

MICROCALORIMETRY IN THE CEMENT HYDRATION PROCESS

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Abstract

This paper presents a differential microcalorimetric system made in laboratory, designed to enable scientific research into the process of hydration in setting materials. The differential calorimeter presented has neither isothermal nor adiabatic properties, and may be listed among both isoperibolic and conduction calorimeters. This paper describes the microcalorimeter and its operation, indicating properties required and the calibration of the device. The reproducibility and the statistical processing of the results obtained by means of this device were established when the microcalorimeter was used to determine the hydration heat in a sample of Portland cement. The results were processed by a computer, which provided a basis for calculation of hydration kinetics, the rate constant, and the activation energy of hydration.

The development of various types of calorimeters applied in the determination of thermodynamic values made it possible to determine kinetic parameters in various chemical processes. Depending on the purpose and the type of the calorimeter used to examine cement hydration a number of methods have been developed, some of which have been standardized in practice.

Recently, microcalorimetry has developed as a direct method which enables a more accurate determination of the dynamics and kinetics of cement hydration. Although the prices of commercial microcalorimetric systems are high, their expanding use in cement research has been justified by the high precision and accuracy and the fact that they require only a small quantity of the sample (2–5 g). They also help to determine the influence of various parameters (water-to-cement ratio, additives, temperature, particle size etc.) on the course of cement hydration.

A microcalorimeter is a device which measures heats from $4 \cdot 10^{-4}$ J upwards, and has a high resolution power [1, 2, 3].

This paper presents a differential microcalorimeter made in the laboratory to measure the hydration heat of cement. The microcalorimetric system has been tested on a cement sample chosen; the reproducibility and accuracy of its measurements were determined, as well as its applicability to the investigation of hydration processes in binding materials.

Experimental

Design

The measuring device is a microcalorimetric system made in our own laboratory, consisting of the following basic parts:

- a differential microcalorimeter (A)¹ formed by two brass sample holders connected to one another by thermocouples (copper-constantan) [4], placed into polyurethane resin, with two pins protruding in order to make contact with the recording device.
- a thermostat (B),
- a recorder (D).

Figure 1 shows the design of the microcalorimetric system.

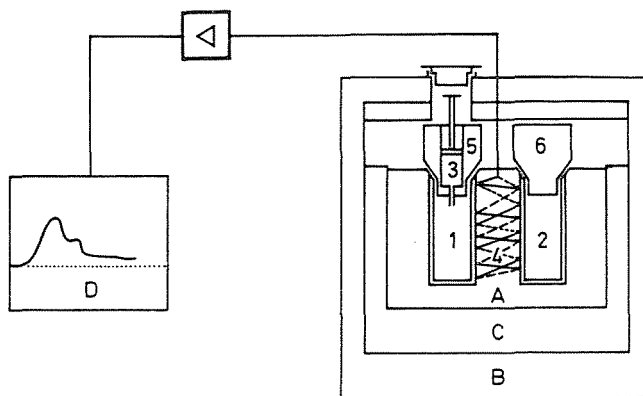


Fig. 1. The differential microcalorimetric system design

A — a differential microcalorimeter; B — a thermostatic device; C — insulating material "stiropor"; D — recorder; 1 — measuring cell; 2 — reference cell; 3 — reagent holder (a syringe); 4 — thermocouple; 5 — measuring cell cover; 6 — reference cell cover

Calculation of the heat evolved

The basic principles valid for isoperibolic and conduction calorimeters were taken in order to apply the finite expression for cement hydration heat evolution to differential microcalorimeters [4].

¹ This part of the calorimeter was made at the Faculty of Civil Engineering in Budapest, at the Institute for Constructions and Materials.

In these systems, a part of the heat q_1 increases the temperature within the measuring cell, while the other part of the heat, q_2 , is exchanged with the surroundings so that the total heat (Q) set free by the reaction in the calorimeter equals the sum of heats q_1 and q_2 , in time t .

$$Q = q_1 + q_2 \quad (1)$$

where

$$q_1 = C_p \cdot d\Theta(t) \quad (2)$$

$$q_2 = \alpha \cdot \Theta(t) dt \quad (3)$$

C_p is the heat capacity of the calorimetric system, J/°C.

α is the leakage constant, related to the cooling constant β by the expression

$$\alpha = C_p \cdot \beta \quad (4)$$

We introduce the proportionality factor, g , which relates the change in temperature, Θ , to the recorded change in voltage, Δ , expressed as:

$$\Theta = 1/g \cdot \Delta \quad (5)$$

From Eq. 1 we obtain

$$Q(t) \int_{t_1}^{t_2} = (C_p/g) \int_{t_1}^{t_2} d\Delta(t) + (C_p/g) \cdot \int_{t_1}^{t_2} \beta[\Delta(t)] \cdot (t) dt \quad (6)$$

i.e.

$$Q(t) = C_p/g \cdot \Delta + C_p/g \cdot \beta \cdot P \quad (7)$$

where $P = \int_{t_0}^{t_x} \Delta(t) dt$, i.e. P is the area under the curve $\Delta = f(t)$ where Δ is the deflection of the pen from the zero position, while t is the duration of the

Table 1

Technical data for the microcalorimetric device

Parameter	Value
Measuring cell volume	8 cm ³
Reference cell volume	8 cm ³
Temperature range of operation	15–50°C
Leakage constant,	3.436 · 10 ⁻³ J min ⁻¹ μV ⁻¹
Cooling constant,	2.35 · 10 ⁻² min ⁻¹
Time constant,	2749 s
Heat capacity of the empty microcalorimeter	22.2371 J K ⁻¹
Proportionality constant, g , in the temperature change recording	230.5 μV K ⁻¹

hydration process. To indicate the area P in cm^2 , a factor S is now introduced, showing how many $\mu\text{V min}$ correspond to an area of 1 cm^2 , so that the expression [7] becomes Eq. 8:

$$Q(t) = C_p/g \cdot \Delta(t) + C_p/g \cdot \beta \cdot S \cdot P(t) \quad (8)$$

C_p of the calorimetric system is obtained by summing the product of the mass of the individual substances entering the calorimetric system and their specific heats [9, 7].

The heat produced during hydration per unit sample mass is

$$q(t) = \frac{Q(t)}{G} \quad (9)$$

where G is the sample weight.

Table 1 shows some characteristic values for the operation of differential microcalorimeters.

Calibration of the differential microcalorimeter

The microcalorimeter was calibrated by means of electric current. An aluminium block with a heater of known resistance was prepared. According to the expression for Joule's heat $Q = I^2 R t$, a precisely defined heat quantity has been introduced into the microcalorimeter, the thermal effects recorded resulting a DMCA curve which was then used to determine the heat quantity recorded in the experiment according to Eq. 8. Table 2 lists the results of measurements.

Measuring hydration heat on cement samples

The cement sample used was an industrial Portland cement type PC-45 with a 30% addition of blast furnace slag and pozzolana in a 4:1 ratio. Table 3 presents the basic data of the cement sample.

Determination of the hydration heat of cement

The heat of hydration was determined as follows: a certain amount of the sample weighed (4 g) was placed in a previously prepared sample holder (the inner part is made of polyethylene foil-PE-foil-while the outer part of aluminium foil-Al-foil), and then placed in the measuring cell of the microcalorimeter. The dimensions of the sample holder should match the dimensions of the measuring cell in order to ensure a good heat transfer from the sample to the cell walls. After that a syringe placed on the top of the calorimetric

Table 2

Test results for the differential microcalorimeter

No of measurements	I mA	R Ohm	t s	Q _A J	Δ μV	P cm ²	q ₁ J	q ₂ J	Q _B =q ₁ +q ₂ J	Q _A -Q _B J
1	72.0	31.2	120	19.4089	94	25.90	14.6170	4.7322	19.3490	0.0599
2	72.0	31.2	180	29.1133	26	137.10	4.0430	25.0480	29.0910	0.0223
3	73.75	31.2	60	10.1819	37	23.73	5.7535	4.3355	10.0890	0.0929
4	74.5	31.2	180	31.1702	145	46.85	22.5475	8.5600	31.1075	0.0627
5	74.5	31.2	270	46.7640	96	174.3	14.9280	31.8450	46.7730	0.0090

Q_A=heat introduced into the microcalorimeter Q=I² R t, J

Q_B=heat determined from the DMCA curves, J

Q_A-Q_B=difference between introduced and experimentally determined heat, J

Table 3

The PC-45 cement sample

Average mineralogical composition mass %	Mill fineness as remains on a 0.09 mm sieve %	Blaine's specific surface cm ² g ⁻¹	Setting duration		
			Start	End	
			hour		
C ₃ S	62.10	3.45	3450	2.3	3
C ₂ S	17.60				
C ₃ A+Fe	19.40				
CaO _{free}	0.90				

Table 4

Hydration heat measured with a differential calorimeter on a PC-45 sample

Hydration duration h	Hydration heat, q J/g					\bar{x} J/g	σ ±J/g	V %	$\frac{dq}{dt}$ Jh ⁻¹ g ⁻¹
	1	2	3	4	5				
1	7.030	6.980	7.030	6.990	7.020	7.010	0.023	0.328	7.01
5	13.148	12.990	13.148	12.892	13.130	13.062	0.156	0.885	2.12
10	35.198	35.171	35.198	35.202	35.202	35.194	0.013	0.037	5.72
15	65.298	65.364	65.298	65.655	65.298	65.383	0.155	0.237	5.96
20	93.798	94.075	93.800	94.406	94.050	94.026	0.250	0.266	5.48
24	114.073	114.512	114.841	114.510	114.300	114.447	0.285	0.249	4.80
30	138.658	139.146	138.800	139.257	138.915	138.955	0.246	0.177	3.45
36	153.673	154.363	154.130	154.930	154.435	154.306	0.458	0.297	1.95
40	161.040	161.354	161.877	161.350	160.930	161.310	0.316	0.196	1.58
48	171.846	171.651	172.301	171.930	172.100	171.966	0.247	0.149	1.20

\bar{x} — average value

σ — standard deviation

$V = \frac{\sigma \cdot 100}{\bar{x}}$ — variation coefficient

$\frac{dq}{dt} = f(t)$ — heat evolution rate as a function of time

cell (also serving as a reagent holder) was used to add a measured quantity of water to the cement sample, according to the water/cement factor chosen.

A sample of previously completely hydrated cement was placed in the reference cell, serving as the thermal tare. When the sample was inserted and the calorimetric system closed, thermostation of the reacting components was carried out until the stability of the zero signal of $\pm 1 \mu\text{V}/\text{h}$ was achieved. Then water was injected into the cement, and the reaction was followed by a curve drawn on the plotter.

The process conditions were the same in all experiments where the microcalorimeter was used to follow the cement hydration process:

- Thermostat temperature $20 \pm 0.005^\circ\text{C}$,
- cement weight 4,000 g,
- water weight 2,000 g,
- measuring range set for registering 500 μV ,
- measuring range sensitivity 2 mm = 5.0 μV ,
- chart width 200 mm,
- chart speed 30 mm/h,
- 1 cm² of area under the curve corresponds to 500 $\mu\text{V min}$,
- Al-foil weight for the sample holder 0.2600 g,
- PE-foil weight for the sample holder 0.0460 g.

Table 4 shows the results obtained for the hydration heat measured by the microcalorimetric system described and obtained from DMCA curves by Eqs 8 and 9 and by statistical data processing. In order to calculate all the values listed, a computer program has been made, and the first kinetic data for hydration heat evolution in time ($dq/dt = f(t)$) were obtained.

Discussion

Our purpose was to construct a differential microcalorimetric system in the laboratory and to apply it for following the early cement hydration by means of the thermal effects of the reaction. As has been shown previously, this aim has been achieved.

Measurements listed in Table 4 indicate a high degree of precision. Individually measured values for the hydration heat differ very slightly from the mean value. The standard deviation (σ) for hydration times up to 24 hours (very sensitive regions) is less than $\pm 0.3 \text{ J/g}$, reaching ± 0.2 to $\pm 0.4 \text{ J/g}$ for hydration times up to 48 hours. When these values are compared to those obtained by standard calorimetric systems, notwithstanding the type of standard, the former show much smaller deviations. In standard calorimetric measurements the allowed deviation from the mean value is $\pm 8.38 \text{ J/g}$ [8, 9]. When compared to values obtained by means of similar types of

microcalorimeters described in literature in respect of reproducibility and standard deviations (σ), approximately similar results are obtained: ± 2.0 J/g at 24 hrs and ± 0.6 J/g at 48 hrs [5].

The variation coefficient (V) shows a high degree of precision for some measuring periods and its average value is roughly 0.3% or less. This confirms that the differential microcalorimeter presented may be used for scientific research in the field of cement hydration — e.g. calculation of reaction rate constant and activation energies.

The differential microcalorimeter described may be used successfully for quantitative determination of cement hydration heat. The results measured are very precise and accurate, with a very high degree of reproducibility. The differential microcalorimeter can be used not only for the determination of hydration heats, but also for the examination of the course of hydration under different conditions. The mathematical processing of data from DMCA curves yields thermokinetic parameters which help to understand the kinetics and mechanism of cement hydration.

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