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DEHYDRATION KINETICS BY NON-ISOTHERMAL TECHNIQUES

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The kinetics of thermal degradation of some cementitious calcium aluminates, sulfoaluminates, sulfoferrites and carboaluminates were studied. Activation energies, obtained by Morris and Rogers and Kissinger techniques, were found to be in good agreement with each other.

A knowledge of the kinetics and energetics of thermal degradation of the hydrates of cement components is very important in view of their sensitivity to the conditions of curing and use of cement. The research activities in this are have been limited to observations of the crystal structure and morphology changes with temperature, or measurements of the weight loss as a function of temperature. In studies of kinetics and energetics of solid state decomposition reactions, mostly isothermal methods have been used. In order to determine the kinetic parameters of a reaction with isothermal methods it is necessary to evaluate a series of experiments performed at constant temperature. This requires a considerable amount of time for experimental work. It would be of greater value if one were able to estimate the kinetic parameters of a solid state decomposition reaction from a single DTA curve.

Kinetic data on the thermal decomposition of some siliceous cementitious hydrates have been reported by the authors [1, 2]. In this article the activation energy results are reported on selected calcium aluminate (ferrite, sulfate) hydrates estimated from data obtained under non-isothermal conditions from one [3] or more [4, 5] curves.

Experimental

The four double salts studied, tetracalcium aluminate monosulfate-12-hydrate, 6-calcium aluminate trisulfate-32-hydrate (ettringite), 6-calcium ferrite trisulfate-32-hydrate (iron-ettringite), and tetracalcium aluminate carbonate-11-hydrate were obtained from the Portland Cement Association, Skokie, Illinois. Tricalcium aluminate-6-hydrate was prepared by hydrating $Ca_3Al_2O_6$. Reagent grade calcium sulfate dihydrate (gypsum) was purchased from the Baker Chemical Company.

All the materials were characterized by X-ray diffraction and differential thermal analysis, using a Phillips XRD-3000 diffractometer and Mettler Thermoanalyzer 1, respectively. DTA curves of these compounds are shown in Fig. 1. X-ray diffraction analyses have shown all the *d*-spacing characteristic of the compounds studied with no minor impurities detected [6]. Thermogravimetric results revealed that a small portion of the loosely bound water in the higher hydrates was lost in sample handling. Experimental data used in the calculation of activation energies were obtained with a Mettler DTA-2000 system, using 2 to 5 mg samples and an optimum ΔT sensitivity of 115 $\mu V/°$. High purity Indium metal was used for calibration.

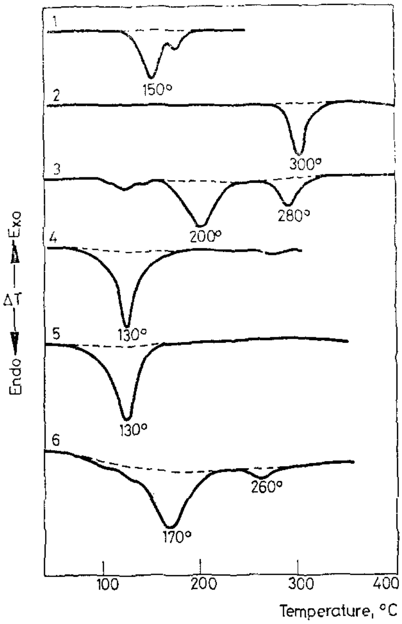

Fig. 1. DTA curves of the compounds studied

Results and discussion

Typical examples of data obtained by the Rogers and Morris [3] and by the Kissinger [4, 5] methods on some of the material studied are depicted in Figs 2 through 4. The Rogers and Morris method analyzes the data from a single curve in the form of distances between the reaction curve and the base line at selected temperatures. The distance measured from the base line to the reaction curve is proportional to the rate of heat evolution or absorption and, therefore, is proportional to the reaction rate constant. The activation energy for the decomposition reaction is estimated from the plots of ln d vs. $\frac{1}{T}$ using the equation:

$$\frac{\ln d_1 - \ln d_2}{\frac{1}{T_2} - \frac{1}{T_1}} = -\frac{E}{R} \tag{1}$$

where d_1 and d_2 are any two distances from the base line to the reaction curve on the low temperature side of the peak, corresponding to temperatures T_1 and T_2; R is the universal gas constant, and E is the activation energy for the reaction represented by the given endotherm.

The Kissinger method [4] utilizes the shift in the peak temperature with heating rate. The working form of the expression is:

$$\frac{d\left(\ln \frac{\phi}{T_m{}^2}\right)}{d\left(\frac{1}{T_m}\right)} = -\frac{E}{R} \tag{2}$$

where the heating rate $\phi = \frac{dT}{dt}$, T_m is the temperature of the peak (K), E is the activation energy, and R is the universal gas constant. The method is based on the premise that the maximum reaction rate takes place at the apex of the peak. In reality, however, the maximum reaction rate occurs at some temperature between the low temperature inflection point and the peak temperature. In fact, the peak temperature is the point at which the rate of heat evolution (or absorp-

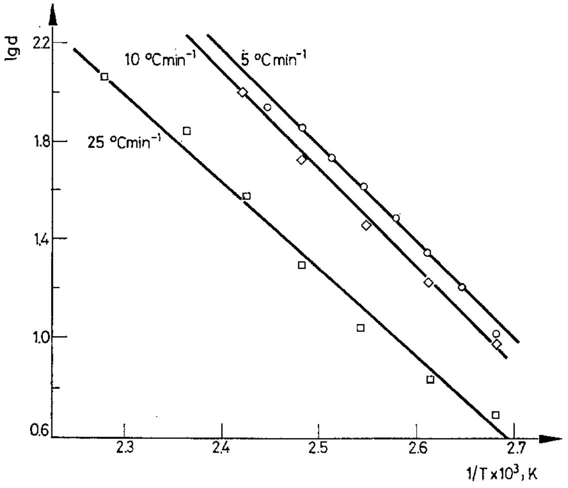

Fig. 2. Arrhenius plots of Ettringite decomposition using the Rogers and Morris method

tion) is equal to the rate of heat transfer to the sensing element. Mathematical justification of the above assumption is given by Kissinger [5] and also has been demonstrated graphically by Vold [6].

In addition to the above assumption, a number of other assumptions (e.g., uniform cell temperature; constant Cp, K and ΔH values with temperatures; and heat transfer by conduction alone) are implicitly included in the treatment of the kinetic data by the method. In the original work of Kissinger [4], these assumptions were very difficult to justify due to use of very large sample sizes (in the order of 500 to 1000 mg) and the lack of precision in the temperature measurements. In the present work, however, most of these assumptions could fully be justified by use of very small samples size (e.g., 2.0 mg) and by very high precision in temperature measurement.

Another assumption, important in the Rogers and Morris method, is the constant mass of sample throughout the reaction. Kirby [7] has shown that even

Table 1

Activation energies and enthalpies of dehydration of the compounds studied

Material and chemical formula	DTA peak temp, °C	Activation energies of dehydration, kcal mol^{-1}					Enthalpy of dehydration, cal/g
		Kissinger method	Rogers and Morris method				
			5°/min	10°/min	15°/min	25°/min	
1 Calcium sulfate dihydrate $CaSO_4.2H_2O$	~150	—	39	—	35.5	39.5	100
2 Tricalcium aluminate hexahydrate $Ca_3Al_2(OH)_{12}$	~300	—	34	—	36	36	42
3 Tetracalcium aluminate monosulfate-12-hydrate	~200	16.5	—	—	—	—	68
$[Ca_2Al(OH)_6]$ $[0.5(SO_4).3H_2O]$	~280	64(?)	—	—	—	—	
4 Hexacalcium aluminate trisulfate-32-hydrate (Ettringite) $Ca_6[Al(OH)_6]_2.24H_2O$ $[(SO_4)_3.1\ H_2O]$	~130	17.5	17.3	17.5	16	16	148
5 Hexacalcium ferrite trisulfate-32-hydrate (Fe-ettringite) $Ca_6[Fe(OH)_6]_2.24H_2O$ $[(SO_4)_3.1\ H_2O]$	~130	20.5	18	—	21	21	100
6 Tetracalcium aluminate carbonate-11-hydrate	~170	13.5	17	16	17	17	98
$[Ca_2Al(OH_6)]$ $[0.5(CO_3).$ $2.\ 5H_2O]$	~260	16	15	14	—	—	

though the heating rate per unit mass increases with temperature, a point is eventually reached at which the mass remaining is so small that the combined effect begins to decrease and reaches zero when the reacting mass approaches zero. This could not be the case in our experiments where the total weight loss never exceeded 40% of the original weight.

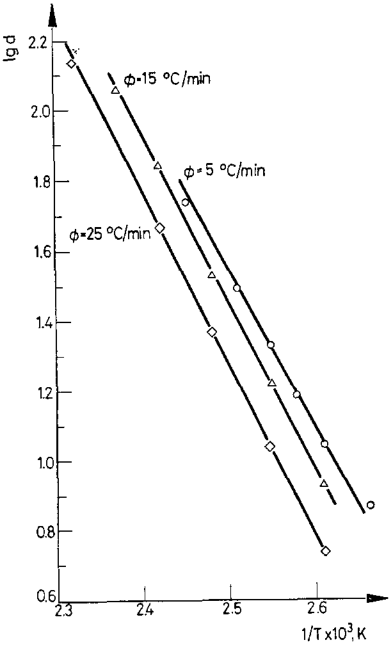

Fig. 3. Arrhenius plots of Ironanalog of Ettringite decomposition using the Rogers and Morris analytical approach

The activation energies obtained using the two methods are summarized in Table 1. It shows a general consistency of activation energy values between the Rogers and Morris data obtained for various heating rates, as well as good agreement between these data and those calculated by the Kissinger approach. Only the Kissinger values were obtained for tetracalcium aluminate monosulfate-12-hydrate. It decomposes in several steps, the low temperature one being by itself a multiple peak. This has been shown also by TG, EGA, and X-ray analysis [8]. Similarly, the tetracalcium aluminate carbonate-11-hydrate decomposes in at least three steps, the two higher temperature peaks occurring at somewhat lower temperatures than those of monosulfate. Note the difference in their activation energies for the peaks at 260–280°. Ettringite and its iron-analog have activation energies in good agreement with each other and the decomposition peaks appear at similar temperatures. In contrast with the ettringite used, the iron-ettringite did not show a small endotherm at about 270°.

Rogers and Smith [8] provide a means of estimating the pre-exponential factor A for the Arrhenius expression using DSC. Their method describes the deflection from the baseline, D, by the equation:

$$D = a m A \exp(-E/RT), \tag{3}$$

where a is the heat of reaction per unit weight of the sample divided by the sensitivity factor of the instrument, and m is the mass at any time. They differentiate this equation with respect to time and set $\mathrm{d}D/\mathrm{d}t$ equal to zero at the peak of the curve to obtain:

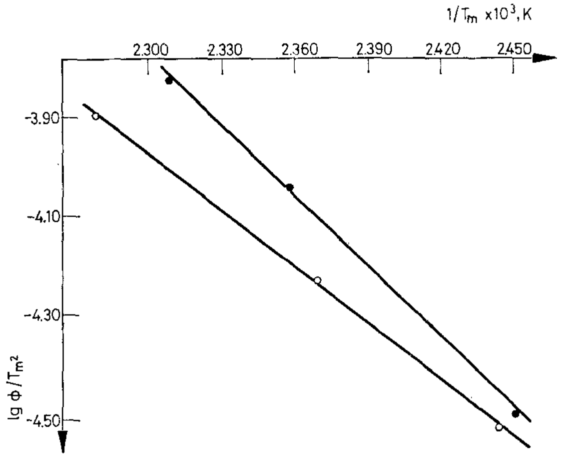

Fig. 4. Arrhenius plots of Ettringite (○) and its iron-analog (●) using the Kissinger method

$$A = \frac{\mathrm{d}T/\mathrm{d}t\, E \exp(-E/RT_\mathrm{m})}{RT_\mathrm{m}^2}, \tag{4}$$

where T_m is the temperature at which D reaches its maximum and $\mathrm{d}T/\mathrm{d}t$ is the programmed heating rate. The values of A, calculated for the studied substances, compare well with those of clay minerals reported by Kissinger [5]. Expression (4) is applicable only to first-order reactions [5]. The degree of asymmetry of the DTA peak can be expressed in terms of reaction order providing that the peak shape is independent of the heating rate and the values of the kinetic constants. To quantitatively describe the peak shape, Kissinger [5] defines a "shape index" as the absolute value of the ratio of the slopes of tangents to the curve at the inflection points. Using the above technique, the calculated reaction orders of the studied decomposition reactions were found to be between 1.005 and 1.09. This shows that the dehydration reaction rates of these materials can be assumed to be first order as a first approximation.

In conclusion it can be stated that, under the experimental conditions used, the Kissinger method can give as good results as the Rogers and Morris method. The close agreement between the respective results, and better justification of the assumptions concerning some thermodynamic (C_p, ΔH) and thermal parameters (heat conduction rate and mechanism) enables the use of Kissinger technique in studying thermal decomposition of solid materials.

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Résumé — On a étudié la cinétique de la décomposition thermique de plusieurs constituants du ciment tels les aluminates, sulfoaluminates, sulfoferrites et carboaluminates de calcium. Les énergies d'activation obtenues en appliquant la méthode de Morris et Rogers ainsi que celle de Kissinger sont concordantes.

Zusammenfassung — Die thermische Zersetzungskinetik einiger im Zement befindlicher Kalziumaluminate, Sulfoaluminate, Sulfoferrite und Karboaluminate wurde untersucht. Die nach den Methoden von Morris und Rogers, sowie Kissinger erhaltenen Aktivierungsenergien stimmten gut überein.

Резюме — Была изучена кинетика термического распада некоторых цементирующих алюминат-, сульфоалюминат-, сульфоферритов и карбоалюминатов кальция. Установлено, что энергии активации, полученные по методу Морриса и Роджера, а также Киссинджера, хорошо согласуются друг с другом.