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APPLICATION OF DTA FOR INVESTIGATION OF HYDRATION AND DEHYDRATION OF CRYSTAL HYDRATES

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The results of the investigation of the hydration processes of the dehydration products of magnesium carbonate trihydrate are shown. The DTA curve was used to calculate the function $Q(t)$. It was found that the results were in good agreement with the equation $\lg \frac{Q - Q_0}{Q_f - Q} = k_1 t - k_2$, where Q is the heat evolved during the hydration time t; Q_0, Q_f are the same for the initial and final products, respectively, k_1 and k_2 are the hydration constants.

The results of our experiments have shown the possibility and usefulness of the application of differential thermal analysis (DTA) for the study of kinetics of both the dehydration of various crystal hydrates and the hydration of their anhydrous form. In this connection the changes in the absorbed or evolved heat in dependence on time have been studied. From the DTA curves of hydration and dehydration products, the values of heat effects necessary for the construction of corresponding curves have been calculated. The relationships $Q(t)$ (Q is the absorbed or evolved heat during the time t) obtained in the above-mentioned way permit the reconstruction of dehydration or hydration curves.

In order to examine the usefulness of the method the kinetics of the dehydration of calcium sulphate dihydrate and magnesium carbonate trihydrate as well as that of the hydration of their dehydration products have been studied. The relationships $Q(t)$ were compared with analogous curves $n(t)$, where n is the molar ratio H_2O/CaO or H_2O/MgO. Within the limits of error the results proved to be in good agreement.

As an example, the results of the study of the hydration process of magnesium carbonate trihydrate dehydration products are detailed.

Experimental

As an initial substance, magnesium carbonate trihydrate precipitated from magnesium chloride solution by sodium carbonate [1] was used. The chemical composition of the crystal hydrate was: MgO 29.5%, CO_2 32.0%, H_2O 38.5%. The product was dried at 110° up to the partial loss of crystallization water and the formation of magnesium carbonate hydrate with molar ratio $H_2O/MgO = 1.45$. For hydration the water suspension method [2, 3] was used.

Differential thermal analysis was carried out in an apparatus Model FPK-55 U.S.S.R.) equipped with a cylindrical chrome-nickel cell and porcelain sample and reference containers. Temperature was measured by thermocouples Pt—Pt/10% Rh located in the centres of the containers. The weight of the sample was 0.1 g, the heating rate 10—12° per min. As a standard compound Al_2O_3 heated at 1450° was used. All DTA experiments were carried out in air at atmospheric pressure.

Results and discussion

Thermal studies of hydration products (Fig. 1) have proved that during hydration only the peak area of the first endothermic effect on DTA curves can alter.

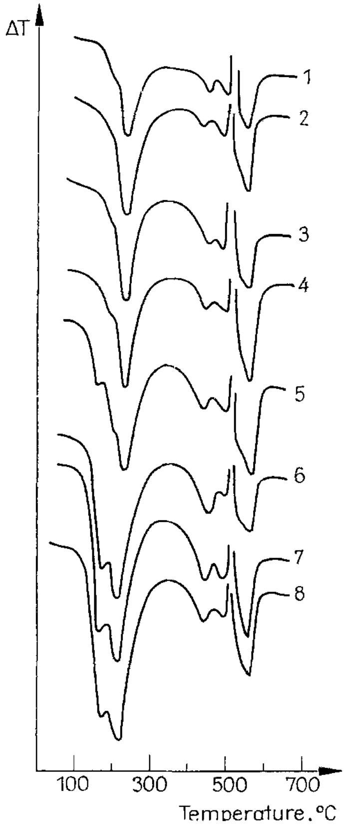

Fig. 1. DTA curves of hydration products of magnesium carbonate at 20°. 1: the initial product, 2: the sample after 20 min of hydration, 3: 30 min, 4: 45 min, 5: 60 min, 6: 90 min, 7: 120 min, 8: 1440 min

In order to investigate the kinetics of hydration the change of reaction heat as a function of the time was studied. The heat of reaction was determined from the peak area of the first endothermic effect. The area of the effect mentioned above was measured with a planimeter.

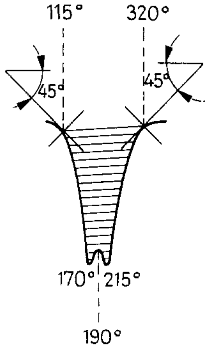

Fig. 2. The construction of the thermal effect area (hydration product at 40° after 90 min)

The area was limited as follows (see Fig. 2): tangents were drawn to both the beginning and end of the differential curve at a 45° angle to the time axis. Contact points of the tangents and curve were linked by a straight line. As the

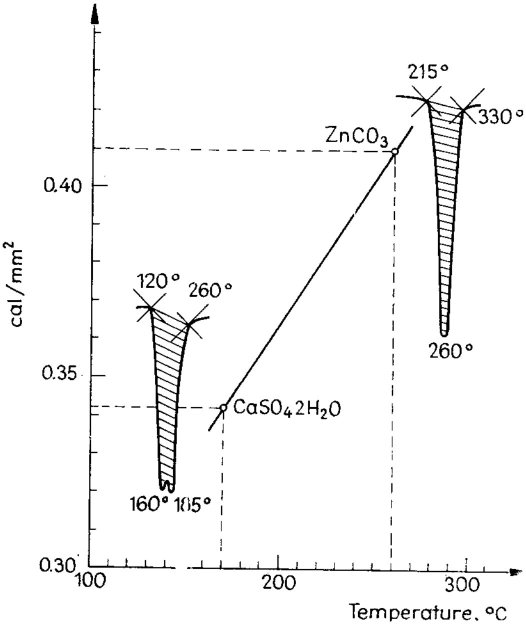

Fig. 3. The graphical interpretation of the change of the thermal effect areas "heat content" in dependence on temperatures

value of thermal effect is not proportional to the calorimetric effect of the process, but depends on the specific heat of a substance, heat conductivity of the apparatus was determined. $CaSO_4 \cdot 2H_2O$ and $ZnCO_3$ were used as standards because their heats of dehydration and dissociation are known. By measuring the areas and temperatures of the thermal effects of these substances and with a knowledge of calorimetric data the change of the "heat content" of the peak areas in dependence on temperature was established. A straight line can be obtained when the data are interpreted graphically (Fig. 3). The graph allows the real heat content of the thermal effects of samples to be determined. The error of the determination does not exceed 3—5%.

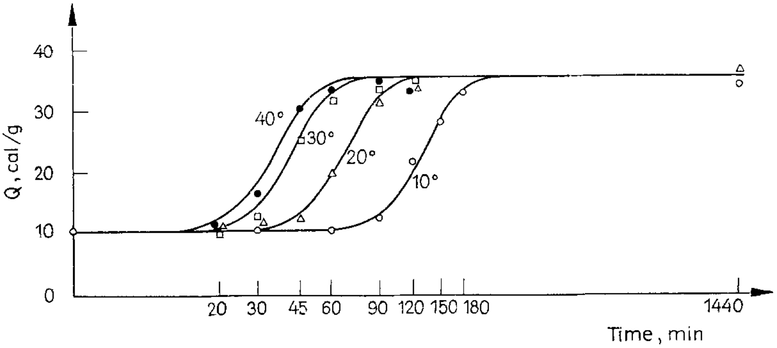

Fig. 4. Hydration curves at 10, 20, 30 and 40°

$Q(t)$ hydration curves were constructed on the basis of the data obtained in this way (Fig. 4). The real relationship $Q(t)$ can be described by an S-form curve characteristic of autocatalytic reactions. The experimental data of $Q(t)$ are in good agreement with the modified Prout—Tompkins equation

$$\lg \frac{Q - Q_0}{Q_f - Q} = k_1 t - k_2 , \tag{1}$$

where Q is the heat evolved during the hydration time t; Q_0 and Q_f are the same for the initial and final products; k_1, k_2 are hydration constants. Using equation (1), the constants k_1 and k_2 were calculated on the basis of experimental data (Table 1) and the straight-line character of the dependence of $\lg \frac{Q - Q_0}{Q_f - Q}$ on t examined.

With the aim of examination the relationships $Q(t)$ were compared with analogous curves $n(t)$ [3], where n is molar ratio H_2O/MgO. A good agreement of results allows the use of the data of thermal and chemical analysis with equal precision for the investigation of either hydration or dehydration processes.

Table 1

The constants in equation 1

Temperature of hydration, °C	k_1, min^{-1}	k_2
10	0.0237	3.100
20	0.0433	2.856
30	0.0643	2.644
40	0.0673	2.404

References

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Résumé — Pour illustrer la méthode employée, on communique les résultats se rapportant à l'étude du phénomène d'hydration des produits de déshydratation du carbonate de magnésium trihydraté. On calcule la fonction $Q(t)$ à l'aide des courbes d'A.T.D. Les résultats obtenus sont en bon accord avec les valeurs de l'équation $\log \frac{Q-Q_0}{Q_f-Q} = k_1 t - k_2$ où Q est la chaleur dégagée pendant le temps d'hydratation t, Q_0 et Q_f sont les valeurs correspondantes pour les produits initiaux et finals, k_1 et k_2 les constantes d'hydratation.

Zusammenfassung — Die benutzte Methode wurde am Beispiel der Untersuchung des Hydrationsvorganges der Dehydratisierungsprodukte des Magnesiumkarbonat-Trihydrats demonstriert. Zur Errechnung der Funktion $Q(t)$ dienten die DTA-Kurven. Die Ergebnisse folgten gut der Gleichung $\lg \frac{Q - Q_0}{Q_f - Q} = k_1 t - k_2$, wo Q die freigesetzte Wärme während der Hydratationszeit t, Q_0, Q_f dieselbe für die Anfangs- und Endprodukte, k_1, k_2 die Hydratationskonstanten bedeuten.

Резюме — Показаны полученные результаты исследования процесса гидратации дегидратированных продуктов трёхводного карбоната магния. Функция $Q(t)$ рассчитана по кривой дифференциального термического анализа (ДТА). Хорошо совпадали полученные данные и результаты, рассчитанные по уравнению $\lg \frac{Q - Q_0}{Q_f - Q} = k_1 t - k_2$ где Q — теплота, выделившаяся во время гидратации, t, Q_0 и Q_f — те же теплоты, соответствующие исходному и конечному продуктам, κ_1 и κ_2 — постоянные гидратации.