Cement and Concrete Research 40 (2010) 867–874

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

A method based on isothermal calorimetry to quantify the influence of moisture on the hydration rate of young cement pastes

Michael Gerstig, Lars Wadsö *

Building Materials, Lund University, Box 118, 221 00 Lund, Sweden

ARTICLE INFO

Article history:
Received 9 October 2009
Accepted 3 February 2010

Keywords:
Calorimetry (A)
Drying (A)
Hydration (A)
Kinetics (A)

ABSTRACT

Cement hydration needs water to proceed and if water is lost by drying, the hydration rate will decrease. This can be of importance in cases when concrete surfaces are exposed to drying so that their strength development will be retarded. We describe a method based on isothermal calorimetry to assess how the rate of cement hydration is influenced by removal of water (drying) at different times up to three days after mixing. Thin samples of cement pastes are hydrated in a calorimeter and at different times exposed to one hour drying periods. The resulting decrease in thermal power following the removal of water is quantified as a measure of the reduction in hydration rate. The mass loss is found by weighing the samples before and after a measurement, and the change in water activity of a sample during drying can be found from the slope of the thermal power during the drying period.

1. Introduction

Cementitious systems like concrete harden when the dry cement powder reacts with water (hydrates). For these reactions to take place, anhydrous substances in the cement are dissolved and combined into hydrated phases that constitute the solid end-product. Water is essential for these reactions. Water content influences which phases are formed, their morphology, and the rate of hydration. This paper describes a calorimetric method to quantify how the hydration rate at an early age is influenced by the amount of available water.

Although water–cement ratio has a high influence on strength, permeability and other properties of the hardened concrete, the initial rate of cement hydration is normally not very dependent on the water–cement ratio as there is in the beginning of the hydration a surplus of water [1]. However, at later times, when part of the water has been used in the hydration, water content can become a critical factor for the rate of continued hydration. In calorimetric measurements, it can be seen that the hydration rate of low water–cement ratio cement pastes goes to low values after 1–3 days, while pastes with higher water–cement ratios continue their hydration [1,2]. The low water–cement ratio pastes have then run out of space for new hydration products to form in.

The mixing water will as hydration proceeds end up either as chemically bound (hydrate) water, physically bound (absorbed) water, or remain as free water. The chemically bound water is part of the solid hydrated phases. The physically bound water includes both adsorbed water and capillary condensed water. The latter is bound in small pores in the formed structure, and is not as freely available for the continued hydration as the free water. Note that this division into three types of water is a simplified description, as there is a continuous scale of differently chemically and physically bound water.

The free water is the water that is the most readily available for hydration and if too little free water is left, hydration will slow down or come to an end. Chemical and physical binding are always intimately linked, as chemical binding gives a fine pore structure in which physical binding takes place. The two of them are jointly responsible for self-desiccation; the general process that causes the relative humidity to decrease in low water–cement ratio concretes [3]. A third process that can cause a decrease in free water content is drying, i.e., when water is lost to the surroundings. The method described in this paper concerns this type of drying.

Above, water is discussed in terms of *water content*, i.e., the mass of water. A complementary – and possibly more useful – description is to use a measure of the state of the water, instead of its amount. We will here use the *water activity*. This can be seen as a thermodynamic measure of the availability of the water. If the water activity is one, then we have free water, and if the water activity is zero (or close to zero) the water is so strongly bound that it is not available for any other processes. In the gas phase (water vapour) the activity is virtually equal to the relative humidity (RH), i.e., the ratio of the vapour pressure to the saturation vapour pressure, and at equilibrium the water activity in a sample equals the RH of the surrounding gas phase. As activity and RH have slightly different definitions, their values are not exactly the same, but the equality (at equilibrium) holds to better that 0.1% at ambient temperature and pressure conditions [4].

---

* Corresponding author.
E-mail address: lars.wadso@byggtek.lth.se (L. Wadsö).

0008-8846/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2010.02.005

How then is the rate of hydration of a cement paste at a certain time after mixing related to the water content or water activity? If we remove all water there will be no reaction and if we have plenty of water there will be a reaction, but at what point will the hydration rate begin to decrease? Only a few attempts to measure this have been made. Powers [5] reviewed some earlier measurements of self-desiccation and hydration rate as a function of relative humidity (RH), and then reported on experiments in which dry cement powders were exposed to different RH for six months. The degree of hydration was about 0.6 at 100% RH, but only about 0.12 for samples kept at 80% RH. At lower RH, the degree of hydration was even lower, and below 30% RH no hydration had taken place. According to Powers, cement hydration can only take place in the water phase and at reduced RH this will be in the condensed menisci between the cement particles [5]. Possibly, this result is relevant also for the present investigation, in which we study how the rate of hydration is reduced when water is removed from a hydrating cement paste, but in our case a structure of hydrating products has already been formed. Jensen et al. [6] has also made a similar study as Powers, but on pure clinker minerals.

Patel et al. [7] made Portland cement pastes with a water–cement ratio of 0.59 and – after curing them for 2 days – they were exposed to different RH ranging from 33 to 100% for 14 and 90 days. When the degree of hydration was measured with X-ray diffraction and thermogravimetry, each of the four main phases had reacted more slowly with decreasing RH. Even a small drop in RH below 95% significantly limited the hydration, and it was severely restricted below 80% RH.

Norling Mjörnell [8] measured degree of hydration on thin samples of cement mortars that had been stored at four different RH from time of mixing to up to 90 days. She found that the rates of reaction (at the same degree of hydration) decreased with decreasing RH. Snyder and Bentz [9] measured the difference in degree of hydration on pastes initially hydrated at saturated conditions, but later stored at 90% RH. They found that the hydration was retarded at 90% RH compared to saturated conditions.

The reduction in reaction rate caused by the decrease in the amount of available water is of interest for the modelling of concrete property development. Generally, one has used Powers' results [5], and then often in the form of an equation proposed by Bažant [10], see for example [11,12]. Norling Mjörnell [13] used her own measurements [8] to formulate a model. Bažant's and Norling Mjörnell's models are similar: a hydration rate reduction factor independent of temperature and degree of hydration is 1.0 at 100% RH and then decreases to low values at 70–80% RH.

The practical importance of the present paper stems from the fact that the property development of concrete structures is dependent on available water and if such water is lacking or scarce we will not achieve the strength, the impermeability etc. we require. If a low water–cement structure dries on its surface during the first days of hydration, this may result in a weaker and less durable surface that may contribute to surface cracking and/or not give the desired protection for the reinforcement [14–16]. This influence of RH is also seen in that concrete cylinders exposed to decreased RH during curing have lower compressive strengths than those cured in moist conditions [17,18].

In the method described in this paper, a fresh cement paste sample is placed in a calorimeter to hydrate and at different times exposed to drying inside the calorimeter. This way, one can follow how the thermal power – which is a function of the hydration rate [19] – is influenced by a decrease in moisture content at any time during the hydration. From the same experiment, one can also assess the decrease in water activity.

2. Materials

Cement pastes were made with a Portland-limestone cement (CEM II A-LL 42.5 R) at a water–cement ratio of 0.45. Batches of 290 g were mixed with a high speed hand-held blender for 60 s, then allowed to rest for 60 s, and finally mixed again for 60 s.

3. Method

3.1. Isothermal calorimetry

Isothermal calorimetry is a general way of studying all types of reactions by measuring the heat production rate (thermal power) produced by the reactions (see for example [20]). At least for a single process, the thermal power is proportional to the rate of a reaction and the produced heat is proportional to the extent of reaction (the nomenclature is given in Table 1):

$$P = \frac{d\xi}{dt} m_0 \Delta h \tag{1}$$

$$Q = \xi \cdot m_0 \cdot \Delta h \tag{2}$$

The above two equations connect the rate and extent of reaction with thermal power and heat, both of which can be measured with an isothermal calorimeter. Isothermal calorimetry can thus be used both in kinetic and thermodynamic studies. A complication with such complex reacting systems as cement paste is that there are several part-reactions in parallel or sequential. In such a case, the enthalpy in Eqs. (1) and (2) should be seen as an overall enthalpy that can be a function of the extent of reaction (see for example [19]).

3.2. The present method

In this study a TAM Air (Thermometric AB, Järfälla, Sweden; now manufactured by TA Instruments, New Castle DE, USA) isothermal (heat conduction) calorimeter was used [21]. This instrument has eight calorimeters fitted inside one thermostat so that one can make eight measurements simultaneously. Each calorimeter is a twin-instrument

Table 1
Nomenclature.

a	Activity of water	1
Δc	Change in moisture content during drying based on dry cement mass	1
F	Gas flow rate	m^3/s
Δh	Reaction enthalpy	J/g
$\Delta_{vap}h$	Vaporization enthalpy of water	J/g
m_0	Initial mass of cement	g
Δm	Change in mass during drying	g
P	Thermal power	W/g_{cement}
P_c	Thermal power corrected for thermal inertia of calorimeter	W/g_{cement}
Q	Heat of hydration	J/g_{cement}
Q_{vap}	Heat of vaporization during drying period	J
t	Time	s
U	Voltage output of calorimeter	V
U_0	Baseline voltage	V
v_{sat}	Saturation vapour content	g/m^3
β	Reduction in reaction rate from drying (Eqs. (5) and (6))	1
ε	Calibration coefficient	W/V
γ	Reduction in water activity from drying (Eq. (12))	1
η	Drying efficiency	1
φ	Relative humidity	Pa/Pa
τ	Time constant	s
ξ	Extent of reaction (degree of hydration)	1
Suffixes		
A	At start of drying	
B	At end of drying	
R	Reference sample (not dried)	
S	Sample being dried	
1	Before drying	
2	After drying	

with one sample and one reference. Calibration coefficients were determined electrically and the baselines were taken from two days measurements. The experiments were performed at 20 °C.

The method uses seven thin cement paste samples (ca. 1 g) from which water is removed by in-situ drying using a flow of dry nitrogen. The eighth calorimeter contains a larger cement paste sample (ca. 7 g), more typical of samples normally used in this type of calorimeter. To get thin samples of an appreciable size – thus reducing the effect of gradients, while still achieving a measureable calorimetric signal – we use helix-shaped lath cuttings of stainless steel (Fig. 1). These are dipped in the cement paste so that about 500 mg of paste is attached to each helix. In the reported measurements, the mean thickness of the cement paste layer was ca. 0.23 mm. The thickness increased towards the centre of the helix cross-section due to the surface tension of the cement paste. The paste was also thicker towards the bottom of the helixes due to gravitation. Two such helixes were placed in each of the first seven 20 mL plastic vials and the mass was determined with a 0.1 mg resolution balance (AC211S, Sartorius, Göttingen, Germany). There are two tubes through each lid permitting gas to flow through the vials. One of the tubes in each lid is connected to one of seven valves that control the flow of nitrogen; the other tubes exit outside the instrument to reduce the risk of condensation inside the instrument and make it possible to check the gas flow rate. The gas flow comes from a flask with a standard reduction valve. To reduce the flow rate, a 1 m long 0.13 mm inner diameter PEEK (polyether ether ketone) tubing is connected before each valve. The valves are computer controlled and can be programmed to different drying schedules. We have used a flow rate of about 50 mL/min.

In the five measurement series presented here, the samples were dried for a duration of 1 h at different times after mixing (other schedules – including repeated dryings – are of course also possible). The first drying (sample 1) was started at 11 h and the last drying (sample 7) was started at up to 70 h after mixing. Each specimen was weighed before and after the experiment to assess the mass of water lost. Typically 35 mg of water was lost during a 1 h drying, which corresponds to about 10% of the mixing water in a sample. Control experiments with water in the vials showed that no more than 2 mg water was lost if no gas flow was applied. Fig. 2 shows an example of a measurement with a drying at about 32 h.

3.3. Evaluation

In this measurement technique many parameters can be evaluated from each drying period:

- The change of thermal power (reaction rate).
- The moisture content decrease.
- The enthalpy of vaporization.
- The decrease in relative humidity (water activity).

Fig. 1. A helix-shaped support on which the cement paste samples were applied.

To make this evaluation we make the following assumptions:

1. The moisture state is homogeneous in each specimen.
2. The flow rate and flow pattern of the drying gas is constant in each vial during each drying.
3. The relative humidity of the gas leaving the ampoule is a constant fraction of the water activity of the sample.
4. The enthalpy of vaporization of water from the pore solution is constant during a drying.
5. It is only the rate of the hydration that is influenced by a drying; the same chemical reactions are active.

3.3.1. Step 1: baseline and calibration coefficient

The raw data U from the calorimeter was recalculated to thermal power P:

$$P = \varepsilon(U - U_0) \tag{3}$$

3.3.2. Step 2: Tian correction

The curves are Tian corrected for the thermal inertia of the calorimeter [21]:

$$P_c = P + \tau\frac{dP}{dt} \tag{4}$$

The time constant was chosen for each measurement so that the drying peaks were as trapezoidal in shape as possible. They were about 180 s. As the Tian correction with one time constant is based on a simplified model of a heat conduction calorimeter, it will not be a perfect time-lag correction of the measured curves and some overshoots were accepted.

3.3.3. Step 3: decrease in thermal power during drying

Two methods were used for this. Firstly, the decrease in thermal power during drying was calculated from the extrapolated values of the thermal power half-way into the drying. The extrapolations were made both from before the drying and from after the drying as is shown in Fig. 3A. The *decrease* in thermal power – assumed to be equal to the change in reaction rate – was then calculated as:

$$\beta = 1 - \frac{P_2}{P_1} \tag{5}$$

Note that β is zero if the thermal power does not change and positive if the thermal power decreases during a drying.

The second method used was to compare the thermal powers before and after the drying with the corresponding thermal powers of a reference curve. This is shown in Fig. 3B. For the reference curve, a mean value of all the undried samples was used. As there were seven samples dried at different times in each experiment, the reference for the first sample consisted of the mean of samples 2–7, while the reference for sample 6 was sample 7. This method was not used for sample 7. The decrease in thermal power was calculated as:

$$\beta = 1 - \frac{P_{S2}/P_{S1}}{P_{R2}/P_{R1}} \tag{6}$$

These two methods complement each other and for each sample, we have manually chosen the more appropriate of these two methods. Eq. (5) works best at later times when the thermal power is a continuously decreasing function, while it cannot be used around the main peak or when there are smaller peaks or disturbances on the curve. Then, Eq. (6) is used as it is not dependent on being able to

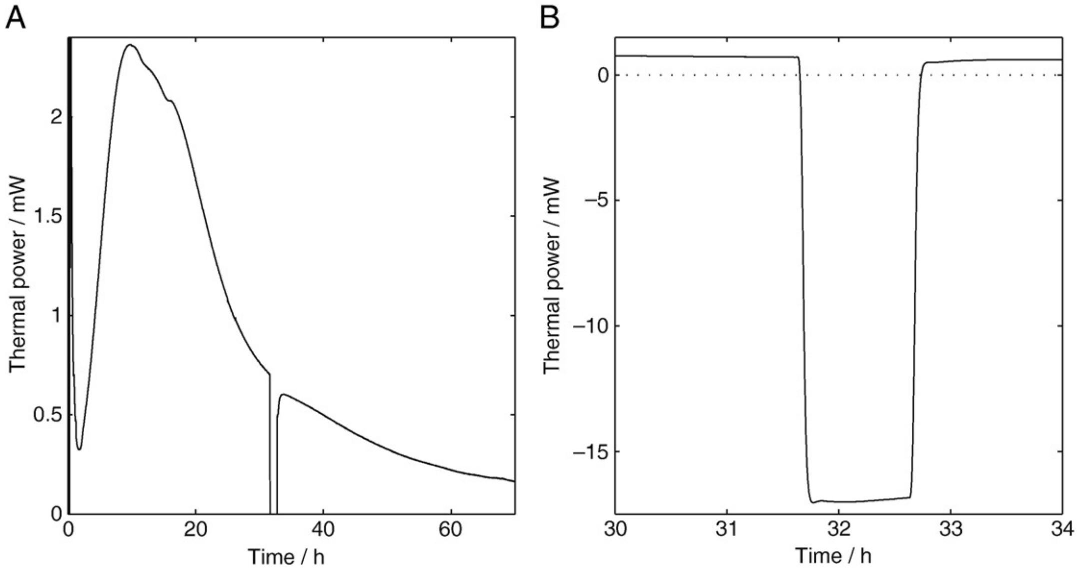

Fig. 2. An example of a measurement. (A) The hydration curve with a 1 h drying at about 32 h. (B) The drying produces a large endothermic peak that is superpositioned on the comparatively low hydration thermal power.

make curve fittings. However, at late dryings with low thermal powers, Eq. (6) does not give reliable results.

3.3.4. Step 4: produced heat when drying started

The specific heat of hydration at the time of drying was calculated by integrating the specific thermal power from the start of the main hydration peak to the start of the drying period. The integration was started at a point close to when the main hydration started. This point was calculated as the crossing point between a horizontal line through the lowest thermal power during the dormant period, and a linear curve fit of the initial part of the accelerating phase of the main hydration peak. The latter was taken 3600 s after the lowest thermal power during the dormant period. This heat is used as a measure of the extent of reaction.

3.3.5. Step 5: heat of vaporization

The heat of vaporization from the drying was calculated by integrating the thermal power from the start to the end of the drying. As the thermal power during the drying is the sum of the hydration and vaporization thermal powers, an interpolated thermal power of hydration curve was subtracted from the measured thermal power before integrating.

3.3.6. Step 6: enthalpy of vaporization of pore water

The enthalpy of vaporization of pore water was calculated by dividing the heat of vaporization with the mass loss measured by weighing the samples before and after an experiment:

$$\Delta_{vap}h = \frac{Q_{vap}}{\Delta m} \tag{7}$$

Note that the water is evaporating from a concentrated ionic solution and the enthalpy of vaporization may differ from that of pure water.

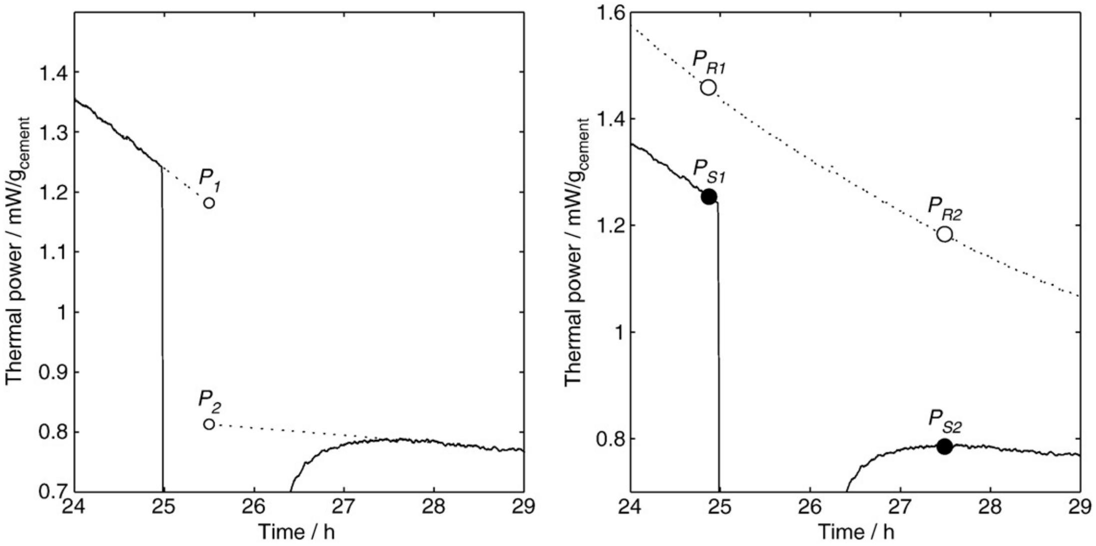

Fig. 3. Schematic descriptions of how the change in thermal power was evaluated. (a) The measured signals before and after the drying were extrapolated to the mid-time of the drying. The change was calculated as the ratio of the mid-time values marked with circles (Eq. (5)). (b) The shape of the thermal power curve for each dried sample was compared with the mean thermal power curve from the non-dried samples. The change in reaction rate was calculated as the fractional decrease in thermal power for the dried sample divided by the corresponding fractional decrease for the undried sample (Eq. (6)).

3.3.7. Step 7: moisture content change during drying

The moisture content change was calculated as:

$$\Delta c = \frac{\Delta m}{m_0} \tag{8}$$

3.3.8. Step 8: water activity change during drying

Generally, when a constant flow of dry gas is passed through a vessel with a humid sample the vaporization thermal power is:

$$P = \Delta_{vap} h \cdot F \cdot v_{\mathrm{sat}} \cdot \varphi \tag{9}$$

Here, φ is the RH of the exiting gas, which need not be equal to the water activity of the sample, as the efficiency of the process may be less than one, i.e., the gas leaving the vessel may not be at water vapour equilibrium with the sample. The efficiency of the humidification of the gas stream is assumed to be constant for a sample during a drying process, and is the ratio between the RH of the exiting gas and the water activity of the sample:

$$\eta = \frac{\varphi}{a} \tag{10}$$

From this, it follows that if we see a decrease in the absolute vaporization thermal power during a drying; this indicates that the activity of the sample is decreasing in the same proportion:

$$\frac{\varphi_A}{\varphi_B} = \frac{P_A}{P_B} \tag{11}$$

This is illustrated in Fig. 4. It is then possible to calculate how much the activity of a sample has *decreased* during a drying as:

$$\gamma = 1 - \frac{P_B}{P_A} \tag{12}$$

If γ is zero there has been no change in water activity. Note that γ is the change in water activity divided by the water activity before the drying; it cannot say anything about the absolute activity as the flow rate and the efficiency were not well known in the present experiments. However, it is reasonable to assume that the initial activity of the cement pastes is about 0.98 because of the dissolved ions but that this value may have decreased at the end of the measurement because of self-desiccation [22].

4. Result and discussion

A total of five measurement series were made with a total of 35 experiments. The results from all experiments, except one failure, are reported here. Fig. 5 shows the reduction in thermal power as a function of the time at which each sample was dried. A first order (linear) curve fit and the result of an error analysis are also shown. The error analysis was made by assuming that the uncertainty (standard deviation) of each thermal power determination was 0.010 mW. The errors increase at later times as the measured thermal powers then are lower. It is seen that there is a reasonable agreement between the spread in the measured data and the error analysis.

Fig. 6 shows the reduction in activity calculated for all the measurement series. A similar drying, but at a later time, gives an increased reduction in sample water activity. This is expected as there is less free water when the hydration has proceeded further.

Note that there is a principal difference between the present study and that of Snyder and Bentz [9]. We essentially remove a certain mass of water (about 10% of the mixing water), whereas they removed all water down to 90% RH. When we dry at early ages, there is still a lot of water left and we do not lower the sample RH appreciably, but when we dry at later ages, a 10% loss of water will remove a larger part of the water available for hydration. Snyder and Bentz did with their method remove most of the water when they dried at early ages, but removed little water at later ages as the samples had then began to self-desiccate.

In all measurement series, it was seen that the scatter in the specific thermal powers of the seven samples on helix supports was quite high and that they were generally slightly lower than that of the larger sample. An example of this is seen in Fig. 7. The scatter is possibly caused by different cement contents in the different samples, or by errors in the mass determinations. The lower thermal powers of the samples on helices may have been caused by these samples

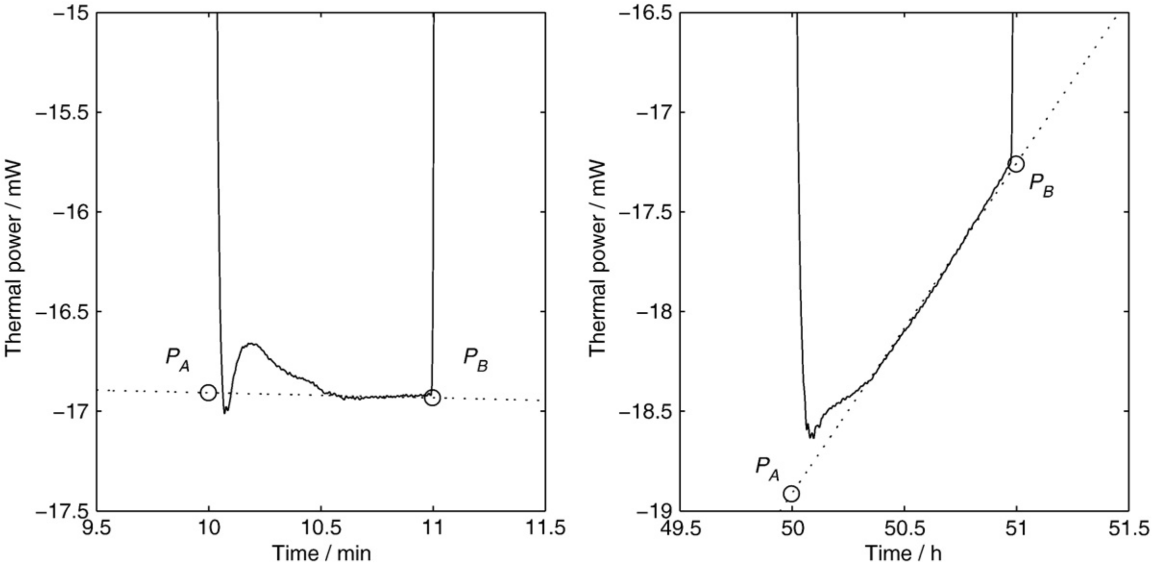

Fig. 4. The change in relative humidity during a drying period was calculated as the ratio between the extrapolated values (circles in the figure) after and before the drying period. The figure shows two examples from one measurement series. (a) The earliest drying at 10 h. (b) The latest drying at 50 h that shows a clear trend to lower absolute thermal powers, indicating a decrease in sample water activity. The linear regressions were made on the latter part of the peaks as the first parts were often disturbed, as is seen both figures.

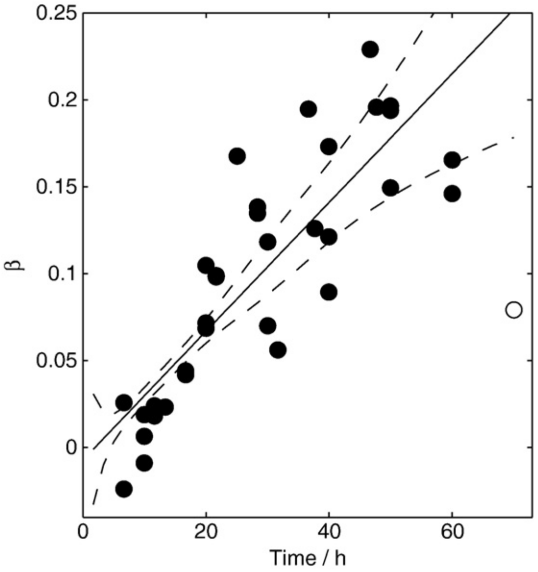

Fig. 5. The relative reduction in thermal power (hydration rate) caused by 1 h drying at different times as a function of the time of drying. The more suitable of the two described methods was used in each case. The solid line is a linear regression using all data points except the unfilled circle which was considered to be an outlier. The dashed lines indicate one standard deviation from the error analysis described in the text.

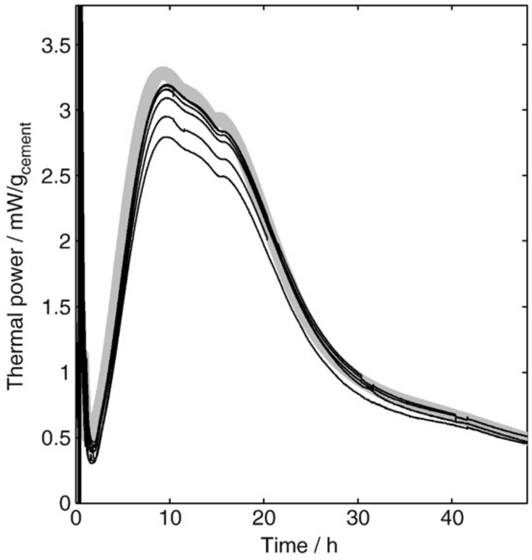

Fig. 7. Specific thermal powers for all eight measurements in one experiment. The thick gray line is from the larger 6.4 g sample and the thinner lines are for the other seven samples with masses in the range 0.64 - 1.07 g. Only the parts of the curves before the drying are shown.

containing less cement, the hydration being delayed by the large surface to volume ratio of these samples, or some of the produced heat not being measured by the calorimeters (as the helices were not in such good contact with the bottom of the ampoule as were the larger samples). However, we believe that none of these explanations fully explains the scatter or the lowering seen.

As the heat of hydration is a measure of the extent of hydration, it is interesting to plot the calculated parameters as a function of the heat instead of the time. In Fig. 8, the heat calculated for each sample at the time of drying is seen. The heat is a steeply increasing function up to about 37 h. After that the thermal power is comparatively low and the heat produced by 70 h is about 260 J/g.

One major contributor to the scatter seen in Fig. 5 is that the samples had different masses and the drying conditions (for example the flow rates) were not exactly the same for all samples. One way to remove these influences from non-similar conditions is to divide the calculated effect-parameters β and γ by the moisture content change. One will then get water activity reduction per moisture content change, and hydration rate reduction per moisture content change. These parameters are shown in Fig. 9 as a function of the heat. The scatter is rather high, but the increasing trends are visible in both cases. The relative change in rate of hydration is about twice that of the relative change in water activity, which indicates that the reduction in hydration rate is not as high as in previously published experiments [5,7,9,13], but these different sets of results are not easily comparable as they have been

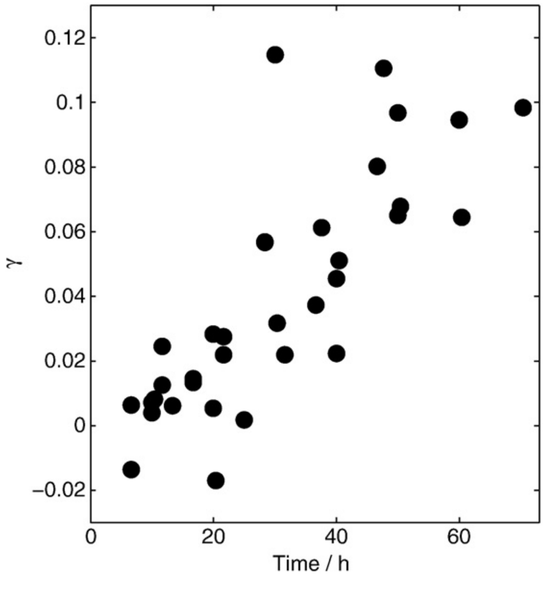

Fig. 6. Relative reduction in water activity caused by 1 h drying at different times after the start of the hydration. One data point outside the plot was considered an outlier.

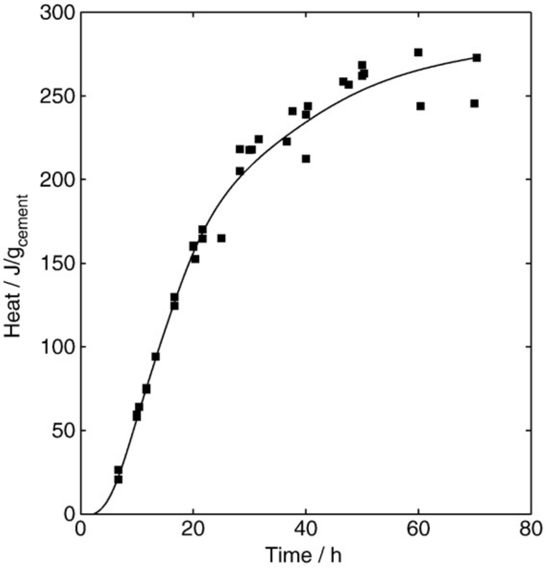

Fig. 8. The specific heat produced by each sample at the time of drying (filled squares) and the cumulative heat calculated for one of the two samples that was dried after the longest time of hydration. The heats were calculated by integrating the measured thermal powers. The integration was started at a point close to when the main hydration started. This point was calculated as the crossing point between a horizontal line through the lowest thermal power during the dormant period, and a linear curve fit of the initial part of the accelerating phase of the main hydration peak. The latter was taken 3600 s after the lowest thermal power during the dormant period.

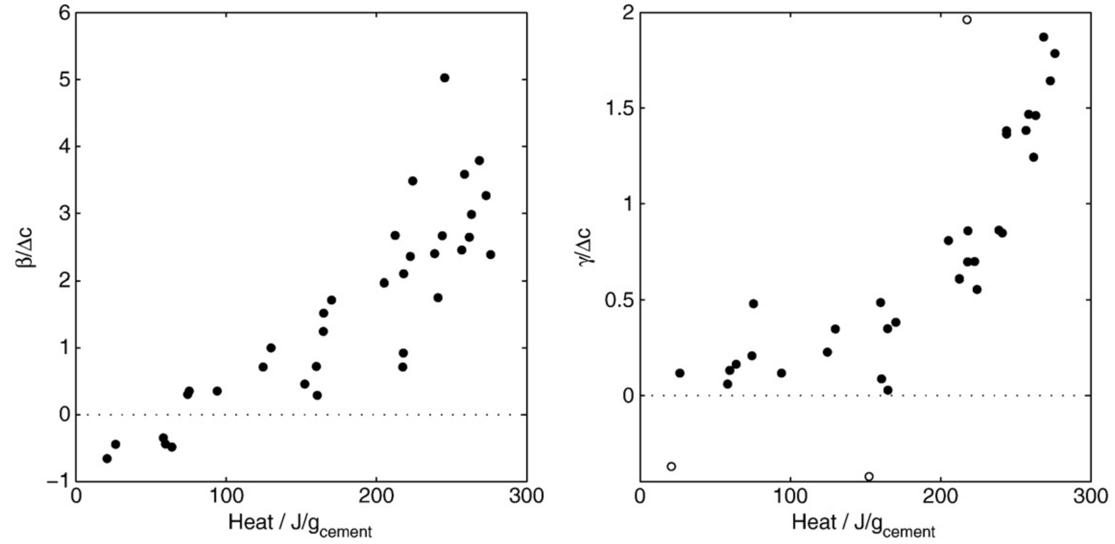

Fig. 9. The effect of drying on water activity and reaction rate. (a). The decrease in reaction rate per decrease in moisture content as a function of specific heat. (b) The decrease in water activity per decrease in moisture content as a function of specific heat. Note that heat is a function of the extent of reaction, i.e., the degree of hydration.

made under quite different conditions. Powers [5] made long term studies of the uptake of water by dry cement — similar to what is termed pre-hydration today [23]. Patel et al. [7] and Snyder and Bentz [9] let samples hydrate normally before placing them in lower RHs. Norling Mjörnell [13] placed thin samples in different atmospheres right after mixing. In all these studies the degree of hydration was measured at different times to assess the effect of drying. In the present measurement, the idea was to study the immediate effect of a short and intensive drying, with the aim of quantifying how a drying would affect the hydration rate at different times during the hydration. So, although these studies all show that the rate of hydration is dependent on RH, the results are not easily comparable.

In Fig. 3B, it is seen that the two curves before the drying event show similar behaviour, but that after the drying the lower curve from the dried sample has a significantly lower slope than the mean curve of the undried samples. Because of this, the evaluated value of β will be dependent on at what point one takes the values after the drying. Generally, less effect of drying will be seen if these values are taken at a later point. This puts into question what takes place at a microscopic level when we remove water by drying. In a hydrating cement system unhydrated phases are continuously dissolved and diffuse out into the pore solution, where they form new solid hydrated phases. If water is suddenly removed, the ionic concentrations will momentarily increase and if saturation is reached, precipitation will take place (or a supersaturated solution will be formed). Higher concentrations will probably give higher reaction rates, until a steady concentration levels are reached again, but then in a smaller volume of water and with a lower reaction rate. The time scales of these processes could be investigated and used to adjust the evaluation time after the drying, so that a new dynamic steady-state has been reached.

It should be noted that the parameters $\beta/\Delta c$ and $\gamma/\Delta c$ shown in Fig. 9 are of general importance for the studied phenomena as they are both expressed per change in moisture content. If water is removed by drying from a hydrating cement paste at a certain age (expressed as heat of hydration) the decreases in reaction rate and water activity are given by the above two parameters multiplied by the moisture content change. Although the limits of this approach have yet to be investigated, it is clear that the present calorimetric technique makes it possible to directly study the effects of drying on hydrating cement systems.

We also evaluated enthalpies of vaporization, but these showed a high scatter and it was not possible to determine any trends. The mean value was about 2000 J/g (standard deviation 170 J/g), which is lower than the literature value for pure water of about 2460 J/g [24]. It should be noted that the vaporization of water from a saturated ionic solution will be accompanied by the precipitation of ions (unless a supersaturated solution is formed) and the measured heat is the sum of the heats from these two processes. Enthalpies of vaporization are always positive (endothermic), but enthalpies of crystallization from an aqueous solution can be either positive or negative.

As the pore solution has a high concentration of various ions, its activity is about 0.98 at the start of the hydration, but this value will later decrease due to self-desiccation. As the self-desiccation was not known for the used recipe, it has not been possible to calculate to what values the activity decreased in each experiment. As noted above, the parameter γ is only the ratio between the change in activity and the activity; it does not give any information about the absolute value of the activity before or after the drying.

Although the results of the present measurements show a decrease in both water activity and reaction rate as drying was made, the measurements show a rather high scatter. This is not surprising as the evaluation of for example $\beta/\Delta c$ involves two extrapolations of measured curves and the determination of a small mass loss. The present method is not trivial to use, but it is interesting as it makes it possible to gain a direct insight into how the water state controls hydration rate. To improve the method one could:

- Use a mass flow controller to achieve a more constant gas flow rate.
- Study the dynamics of the calorimetric system and design an improved 'Tian correction', e.g., with two time constants, that better describes the calorimetric system.
- Use thinner samples, possibly spread out in more uniform way to achieve more homogeneous drying.
- Have better control of the cement content of each specimen.
- Have a better control of the mass determinations, for example to make sure that no mass is lost through diffusion.
- Make a measurement of the decrease in RH from self-desiccation on a parallel sample to be able to calculate the RH after each drying.
- Use a more sensitive calorimeter for longer measurements.

5. Conclusions

We have presented a calorimetric method to study the influence of drying of young cement paste samples. It was shown that it was possible to evaluate the reductions in both water activity and hydration rate following an intense drying. The method has the potential to be used to assess the effect of early drying on mortars and concrete.

Acknowledgement

The support of The Swedish Nuclear Power Inspection is gratefully acknowledged.

References

[1] C. Wang, W.H. Dilger, Modeling of the development of heat of hydration in high-performance concrete, 2nd CANMET/ACI International Symposium, Am. Concrete Institute, Las Vegas, 1995.

[2] J.H. Taplin, A metod for following the hydration reaction in Portland cement paste, Austral. J. Appl. Sci. 10 (1959) 329–345.

[3] B. Persson, D. Bentz, L.-O. Nilsson (Eds.), The Fourth International Research Seminar on self-desiccation and its importance in concrete technology held in Gaithersburg, Maryland, USA, Building Materials, Lund University, Sweden, 2005, Report TVBM-3126.

[4] S. Gal, Uber die Ausdrucksweien der Konzentration des Wasserdampfes bei Wasserdampf-Sorptionsmessungen, Helvetica Chim. Acta 55 (5) (1972) 1752–1757.

[5] T.C. Powers, A discussion of cement hydration in relation to the curing of concrete, Proc. Highway Res. Board 27 (1947) 178–188.

[6] O.M. Jensen, P. Freisleben Hansen, E.E. Lachowski, F.P. Glasser, Clinker mineral hydration at reduced relative humidities, Cement Concrete Res. 29 (1999) 1505–1512.

[7] R.G. Patel, D.C. Killoh, L.J. Parrott, W.A. Gutteridge, Influence or curing at different relative humidities upon compound reactions and porosity in Portland cement paste, Mater. Struct. 21 (1988) 192–197.

[8] K. Norling Mjörnell, Moisture conditions in high performance concrete — mathematical modelling and measurements, Department of Building Materials, Chalmers University of Technology: Göteborg, Sweden, 1997.

[9] K.A. Snyder, D.P. Bentz, Suspended hydration and loss of freezable water in cement pastes exposed to 90% relative humidity, Cement Concrete Res. 34 (2004) 2045–2056.

[10] Z.P. Bažant, Nonlinear water diffusion in nonsaturated concrete, Mater. Struct. 5 (25) (1972) 3–18.

[11] G. di Luzio, G. Cusatis, Hydro–termo–chemical modeling of high performance concrete I. Theory Cem. Concr. Compos. 31 (2009) 301–308.

[12] D. Gawin, F. Pesavento, B.A. Schrefler, Hygro–thermal–chemo–mechanical modelling of concrete at early ages and beyond. Part I: Hydration and hygro–mechanical phenomena, Int. J. Numerical Meth. Eng. 67 (2006) 299–331.

[13] K. Norling Mjörnell, A model on self-desiccation in high-performance concrete, Self-desiccation and its Importance in Concrete Technology, Building Materials, Lund University, Lund, Sweden, 1997, Sweden (TVBM-3075.

[14] V. Baroghel-Bouny, Hydration and moisture distribution, in Early age cracking in cementitious systems, in: A. Bentur (Ed.), RILEM Technical Committee TC 181-EAS: Bagneux, France, 2003, pp. 39–45.

[15] V. Baroghel-Bouny, J. Godin, Experimental study on drying shrinkage of ordinary and high-performance cementitious materials, Concrete Sci. Eng. 3 (March 2001) 13–22.

[16] A.M. Neville, Properties of concrete, Longman Group Ltd., Harlow, Essex, UK, 1995.

[17] W.-C. Liao, B.J. Lee, C.W. Kang, A humidity-adjusted maturity function for the early strength prediction of concrete, Cem. Concr. Compos. 30 (2008) 515–523.

[18] M.F.M. Zain, M. Safiuddin, K.M. Yusof, Influence of curing conditions on strength and durability of high-performance concrete, 4th International Conference on Repair, Rehabilitation, & Maintenance of Concrete Structures, & Innovation in Design & Construction, 2000, Seoul, South Korea.

[19] L.J. Parrott, M. Geiker, W.A. Gutteridge, D. Killoh Monitoring, Portland cement hydration: comparison of methods, Cement Concrete Res. 20 (1990) 919–926.

[20] L.D. Hansen, Calorimetric measurements of the kinetics of slow reactions, Ind. Eng. Chem. Res. 39 (2000) 3541–3549.

[21] L. Wadsö, Applications of an eight-channel isothermal conduction calorimeter for cement hydration studies, Cement Int. 5 (2005) 94–101.

[22] G. Hedenblad, Influence of salt on the sorption isotherm (in Swedish), Building Materials, Lund University, Lund, Sweden, 1987.

[23] E. Dubina, R. Sieber, J. Plank, L. Black, Effects of pre-hydration on hydraulic properties on Portland cement and synthetic clinker phases, 28th Cement and Concrete Science, 2008, Manchester, England.

[24] D.R. Lide, Handbook of Chemistry and Physics89th edition, CRC Press, Boca Raton FL, USA, 2009.