Journal of Thermal Analysis, Vol. 43 (1995) 497-504

CALORIMETRY IN THE SCIENCE OF BUILDING MATERIALS

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Abstract

A new conceptual approach is proposed for evaluation of the most important properties of cement-containing composites on the basis of the rate and degree off completeness of hardening processes and study of the porous structure during material formation, within the limits of the system "composition–structure–process–property".

Keywords: calorimetry, cement-containing materials, kinetics

Introduction

Cement-containing building materials are the most frequently used in civil engineering. However, they are very complex, due to the dispersion character of the components, the time dependence of their material properties, the heterophase nature of the reaction products, the composition and the structure. Therefore, measurement of their thermophysical properties requires special treatment (see, e.g. [1]). One of the promising approaches to the study of the properties of cement-containing composites consists in studying the system "composition–structure–process–property" [2]. Thermokinetic and thermodynamic methods [3, 4] are accepted as most powerful tools in this concept.

The features of heterogeneous interactions in dispersion systems impose a number of requirements on experimental calorimetric methods. The most important of them are the isolation of the reagents before the beginning of the interaction and the high degree of mixture homogeneity independently of the water-solid ratio.

Original devices have been developed for the isolated location of the reagents, the control of their being brought into contact and homogenization by means of the free delivery of powders into the reaction cell, mixing with the liquid components, adsorption interaction or forced mixing, depending on the liquid, solid or gaseous nature of the reagents. The processes were studied in the temperature interval of 5–180°C.

0368–4466/95/ $ 4.00

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Thermokinetics

In thermokinetic studies, a fixed limitation is set between conceptual and formal kinetic devices of identification and interpretation of the experimental results. Use of the mathematical model of kinetic reactions leads to a complex of interconnected problems related to the four stages shown in Fig. 1.

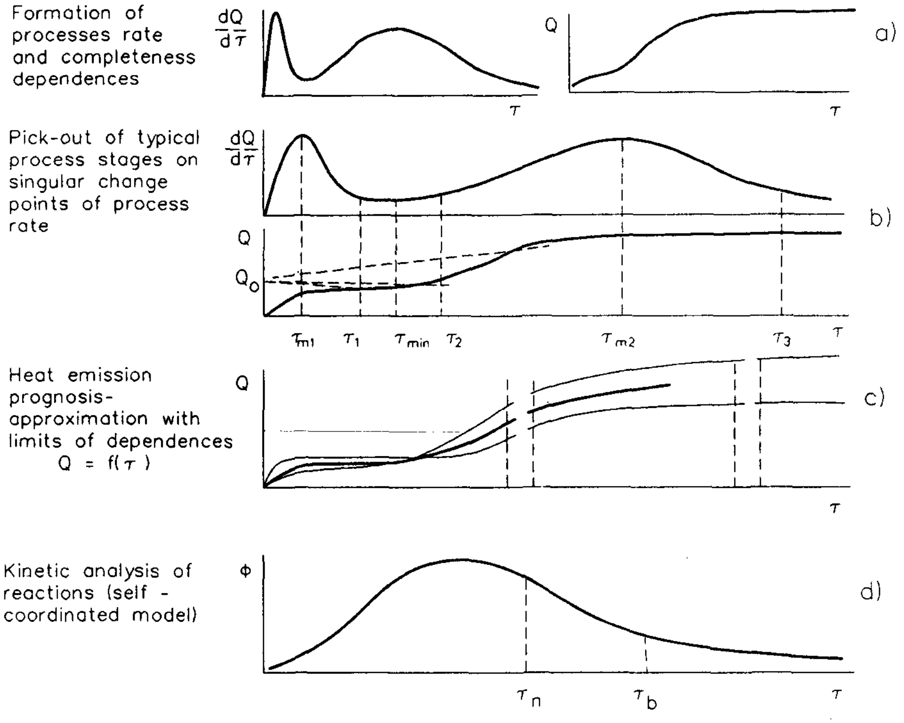


Fig. 1 Thermokinetic analysis

The primary processing consists in the dynamic correction of the measurement results by the Tian equation, and the formulation of two differential and integral dependences, $dQ/d\tau = f_1(\tau)$ and $Q = f_2(\tau)$.

The integral dependence is calculated by using the quantitative method of Ermit, considering the value of the second derivative of dQ/dt determined by the Lagrange method of the second kind.

We connect the pick-out of typical reaction stages and periods with a relative conception of slow and rapid processes. These parameters are characterized by a relation between two values having rate measures connected with the process itself, hardening for example. One of them is the momentary heat emission rate, $\mu = Q(\tau)$; the other is obtained by time-averaging of $Q(\tau)$:

$$w = 1/\tau \int Q(\tau)\mathrm{d}\tau$$

For $w/\mu > 1$ the reactions proceed rapidly, and for $w/\mu < 1$ they proceed slowly. Three singular change points (from rapid to slow and vice versa) are to be observed in thermokinetic curves.

In a long-term prognosis, the forestall time exceeds the observation time. The problems under study depend on the choice of formal approximation models. As a rule, the functions $Q=f(\tau)$ are represented by monotonously rising asymmetric sygmoid curves tending to a thermodynamically determined limit. The prognosis procedure is interconnected with the error-evaluation treatment. This is feasible by using an approximation with limits. The important condition is the existence of a point (τ_x, Q_x) on the curve $Q=f(\tau)$, such that for $\tau > \tau_x$ the reaction system does not undergo any changes. Approximation functions without local extrema are considered upper and lower estimates in this case. Extrapolations of the thermokinetic function in the prognosis interval fall into the "corridor" of two approximation functions.

The probabiliy model of Kolmogorov for systems involving chemical interactions is employed in the kinetic analysis of processes. This model, which has been repeatedly supplemented, does not take into account a number of essential factors, e.g. endogenetic effects generated in surface layers of a liquid phase, the formation of non-steady concentration fields, electrokinetic changes, etc. The unity conditions of the rate of growth of new phase germs are disturbed. The development of the approach is based on the construction of a self-coordinated model with the solution of an inverse kinetic problem. Changes resulting in new formations being transformed from a metastable into a stable condition are taken into consideration.

The cement – water interacting system should be regarded as an open thermodynamic system with three basic phases, solid – cement stone, liquid – water, and a vapor – gas mixture. A rigid solid cube of cement stone interacting with liquid and vapor is examined. The interaction depends on the dimensions of the pores and the degree of absorbability of water by their walls. The interaction analysis is based on the thermodynamics of surface phenomena. The method of differential scanning calorimetry (DSC) (Fig. 2) is the experimental base.

According to Stockhausen *et al.* [5], in a capillary-porous body four modifications of the adsorbed and capillary condensed water can be distinguished. The water in the pores has a foliated structure and its properties (primarily the crystallization temperature) vary with the distance between pore centers. The solid surface of the pores adsorbs the molecules of water. Such an interaction distorts the water structure and this is the kinetic obstacle to liquid crystallization [6].

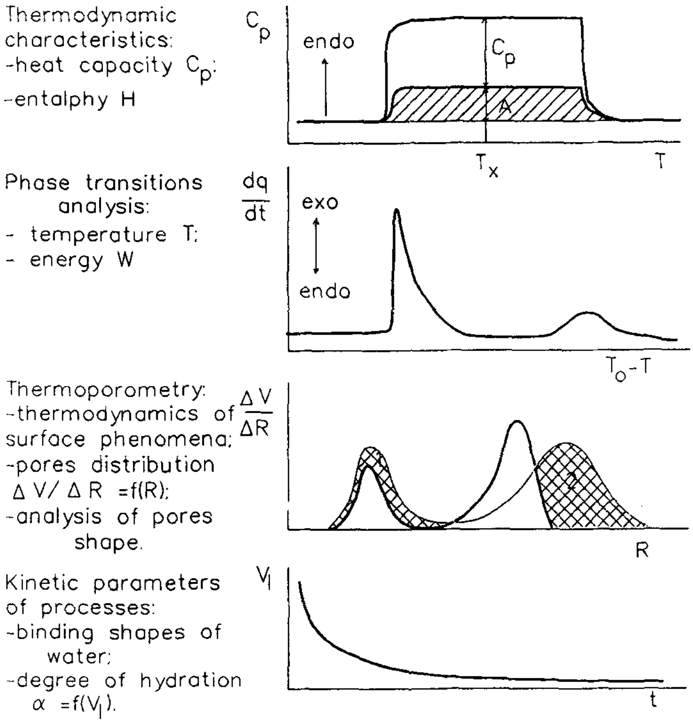


Fig. 2 Thermodynamic analysis

The dependence of the crystallization temperature of the water in the pores on their dimensions is derived, taking into consideration the thermodynamic water – ice balance, and the chemical potential equilibrum [7]. We have

$$\frac{1}{R}=\frac{1}{2\gamma}\int_{T_o}^{T}\frac{\Delta S\,dT}{v} \tag{1}$$

where γ is the free surface energy on the limit of the division liquid–solid; ΔS is the entropy chang during crystallization; and v is the liquid phase volume. After integrating Eq. (1), we get

$$R=\frac{A}{(T_o-T)}+B \tag{2}$$

where A and B are experimental factors.

The pore-distribution curve is a function $\Delta V/\Delta R=f(R)$.

In the time interval $d\tau$, the phase transition energy is proportional to the area $yd(T_o-T)$ (Fig. 2).

When crystallization takes place in the system, the volume of the pores is directly proportional to this energy and inversely proportional to the apparent crystallization energy W:

$$\Delta V=\frac{Cyd(T_o-T)}{W} \tag{3}$$

where y is the deflection from the baseline; and C is the coefficient factor.

Consequently, the distribution curve equation will be

$$\frac{\Delta V}{\Delta R}=\frac{ky(T_o-T)^2}{W} \tag{4}$$

where k is the factor including the influence of the chosen method of investigation and the sensitivity of the calorimeter.

From a comparison of the water crystallization and melting curves for porous materials, it is possible to determine the pore shape by analysing R and the temperature decrease for each case. Thus, it is supposed that all pore shapes can be reduced to two types: spherical and cylindrical. In the former case, the solid phase curvature does not change with melting and crystallization and consequently hysteresis does not appear.

For cylindrical shape pores a considerable hysteresis is observed between melting and crystallization. The melting curve does not provide the pore distribution, but it contains information on their shape.

As a result, two hypothetical curves can be plotted (Fig. 2), one of them being spherical (2), the other one cylindrical (1). Comparison of these curves with the pore-distribution curve of a material under study allows an estimation of the pore shape.

Water – ice phase transition analysis provides information on the free water content in the material. Its amount is proportional to the mass of water in the material and to the peak surface of the phase transition. A comparison of these values for samples with different hardening times permits quantification of the change in the degree of hydration from the free water content in the hardening material.

Application

The indirect prognosis of the strength duration and the, freeze-thaw durability depending on the parameters of the porous structure is based on a thermodynamic analysis of the binder-water system.

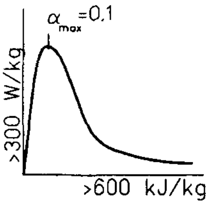
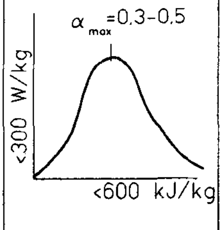
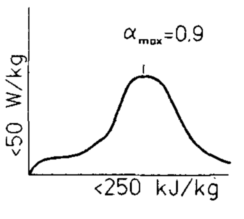
Type of dependences	I	II	III
View of thermo-kinetic dependence $\frac{dQ}{d\tau}=f(Q)$			
Binders	CaO, $3CaO*Al_2O_3$ $4CaO*Al_2O_3*Fe_2O_3$ phosphates	$CaSO_4*0,5H_2O$ $3CaOSiO_2$ $CaO*Al_2O_3$ cementes	CaO/SiO_2 $2CaO*SiO_2$ slags ashes

Fig. 3 Thermokinetic classification of binding materials, hardening processes and properties

The thermokinetic analysis of inorganic-binder hardening leads to a classification based on the reaction rate and degree of completeness (Fig. 3).

High-reaction binders belong in the first type: CaO, $3CaO\cdot Al_2O_3$ and others. The periods of acceleration and slowing down are apparent from the functions $Q/d\tau=f(\tau)$.

The maximum rate of the process corresponds to the beginning of transformation when $\alpha=0.15-0.3$. This kind of hardening does not lead to the formation of strong structures under common conditions.

The second type includes the majority of traditional binders having given strength characteristics (cement, building gypsum, $3CaO\cdot SiO_2$ and others). The reaction course, whose maximum rate corresponds to an α of approximately 0.3–0.5, provides chemical properties.

The low reaction intensity in the time interval from several days to several months, and sometimes to several years, is characteristic of binders whose reaction activity is practically not displayed under normal conditions (slags, ashes, calcium silicates: $2CaO\cdot SiO_2$, and mixtures of CaO and SiO_2). Maximum values of the transforming rate appear at $\alpha>0.7$. This type of binder cannot harden and the required strength is produced only when activation is applied: pressure and mechanical-chemical activation.

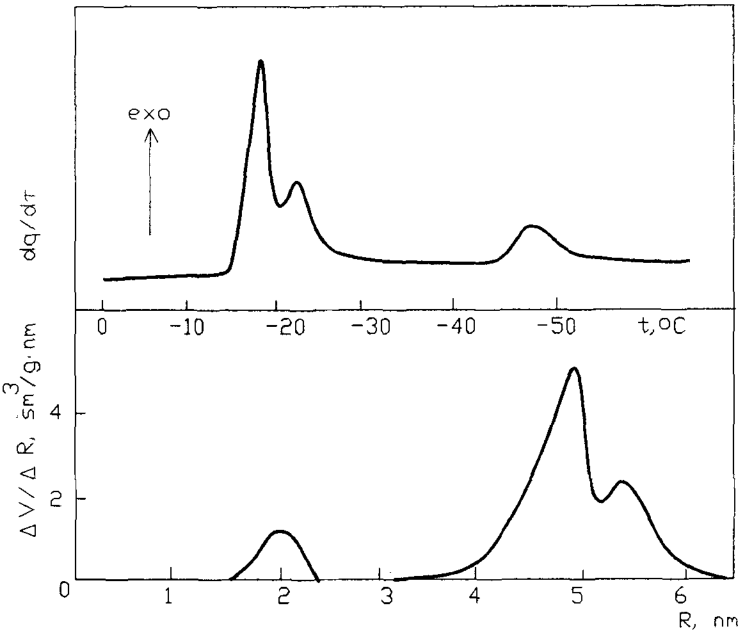


Fig. 4 Thermoporometry of tricalcium silicate

Thus, thermokinetic analysis allows prediction of the main physical-mechanical materials and determination of the conditions necessary to obtain the required properties.

The thermodynamic analysis of hardening binders confirms the change in the water crystallization temperature during the hydration process (Fig. 4a). The dimensions of the pores decrease, due to the growth of new formations inside. In the freezing curves (Fig. 4), we can see the water – ice phase transition and the respective dimensions of the pores. Thus, in $3CaO\cdot SiO_2$ hardening, at least three different types of pores are formed (Fig. 4b).

The pore-shape analysis of hardening binders assumes that near-spherical pores prevail in the early hydration stages. However, due to the hysteresis in the crystallization-melting process, "bottle-neck" pores [8] appear. In later hydration stages, the volume of fine cylindrical pores increases.

Thermoporometry is limited by the minimum pore size of 1.6 nm, because adsorption water does not freeze in smaller pores.

The kinetic and thermodynamic parameters of the processes of structure formation of cement – containing compounds should become the basis for a computer data bank, and a knowledge base for new information technologies for building materials.

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Zusammenfassung — Im Rahmen des Systems "Komposition – Struktur – Prozess – Eigenschaft" ist ein neuer konzeptualer Zutritt zur Bewertung der wichtigsten Eigenschaften der zementhaltigen Kompositen aufgrund der Interpretierung der Geschwindigkeit der Erhartung und Formierung der Stoffporenstruktur vorgeschlagen. Theoretische und experimentelle Grundlagen der thermokinetischen und thermodynamischen Analysen der Gesetzmässigkeiten der Formierung von Eigenschaften der zu erforschenden Objekte sind dargestellt. Der Zusammenhang der kinetischen und energetischen Parametern mit physikalisch-mechanischen Kennziffern der zu erhartenden Stoffe ist auch gezeigt.