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METHOD FOR CORRECTING THE TIME LAG OF A CONDUCTION CALORIMETER AND ITS APPLICATION *

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ABSTRACT

A microcomputer system is applied in a conduction calorimeter to reconstruct the thermal inertia of the instrument. In this method, the measured data were sampled automatically and calculated from the general heat transfer equation to obtain the real thermokinetic curves. Therefore a fast reaction can be studied correctly in a conduction calorimeter. Electric heat impulse experiments verify that this method, system and program are feasible. An application of the method to the study of the early stages of the hydration of cement, clearly shows the details of the process.

INTRODUCTION

Since the heat–power curves within the calorimeter cells can be recorded using a conduction calorimeter (heat flow calorimeter), these calorimeters have recently been applied as instruments to study reaction processes in various fields. However, the measured signal is delayed relative to the reaction in the cells owing to the thermal inertia of the instrument, and thus the recorded curves are unable to represent the real process correctly. When the exothermic rate is significantly greater than the rate of heat transfer, the time lag will be serious. Using the distorted thermograms in studying the process under investigation, some errors may occur and wrong conclusions may be drawn. Therefore, the first important step for evaluating the kinetic parameters is to reconstruct thermokinetic curves into their original forms.

BASIC PRINCIPLES

The transfer characteristics of these instruments are correctly described by a linear relationship, especially under the isothermal condition (e.g. 0.2%

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temperature difference [1]). This means that the temperature or potential gradients across the thermoelements and the resulting flux of heat or electricity conform with linear Onsager equations [2]. Then, the correlation between the exothermic rate $x(t)$ in the cells (and the response which is the measured signal $y(t)$, namely, the general heat transfer equation of a conduction calorimeter, can be deduced [3]:

$$
\begin{aligned}
x(t) = \sum_i K_i\tau_i \Bigg[& y(t) + \sum_i \tau_i \frac{dy(t)}{dt} + \sum_{i\neq j} \tau_i\tau_j \frac{d^2y(t)}{dt^2} \\
& + \cdots + \sum_{i\neq j\neq k} \tau_i,\ \tau_j, \cdots, \tau_k \frac{d^k y(t)}{dt^k} + \cdots \\
& + \tau_1,\ \tau_2, \cdots, \tau_k, \cdots, \tau_n \frac{d^n y(t)}{dt^n} \Bigg]
\end{aligned}
$$

$(i = 1, 2, \cdots, n. \qquad n \to \infty)\ (K_i = \text{calorimeter constant})$

The commonly used Tian's equation is the first-order approximation of the general equation, since it is based on two simplifying hypotheses. The first is that the temperature of the test samples in the cells equals the temperature of every spot on the internal boundary, and the second is that the temperature of every spot on the outer boundary remains constant and uniform throughout the experiment [4]. Both hypotheses are often grossly approximate, so that the equation can only be used for slow processes. For a common chemical reaction, the general heat transfer equation must be employed to reconstruct the recorded curves correctly, but according to the precision of the measured value and the sharply decreasing value of the time constants of successive orders [5,6], the third-order approximation is simply used under normal conditions.

DATA-PROCESSING SYSTEM AND CORRECTION METHOD

A computer system is used in this experimental apparatus to reconstruct the measured data directly. The block diagram is shown in Fig. 1. Analogue signals resulting from calorimeter cells A and B [7] were fed through preamplifiers, electric filters and a 12-bit analogue-to-digital converter separately. The digital signals were sampled by the computer according to the selected frequency and scale range. Then, the first-, second- and third-order approximations were calculated from the general equation by means of numerical differentiation of the discontinuous measured $y(t)$ data in order to obtain $x(t)$, the real heat–power curves in the cells, which were printed by the computer.

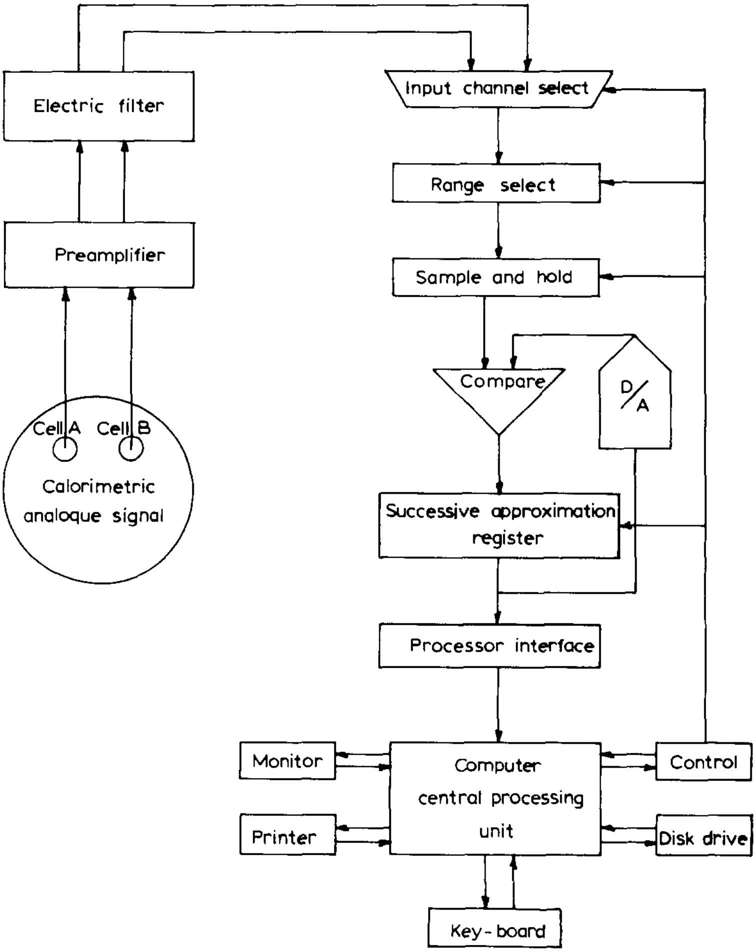

Fig. 1. Block diagram of the computer system.

EXPERIMENTAL VERIFICATION USING ELECTRIC HEAT IMPULSES

Measurement systems composed of different reactants in differently constructed cells of different materials have different time constants under various experimental conditions. In order to achieve sufficiently precise correction, the time constants of the first three orders of every system under investigation must be measured respectively by using a similar known chemical reaction or an electric heat impulse. Figure 2(a) shows a recorded curve y(t) printed by the computer which is the response of a certain system to an electric impulse. After third-order correction, the curve x(t) is shown in Fig. 2(b). In this case the first-order time constant τ_1 equals 172.5 s, the second-order time constant τ_2 equals 42 s and the third-order time constant

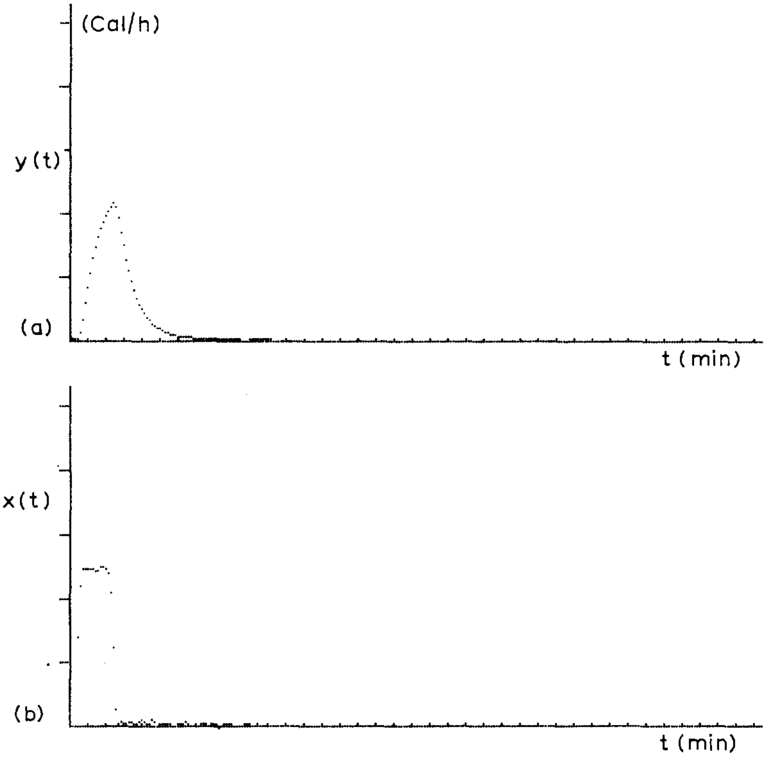

Fig. 2. Computer generated curves: (a) y(t), (b) x(t).

τ_3 equals 9 s. It can be seen from Fig. 2 that the process curve represented by x(t) is more correct than that represented by y(t).

APPLICATION

As an example, the above system and program are applied to the study of the early stages of the hydration of cement and various minerals. The results of four representative samples are shown in Table 1 and Fig. 3.

In Fig. 3, the first curves are the hydration curves of neat cement in the first hour. Because the water adsorption of C_3A and C_3S ($A = Al_2O_3$, $C = CaO$ and $S = SiO_2$) on the surface of cement particles and the fast reaction forming silicates and ettringite took place almost at the same time, these two exothermic peaks overlapped. When the surface of the cement particles were covered with hydrate, the hydration was impeded and the exothermic rate decreased rapidly. Hence the hydration reaction entered the induction period. The experimental (A) and corrected (B) calorimetric curves had the same peak area, but peak (B) shifted forward and rose significantly. This conformed to reality. In the second curves, the retardative superplasticizer JSM-B was added and the corrected curve was split into

TABLE 1
Experimental samples and results

No.	Cement [a] (g)	Superplasticizer	Water: cement (wt./wt.)	Superplasticizer: water (wt./wt.)	Hydration heat in first hour (cal g^{-1})
1	3.0788		0.5	0	4.3545
2	3.0861	JSM-B [b]	0.5	4%	5.3873
3	3.0760	SN-II [c]	0.5	4%	4.3344
4	3.1173	Sodium/sulphate	0.5	2.2%	4.8487

[a] The cement is a Portland cement produced by Chinese cement plant; cement brand, Wu Yang; cement mark, 525.

[b] Melamine sulphonate formaldehyde polymer.

[c] Naphthalene sulphonate formaldehyde polymer.

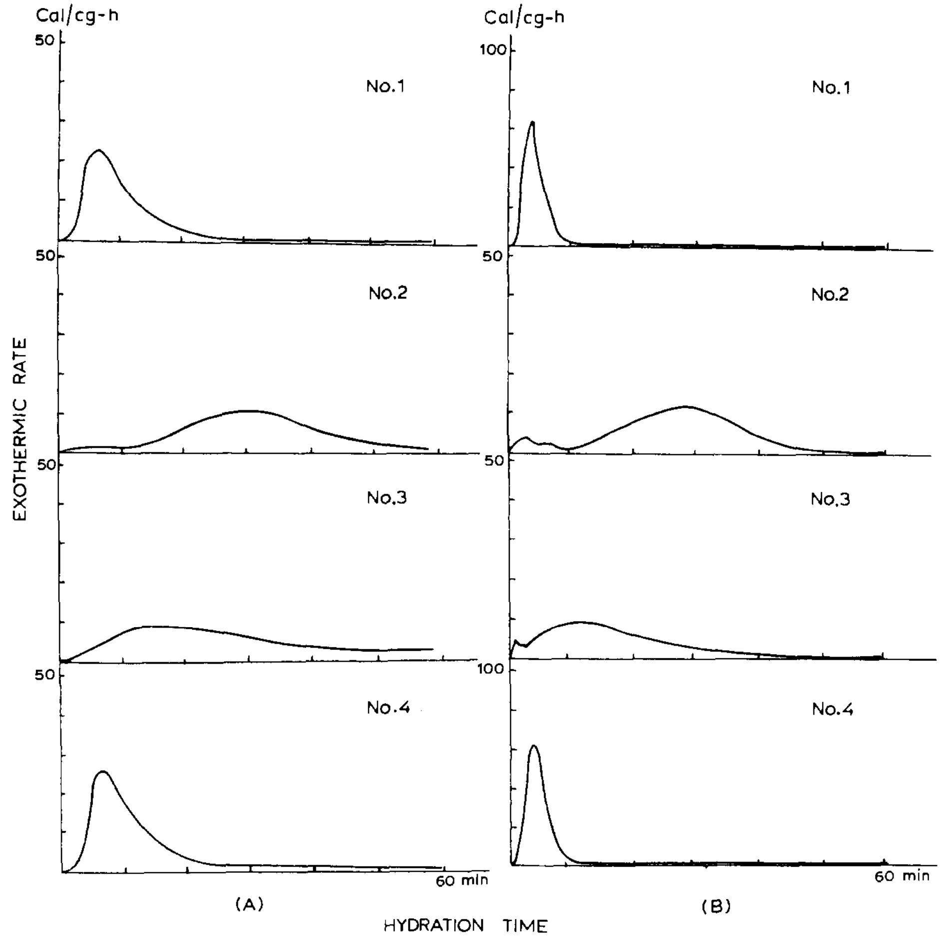

Fig. 3. Hydration curves of 4 samples (see Table 1 also). (A) Experimental; (B) corrected.

three peaks. The first was a peak of water adsorption. The second, a peak of hydrate reaction, was small since the reaction was reduced by the monomolecular film of the superplasticizer adsorbed on the surface. The third peak was due to fast hydration when the film of JSM-B and hydrate was broken by C_3A and C_3S. Owing to the dispersive action of the superplasticizer, the cement particles were uniformly distributed and the hydrate surface was increased, and thus the peak became large. Then the hydration reached the induction stage. In the third corrected curve, the first and the second peak overlapped because the retardative function of the superplasticizer SN-II was smaller than that of JSM-B. Sulphate could speed up the cement hydration. Therefore the fourth curves were similar to the first curves, but the hydration heat in the first hour was larger than that for neat cement.

It can be seen from Fig. 3 and its analyses that the details of the rather violent cement hydration in the early stage are further clarified in the corrected curves by using this method. This is advantageous in the study of crystal formation and transition in hydration process, and will contribute to the selection and application of superplasticizers in projects.

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