

WATER VAPOUR SORPTION ISOTHERMS OF HARDENED CEMENT PASTE AT DIFFERENT TEMPERATURES

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ABSTRACT

The impact of the sample preparation method on the experimental results of water vapour sorption isotherms measured by the volumetric method has been identified and an experimental protocol for measuring at different temperatures is presented here. The results showed the same trends as observed on the data obtained by the gravimetric methods. Further, possible phenomena in the nature of C-S-H hydrates at the beginning of the adsorption process were discussed using the heat of adsorption calculated by the Clausius–Clapeyron relation.

Keywords: water sorption isotherms, pre-drying, temperature, heat of sorption, C-S-H

1. INTRODUCTION

Measurement of water vapour sorption isotherms is a great significance for cement and concrete industry. For example, for engineering applications, it gives a useful relationship between the water content and relative humidity (RH) at given temperature and, from the scientific point of view, it can be used to characterize the microstructure of the adsorbent in terms of surface area, pore size distribution, pore connectivity, surface chemistry etc.

In the pioneer studies, the correlation of water sorption isotherms with shrinkage of the hardened cement paste was emphasized as can be found in the work of Powers [1] or Feldman [3]. In the recent years, attention has been given to the effects of elevated temperatures on the sorption properties of cement and concrete. It has been well established that increase in the temperature shifts the equilibrium at given a RH towards lower water uptake e.g. [7], [8], [11], [17]. This trend can be observed both on the adsorption and desorption branch of the isotherm however, on the latter one is more apparent.

Even though studies dealing with the heat involved in a sorption process are common for other engineering materials [22] or in the food industry [23], very scarce data are available for cementitious materials. Empirical relationship was given by Powers and Brownyard [2] and more recently Poyet and Charles [17] published calculations based on two sets of experimental data obtained from the first desorption of hardened cement paste.

In this proceeding, we calculate the heat of adsorption using water vapour sorption isotherms in the low RH region and use the results for discussing possible phenomena in the nature of C-S-H hydrates. The main goal of this text is to show possible application of water vapour sorption isotherms and heat of sorption for further study of the binding agent of concrete.

2. EXPERIMENTAL PROGRAM

2.1 Material

Samples of 0.52 w/c ratio were prepared using the European-produced ordinary Portland cement CEM I 52.5 N (ordinary Portland cement, 52.5 MPa standard strength, normal early strength). Properties of the material are listed in Table 1 and the characteristics of the hardened cement paste were given in the last year proceeding [9]. Mixing of the cement with deionized water was done in 2 steps by a dual centrifugal mixer. Firstly, the paste was mixed to 0.40 w/c for 2 minutes, then the remaining water was added to obtain the desired w/c and the paste was mixed for another 2 minutes. All the materials were stored in a temperature controlled room ($20 \pm 2^\circ\text{C}$) for couple days prior to the mixing. Before pouring into the molds, the fresh paste was repeatedly remixing for 4 to 6 hours to prevent bleeding during the dormant period. The cement paste was compacted on a vibrating table once placed into the molds, then sealed and kept in the temperature control room until analysing.

2.1 Analysis method

The sorption isotherms were measured by the volumetric method using the VSTAR vapour sorption analyser (Quantachrome Instruments) at temperatures 20, 40, 60 and 80°C . All the experimental data of sorption isotherms were obtained at the age of the material more than 3 months while the water sorption isotherms at different temperatures were obtained within 22 days. Prior to a measurement, the hardened cement paste was crushed and powder fraction of 25 – 75 μm was used for the analysis.

Since the applied method requires a dry sample at the beginning of an analysis, the effect of sample pre-drying on the experimental data was investigated by a comparison of vacuum drying at 2 different temperatures. Sample of 25 - 26 mg in terms of a wet mass was vacuum-dried at 105°C for 30 minutes

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Table 1 Properties of the cement

Density (g/cm ³)	Blaine value (cm ² /g)	Loss on ignition (%)	Chemical composition (%)											
			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	Total
3.17	4 300	1.48	21.51	3.62	4.24	63.11	2.01	2.60	0.17	0.57	0.38	0.05	0.32	98.58

followed by additional 30 minutes drying at the analysis temperature in order to equilibrate the system before the measurement. The second method consist of sample pre-drying at the analysis temperature for 75 minutes in total. All the sorption data presented in this manuscript were normalised with respect to the dry mass of sample determined by vacuum-drying at 105°C at the end of each analysis.

3. RESULTS AND DISCUSSION

3.1 Effect of sample pre-treatment method

The influence of the sample vacuum-drying temperature on the measured sorption isotherm is shown in Fig. 1 (equilibrium points are connected by a straight line to guide the eye). It can be observed that the isotherms are comparable until approximately 60% RH, then a discrepancy in the water content arises and is kept almost constant throughout the measurement until the sudden drop in the desorption branch which typically occurs around 35% RH in case of a measurement at 20°C.

It is generally accepted that cement hydrates are unstable even below 100°C [20]. Normally, in the cement system, one mole of ettringite bounds 32 molecules of water however, it loses its chemically bound water if it is dried at elevated temperatures and the number of the water molecules is reduced to approximately 10 – 13 [10]. This behaviour is reversible, ettringite can be rehydrated and the original number of water molecules can be restored. This was confirmed by measuring of a water vapour sorption isotherm of ettringite which was prepared by hydration of synthesized tricalcium aluminate in presence of gypsum. The purity of the resulting product was checked by X-ray diffraction. As can be seen in Fig. 2, after sample vacuum-drying at 105 °C, the re-hydration occurs around 60% RH and, since the measurement temperature is kept at 20 °C, water content at the end of

the measurement is higher than at the beginning.

Another issue related to the sample preparation can be observed on the experimental data if the vacuum-drying time is excessively prolonged. This causes flattening of the typical kink at the sudden drop of water content on the desorption branch as can be seen in Fig. 3. Therefore, same as in the previous case, the information given by the isotherm is inaccurate. More experimental data are needed to explain this behaviour but one possible hypothesis is that the C-S-H sheets become strongly agglomerated as a result of prolonged vacuum-drying which makes the pores responsible for the sudden drop either isolated or their response for a change in RH is delayed due to high tortuosity of the diffusion path of water molecules.

Below the sudden drop in the water content on the desorption branch, a low RH hysteresis can be observed. Its presence is still subjected to study and there are 3 generally accepted hypotheses, namely (1) irreversible reaction of the adsorbate with the adsorbent similarly as was shown for ettringite, (2) swelling of layered structures and opening new adsorption sites observed at clay minerals [15] and (3) lack of equilibrium time on the adsorption branch of the isotherm [16].

3.2 Sorption isotherms affected by temperature

Based on the aforementioned effect of the pre-treatment procedure on the obtained data, sample pre-drying at the analysis temperature was implemented into the experimental protocol. The typical reproducibility of the measurements is shown in Fig. 4.

The water vapour sorption isotherms measured at different temperatures are shown in Fig. 5. It can be observed that with increasing temperature the equilibrium is shifted towards lower water content and this behaviour is particularly obvious on the desorption branch. Moreover, the sudden drop in water content which is typically observed at 35% RH at 20°C is

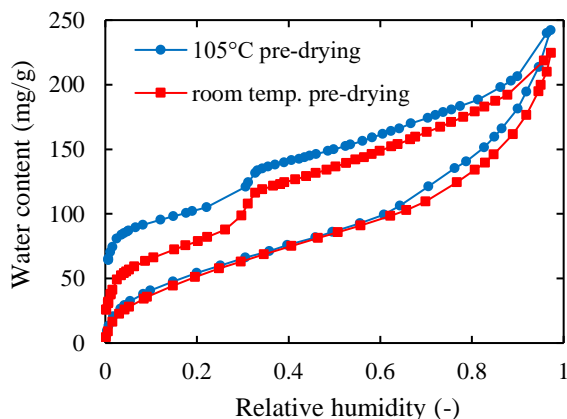


Fig. 1 Effect of the temperature of pre-drying

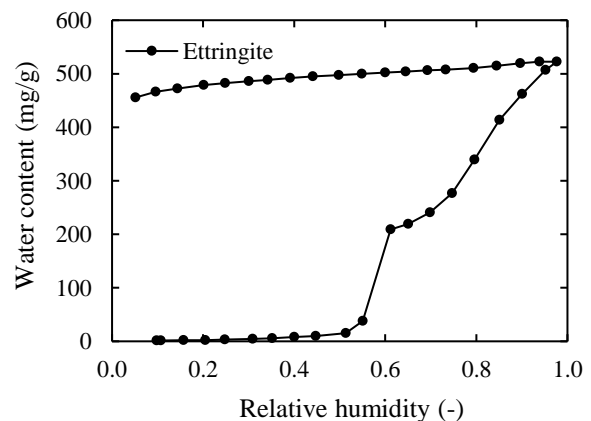


Fig. 2 Water sorption isotherm of synthesized ettringite

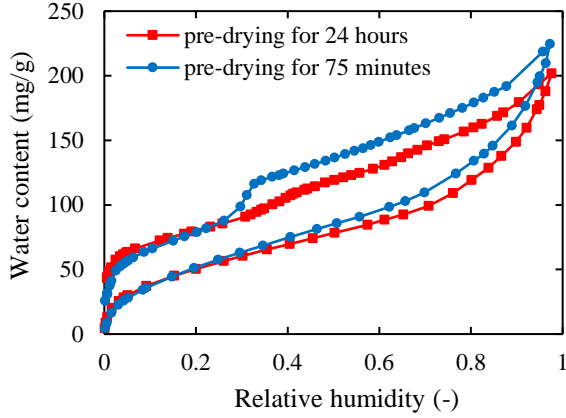


Fig. 3 Effect of prolonged vacuum-drying

shifted toward higher RHs with increasing temperature while the water content at the beginning of the drop appears to be unchanged. Another interesting feature is that the hysteresis in the low RH region (below the sudden drop) is reduced however, even at 80°C, it is still present.

The reduction in the retained water content in desorption process with increasing temperature for cementitious materials can be found in the work of Hundt and Kantelberg [7] and it was well reproduced by several researchers dealing with water sorption isotherms affected by temperature published in the recent years [7], [8], [11], [17]. Those data are typically obtained by the gravimetric methods when the samples are equilibrated above saturated salt solutions or in a dynamic vapour sorption analyser. The time frame of sample equilibration is usually several days or months in this case therefore, even though some studies claimed opposite [11], alternation of the microstructure of the hardened cement paste influences the obtained data [12-14]. Also, the span of equilibrium points is rather coarse which does not allow to obtain accurate information especially at the onset of the capillary condensation or at the sudden drop in the desorption branch. Moreover, due to the absence of equilibrium points in the very low RH range, the adsorption/desorption process cannot be precisely examined at this region as will be demonstrated in the next part of this text.

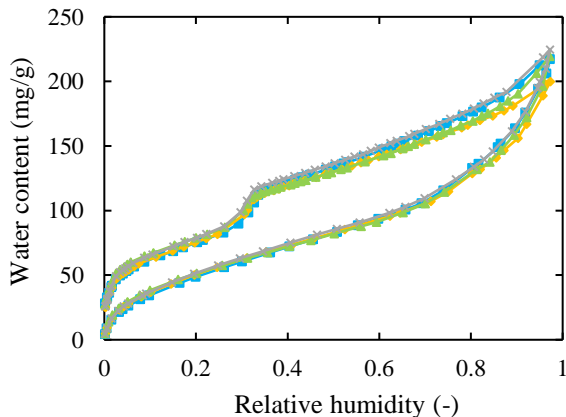


Fig. 4 Typical reproducibility of the measurements (measurement at 20 °C, pre-drying for 75 min)

3.1 Heat of sorption

Similarly as in [17], [23] the experimental data of water vapour sorption isotherms at different temperatures were fitted to the GAB equation [4-6] which expands the applicability of the well-known BET model. It states:

$$w = \frac{C \cdot k \cdot w_m \cdot h}{(1 - k \cdot h)[1 + (C - 1) \cdot k \cdot h]} \quad (1)$$

where,

- w : mass of water per gram of cement paste dried at 105°C (mg/g)
- h : relative humidity (-)
- C, k, w_m : GAB model parameters (-, -, mg/g).

The inverse relationship was used to predict the water vapour pressure for given water content at different temperatures:

$$p = \frac{p_{sat}}{2 \cdot k(1 - C)} \left[\alpha - \sqrt{\alpha^2 - 4(1 - C)} \right] \quad (2)$$

$$\alpha = 2 + \left[\frac{w_m}{w} - 1 \right] C \quad (3)$$

where,

- p : predicted water vapour pressure (Pa)
- p_{sat} : saturated water vapour pressure (Pa).

At least 3 experimental isotherms were used for fitting of the adsorption branch to the GAB model by the method of least squares. An example of the fit is shown in Fig. 6. The resulting parameters as well as the values of the specific surface area evaluated by the BET theory between 5% and 35% are summarised in Table 2. The cross-section area of the water molecule was corrected for the specific surface calculation using the relationship between water density and temperature as follows:

$$s_t = s_{20} \left(\frac{\rho_{20}}{\rho_t} \right)^{2/3} \quad (4)$$

where,

- s_t : water molecule cross-section area at given temperature (nm²)
- s_{20} : water molecule cross-section area at 20°C (0.114 nm² [21])
- ρ_t : water density at given temperature (kg/m³)
- ρ_{20} : water density at 20°C (kg/m³).

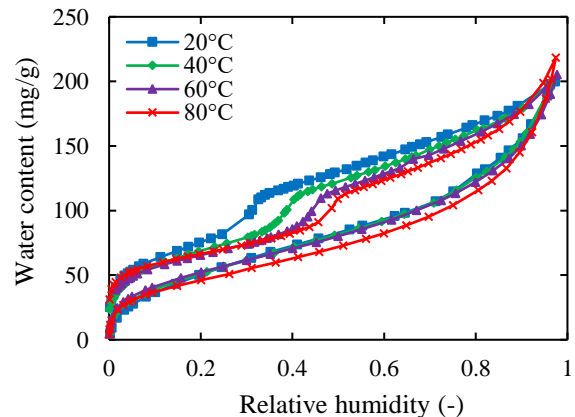


Fig. 5 Water vapour sorption isotherms measured at different temperatures (pre-drying for 75 min)

The fitted water vapour sorption isotherm at different temperatures were used to calculate the heat of sorption. The heat involved in an adsorption/desorption process for a given water content can be derived from Eq. 5 using the Clausius–Clapeyron relationship and, if the derivative is substituted by a difference as in Eq. 6, the fitted experimental isotherms can be used for calculations of the isosteric heat of sorption [17], [23], [24]:

$$Q_{ST} = -R \left[\frac{\partial \ln(p)}{\partial \left(\frac{1}{T}\right)} \right]_w \quad (5)$$

$$Q_{ST} \approx R \cdot \ln \left[\frac{p_1(w)}{p_2(w)} \right] \cdot \left(\frac{T_1 \cdot T_2}{T_1 - T_2} \right) \quad (6)$$

where,

- R :gas constant (8.314 J/mol/K)
- p_1, p_2 :equilibrium water vapour pressures (Pa)
- T_1, T_2 :absolute temperatures (K).

The adsorption is defined as bonding of adsorbate molecules to the surface of an adsorbent and a release of energy is associated with this process. Therefore, since it is exothermic, the heat of sorption is negative. However, assumption that adsorption and desorption are completely reversible processes allows us to compare the previously published data of the heat of desorption with our data of the heat of adsorption. Using this terminology, the energies involves in both processes would be positive and can be plotted in one chart. Fig. 7 shows development of the sorption heat as a function of adsorbed layers. In this case, the average thickness of water layer at 2 temperatures was used in order to take into the account the change in water density similarly as in case of the BET specific surface area calculations.

In Fig. 7 we also plot the empirical formula given by Powers and Brownyard [2] for estimation of the differential heat of sorption of cementitious materials which was later modified by Poyet and Charles [17], who incorporated the latent heat of condensation/vaporisation of water (42.7 kJ/mol [19]) and gave a relationship for estimation of the isosteric heat of sorption Q_{st} in form:

$$Q_{st} = 42.7 + \frac{64.6}{\left(1.31 + \frac{w_m}{w}\right)^2} \quad (7)$$

From Eq. 7, it is visible that the isosteric heat decreases with increasing number of adsorbed water layers.

Table 2 parameters of the GAB model

Temperature (°C)	S_{BET} (m ² /g)	C (-)	k (-)	w_m (mg/g)
20	180.1	27.3	0.767	50.7
40	180.0	48.4	0.753	51.2
60	172.7	74.7	0.790	46.3
80	160.3	115.5	0.847	39.7

Poyet and Charles calculated the heat of desorption from their data obtained at 30°C and 80°C and they applied the same approach on the data given by Hundt and Kantelberg at 20, 45, 57.5 and 70°C. It is worth to mentioned that all those data were obtained on the first desorption. Contrary from the relationship given by Powers, their data does not gradually converge to the average heat of condensation/vaporisation with increasing number of water layers but the isosteric heat firstly increases and then falls similarly as predicted by the empirical formula. Another interesting feature of those data is that it does not peak at the same water content therefore, the heat of desorption appears to vary within different cement types [17]. However, as the authors admit, this conclusion can be affected by inaccuracies due to the lack of fit of the desorption data which serve as an input for the calculations. In our case, plenty of data at low water contents are available which makes subsequent data fitting and calculations more reliable.

The calculated results differ based on which two temperature of sorption isotherms are used for the calculation. This is not novelty and a similar, however milder, trend can be observed on the calculation given by Poyet and Charles. This can be attributed to different surface chemistry since different amount of water is evaporated if the sample is dried at different temperatures as is shown in Fig. 8. It suggests that different drying potential empties sorption sites of different type therefore, the subsequent adsorption process changes based on the analysis temperature.

Another discrepancies in the trends in Fig. 7 also need to be discussed. Heat of adsorption lower than the latent heat of water condensation/vaporisation was reported in case of porous carbon materials (15–25 kJ/mol) and this low value was attributed to the hydrophobic property of the adsorbate surface [22]. Subsequent increase in the heat of adsorption can be associated with creation of new adsorption sites either around the first bonded water molecule [22] or with adsorption on other sites which become newly available due to alternation of the adsorbent matrix [23].

After the increase in the heat of adsorption, there are two possible mechanisms which can be responsible for decrease in the heat of adsorption in case of cement paste. The first one is reduction of the hydrophilic

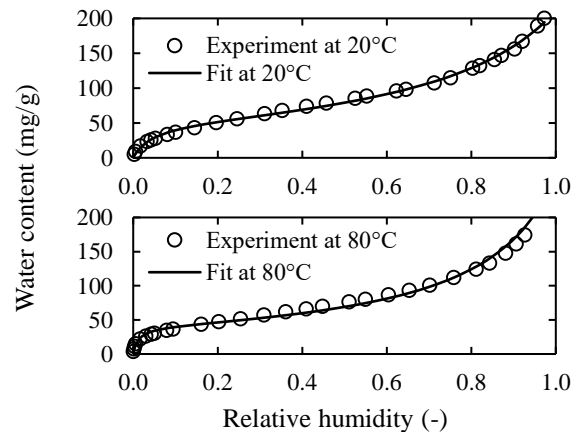


Fig. 6 Examples of data fitting

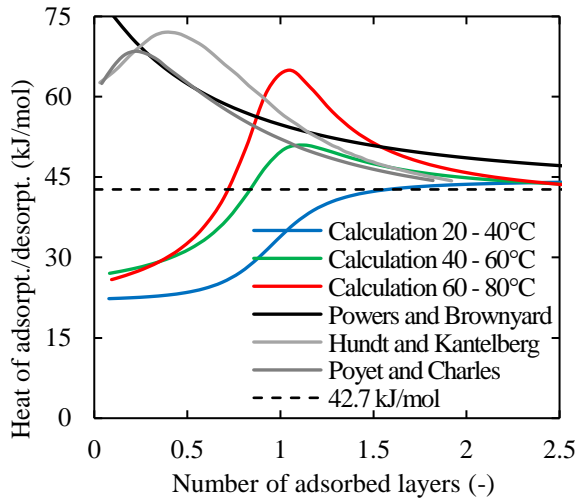


Fig. 7 Heat of adsorption/desorption as a function of adsorbed water

property of the surface due to the fact that new water molecules are adsorbed further from the surface [18]. The second one is associated with dissipation of the energy due to expansion of structural layer distance of the adsorbent as was shown in case of montmorillonite [25]. The calculations using the data at 60 and 80°C shows firstly an increase in the heat of adsorption above the value of the latent heat of condensation/vaporisation of water followed converging to this value. Contrary, in the case of the data calculated between 20 and 40°C, the initial stage can be interpreted as bonding of the hydrogen in a water molecule to the vacant position in the structure of C-S-H and the following increase in the heat of adsorption suggests formation of a cluster around this first water molecule.

The fact that the heat of adsorption exceeding the value of the latent heat of condensation/vaporisation of water only in case of calculation between 40 – 60°C and 60 – 80°C suggests that the hydrophilicity of cement paste indicated by this is an artefact of sample drying at elevated temperatures which empties additional adsorption sites. Since, as was shown previously, ettringite is rehydrated in the later stage of the adsorption process, those available adsorption sites can be probably associated with some other aluminium-based phases such as Monocarbonate, Hemicaluminate or Hydrogarnet.

Interestingly, the first derivative of the heat of adsorption in Fig. 9 has its first peak always in the

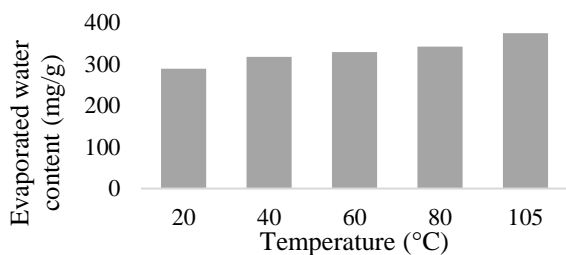


Fig. 8 Evaporable water at different vacuum-drying temperature

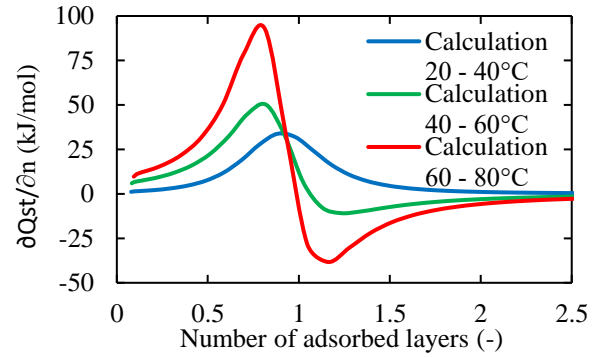


Fig. 9 Derivative of the heat of adsorption

similar position just below 1 adsorbed water layer in all calculated cases. To explain the meaning of an adsorbed layer in this context, it does not necessarily need to be a complete monolayer in sense of the adsorption theory because, as mentioned before, there is a possibility of a cluster formation around one adsorption site. Therefore, since the decrease is always observed at similar water contents, it suggests that the mechanism responsible for decrease in the heat of adsorption is expansion of the C-S-H sheets.

We are well aware that our interpretation of possible surface chemistry in the very low RH region is based on the calculations using the fitted isotherms and, even though there are multiple equilibrium points in the low RH region, this induces inaccuracies of the results.

4. CONCLUSION

The temperature dependency of water vapour sorption isotherms of hardened cement paste was measured by the volumetric method. It has been found that the sample preparation method strongly influences the measurement results. Specifically:

- (1) Vacuum-drying of a sample at elevated temperatures causes ettringite dehydration and subsequent irreversible rehydration contributes to the low RH hysteresis.
- (2) The excessive pre-drying time causes flattening of the sudden drop on the desorption branch of the isotherm.

Subsequently, the GAB model was used for fitting of the experimental isotherms and served as an input for calculations of the heat of adsorption. Using this approach, we attempt to extend the application of water vapour sorption isotherms from characterising of the microstructure to interpretation the adsorption process in terms of surface chemistry and reversible microstructural alternation of the C-S-H. The initially low heat of sorption is due to adsorption of water molecules within the layered structure of the C-S-H, subsequent increase is caused by creation of a cluster around the first adsorbed water molecule and following decrease can be associated with energy dissipation due to expansion of the C-S-H layers. Additionally, in case of samples dried at elevated temperatures, the emphasized increase in the heat of adsorption can be caused by rehydration of the aluminium-based phases of the material.

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