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A simple method to measure the isosteric energy of adsorption

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ABSTRACT

The effect of temperature on water vapour desorption isotherms can be described simply using the Clausius-Clapeyron equation and the isosteric energy of adsorption, the latter conventionally estimated using two (or more) isotherms obtained at different temperatures. This approach has some disadvantages, however, and this article puts forward a simple alternative methodology for characterising this isosteric energy experimentally. Our method is based on monitoring the relative humidity of a cementitious material heated under sealed conditions. The evolution of the relative humidity as a function of temperature makes it possible to directly evaluate the isosteric energy. In practice, the tests are performed using a cell of the type that is used for self-desiccation studies.

1. Introduction

Temperature has a significant influence on the adsorption of water vapour in cementitious materials: for a given relative humidity (RH) value, it induces (inter alia) a drop in the quantity of water retained in the porous network at equilibrium when it increases [1–9]. This phenomenon has been attributed to thermal desorption [10]. According to Le Chatelier's principle [11], a change in temperature in a system at equilibrium moves the position of equilibrium to counteract the change. Because adsorption is an exothermic process, an increase in temperature displaces the equilibrium between the water vapour and the adsorbed water towards the endothermic reaction, i.e. desorption. As a result, the amount of water retained in the pores decreases, as mentioned above. This effect may be described simply but effectively by means of the Clausius-Clapeyron equation [12–15] (note that the derivation is carried out with the water content w constant):

$$q_{st}(w) = -R\left.\frac{\partial ln(p_v)}{\partial\left(\frac{1}{T}\right)}\right|_w \quad (1)$$

where q_{st} is the isosteric energy of adsorption of the water vapour (J/mol); R the constant of ideal gases (8.3145 J/mol/K); p_v the vapour pressure (Pa) at equilibrium with the mass water content w (wt%) and the absolute temperature T (K).

When the isosteric heat q_{st} is known (i.e. when the variations in the q_{st} value as a function of the water content w are known), it is easy to estimate the equilibrium displacement induced by a change in temperature in terms of the relative humidity h or vapour pressure p_v by integrating Eq. (1). We then obtain:

$$p_v(w,T) = p_v(w,T_0)exp\left[q_{st}(w)\frac{(T-T_0)}{RT_0T}\right] \quad (2)$$

$$h(w,T) = h(w,T_0)\frac{p_{vs}(T_0)}{p_{vs}(T)}exp\left[q_{st}(w)\frac{(T-T_0)}{RT_0T}\right] \quad (3)$$

where $h(w,T)$ is the value of the relative humidity at equilibrium with the water content w and the temperature T; $p_{vs}(T)$ is the saturated vapour pressure (Pa) at temperature T and T_0 is a temperature for which the isotherm is known (i.e. the relation between w and h). It should be noted that T_0 generally corresponds to the ambient temperature (ca. 20 °C).

We should emphasise here that this simple approach does not factor in possible changes in the distribution of the size of the pores, linked (for example) to the modification of the calcium-silicate-hydrates (CSH) [16–20] and/or the partial dissolution of the calcium sulfoaluminates [21,22], which could impact the adsorption/desorption isotherms. This in no way implies that these phenomena do not occur; rather that their influence on the isotherms is negligible compared to that of thermal desorption.

From a practical point of view, the isosteric heat of adsorption q_{st} can

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be evaluated simply by measuring the isotherm at two different temperatures (T_0 and T_1); Eq. (1) then becomes [10]:

$$q_{st}(w) = R\left(\frac{T_0 T_1}{T_{0-}T_1}\right) ln\left[\frac{p_v(w,T_0)}{p_v(w,T_1)}\right] \quad (4)$$

where $p_v(w,T_0)$ and $p_v(w,T_1)$ are the vapour pressures at equilibrium with the water content w and temperatures T_0 and T_1 respectively.

Even though the above approach is very simple, it nevertheless does have some disadvantages. In the first instance, it requires experimental results at two different temperatures (or more if possible). Although the characterisation of isotherms at ambient temperature may be considered a routine operation for many laboratories, the same cannot be said for tests at other temperatures: we need only note how few results are published in this field to recognise this. Secondly, since the derivation of Eq. (1) must be performed at a constant water content, a mathematical function must be used to extrapolate the value of the vapour pressure $p_v(w,T)$ based on the experimental results available at temperature T. In practice, different functions can be used such as adsorption models, for example BET [23], GAB [24,25], Pickett [26] or any other bijective function [27]. Unfortunately, the choice of function is far from a trivial matter in that the $q_{st}(w)$ values obtained in this way depend on the model used. For example, significant differences were obtained using the GAB and Pickett models [6]. These two points highlight the need for an experimental method that can evaluate the isosteric energy more directly while avoiding any descriptive model. The aim of this article is to suggest an alternative methodological approach and to compare it with the available results (desorption isotherms at different temperatures).

2. Material and methods

First, it should be mentioned that the approach presented here is not new; contrary to what the authors initially thought. A similar approach has recently been proposed [28,29] and used for the study of food products [30–33]. It may be possible that other similar studies have been published, and especially in other scientific fields, although no other papers could be found by the authors.

Rather than performing tests using a conventional approach - i.e. at a constant temperature measuring the water content at equilibrium with different RH values (regulated with saturated salt solutions, for example) - it seemed more relevant and practical with a view to using Eq. (1) to work at a constant water content w while varying the temperature T and measuring the vapour pressure $p_v(w,T)$ at equilibrium. This type of approach is commonly used to characterise the hygrothermic coefficient [34,35] that links the increase in RH induced by an increase in temperature [2,36–40].

The easiest way to conduct this type of test is to take advantage of the experience gained from studies on self-desiccation: the methods and devices developed have proved their ability to prevent any water loss from the sample tested [41] and, it follows, to the water content during the test. For practical reasons, it was decided in this instance to use the device designed by Garcia Boivin [42]: this consists of a stainless steel body (Fig. 1) which can accommodate a sample in a small cavity equipped with a thermo-hygrometer (Rotronic HygroClip IM-3 capacitive probe), which can be used to measure the RH at equilibrium with the sample. The device is immersed in a thermostated bath during a test to limit temperature fluctuations. Water tightness is achieved by means of a PTFE cylinder and O-rings (as well as screws not shown in Fig. 1).

Two such devices were used in this study, and were first tested using saturated salt solutions: these tests confirmed the tightness of the devices, making it possible to estimate the uncertainty of the temperature and RH measurements (±0.3 °C and ±2% RH respectively; see Appendix 1).

A CEM I paste (Ordinary Portland Cement, OPC) was selected as the material for this study since it has been analysed in the past and the q_{st} isosteric energy was evaluated on the basis of Eq. (4) by Drouet et al. [6]. The paste was prepared in 2009 using a 2 L batch and then poured into cylindrical plastic moulds (diameter 50 mm, height 80 mm). The cylinders were demoulded 24 h later and stored in an airtight container and submerged in water. Excess portlandite was added to limit calcium leaching and carbonation. Nine years later (in 2018), cylinders were removed from the containers and thin discs (3 mm thick) were cut using a diamond disc saw on the central part of the cylinders. They were then resaturated under vacuum [43] and placed in desiccation cabinets above saturated salt solutions to equilibrate them to the given RH values [44]. The saturated salt solutions used are summarised in Table 1 together with the RH obtained. Finely-divided calcium oxide (CaO) was added to the desiccation cabinets to prevent the carbonation of the samples; it should be noted that the presence of CaO did not interfere with the maintenance of the RH by the various salt solutions. This was verified from time to time by checking the RH value in the different cabinets.

The discs were left for at least one year in the desiccation cabinets so they could reach water equilibrium. They were then removed, weighed and immediately introduced into the self-desiccation devices. The temperature of the thermostated bath was increased in steps up to a maximum of 50 °C in order to limit the destabilisation of the minerals of

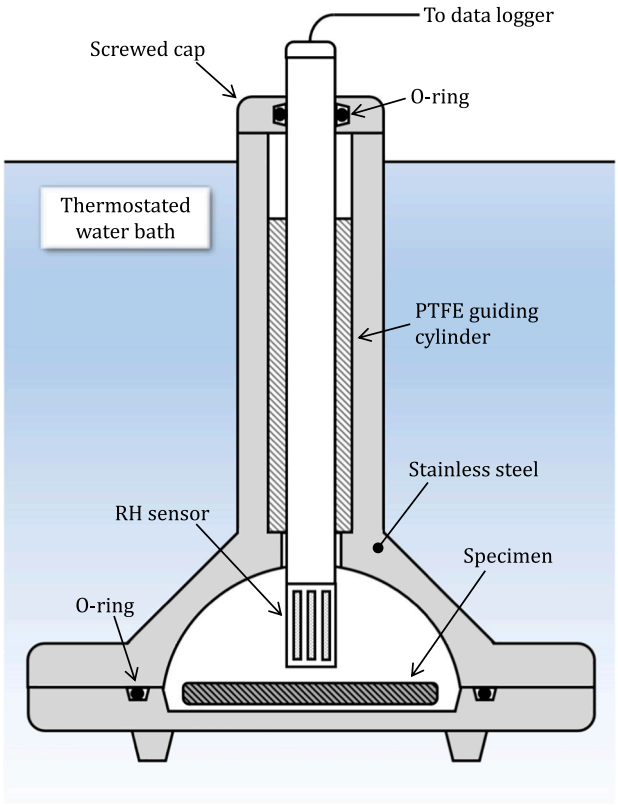

Fig. 1. View of the self-desiccation device used in this study. Adapted from [42].

Table 1
Saturated salt solutions used to dry the samples prior to the tests [44].

Salt	Formula	RH at 20 °C
Calcium chloride	$CaCl_2$	≈3%
Lithium chloride	LiBr	11%
Potassium acetate	CH_3COOK	23%
Magnesium chloride	$MgCl_2$	33%
Potassium carbonate	K_2CO_3	43%
Magnesium nitrate	$Mg(NO_3)_2$	54%
Sodium bromide	NaBr	59%
Potassium iodide	KI	70%

the cement paste. The temperature and RH values were recorded throughout the tests. Following the tests, the discs were dried at 80 °C (with $CaCl_2$ as a desiccant) in order to estimate their water content. This protocol was chosen so that the results could be compared with the data acquired by Drouet et al. [6]. It should also be noted that for Portland cements, this drying protocol essentially gives the same results as drying at 105 °C (see Table 8 of reference [6]).

3. Results

Fig. 2 shows, by way of example, the results obtained with the disc initially dried at 43% RH with the K_2CO_3 solution (Table 1). The vapour pressures p_v were calculated from RH values using Rankine's formula:

$$p_v = RH \times p_{vs} \text{ with } p_{vs}(T) = p_a exp\left(A + \frac{B}{T}\right) \quad (5)$$

where p_{vs} represents the water vapour saturation pressure (Pa), p_a the atmospheric pressure (101.3 kPa) and A and B are two constants (A = 13.7 and B = 5120 K).

For this test, the measurement device was stored in ambient air (20 °C ± 2 °C) before being immersed in the thermostated bath, which explains the temperature fluctuations observed during the first week of the test. It is interesting to observe that the RH value at equilibrium with the disc at ambient temperature is approximately 44% (i.e. a vapour pressure of 1.05 kPa), consistent with the expected value (Table 1). This indicates that the one-year period in the desiccation cabinet was enough to achieve water equilibrium. When the temperature increases, the vapour pressure at equilibrium also increases: this indicates that the water is released by the cement paste. This water loss does not give rise to a significant variation in the sample's water content, as was verified by weighing the sample after the test. It must be noted here that equilibrium was obviously not reached at each RH-step (Fig. 2). For practical reasons, equilibrium was assumed to be reached when the RH-increase rate was lower than 0.2%/day, just like in sorption balance experiments [45]. The use of this criterion made it possible to reduce the duration of the tests while ensuring the measurement stability of the ln (p_v) values (Fig. 3) necessary for the evaluation of the isosteric energy of adsorption q_{st} (see Eq. (1)).

Fig. 4 compiles the vapour pressure values (log scale) at the end of each temperature step as a function of the inverse of the temperature (1000 / T). It should be noted that the uncertainty in the values presented is much lower than the size of the points used to represent them. The slope of the regression line is used to estimate the energy q_{st} = 56.2 kJ/mol (as an absolute value).

All the q_{st} values obtained by testing all the dried discs with the salt solutions in Table 1 are presented in Fig. 5 as a function of the RH measured at ambient temperature. The horizontal error bar represents

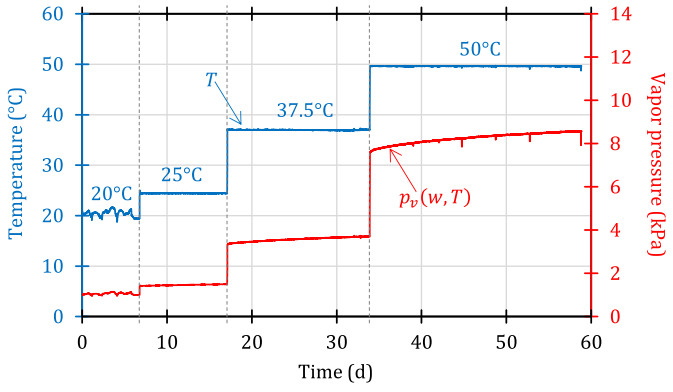

Fig. 2. Example of temperature and vapour pressure results obtained during a test (paste dried using K_2CO_3).

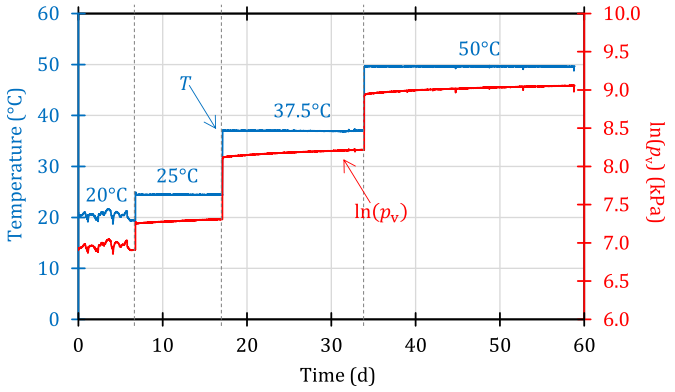

Fig. 3. Example of stability of ln(p_v) measurements obtained during a test (paste dried using K_2CO_3).

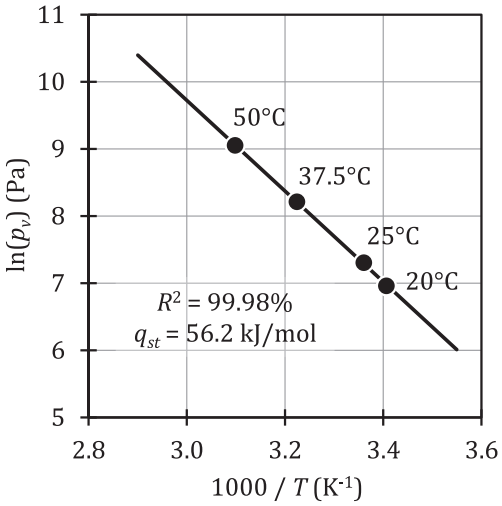

Fig. 4. Assessment of q_{st} average value using a paste sample initially equilibrated at 43% HR (using K_2CO_3 at ambient temperature).

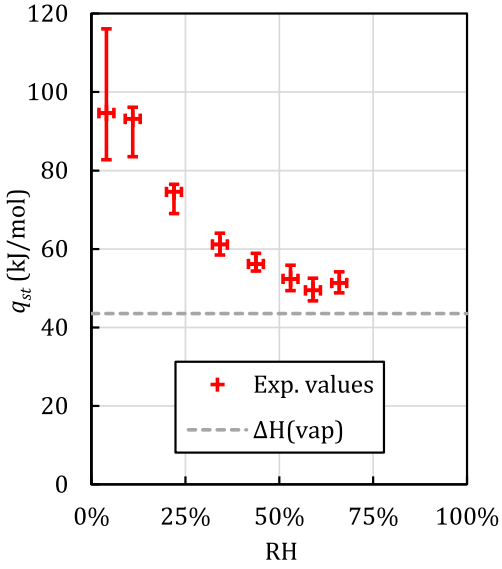

Fig. 5. q_{st} versus relative humidity of the disc at ambient temperature.

the constant uncertainty of ±2% for the RH measurement while the vertical error bar represents the uncertainty in the q_{st} isosteric energy. The vertical bars represent the q_{st} minimum and maximum values that were determined as explained in the Appendix. The q_{st} uncertainty is not constant and increases when the RH at equilibrium decreases; this point is discussed in Appendix 1. The q_{st} values decrease when the RH increases, and are all higher than the mean value of the latent heat of the water vaporisation ($\Delta H_{vap} \approx 43.6$ kJ/mol between 20 °C and 50 °C); this point is discussed below.

Knowing the water content and RH value at equilibrium at ambient temperature (approximately 20 °C) for each disc meant it was possible to estimate the desorption isotherm of the paste (Fig. 6). As for Fig. 5, the error bars correspond to the uncertainties of the measurements (±2% for the RH and ±0.5% for the water content). The comparison with the desorption isotherm obtained by Drouet et al. [6] with larger samples is good. This demonstrates the absence of a significant parasitic effect of atmospheric carbonation [46] despite the thinness of the discs used here (3 mm thick).

Fig. 7 shows the q_{st} isosteric energy as a function of the water content of the discs. As with Fig. 5, when the water content increases, the q_{st} isosteric energy decreases and tends towards the mean value of the latent heat of the water vaporisation (ΔH_{vap}). This indicates that the further a water molecule is from the substrate, the more it behaves like free water. Conversely, the closer it is to the substrate, the higher its adsorption energy. The measurements performed in this study with the self-desiccation device are consistent with the results obtained by Drouet et al. [6], even if there are significant differences in the steepest section of the curve (approximately 20 kJ/mol deviation around w = 5%). We should bear in mind that the uncertainty in the isosteric energy assessed by Drouet et al. [6] is of the order of ±10 kJ/mol and may, therefore, contribute significantly to the differences observed here.

These results show that the self-desiccation device can be used to assess the values of the q_{st} isosteric energy of adsorption with a level of confidence equivalent to the conventional method (using isotherms at different temperatures). As is seen in Fig. 7, there are no results at low moisture contents (in the monolayer, i.e. for 0% ≤ w ≤ 4.8%). This is due to the form of the isotherm (a very rapid rise in the water content at low RH; see Fig. 6), which does not allow easy access to water content values below 5% (in this particular case) by means of the usual salt solutions. As it stands, this methodology cannot be used to obtain information on the q_{st} variations in the monolayer (and more particularly on the validity of the optimum).

4. Conclusion

This article presents an alternative methodology for evaluating q_{st} isosteric energy of adsorption, which can be used to simply describe the effect of temperature on water desorption isotherms using the Clausius-Clapeyron relationship. The method consists of introducing a sample - previously conditioned to a water content - in an airtight container and monitoring the RH variations at equilibrium as the temperature increases. From a practical perspective, this methodology is simple to set up and requires only common laboratory equipment (a thermostated bath and thermo-hygrometer). The self-desiccation cell used here can be replaced by any type of container that is small in volume and that can be sealed effectively.

The results obtained in this study show that this approach can be employed to assess the value of the q_{st} isosteric energy with a level of confidence that is at least equivalent to the usual method (using Clausius-Clapeyron and isotherms at different temperatures). It is difficult, however, to obtain results for low water contents (i.e. for water content values that are smaller than the monolayer). Furthermore, uncertainty in the q_{st} value obtained increases as the RH tested decreases in relation to the uncertainty linked to the thermo-hygrometer used here.

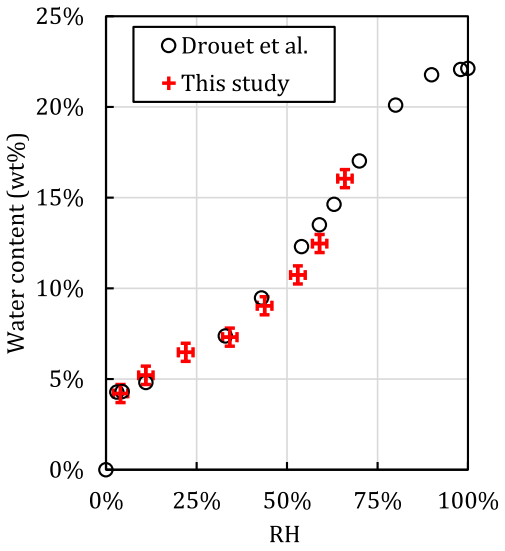

Fig. 6. Paste desorption isotherm at ambient temperature (approx. 20 °C) and comparison with data from Drouet et al. [6].

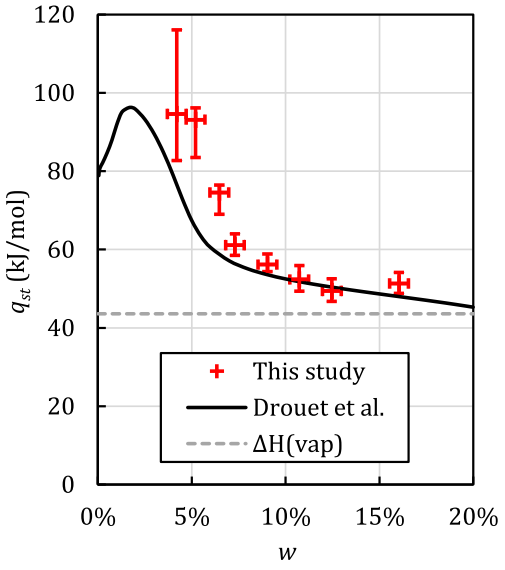

Fig. 7. Isosteric energy q_{st} versus water content w and comparison with the results of Drouet et al. [6].

CRediT authorship contribution statement

S. Poyet: Conceptualization, Methodology, Validation, Investigation, Data curation, Supervision, Writing – Original draft
G. Touze: Investigation, Data curation
J.-L. Adia: Validation, Writing – Review & editing, Project administration, Funding acquisition
L. Charpin: Validation, Writing – Review & editing, Project administration, Funding acquisition
S. Michel-Ponnelle: Validation, Writing – Review & editing, Project administration, Funding acquisition.

Declaration of competing interest

No potential conflict of interest was reported by the authors.

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Appendix 1. Estimation of uncertainties

The two self-desiccation cells were tested prior to the tests: cups containing saturated salt solutions (KNO_3, KI, K_2CO_3, CH_3COOK and LiBr) were introduced into the devices, which were sealed and then immersed in the thermostated bath. The temperature of the bath was increased from 20 °C to 65–70 °C in 5 °C steps. The temperature and RH in the gaseous atmosphere above the salt solutions were continuously recorded. It became clear that both hygrometers return similar temperature values (Fig. 8-a) but that the difference between the two probes can reach ±0.3 °C (Fig. 8-b). In terms of the RH, the measured values (Fig. 9) correspond satisfactorily to the values available in the literature [44,47–50] although the deviation may reach ±2% at the two extremes of the RH range (11% at 20 °C with the LiBr solution and 93% at 20 °C with the KNO_3 solution).

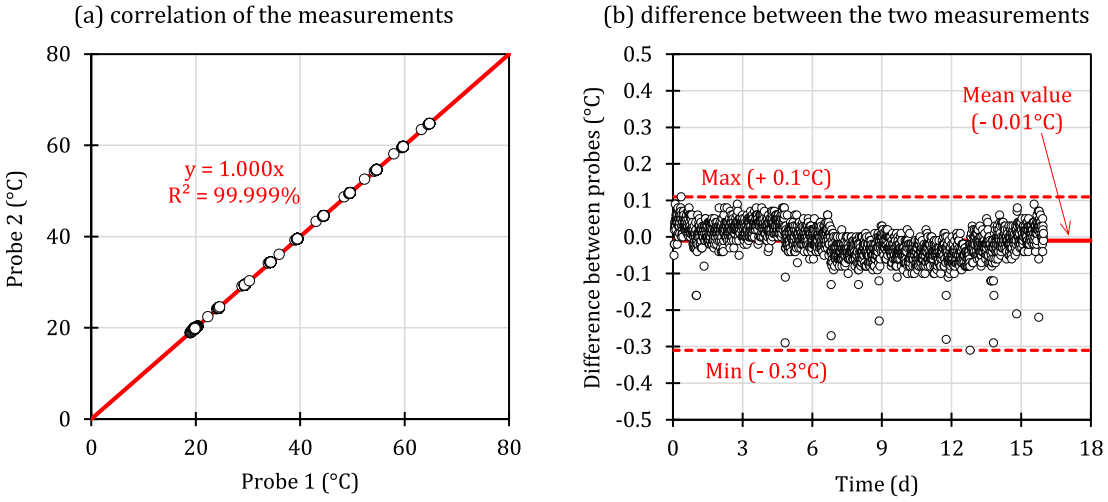

Fig. 8. Comparison of the temperature values measured using two different hygrometers.

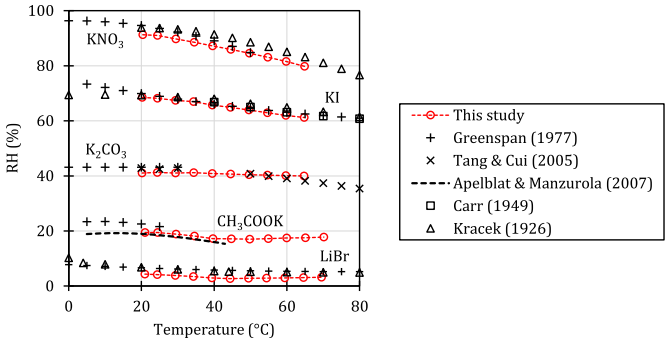

Fig. 9. Comparison of the RH measured using the two hygrometers and comparison with tabulated values from the literature [44,47–50].

The uncertainty in the isosteric energy value was estimated by considering that the position of the points in Fig. 4 - line ln (p_v) as a function of $\frac{1000}{RT}$ - may vary depending on the uncertainties outlined above. By only taking into account the two points corresponding to the lowest and highest temperature, and by considering the suitable combinations of uncertainties, we maximize the impact of the slope on the line (Fig. 10) and can estimate the minimum and maximum q_{st} values.

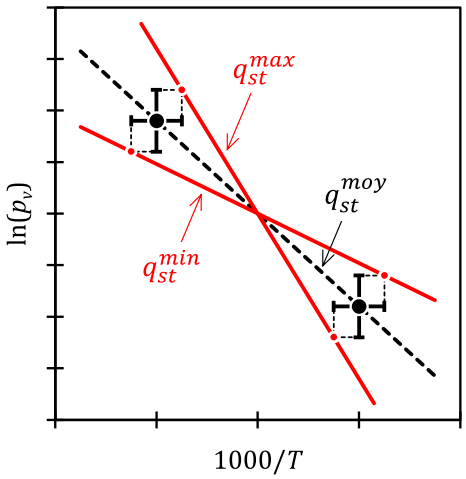

Fig. 10. Illustration of the uncertainty assessment of q_{st} values.

When the value of the initial RH is above about 20%, the uncertainty in the value of the isosteric energy q_{st} remains limited, i.e. between ±2 kJ/mol and ±5 kJ/mol approximately (Fig. 5). This is due to the fact that the uncertainties in the temperature and RH do not significantly modify the position of the points and, therefore, the value of the slope of the line (0.3 K is low compared to the temperature value and 2% is low compared to the RH value). On the other hand, the more the value of the initial RH drops, the greater the uncertainty becomes in relation to the RH value and modifies the position of the points on Fig. 10. For example, in the case of $CaCl_2$ (Table 1), the initial RH is of the order of 4% (at 20 °C); the uncertainty therefore represents half of its value, which maximizes the uncertainty in the q_{st} value. In this particular case, the evaluation gives the following result with a high degree of uncertainty: $q_{st} = 94.6^{+21.0}_{-12.0}$ kJ/mol. The uncertainty at low RH could be significantly reduced by limiting the uncertainty relating to the RH measurement by using more suitable sensors: dew point sensors, for instance.

References

[1] J. Hundt, H. Kantelberg, Sorptionsuntersuchungen an zemenstein, zementmörtel und beton (in German), Dtsch. Aussch. Stahlbet. 297 (1978) 25–39.

[2] F. Radjy, E.J. Sellevold, K.K. Hansen, Temperature data for water sorption in hardened cement paste: enthalpy, entropy and sorption isotherms at different temperatures, Report 057, Technical University of Denmark (Lyngby Denmark), 2003.

[3] T. Ishida, K. Maekawa, T. Kishi, Enhanced modeling of moisture equilibrium and transport in cementitious materials under arbitrary temperature and relative humidity history, Cem. Concr. Res. 37 (2007) 565–578, https://doi.org/10.1016/j.cemconres.2006.11.015.

[4] S. Poyet, Experimental investigation of the effect of temperature on the first desorption isotherm of concrete, Cem. Concr. Res. 39 (2009) 1052–1059, https://doi.org/10.1016/j.cemconres.2009.06.019.

[5] F. Brue, C.A. Davy, F. Skoczylas, N. Burlion, X. Bourbon, Effect of temperature on the water retention properties of two high performance concretes, Cem. Concr. Res. 42 (2012) 384–396, https://doi.org/10.1016/j.cemconres.2011.11.005.

[6] E. Drouet, S. Poyet, J.-M. Torrenti, Temperature influence on water transport in hardened cement pastes, Cem. Concr. Res. 76 (2015) 37–50, https://doi.org/10.1016/j.cemconres.2015.05.002.

[7] J.M. De Burgh, S.J. Foster, H.R. Valipour, Prediction of water vapour sorption isotherms and microstructure of hardened Portland cement pastes, Cem. Concr. Res. 81 (2016) 134–150, https://doi.org/10.1016/j.cemconres.2015.11.009.

[8] F.N.G. Brue, C.A. Davy, N. Burlion, F. Skoczylas, X. Bourbon, Five year drying of high performance concretes: effect of temperature and cement-type on shrinkage, Cem. Concr. Res. 99 (2017) 70–85, https://doi.org/10.1016/j.cemconres.2017.04.017.

[9] I. Maruyama, J. Rymeš, Temperature dependency of short-term length-change and desorption isotherms of matured hardened cement, J. Adv. Concr. Technol. 17 (2019) 188–194, https://doi.org/10.3151/jact.17.5.188.

[10] S. Poyet, S. Charles, Temperature dependence of the sorption isotherms of cement-based materials: heat of sorption and Clausius-Clapeyron formula, Cem. Concr. Res. 39 (2009) 1060–1067, https://doi.org/10.1016/j.cemconres.2009.07.018.

[11] H. Le Chatelier, Sur un énoncé général des lois des équilibres chimiques (in French), C. R. Hebd. Seances Acad. Sci. 99 (1884) 786–789. https://gallica.bnf.fr/ark:/12148/bpt6k3055h.image.f786.pagination.langFR.

[12] H. Pan, J.A. Ritter, P.B. Balbuena, Examination of the approximations used in determining the isosteric heat of adsorption from the Clausius-Clapeyron equation, Langmuir. 14 (1998) 6323–6327.

[13] S. Sircar, R. Mohr, C. Ristic, M.B. Rao, Isosteric heat of adsorption: theory and experiment, J. Phys. Chem. B 103 (1999) 6539–6546.

[14] A.A. Fomkin, Adsorption of gases, vapors and liquids by microporous adsorbents, Adsorption. 11 (2005) 425–436, https://doi.org/10.1007/s10450-005-5636-x.

[15] S. Builes, S.I. Sandler, R. Xiong, Isosteric heats of gas and liquid adsorption, Langmuir. 29 (2013) 10416–10422, https://doi.org/10.1021/la401035p.

[16] Y. Aono, F. Matsushita, S. Shibata, Y. Hama, Nano-structural changes of C-S-H in hardened cement paste during drying at 50°C, J. Adv. Concr. Technol. 5 (2007) 313–323, https://doi.org/10.3151/jact.5.313.

[17] E. Gallucci, X. Zhang, K.L. Scrivener, Effect of temperature on the microstructure of calcium silicate hydrate (C-S-H), Cem. Concr. Res. 53 (2013) 185–195, https://doi.org/10.1016/j.cemconres.2013.06.008.

[18] S. Bahafid, S. Ghabezloo, M. Duc, P. Faure, J. Sulem, Effect of the hydration temperature on the microstructure of Class G cement: C-S-H composition and density, Cem. Concr. Res. 95 (2017) 270–281, https://doi.org/10.1016/j.cemconres.2017.02.008.

[19] S. Bahafid, S. Ghabezloo, P. Faure, M. Duc, J. Sulem, Effect of the hydration temperature on the pore structure of cement paste: experimental investigation and micromechanical modelling, Cem. Concr. Res. 111 (2018) 1–14, https://doi.org/10.1016/j.cemconres.2018.06.014.

[20] F. Avet, K. Scrivener, Effect of temperature on the water content of C-A-S-H in plain Portland and blended cements, Cem. Concr. Res. 136 (2020) 106124, https://doi.org/10.1016/j.cemconres.2020.106124.

[21] R.B. Perkins, C.D. Palmer, Solubility of ettringite (Ca6[Al(OH)6]2(SO4)3 26H2O) at 5–75°C, Geochim. Cosmochim. Acta 63 (1999) 1969–1980.

[22] Q. Zhou, F.P. Glasser, Thermal stability and decomposition mechanisms of ettringite at <120°C, Cem. Concr. Res. 31 (2001) 1333–1339, https://doi.org/10.1016/S0008-8846(01)00558-0.

[23] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60 (1938) 309–319, https://doi.org/10.1021/ja01269a023.

[24] R.B. Anderson, Modifications of the Brunauer, Emmett and Teller equation, J. Am. Chem. Soc. 68 (1946) 686–691, https://doi.org/10.1021/ja01208a049.

[25] C. van den Berg, Vapour Sorption Equilibria and Other Water-Starch Interactions; a Physico-chemical Aproach, Ph.D. Thesis, University of Wageningen (Netherlands), 1981. http://library.wur.nl/WebQuery/wurpubs/75143.

[26] G. Pickett, Modification of the Brunauer Emmett Teller theory of multimolecular adsorption, J. Am. Chem. Soc. 67 (1945) 1958–1962, https://doi.org/10.1021/ja01227a027.

[27] S. Poyet, Determination of the intrinsic permeability to water of cementitious materials: influence of the water retention curve, Cem. Concr. Compos. 35 (2013) 127–135, https://doi.org/10.1016/j.cemconcomp.2012.08.023.

[28] R.M. Syamaladevi, R.K. Tadapaneni, J. Xu, R. Villa-Rojas, J. Tang, B. Carter, S. Sablani, B. Marks, Water activity change at elevated temperatures and thermal resistance of Salmonella in all purpose wheat flour and peanut butter, Food Res. Int. 81 (2016) 163–170, https://doi.org/10.1016/j.foodres.2016.01.008.

[29] R.K. Tadapaneni, R. Yang, B. Carter, J. Tang, A new method to determine the water activity and the net isosteric heats of sorption for low moisture foods at elevated temperatures, Food Res. Int. 102 (2017) 203–212, https://doi.org/10.1016/j.foodres.2017.09.070.

[30] R.K. Tadapaneni, J. Xu, R. Yang, J. Tang, Improving design of thermal water activity cell to study thermal resistance of Salmonella in low-moisture foods, LWT Food Sci. Technol. 92 (2018) 371–379, https://doi.org/10.1016/j.lwt.2018.02.046.
[31] J. Xu, J. Tang, Y. Jin, J. Song, R. Yang, S.S. Sablani, M.J. Zhu, High temperature water activity as a key factor influencing survival of Salmonella Enteritidis PT30 in thermal processing, Food Control 98 (2019) 520–528, https://doi.org/10.1016/j.foodcont.2018.11.054.
[32] Y. Jin, J. Tang, S.S. Sablani, Food component influence on water activity of low-moisture powders at elevated temperatures in connection with pathogen control, Lwt. 112 (2019) 108257, https://doi.org/10.1016/j.lwt.2019.108257.
[33] M.E. Pérez-Reyes, J. Tang, M.J. Zhu, G.V. Barbosa-Cánovas, The influence of elevated temperatures and composition on the water activity of egg powders, J. Food Process. Preserv. 45 (2021), https://doi.org/10.1111/jfpp.15269.
[34] Z.P. Bažant, Delayed thermal dilatations of cement paste and concrete due to mass transport, Nucl. Eng. Des. 14 (1970) 308–318, https://doi.org/10.1016/0029-5493(70)90108-1.
[35] H. Nguyen, S. Rahimi-Aghdam, Z.P. Bažant, Unsaturated nanoporomechanics, Proc. Natl. Acad. Sci. U. S. A. 117 (2020) 3440–3445, https://doi.org/10.1073/pnas.1919337117.
[36] L.-O. Nilsson, Temperature effects in relative humidity measurements on concrete - some preliminary studies, in: J. Kronvall (Ed.), Proc. Symp. Day Build. Phys, Swedish Council for Building Research, Lund, Sweden, 1987, pp. 456–462.
[37] B. Persson, Self-desiccation and chloride migration, in Persson & Fagerlund (eds), in: B. Persson, G. Fagerlund (Eds.), Self-desiccation Its Importance Concr. Technol. Proc. 3rd Int. Res. Semin., Lund University, Lund, Sweden, 2002, pp. 175–194.
[38] Z.C. Grasley, D.A. Lange, Thermal dilation and internal relative humidity of hardened cement paste, Mater. Struct. Constr. 40 (2007) 311–317, https://doi.org/10.1617/s11527-006-9108-x.
[39] T. Colinart, P. Glouannec, Temperature dependence of sorption isotherm of hygroscopic building materials. Part 1: experimental evidence and modeling, Energy Build. 139 (2017) 360–370, https://doi.org/10.1016/j.enbuild.2016.12.082.
[40] H. Wang, C. Hellmich, Y. Yuan, H. Mang, B. Pichler, May reversible water uptake/release by hydrates explain the thermal expansion of cement paste? — arguments from an inverse multiscale analysis, Cem. Concr. Res. 113 (2018) 13–26, https://doi.org/10.1016/j.cemconres.2018.05.008.
[41] L.E. Copeland, R.H. Bragg, Self desiccation in Portland cement pastes, ASTM Bull. 204 (1955) 1–17.
[42] S. Garcia Boivin, Retrait au jeune âge du béton : Développement d'une méthode expérimentale et contribution à l'analyse physique du retrait endogène (in french), Ph.D. Thesis, Ecole Nationale des Ponts et Chaussées, Paris (France), 1999.
[43] H. Hornain, G. Arliguie, GranDuBé - Grandeurs associées à la durabilité des bétons (in French), Presses des Ponts et Chaussées, 2007.
[44] L. Greenspan, Humidity fixed points of binary saturated aqueous solutions, J. Res. Natl. Bur. Stand. Sect. A Phys. Chem. 81A (1977) 89–96, https://doi.org/10.6028/jres.081A.011.
[45] S. Poyet, K. Trentin, E. Amblard, The use of sorption balance for the characterization of the water retention curve of cement-based materials, J. Adv. Concr. Technol. 14 (2016) 354–367, https://doi.org/10.3151/jact.14.354.
[46] M. Auroy, S. Poyet, P. Le Bescop, J.M. Torrenti, T. Charpentier, M. Moskura, X. Bourbon, Impact of carbonation on unsaturated water transport properties of cement-based materials, Cem. Concr. Res. 74 (2015) 44–58, https://doi.org/10.1016/j.cemconres.2015.04.002.
[47] F.C. Kracek, P-T-X relations for systems of two or more components and containing two or more phases, in: E.W. Washburn (Ed.), Int. Crit. Tables Numer. Data, Physics, Chem. Technol. (Vol. 3), Knovel, 1926: pp. 351–385.
[48] D.S. Carr, B.L. Harris, Solutions for maintaining constant relative humidity, Ind. Eng. Chem. 41 (1949) 2014–2015, https://doi.org/10.1021/ie50477a042.
[49] A.-M. Tang, Y.-J. Cui, Controlling suction by vapour equilibrium technique at different temperatures, application to the determination of the water retention properties of MX80 clay, Can. Geotech. J. 42 (2005) 287–296, https://doi.org/10.1139/T04-082.
[50] A. Apelblat, E. Manzurola, The vapour pressures over saturated aqueous solutions of sodium and potassium acetates, chlorates, and perchlorates, J. Chem. Thermodyn. 39 (2007) 1176–1181, https://doi.org/10.1016/j.jct.2006.12.006.