

A CONDUCTION CALORIMETER FOR MEASURING THE HEAT OF CEMENT HYDRATION IN THE INITIAL HYDRATION PERIOD

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Abstract

A new-design conduction microcalorimeter is described, which has been used to measure the heat of cement hydration evolved in the initial period of hydration. The calorimeter is 30 cm³ in volume; the heat loss coefficient is 27.270±0.015 W V⁻¹, the time constant is 300 s.

Keywords: cement hydration, conduction calorimeter

Introduction

The application of conduction calorimeters to study cement hydration heats is a considerable progress, because it does not only enable to determine the total heat of hydration, but it also makes it possible to follow the thermokinetics, i.e., variation of the thermal power in time, and thus the rate of heat release in time under quasi-isothermal conditions [1–5]. This is of particular importance in establishing the effect of various additives in the course of the hydration process. For example, Sakai *et al.* [6] and Cheeseman *et al.* studied the effect of CaCl₂ [7], KCl [8] and of hydroxides of lead, zinc and cadmium as additives [9]; Pushpalal *et al.* studied the effect of phenol-resin composites as additives [10, 11]; alkaline activation of metakaolin was studied by Granizo and Blanco [12] and also by Fernandez-Jimenez *et al.* [13].

Several attempts to measure the heat evolved within the first period of hydration of cement have been made for a long time. Such studies were made possible only after, among other things, the calorimeters designed by Courtault and Longuet [14] and Kamiński [15, 16] have been made available. The former design ensured the contact of cement with water by application of vacuum; the latter design employed a mechanical stirrer enabling a cement mortar to be prepared inside the calorimeter.

This paper describes another conduction calorimeter which enables the total thermokinetics of hydration of cement or cemental materials to be established, starting with the initial moment of the reaction. The design of this calorimeter is based on

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an earlier design of BMR calorimeter constructed at the Institute of Physical Chemistry of the Polish Academy of Sciences [17, 18].

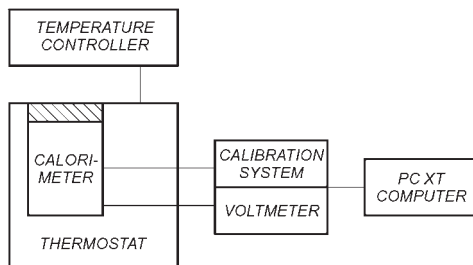


Fig. 1 The calorimetric system

Apparatus

The calorimetric system, presented in Fig. 1, comprises the following elements:

(i) the actual calorimeter comprising two identical calorimetric cells, one of which is the measuring cell and the other is the reference cell. The variation of temperatures in the measuring cell is established via measuring the difference between the temperatures of the measuring cell and the reference cell. The two cells can be used independently. The calorimetric cells adhere tightly to internal metal shields. Between the shields and a copper metal block which forms the external shield of the calorimeter, there are sets of thermocouples mounted;

(ii) a liquid thermostat provided with an electric motor-driven stirrer and a pump which enables the other elements to be supplied with the thermostated liquid. To achieve a precise temperature control, the thermostat is equipped with a platinum thermometer connected with a PID type 650 H temperature controller produced by UNIPAN (Warsaw, Poland). The thermostat is equipped with a water cooler which is supplied with tap water or fed from a preliminary thermostat, and serves to remove the excess of heat outside of the thermostat. When water is applied, the operating range of the thermostat is 20–60°C; the thermostating accuracy is $\pm 0.001^\circ\text{C}$;

(iii) the system involving measuring, acquisition and processing of the data which serves to read and record the output signal of the calorimeter. The system comprises a type V542.1 digital voltmeter and IBM PC computer. The measurement is accurate to within $1\ \mu\text{V}$; sampling time is 0.9 s and its multiple values. A routine has been developed which enables the thermal effect to be evaluated by a dynamic method [19]. The total thermal effect $Q(t)$ is evaluated according to the equation:

$$(1/\alpha)dQ(t) = \tau d\theta(t) + \theta(t)dt \quad (1)$$

and the thermal power evolved $W(t)$ is determined as

$$(1/\alpha)W(t) = \tau d\theta(t)/dt + \theta(t) \quad (2)$$

where $\theta(\tau)$ is the temperature course over time t expressed in terms of variation of the thermoelectric power of the thermocouples, τ and α is the time constant of the calorimeter or the heat transfer coefficient;

(iv) the calibration system which is intended to establish the calorimetric constants α and τ by way of measuring the Joule's effect liberated at a well-defined power and over a well-defined time of duration. The system comprises the blocks to set the time of current flow and current intensity and a direct current source. The calorimetric constants established are: $\tau=300\pm 0.8$ s and $\alpha=27.270\pm 0.015$ W V⁻¹.

A schematic diagram of the actual calorimeter is presented in Fig. 2. The calorimetric cell, 30 cm³ in volume, to hold a cement or another cemental material to be investigated, is made of stainless steel in the form of a truncated cone. A Teflon sleeve (2) equipped with a pipe (3), located above the cell, serves to fix a vacuum hose (4) and to combine with the connector in which a hypodermic syringe (5) is fixed, containing water or a solution. In a calibration measurement, the calorimetric cell holds an electric heater the leads of which are led out through the pipe (3). o-Rings (6) and (7) are used to keep the connections tight. The sleeve (2) serves also to insulate the calorimeter at the top. A Teflon shield is fixed on the pipe (3), which is led out from the calorimeter outside. The shield comprises a hose connected to vacuum and a threaded rod (9) connected by means of an articulated joint with the piston of the syringe. The articulated joint prevents the piston of the syringe to move spontaneously before the reaction has been initiated in the calorimeter. The thread (11) enables the rod (9) to rotate and thus also the syringe's piston to move and to supply wa-

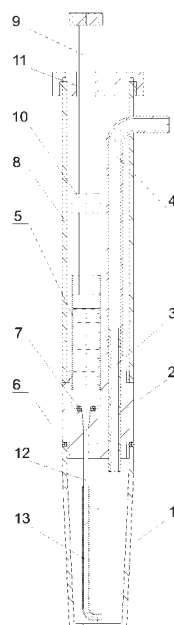


Fig. 2 A schematic diagram of the actual calorimeter

Table 1 Characteristic cement hydration thermokinetic data points

No.	Initial period						Main period						
	$t_{\max}/$ min	$W_{\max}/$ W g ⁻¹	$Q_{\max}/$ J g ⁻¹	$t_{\min}/$ min	$W_{\min}/$ W g ⁻¹	$Q_{\min}/$ J g ⁻¹	t_g/h	$W_g/$ W g ⁻¹	$Q_g/$ J g ⁻¹	$W_{12}/$ W g ⁻¹	$Q_{12}/$ J g ⁻¹	$W_{24}/$ W g ⁻¹	$Q_{24}/$ J g ⁻¹
1	2	24.05	2.26	85	0.33	8.31	7.5	1.43	30.43	1.23	52.23	0.62	91.77
2	2	23.01	2.05	85	0.34	8.32	7.5	1.43	30.34	1.22	52.01	0.62	91.74
3	3	21.11	2.73	85	0.33	8.08	7.5	1.43	29.94	1.25	51.78	0.66	92.94

ter from the syringe to the calorimetric cell. A metal capillary (13) is superimposed on the needle of the syringe which allows water to flow in under the sample of cement and also enables the syringe and the needle to be taken out from the cement hardened during the experiment.

Experimental

Cement, 20 g, is weighed in the calorimetric cell; a metal loop is placed inside the cement sample so as to protrude above the surface of the sample. The loop enables the hardened cement to be taken out from the calorimetric cell. Water, about 10 g (water/cement ratio = ~0.5), is weighed in the syringe, with due precaution to keep water out of the needle of the syringe. The cell holding the cement sample is fixed with a screw to the sleeve (2) and the syringe full of water is placed in a tight fixture. The shield (8) is fixed with screws onto the sleeve and the vacuum hose is led off outside. The equipment thus mounted is placed inside the copper block of the thermostat and is thermally equilibrated; equilibration takes 1.5 to 2 h. After a thermal equilibrium has been attained, water is added to the cement by allowing the piston of the syringe to move. Just before water is brought into contact with the cement, the vacuum hose is connected to the vacuum source, i.e., to an AGA LABOR vacuum pump, to attain a pressure of about 0.04 MPa. Vacuum is applied to make the wetting of cement particles easier. After water has been injected, the vacuum pump is disconnected and the vacuum hose is closed. A slight thermal effect observed when vacuum is being applied has been found to be compensated immediately after vacuum has been disconnected by an opposite thermal effect.

Results

Three control measurements were carried out to determine the heat of hydration of cement III/A 32.5 (Cement Plant 'Wierzbica' S.A., Wierzbica, Poland) at 25°C. Table 1 lists the characteristic data representing the cement hydration thermokinetics: measurement number (No.); time (t_{\max}) in which the heat evolution rate attained a maximum in the initial period; thermal power values corresponding to this maximum, (W_{\max}); and to the total heat (Q_{\max}); time (t_{\min}), in which the heat evolution rate was minimum within the initial period; thermal power values corresponding to this point, (W_{\min}); and total heat (Q_{\min}); time (t_g) corresponding to the maximum heat evolution rate in the main period; the thermal power (W_g); and total heat (Q_g); thermal power (W_{12}); and total heat evolved (Q_{12}) in 12 h of hydration; thermal power (W_{24}); and total heat evolved (Q_{24}) in 24 h of hydration.

As evident from Table 1, the values obtained in 24 h are quite consistent. The calorimeter is thus seen to lend itself to various thermal investigations on cement and conditions have been arranged to start commercial production of this instrument.

References

- 1 T. D. Dyer, J. E. Halliday and R. K. Dhir, *J. Mater. Sci.*, 34 (1999) 4975.
- 2 O. Pawling and R. Trettin, *Thermochim. Acta*, 329 (1999) 7.
- 3 E. Smrckova, M. T. Palou and V. Tomkova, *J. Thermal Anal.*, 46 (1996) 597.
- 4 C. J. Shi and R. L. Day, *Cem. Concr. Res.*, 26 (1996) 439.
- 5 M. T. Palou, J. Majling, I. Janotka, E. Dan and D. Popescu, *Ceramics–Silikaty*, 42 (1998) 105.
- 6 E. Sakai, A. Nakamura, N. Nito, Y. Ohba, T. Yano and M. Daimon, *Nippon Kagaku Kaishi*, 5 (1997) 373.
- 7 C. R. Cheeseman and S. Asavapisit, *Cem. Concr. Res.*, 29 (1999) 885.
- 8 A. Nakamura, E. Sakai, T. Kumata, Y. Ohba, T. Yano and M. Daimon, *Nippon Kagaku Kaishi*, 6 (1998) 433.
- 9 S. Asavapisit, G. Flower and C. R. Cheeseman, *Cem. Concr. Res.*, 27 (1997) 1249.
- 10 G. K. D. Pushpalal, T. Kawano, T. Kobayashi and M. Hasegawa, *Adv. Cem. Bas. Mat.*, 6 (1996) 45.
- 11 G. Kankanamge, D. Pushpalal, T. Kawano, T. Kobayashi and M. Hasegawa, *ibid.*, 6 (1997) 45.
- 12 M. L. Granizo and M. T. Blanco, *J. Therm. Anal. Cal.*, 52 (1998) 957.
- 13 A. Fernandez-Jimenez, F. Puertas and A. Arteaga, *ibid.*, 52 (1998) 945.
- 14 B. Courtault and P. Longuet, *Service chimie – CERILH, Gr VII, Paris*.
- 15 M. Kamiński, *Doctoral Thesis, Polish Academy of Sciences, Institute of Physical Chemistry, Warsaw 1981*.
- 16 M. Kamiński and W. Zielenkiewicz, *Cement, Wapno, Gips*, 6 (1981) 160.
- 17 A. Zielenkiewicz, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, 21 (1973) 333.
- 18 W. Zielenkiewicz, A. Zielenkiewicz, E. Utzig and M. Żółkiewski, *Pomiary, Automatyka, Kontrola*, 3 (1991) 54.
- 19 W. Zielenkiewicz and E. Margas, *Theoretical Fundamentals of Dynamic Calorimetry (in Polish)*, Ossolineum, Wrocław 1990.