture content. Limited by the accuracy of the psychrometer and the condensation caused by temperature fluctuations, these two methods show their best applicable range for capillary pressures below $-1 \cdot 10^5$ Pa. The semi-permeable membrane method and the psychrometer method also feature in low cost, simple handling and application efficiency.

Keywords: porous building material; moisture storage curve; capillary pressure; moisture content; semi-permeable membrane; psychrometer

1. Introduction

Moisture is one of the central issues in buildings in particular and in the built environment in general. It affects the energy efficiency and service life of buildings [1, 2], as well as the indoor climate and air quality [3, 4]. Due to this critical nature of moisture, many hygrothermal models have been established and various numerical tools have been implemented [5-7] to optimally understand and correctly control different moisture-related processes in built structures.

For this spectrum of theoretical models and numerical tools, the hygric properties of porous building materials are always indispensable parameters. They characterize the capability of a material to store and transport moisture, and therefore can be classified as moisture storage and transport properties. In this study we concentrate on the storage properties, while in a future paper of this series we will focus on the transport properties.

Generally speaking, the moisture storage properties express the relation between the moisture content (w , $\text{kg} \cdot \text{m}^{-3}$) and the moisture potential. The moisture potential can be characterized by relative humidity (RH, -), capillary pressure (p_c , Pa) and other parameters, which are mutually convertible. Due to the hysteresis phenomenon, the moisture storage properties are usually not a single function

but rather process-dependent scanning curves. Consequently, at least three important curves are needed for a complete characterization over the full humidity range – one adsorption curve starting from the dry state as well as two desorption curves starting from the saturated moisture content (w_{sat} , $\text{kg}\cdot\text{m}^{-3}$) and the capillary moisture content (w_{cap} , $\text{kg}\cdot\text{m}^{-3}$), respectively. This is illustrated in Fig. 1.

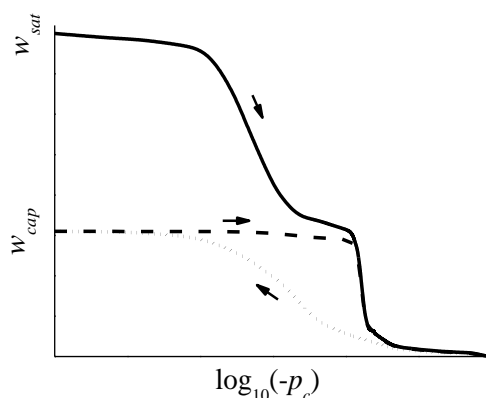


Fig.1 Moisture retention curves for different adsorption/desorption processes

Moisture storage curves can be obtained via simulation or measurement, and experiments at present form the dominant approach. Many methods have been developed in soil science and other disciplines to measure the moisture retention curves of porous materials. As is shown in Fig.2, the main distinction between the different methods is their protocols for imposing or determining the moisture potential. Consequently, these methods can be generally classified into two large categories – suction control methods and moisture control methods [8]. Suction control methods typically impose predetermined moisture potentials on the sample. When equilibrium has been reached, the moisture content of the sample can easily be obtained in a gravimetric way. Contrarily, moisture control methods typically condition the sample for its moisture content and then determine the corresponding moisture potential.

Both suction control methods and moisture control methods can be further elaborated. For suction control methods, there are three main techniques to control the moisture potential – the axis translation technique, the osmotic technique and the ambient RH control technique. The axis translation technique was first invented by Hilf in 1956 to avoid the cavitation of water [9] and later evolved into different forms, the most popular of which is the well-known pressure plate [10-13]. In the osmotic technique solutions of different concentrations – and hence different osmotic pressures – are employed to control the moisture potential [14, 15]. Obviously, both the axis translation and the osmotic technique suit the liquid-dominant cases (in building physics terms: the over-hygroscopic range). For vapor-dominant situations (in building physics terms: the hygroscopic range), the moisture potential control reverts to regulating the ambient RH, typically realized with saturated salt solutions [16, 17] or mixing dry/wet air [18]. With respect to moisture control methods, the moisture content of the sample can be imposed either directly (e.g. by applying tiny water drops on the sample or even through immersion [8, 19, 20]) or indirectly (e.g. by contacting moist soil [21]). The determination of the moisture potential can also be performed directly (e.g. with an RH sensor or a psychrometer [8, 22]) or indirectly (e.g. the filter paper method [10, 18, 23]).

concrete and ceramic brick are performed. After that experimental results from these two methods are analyzed and validated by mutual comparison, as well as by the comparison with data from other existing protocols.

Table 1 Characteristics of methods for measuring moisture retention curves of building materials

Method	Pressure plate	Pressure membrane	Modified pressure plate	Hanging water column	MIP
Standard example	ASTM C1699 [28]	ISO 11274 [29]	Unstandardized	ISO 11274 [29]	ASTM D4404 [30]
Application example	Ref. [31]	Ref. [32]	Ref. [33]	Ref. [34]	Ref. [25]
Equipment cost	Expensive	Expensive	Expensive	Cheap	Very expensive
Availability	Common	Common	Rare	Rare	Common
Toxicity	Low	Low	Low	Low	High (mercury)
Experimental procedure	Complicated	Complicated	Complicated	Moderate	Simple
Data processing	Simple	Simple	Simple	Simple	Complicated
Applicable p_c range (Pa)	$0 \sim -1.5 \cdot 10^6$	$-1.5 \cdot 10^6 \sim -1 \cdot 10^7$	$0 \sim -5 \cdot 10^5$	$0 \sim -5 \cdot 10^4$	$0 \sim -5 \cdot 10^7$
Applicable process	Desorption from w_{sat} and w_{cap}	Desorption from w_{sat} and w_{cap}	Adsorption	Desorption from w_{sat} and w_{cap}	Desorption from w_{sat} only
Duration	Weeks ~ months	Weeks ~ months	Weeks ~ months	Weeks ~ months	Hours ~ days
Additional remarks	Not accurate for $p_c > -1 \cdot 10^5$ Pa [35].				Not suitable for cement-based materials [36, 37].

2. Materials and methods

In this section, we will first present the target materials used for validation experiments. After that, two existing protocols – the desiccator test and the pressure plate test – will be concisely introduced, as they serve as the reference methods in this study. Finally, the basic principles and procedures of the semi-permeable membrane method and the psychrometer method – which belong to the suction control methods and the moisture control methods respectively – for measuring moisture storage curves in the over-hygroscopic range will be proposed.

2.1 Materials

To validate the proposed semi-permeable membrane and psychrometer methods, measurements are performed on three materials – calcium silicate (CS), autoclaved aerated concrete (AAC) and ceramic brick (CB). Table 2 [38] summarizes some crucial properties of these materials: the bulk density (ρ_{bulk} , $\text{kg} \cdot \text{m}^{-3}$) and open porosity (ϕ) obtained from the vacuum saturation test [39], the vapor diffusion resistance factor (μ) derived from the dry cup test [40], the equilibrium moisture content at RH 84.7% ($u_{84.7\%}$, $\text{kg} \cdot \text{kg}^{-1}$) determined through the desiccator test [26], the median pore-throat radius (r_{50} , m) measured from the MIP test [41], as well as the capillary absorption coefficient (A_{cap} , $\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-0.5}$) and capillary moisture content (w_{cap} , $\text{kg} \cdot \text{m}^{-3}$) tested by the capillary absorption test [38].

It is clearly revealed in Table 2 that CS is strongly hygroscopic and capillary, AAC is strongly hygroscopic but weakly capillary, and CB is weakly hygroscopic but strongly capillary. Because of these variations, these three materials are able to represent a wide variety of porous building materials with different hygric characteristics, and are therefore often chosen as target materials for hygric property characterization [31, 38, 42, 43].

For the semi-permeable membrane and psychrometer tests, raw materials are cut into samples with a diameter of 3 cm and a thickness of 0.5 cm. For the desiccator and pressure plate tests, a sample size of 5 cm in diameter and 0.5 cm in thickness is chosen. The dry mass of all samples is determined by an electronic balance with a resolution of 1 mg after drying in a ventilated oven at 70°C, and all later wet masses are measured with the same balance. All measurements are conducted at 23±0.5°C.

Table 2 Fundamental properties of target materials (21-23°C) [38]

Material	ρ_{bulk} (kg·m ⁻³)	ϕ (%)	μ^a	$u_{84.7\%}^b$ (kg·kg ⁻¹ , %)	r_{50} (m)	A_{cap}^c (kg·m ⁻² s ^{-0.5})	w_{cap} (kg·m ⁻³)
CS	271	89.1	2.0	2.9	3.2×10^{-7}	1.01	756
AAC	462	81.4	7.4	3.1	- ^d	0.046	312
CB	1818	32.6	11.6	<0.05 ^d	4.1×10^{-6}	0.61	210

^a Determined from dry cup test (RH 11.3%-53.5%);

^b Adsorption from dry state;

^c Values for 20°C;

^d Cannot be determined accurately.

2.2 Methods

2.2.1 Existing methods for comparison

To verify the semi-permeable membrane test and the psychrometer test (explained later), we perform validation measurements based on two existing methods – the desiccator test and the pressure plate test.



a. The desiccator test



b. The pressure plate test

Fig.3 Existing experimental methods for comparison

As mentioned in Section 1, the desiccator test (Fig.3 a) is a mature and reliable method for measuring the moisture storage curves in the hygroscopic range. During the test, a constant ambient RH is established by a saturated salt solution (or other techniques). A correctly pre-conditioned sample is exposed to this known RH and its moisture content is measured gravimetrically, after reaching equilibrium. By altering the controlled RH, the moisture content changes as well. Finally, the hygroscopic moisture storage curves can be obtained by fitting the discrete points with a proper function.

The curves obtained from the desiccator test should smoothly extend to or overlap with the low-humidity end in the over-hygroscopic range. For this reason, we carry out the desiccator test in the p_c range starting from $-3.6 \cdot 10^6$ Pa for both the adsorption from the dry state and the desorption from w_{sat} , based on our normal procedures [16] as well as the ISO 12571 and ASTM C1498 standards [26, 27]. We do not measure the desorption from w_{cap} , because in the hygroscopic range the desorption curves from w_{sat} and w_{cap} overlap with each other for the target materials in this study, and hence are not distinguishable.

The pressure plate (Fig.3 b) test is another well-established approach, originating from soil science [44] and adopted in many other disciplines [11, 32, 35, 45]. During the test, compressed air is used to exert a constant capillary pressure on the sample. When equilibrium has been reached, the moisture content with respect to that specific pressure is measured gravimetrically. By changing the exerted air

pressure, different points in the moisture storage curves can be obtained.

In this study, we follow our previous experimental protocol [31, 42], which is modified based on the ISO 11274 and ASTM C1699 standards [28, 29]. A Soilmoisture[®] ceramic plate extractor system is used for measuring the desorption curves starting from both w_{sat} and w_{cap} at a p_c range of $-1 \cdot 10^4$ Pa $\sim -1.5 \cdot 10^6$ Pa.

2.2.2 The semi-permeable membrane method

The semi-permeable membrane method can be deemed as a derivative of the desiccator test: while saturated salt solutions are often used in the hygroscopic range for humidity control, unsaturated salt solutions can be similarly utilized for maintaining desired moisture potentials in the over-hygroscopic range. By exposing samples to such environment, the over-hygroscopic equivalent of the desiccator test can be achieved.

There are, however, two critical issues concerning the usage of unsaturated salt solutions in the over-hygroscopic range. First, it is liquid, rather than vapor, that dominates the moisture transfer in the over-hygroscopic range. Consequently, the surface transfer resistance of vapor diffusion will result in an enormous amount of time for the sample to reach equilibrium if directly exposed to humid air. Moreover, a slight temperature fluctuation can cause a large shift of the air humidity in the over-hygroscopic range due to the limited thermal inertia and moisture capacity of air.

To solve these two problems, we keep the sample in close contact with the salt solution, with a piece of semi-permeable membrane in between to allow the moisture transport but block the salt penetration. The salt solution can also effectively buffer the fluctuations of temperature and moisture potential. When equilibrium is reached, the sample should have the same p_c as the solution. This is the basic principle of the semi-permeable membrane method for measuring moisture storage curves (Fig.4). This method is obviously applicable to a wide moisture content range for both adsorption and desorption processes.

During the test, samples are pre-conditioned to a desired initial moisture content (dry state, w_{sat} or w_{cap}) and then laid in a sample holder whose bottom surface is a semi-permeable membrane (Fig.5 a). The top of the sample holder is covered by a piece of plastic film to minimize the impact of condensation caused by temperature fluctuations. Next, multiple sample holders with samples inside are placed into desiccators, floating on unsaturated K_2SO_4 solutions of different concentrations (Fig.5 b). When the mass of samples no longer changes (after approximately 3~4 weeks), the final m_{wet} is recorded. Do to the moisture transfer across the semi-permeable membrane, the concentrations of K_2SO_4 solutions will slightly deviate from the original values, and their p_c will change accordingly. We use a WP4C psychrometer (explained in the next section) to measure the final p_c .

It should be noted that ideally no salt can cross the semi-permeable membrane, while in practice a tiny amount of salt may still penetrate. The membrane used in this study is an industrial-level reverse osmosis membrane (Filmtech[®] Flat Sheet BW30) with a NaCl rejection capability as high as 99.5% [46]. The salt used in our test is K_2SO_4 . Since K^+ is larger than Na^+ in size, and SO_4^{2-} is larger than Cl^- in both size and charge amount, it is more difficult for K_2SO_4 to pass through the membrane. The impact from salt transport can thus be reasonably neglected.

It should be mentioned that semi-permeable membranes have previously been used for determining the moisture storage curves of porous materials [14, 15]. However, since there is no need to study the confining stress effect on our materials, our protocol is very simple and efficient, with the capability to test multiple samples at the same time in easily-available setups.

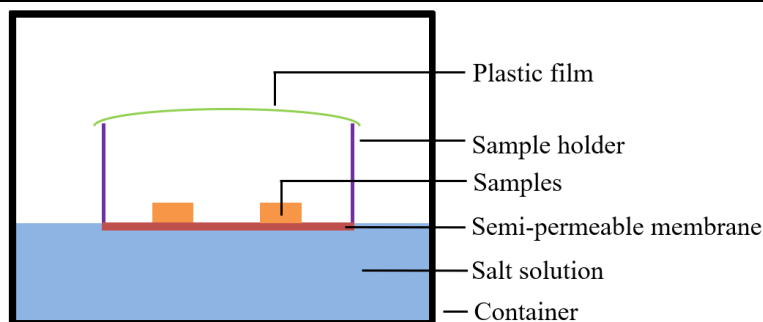


Fig.4 A schematic of the semi-permeable membrane setup



a. Samples lying on the semi-permeable membrane



b. Samples in desiccators with salt solutions

Fig.5 The semi-permeable membrane method for measuring moisture storage curves

2.2.3 The psychrometer method

The psychrometer method is a suction control method. During the test, the sample is conditioned to an arbitrary moisture content first, and the p_c in the sample is then obtained by holding the sample in a sealed chamber and measuring the humidity of the air inside caused by the water evaporation from the sample. In the over-hygroscopic range, the resultant air humidity is rather close to saturation. Consequently, the widely used RH sensors are no longer reliable because they are mainly designed for applications at a lower humidity, while psychrometers specifically designed for the high humidity range become a much better choice instead.

There are different types of psychrometers, such as the transistor psychrometer and the chilled-mirror dew-point psychrometer. Many factors – such as temperature, hysteresis, calibration and equilibrium time – all have an impact on the accuracy. After comprehensive comparisons, Cardoso *et al* [47] recommended the chilled-mirror dew-point psychrometer. In this study, we follow their recommendation and adopt the chilled-mirror dew-point psychrometer for the humidity measurement. The instrument model is WP4C (Fig.6 a and b), produced by Decagon Devices Inc. According to the manufacturer, this psychrometer has an accuracy of $\pm 5 \cdot 10^4$ Pa in the range of $0 \sim -5 \cdot 10^6$ Pa and $\pm 1\%$ for $-5 \cdot 10^6 \sim -3 \cdot 10^8$ Pa [48]. More details about this psychrometer can be found in [49].

As a matter of fact, psychrometers have been widely used in soil science, geology and other disciplines to determine the moisture retention curves for a long time [8, 22, 49]. However, as mentioned before, the function of a psychrometer is measuring, rather than controlling the moisture potential. Consequently, the sample conditioning protocols and the adsorption/desorption processes can differ significantly. Here we propose a method which is optimal for most porous building materials.

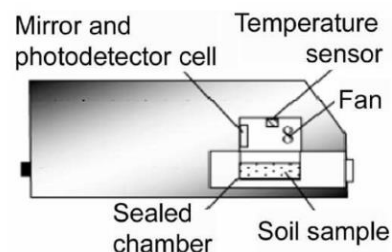
For adsorption measurements, samples are first pre-conditioned at an ambient RH of 97% controlled by a saturated K_2SO_4 solution (Fig.7 a). Next, samples are placed above pure water in desiccators

placed in an insulated chamber for better temperature stability (Fig.7 b and c). From time to time, the adsorption process is interrupted by sealing samples into small sample cups (Fig.7 d). After a standing period, the profiles of moisture content and potential in the sealed samples are assumed equilibrated. The w and p_c of samples are then measured by the balance and by the WP4C psychrometer, respectively. Resultantly, the adsorption curve starting from dry state in the over-hygroscopic range is determined. For calcium silicate and autoclaved aerated concrete, the adsorption progresses very slowly when the humidity is extremely high, while for ceramic brick the adsorption directly from air can hardly result in an observable change in moisture content. For those cases, we apply some tiny water drops directly on the samples for acceleration.

Reversibly, desorption curves starting from w_{sat} or w_{cap} can be obtained. For desorption measurements, the samples are first pre-conditioned to w_{sat} or w_{cap} and then exposed to 97% or 94% ambient RH (controlled by saturated K_2SO_4/KNO_3 solutions). With a similar process, the w and p_c can be measured, and the desorption curves are hence available.



a. A photo



b. A schematic [49]

Fig.6 The chilled-mirror dew-point psychrometer (model: WP4C)



a. Samples under pre-conditioning



b. Samples in the insulation chamber



c. A close look of samples in the test



d. Samples sealed in cups

Fig.7 The psychrometer method for measuring moisture storage curves

It should be noted that in the psychrometer test we always weigh the sample first and then measure its p_c , and the working principle of the chilled-mirror dew-point psychrometer subsequently makes an underestimation of the original sample p_c (or an equivalent overestimation of w), inevitable due to the evaporation. However, the total volume of the sealed chamber can be estimated as 50 mL. A simple calculation reveals that under our experimental conditions 1.1 mg water vapor could yield 100% ambient RH in such a volume. Our sample size is roughly $3.5 \cdot 10^{-6} \text{ m}^3$, corresponding to an overestimation of w around 0.3 kg/m^3 , which is completely negligible.

It should also be mentioned that the purpose for pre-conditioning samples at 97% RH in the adsorption tests is to slow down the moisture absorption process when samples are exposed above pure water, so that the p_c and w profiles inside the sample are more uniform. For the same reason, the desorption tests are carried out at relatively high RHs. In our trial measurements, the p_c evolutions of some samples are monitored after their sealing. It is observed that during the initial hours there are still some p_c changes, which should be mainly attributed to the moisture content re-distribution within the sample. After several hours, equilibrium has almost been reached and the measured p_c only shows minor fluctuations. For this reason, we always carry out the p_c measurements on samples having been standing overnight.

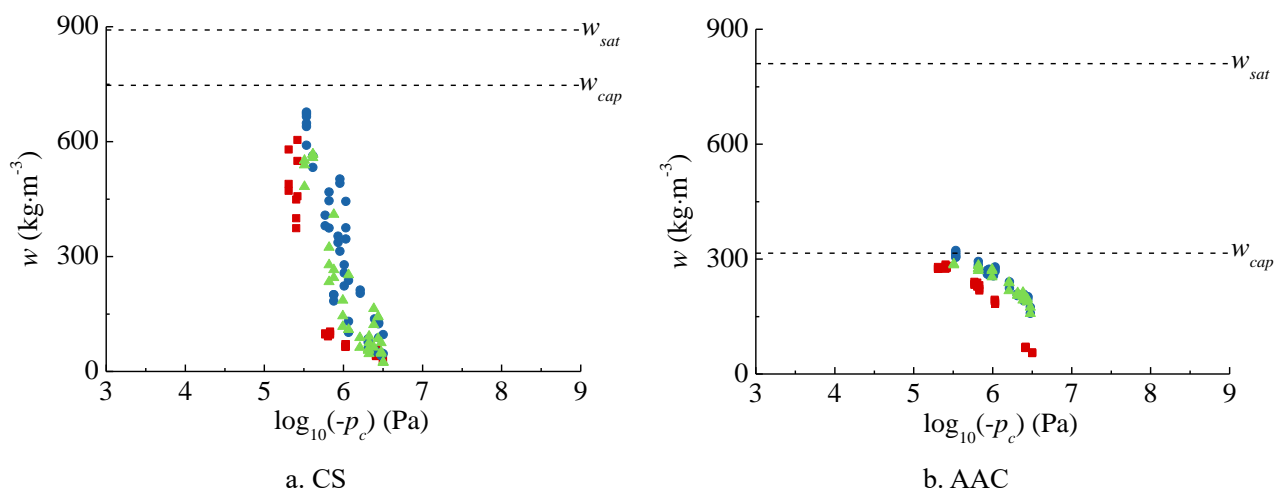
3. Results and discussion

In this section, we will first report the results obtained through the semi-permeable membrane test and the psychrometer test. Next, the desorption results from both tests are confronted with each other, as well as with the outcomes of other tests. After that, the adsorption results obtained from these two methods are compared.

3.1 Results from semi-permeable membrane and psychrometer tests

Fig.8 and 9 illustrate the experimental results obtained from the semi-permeable membrane test and the psychrometer test, respectively. For all three target materials both the adsorption and desorption curves are obtained. Several general remarks can be made to grasp a first interpretation of these results.

To start with, we can observe from both Fig.8 and 9 that within the p_c range lower than $-3.2 \cdot 10^5 \text{ Pa}$ ($\log_{10}(-p_c) > 5.5$), the desorption curves starting from w_{sat} and w_{cap} overlap with each other, whatever the material is. This interesting phenomenon indicates that for these materials the desorption hysteresis is not significant in this p_c range, triggering inspiration for future studies.



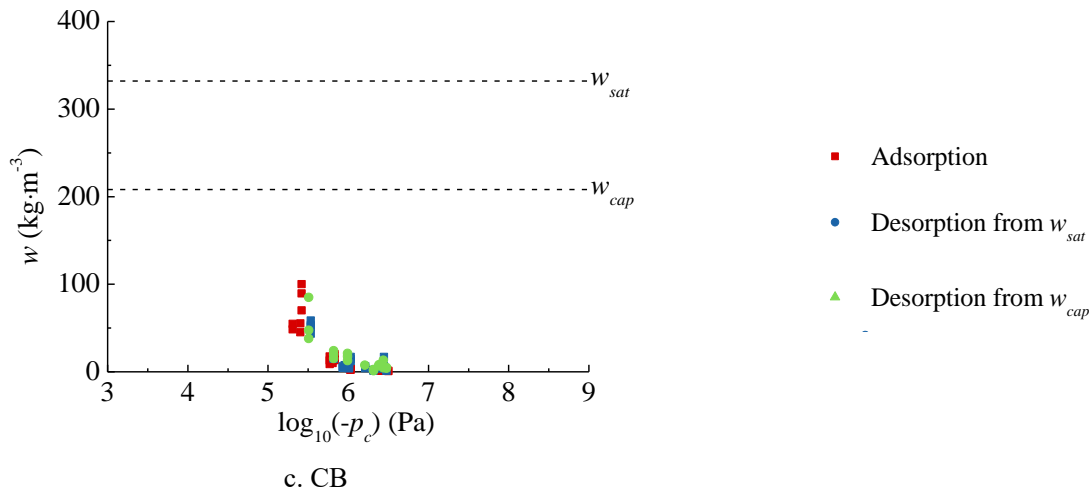


Fig.8 The moisture storage curves obtained from the semi-permeable membrane test

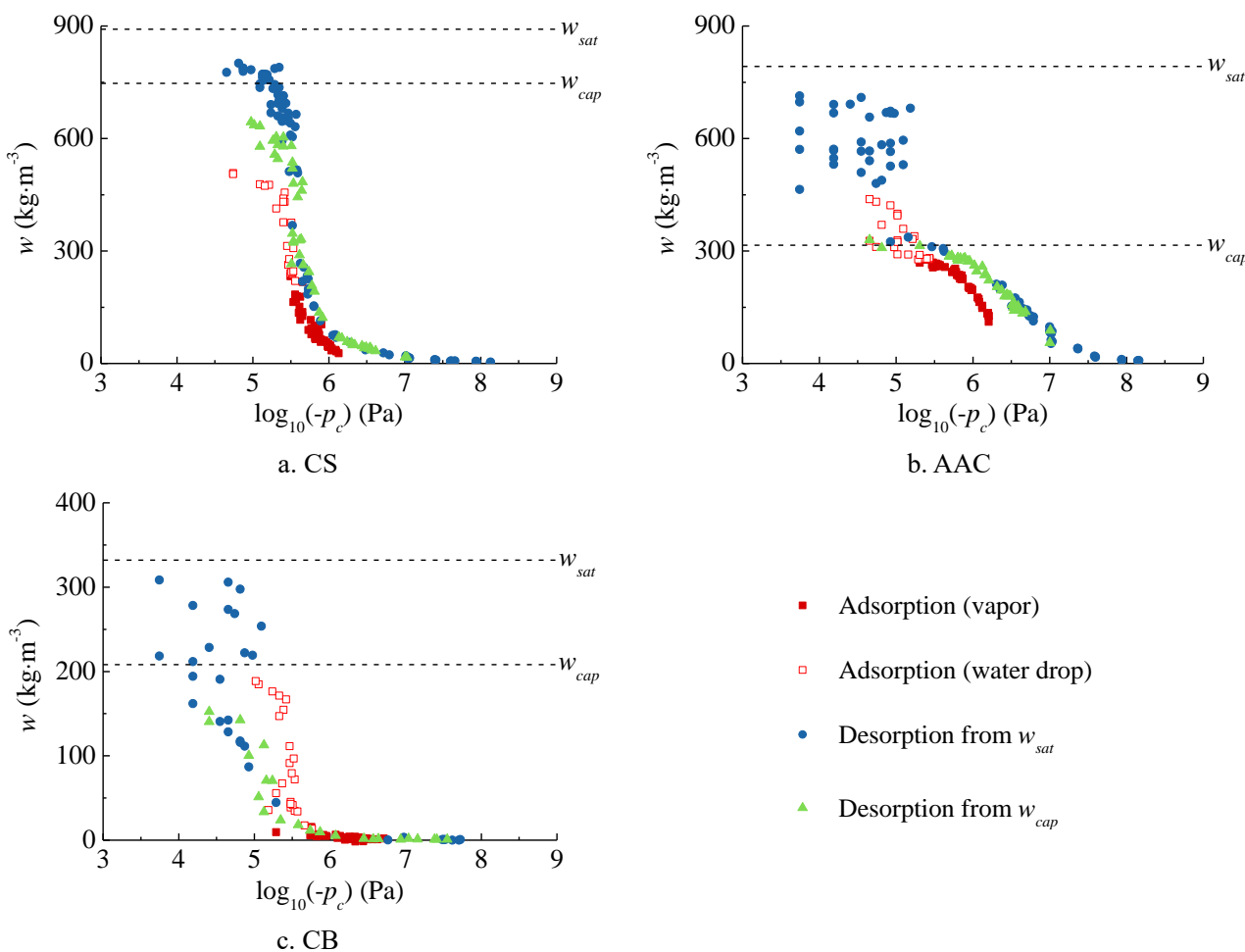


Fig.9 The moisture storage curves obtained from the psychrometer test

What's more, as is clearly revealed in Fig.8, we fail to obtain reliable results for capillary pressures above $-1 \cdot 10^5$ Pa ($\log_{10}(-p_c) < 5$) with the semi-permeable membrane method. The main reason is that this extremely high humidity inevitably leads to severe condensation due to the temperature fluctuations beyond the control capability in our lab.

In addition, the protocol of applying tiny water drops on the sample for accelerating the psychrometer adsorption process appears to yield reasonable results, which is in accordance with other studies [8]. Even with this protocol though, the adsorption measurement is still very slow: its complete execution takes more than 6 months. Consequently, for capillary pressures above $-1 \cdot 10^5$ Pa, no adsorption curve results are collected with the psychrometer test, either.

Moreover, limited by the instrumental accuracy, large scatters of the data points are displayed for the desorption curves obtained from the psychrometer test for capillary pressures above $-1 \cdot 10^5$ Pa. This is especially obvious for CB (Fig.9 c), who has relatively large pores, with a median radius around $4 \cdot 10^{-6}$ m (Table 2). Consequently, a large drop/rise of the storage curves around $-3.2 \cdot 10^4$ Pa ($\log_{10}(-p_c) \approx 4.5$) is expected, beyond the accuracy of our psychrometer ($\pm 5 \cdot 10^4$ Pa in this range). Within this high humidity range the severe condensation incurred by temperature fluctuations also plays a role.

Last but not least, although all other 5 cases are reasonable, the hysteresis phenomenon of CB in the psychrometer test seems illogical (Fig.9 c), as the desorption curves should stay above the adsorption curve. At this moment we don't have a convincing explanation for this exception.

From the discussion above, we can build the first impression that both the semi-permeable membrane test and the psychrometer test work reasonably in the p_c range below $-1 \cdot 10^5$ Pa. Next, we will validate the experimental results.

3.2 Comparison of results from different methods

To validate the results obtained from the semi-permeable membrane test and the psychrometer test, we make a comparison between them on the results of all three materials. The pressure plate test and the desiccator test are used for external verification where applicable. Fig.10-12 illustrate these results.

Fig.10 compares the desorption results obtained from different methods, all starting from w_{sat} . As is clearly reflected, the experimental results obtained from the semi-permeable membrane test and the psychrometer test agree with each nicely in the p_c range below $-1 \cdot 10^5$ Pa. Since these are two independent experimental methods (although the same psychrometer is used for p_c determination) and provide very similar results, it is highly plausible that both methods are capable of delivering reliable results. Moreover, the pressure plate measurements provide almost overlapping results in the over-hygroscopic range, while the results obtained from the desiccator test nicely extend to the results obtained from the semi-permeable membrane test and the psychrometer test. Since the pressure plate and the desiccator tests are well-established methods, their results convincingly support the correctness of the two novel methods.

Fig.11 illustrates the desorption results starting from w_{cap} . Similar to Fig.10, data points obtained from the semi-permeable membrane test, the psychrometer test and the pressure plate test agree with each other almost perfectly in the p_c range below $-1 \cdot 10^5$ Pa, confirming the reliability of all three methods. Although the desiccator results are not available as references in this case, the limited hysteresis of the target materials (discussed in Section 3.1) makes them redundant. We can therefore still assert that both the semi-permeable membrane method and the psychrometer method are trustworthy for the desorption measurement starting from w_{cap} .

Finally, Fig.12 summarizes the adsorption results. Since by far there is no widely accepted protocol for measuring the adsorption storage curve in the over-hygroscopic range, we can only compare the results from the semi-permeable membrane method and the psychrometer method. Fortunately, these two novel methods produce very similar results in the over-hygroscopic range, with the desiccator test as an optimistic external support from the hygroscopic range (for CS and AAC only). Based on this, as well as the success of the semi-permeable membrane method and the psychrometer method for the

desorption processes, it is reasonable to remain confident for their adsorption results. However, the strange hysteresis phenomenon of CB in the psychrometer test (Fig.9 c) calls for further study of its adsorption test, which remains as future work.

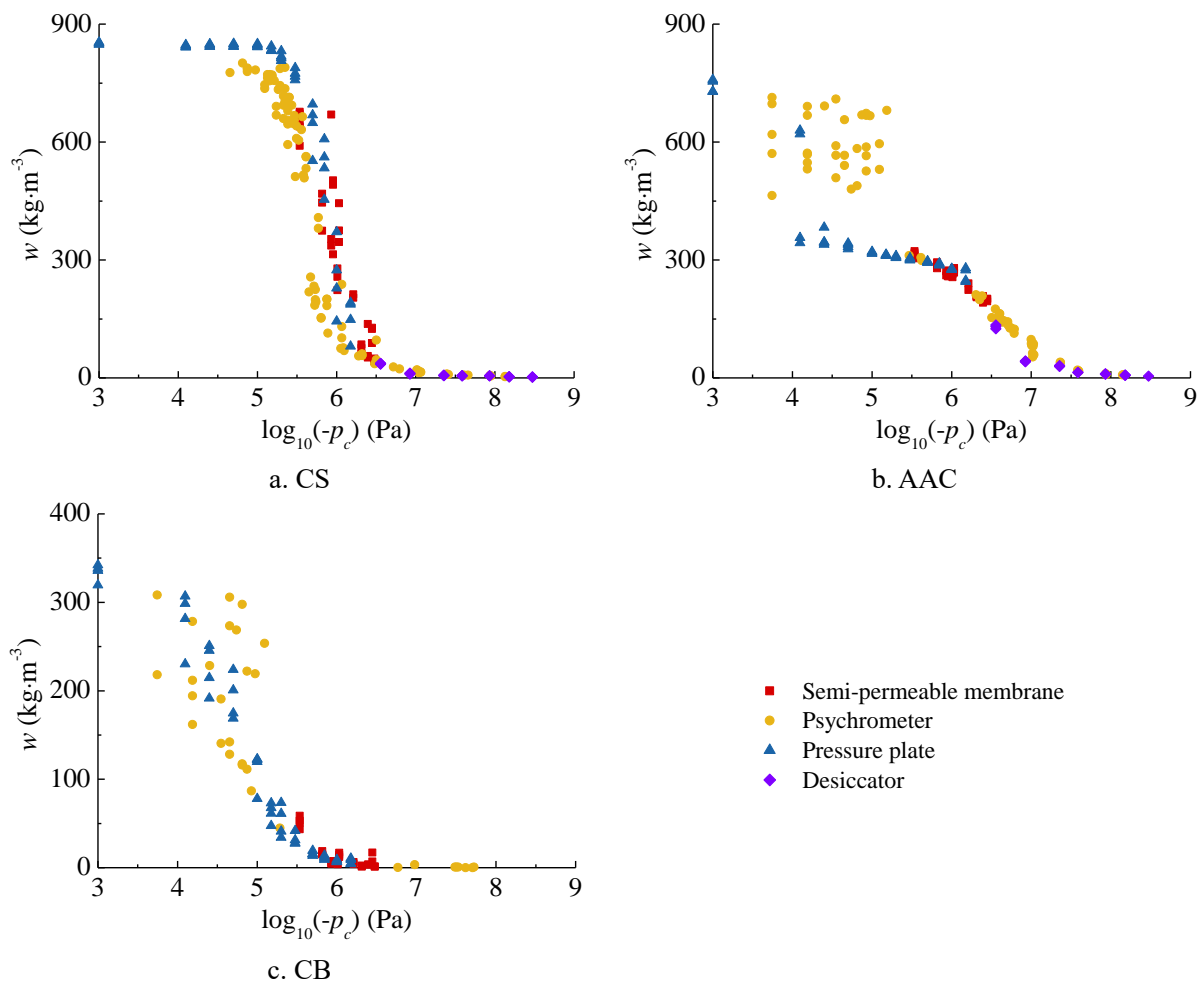
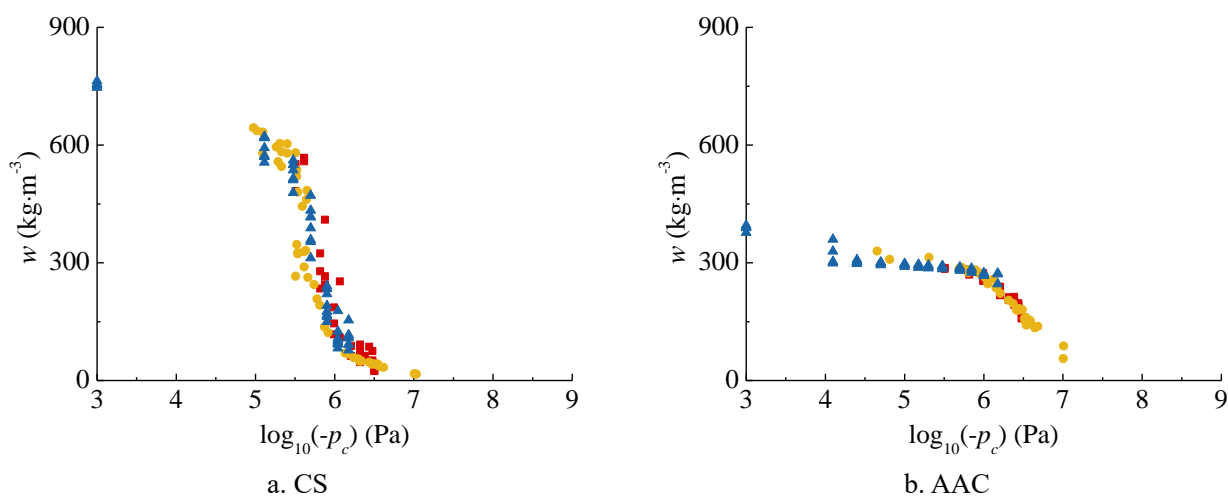


Fig.10 Comparison of the desorption results from different tests (starting from w_{sat})



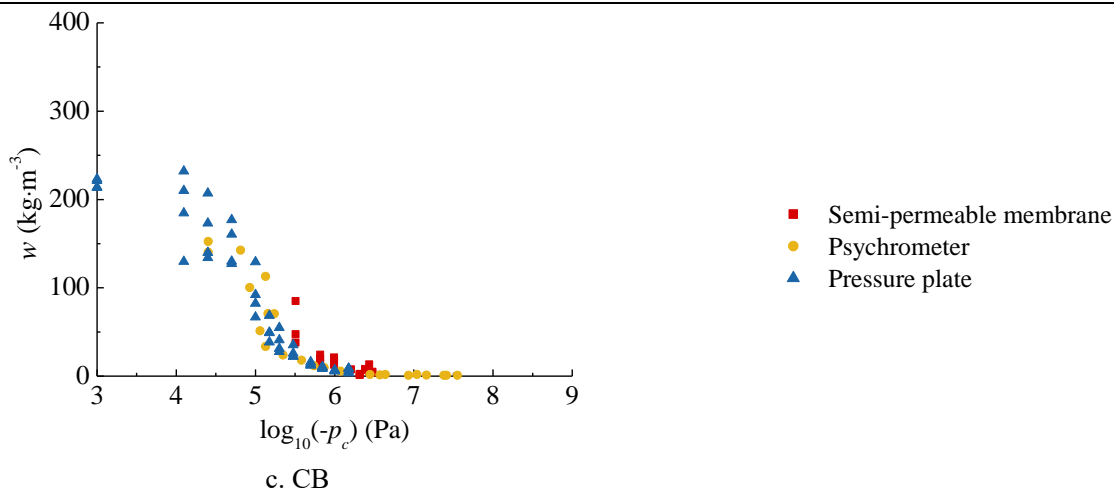


Fig.11 Comparison of the desorption results from different tests (starting from w_{cap})

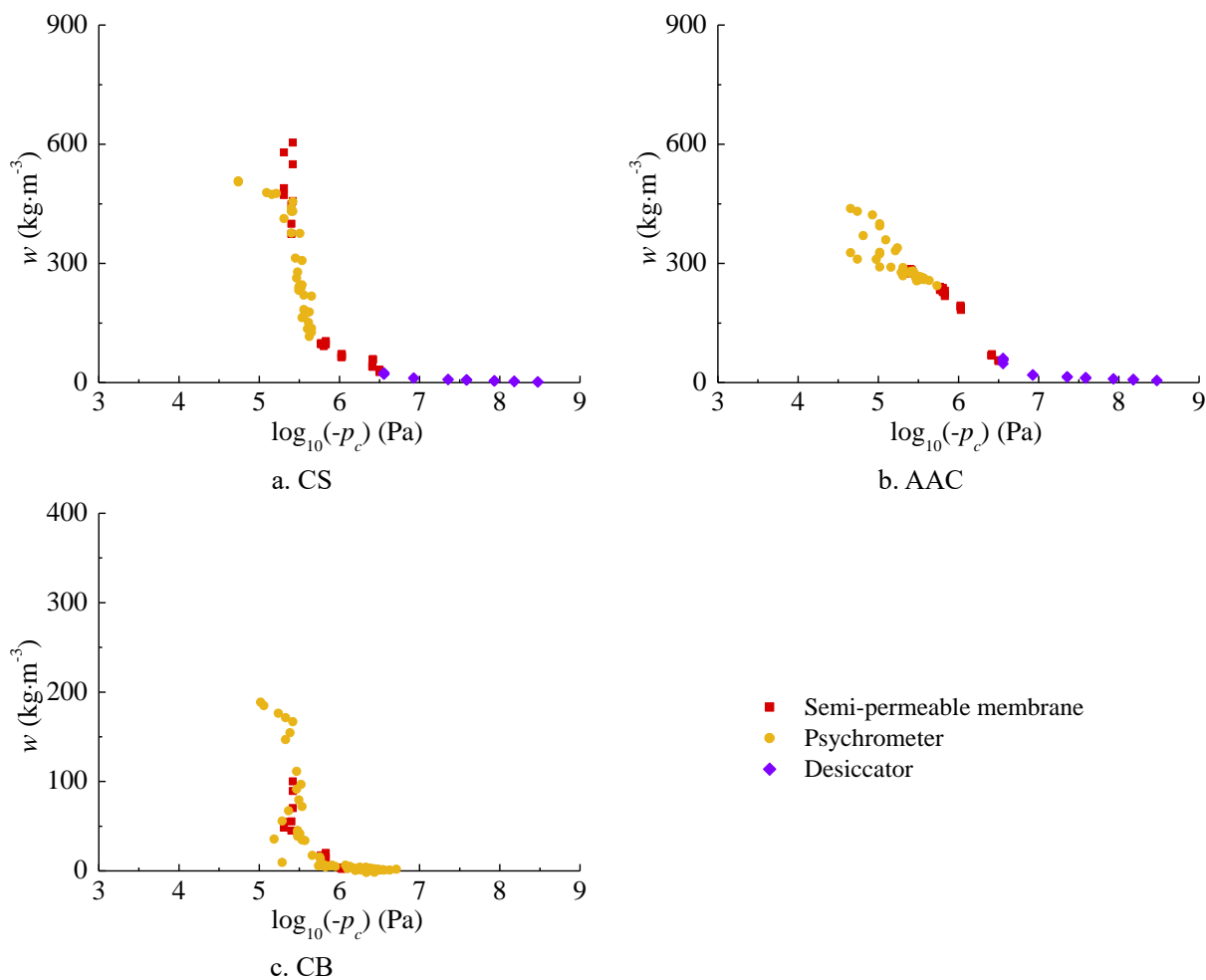


Fig.12 Comparison of the adsorption results from different tests

For more quantitative evaluations, we fit the data points obtained from the semi-permeable membrane method, the psychrometer method and the pressure plate method into respective moisture storage curves. The adjusted R^2 from the fittings directly reflects whether a method produces accurate results or not. Moreover, to evaluate the closeness of data obtained from these three methods, we lump all the data together, repeat the fitting and check the adjusted R^2 again. Since both desorption and

adsorption share the same experimental principle, we focus on the desorption process from w_{sat} only.

For the fittings, the well-known and widely accepted van Genuchten model [50] is adopted:

$$w = w_0 \cdot \sum_{i=1}^k l_i [1 + (a_i \cdot p_c)^{b_i}]^{\frac{1-b_i}{b_i}} \quad (1)$$

where w_0 , a_i and b_i are all fitting parameters, while l_i is the weighing factor for system i with the constraint $\sum_{i=1}^k l_i = 1$. The fitting parameter w_0 is fixed as w_{sat} in our case. Trials show that for $i = 1$ or 2 the fitting results are already very excellent, while additional systems don't provide noticeable improvement. Consequently, we keep $i = 1$ or 2 in all our fittings.

As mentioned before, the semi-permeable membrane method and the psychrometer method are mainly applicable in the p_c range below $-1 \cdot 10^5$ Pa. Thus, for these two methods we only select data in this range for the fittings. Moreover, while conducting the lumped fittings, a total weighing factor of 1/3 is assigned to each method, further averaged by the number of points obtained from that method.

Fig.13 illustrates the respective and lumped fittings for CS as an example, while Fig.14 compares the adjusted R^2 for all fittings. Clearly, the semi-permeable membrane method, the psychrometer method and the pressure plate method have similar adjusted R^2 values, and no method shows a dominant advantage. The adjusted R^2 values for the lumped fittings are also at the same level as for the respective fittings. This indicates that there are not significant and systematic deviations between different methods, otherwise the adjusted R^2 should have decrease obviously.

Based on the analysis above, we conclude that both the semi-permeable membrane method and the psychrometer method are reliable in obtaining the moisture storage curves of porous building materials in the over-hygroscopic range.

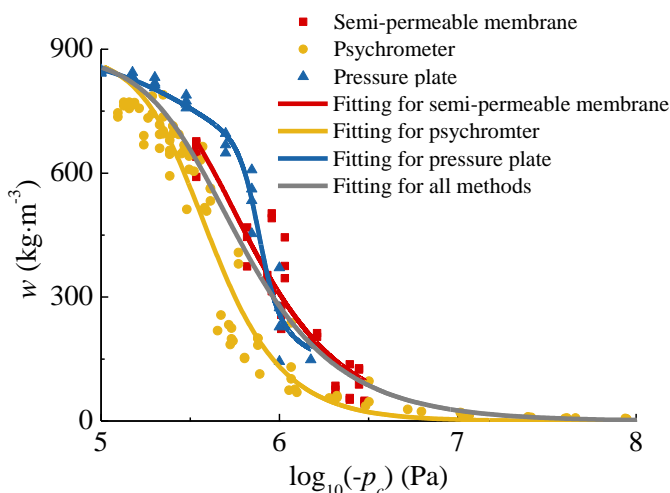


Fig.13 Fittings for the moisture storage curves of CS (desorption from w_{sat})

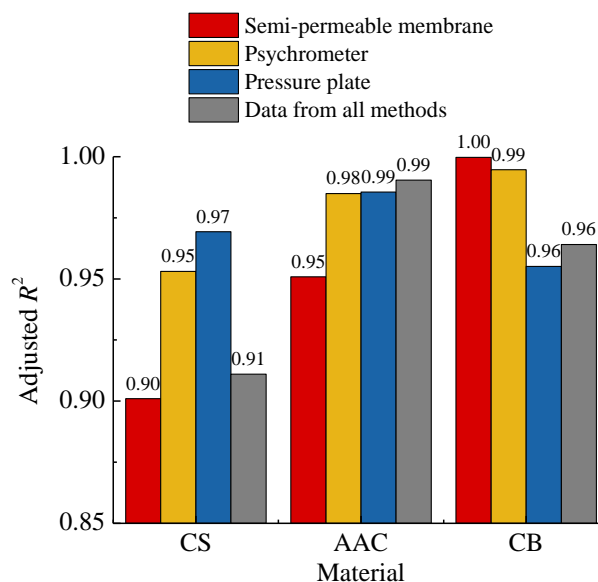


Fig.14 Comparison of the adjusted R^2 for fittings (desorption from w_{sat})

3.3 Discussion

Above we have validated the semi-permeable membrane method and the psychrometer method. To have a thorough understanding of their characteristics, some further remarks are needed.

The most attractive advantage of these two novel methods is their capability of measuring the

adsorption curve (although slightly dubious still on CB). As explained in Section 1, the adsorption measurement on porous building materials in the over-hygroscopic range has been a difficulty for a long time. Although much effort has been made by different researchers and some methods are suggested – such as the modified pressure plate in Lund University [33] – there is no ideal and widely adopted solution. As two novel methods with great potential, both the semi-permeable membrane method and the psychrometer method resolve this problem (at least partially), providing a direct complement to current desorption experimental protocols, and hence making our measurements on the moisture storage curve in the over-hygroscopic range complete.

The next superiority of the semi-permeable membrane method and the psychrometer method is that they don't require expensive set-ups, and their experimental procedures are very simple. Both the semi-permeable membrane and the psychrometer are commercially available in the market at a low price, with a lot of options to choose according to different requirements. The handling is just slightly more complicated than the desiccator method – the most popular method for measuring the moisture storage curves in the hygroscopic range – but is still much easier than the pressure plate and many other tests.

A third benefit of the semi-permeable membrane method and the psychrometer method is their efficiency. For the psychrometer method we admit that it is extremely slow for the adsorption measurement. However, for the desorption measurement 1 month already suffices, consuming the same time as most of the experimental methods listed in Table 1. When it comes to the semi-permeable membrane method, roughly 3~4 weeks are enough for both the adsorption and desorption measurements.

A final strong point is the applicable range of these two methods. In this study we just perform the measurements in the over-hygroscopic range, but the scope is already wider than the combination of the pressure plate method and the pressure membrane method ($0 \sim -1.0 \cdot 10^7$ Pa). Moreover, according to the working principles of the semi-permeable membrane method and the psychrometer method, the lower bound of their applicable range can obviously extend to the hygroscopic range. For the upper bound, both methods are not accurate when the p_c is greater than $-1.0 \cdot 10^5$ Pa (and hence not applicable to CB or other materials with large pores), and some other method – such as the hanging water column [34] – should be employed.

To sum up, both the semi-permeable membrane method and the psychrometer method are satisfactory in measuring the moisture storage curves of porous building materials in the over-hygroscopic range. They are cheap, simple, efficient and widely applicable. For the semi-permeable membrane method, the advantages are especially conspicuous. It is therefore advisable to standardized it as the over-hygroscopic part of the desiccator test, replacing the time-consuming and troublesome pressure plate/membrane test.

4. Conclusions

This paper proposes two novel methods – the semi-permeable membrane method and the psychrometer method – to determine the moisture storage curves of porous building materials in the over-hygroscopic range. Measurements on calcium silicate, autoclaved aerated concrete and ceramic brick are conducted and the results are validated by comparing the experimental results obtained from these two methods, as well as from other existing protocols. It has been proved that both the semi-permeable membrane method and the psychrometer method can provide reliable results up to a capillary pressure of around $-1 \cdot 10^5$ Pa for both adsorption and desorption processes. Their other advantages – low cost, simple procedure, test efficiency and wide applicable range – make them very

advisable.

Acknowledgements

This project is supported by the FWO Odysseus grant "Moisture transfer in building materials: analysis at the pore-scale level" (No. G.0C55.13N). We express sincere gratitude to Prof. Rafaela Cardoso in Instituto Superior Técnico for sharing her experience with the psychrometer, and to Prof. Bart Van der Bruggen in KU Leuven for sharing his expertise about semi-permeable membranes.

References

- [1] van Aarle M, Schellen H, van Schijndel J. Hygro Thermal Simulation to Predict the Risk of Frost Damage in Masonry; Effects of Climate Change. *Energy Procedia*. 2015;78:2536-41.
- [2] Harrestrup M, Svendsen S. Full-scale test of an old heritage multi-storey building undergoing energy retrofitting with focus on internal insulation and moisture. *Building and Environment*. 2015;85:123-33.
- [3] Woloszyn M, Kalamees T, Olivier Abadie M, Steeman M, Sasic Kalagasidis A. The effect of combining a relative-humidity-sensitive ventilation system with the moisture-buffering capacity of materials on indoor climate and energy efficiency of buildings. *Building and Environment*. 2009;44:515-24.
- [4] Fang L, Clausen G, Fanger PO. Impact of temperature and humidity on the perception of indoor air quality. *Indoor Air*. 1998;8:80-90.
- [5] Funk M, Wakili KG. Driving potentials of heat and mass transport in porous building materials: a comparison between general linear, thermodynamic and micromechanical derivation schemes. *Transport in Porous Media*. 2008;72:273-94.
- [6] Hens H, Ojanen T, Künzle HM, Dow G, Rode C, Hagetoft C. IEA Annex 24: Heat, Air and Moisture Transfer in Insulated Envelope Parts. Final Report, Volume 1, Task 1: Modeling. 1996.
- [7] Woloszyn M, Rode C. IEA Annex 41: Whole Building Heat, Air, Moisture Response. Subtask 1: Modeling Principles and Common Exercises. 2008.
- [8] Lu Y, Abuel-Naga H, Bouazza A. Water retention curve of GCLs using a modified sample holder in a chilled-mirror dew-point device. *Geotextiles and Geomembranes*. 2017;45:23-8.
- [9] Hilf JW. An investigation of pore-water pressure in compacted cohesive soils. US Department of Interior Bureau of Reclamation, Technical Memorandum 654, Denver, Colorado. 1956.
- [10] Mavroulidou M, Zhang X, Cabarkapa Z, Gunn M. A study of the laboratory measurement of the Soil Water Retention Curve. 11th International Conference on the Environmental Science and Technology. Chania, Crete, Greece 2009. A 907-15.
- [11] Southen JM, Kerry Rowe R. Evaluation of the water retention curve for geosynthetic clay liners. *Geotextiles and Geomembranes*. 2007;25:2-9.
- [12] Tarantino A, Romero E, Cui YJ. Laboratory and field testing of unsaturated soils: Springer; 2009.
- [13] Abuel-Naga H, Bouazza A. A novel laboratory technique to determine the water retention curve of geosynthetic clay liners. *Geosynthetics International*. 2010;17:313-22.
- [14] Bannour H, Stoltz G, Delage P, Touze-Foltz N. Effect of stress on water retention of needlepunched geosynthetic clay liners. *Geotextiles and Geomembranes*. 2014;42:629-40.
- [15] Delage P, Suraj de Silva GPR, Vicol T. Suction controlled testing of non saturated soils with an osmotic consolidometer. Proceedings 7th International Conference on Expansive Soils. Dallas. 1992:206-11.
- [16] Feng C, Janssen H, Wu C, Feng Y, Meng Q. Validating various measures to accelerate the static gravimetric sorption isotherm determination. *Building and Environment*. 2013;69:64-71.
- [17] Garbalińska H, Bochenek M, Malorny W, von Werder J. Comparative analysis of the dynamic vapor sorption (DVS) technique and the traditional method for sorption isotherms determination — Exemplified at autoclaved aerated concrete samples of four density classes. *Cement and Concrete Research*. 2017;91:97-105.
- [18] Delage P, Mantikos V, Ackerley S, Kirkham A, Tsiampousi A, Taborda DMG, et al. Investigating soil water retention characteristics

Postprint: Feng C, Janssen H. 2019. Hygric properties of porous building materials (IV): semi-permeable membrane and psychrometer methods for measuring moisture storage curves, *Building and Environment*, 152: 39-49.

doi: <https://doi.org/10.1016/j.buildenv.2019.01.054>

at high suction using relative humidity control. *E3S Web of Conferences*. 2016;9:10007.

[19] Vangpaisal T, Bouazza A. Gas Permeability of Partially Hydrated Geosynthetic Clay Liners. *Journal of Geotechnical and Geoenvironmental Engineering*. 2004;130:93-102.

[20] Bouazza A, Vangpaisal T. An apparatus to measure gas permeability of geosynthetic clay liners. *Geotextiles and Geomembranes*. 2003;21:85-101.

[21] Beddoe RA, Take WA, Rowe RK. Water-Retention Behavior of Geosynthetic Clay Liners. *Journal of Geotechnical and Geoenvironmental Engineering*. 2011;137:1028-38.

[22] Madsen HB, Jensen CR, Boysen T. A comparison of the thermocouple psychrometer and the pressure plate methods for determination of soil water characteristic curves. *Journal of Soil Science*. 1986;37:357-62.

[23] Acikel AS, Singh RM, Bouazza A, Gates WP, Rowe RK. Applicability and accuracy of the initially dry and initially wet contact filter paper tests for matric suction measurement of geosynthetic clay liners. *Géotechnique*. 2015;65:780-7.

[24] ASTM D5298 - 16: Standard Test Method for Measurement of Soil Potential (Suction) Using Filter Paper. 2016.

[25] Roels S, Elsen J, Carmeliet J, Hens H. Characterisation of pore structure by combining mercury porosimetry and micrography. *Materials and structures*. 2001;34:76-82.

[26] ISO 12571: 2013(E) Hygrothermal performance of building materials and products - Determination of hygroscopic sorption properties. 2013.

[27] ASTM C1498 - 2010: Standard Test Method for Hygroscopic Sorption Isotherms of Building Materials. 2010.

[28] ASTM C1699 - 09: Standard Test Method for Moisture Retention Curves of Porous Building Materials Using Pressure Plates. 2009.

[29] ISO 11274: 1998(E) Soil quality - Determination of the water retention characteristic - Laboratory methods. 1998.

[30] ASTM D4404 - 18: Standard Test Method for Determination of Pore Volume and Pore Volume Distribution of Soil and Rock by Mercury Intrusion Porosimetry. 2018.

[31] Feng C, Janssen H, Feng Y, Meng Q. Hygric properties of porous building materials: Analysis of measurement repeatability and reproducibility. *Building and Environment*. 2015;85:160-72.

[32] Hansen MH. Retention curves measured using pressure plate and pressure membrane apparatus: Description of method and interlaboratory comparison. *Nordtest Technical Report 367*. 1998.

[33] Fredriksson M, Johansson P. A Method for Determination of Absorption Isotherms at High Relative Humidity Levels: Measurements on Lime-Silica Brick and Norway Spruce (*Picea abies*(L.) Karst.). *Drying Technology*. 2016;34:132-41.

[34] Plagge R, Scheffler G, Nicolai A. Experimental methods to derive hygrothermal material functions for numerical simulation tools. *Building X Conference*. Clearwater, Florida 2007. 1-12.

[35] Bittelli M, Flury M. Errors in water retention curves determined with pressure plates. *Soil Science Society of America Journal*. 2009;73:1453-60.

[36] Day RL, Marsh BK. Measurement of porosity in blended cement pastes. *Cement and Concrete Research*. 1988;18:63-73.

[37] Diamond S. Mercury porosimetry: an inappropriate method for the measurement of pore size distributions in cement-based materials. *Cement and Concrete Research*. 2000;30:1517-25.

[38] Feng C, Janssen H. Hygric properties of porous building materials (III): Impact factors and data processing methods of the capillary absorption test. *Building and Environment*. 2018;134:21-34.

[39] Safiuddin M, Hearn N. Comparison of ASTM saturation techniques for measuring the permeable porosity of concrete. *Cement and Concrete Research*. 2005;35:1008-13.

[40] ISO 12572: 2001(E) Hygrothermal performance of building materials and products - Determination of water vapour transmission properties. 2001.

[41] Gao Z, Hu Q. Estimating permeability using median pore-throat radius obtained from mercury intrusion porosimetry. *Journal of Geophysics and Engineering*. 2013;10:025014.

[42] Feng C, Janssen H. Hygric properties of porous building materials (II): Analysis of temperature influence. *Building and Environment*. 2016;99:107-18.

Postprint: Feng C, Janssen H. 2019. Hygric properties of porous building materials (IV): semi-permeable membrane and psychrometer methods for measuring moisture storage curves, *Building and Environment*, 152: 39-49.

doi: <https://doi.org/10.1016/j.buildenv.2019.01.054>

-
- [43] Roels S, Carmeliet J, Hens H, Adan O, Brocken H, Czerny R, et al. HAMSTAD Work Package 1: Final Report - Moisture Transfer Properties and Materials Characterisation, EU Contract GRD1-1999-20007. 2003.
- [44] Richards L. Porous plate apparatus for measuring moisture retention and transmission by soil. *Soil Science*. 1948;66:105-9.
- [45] Cresswell H, Green T, McKenzie N. The adequacy of pressure plate apparatus for determining soil water retention. *Soil Science Society of America Journal*. 2008;72:41-9.
- [46] <https://www.lenntech.com/Data-sheets/Filmtec-Flat-Sheet-Membrane-Chart-L.pdf>.
- [47] Cardoso R, Romero E, Lima A, Ferrari A. A comparative study of soil suction measurement using two different high-range psychrometers. *Experimental unsaturated soil mechanics: Springer*; 2007. p. 79-93.
- [48] <https://www.metergroup.com/environment/products/wp4c/>.
- [49] Leong E-C, Tripathy S, Rahardjo H. Total suction measurement of unsaturated soils with a device using the chilled-mirror dew-point technique. *Géotechnique*. 2003;53:173-82.
- [50] van Genuchten MT. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal*. 1980;44:892-8.