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STATISTICAL ESTIMATION OF THE RESULTS OF DIFFERENTIAL THERMAL ANALYSIS OF CEMENT MATERIALS

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The paper describes the results of statistical analysis of DTA diagrams. A connection is found between the second and third endothermal effects. An analysis of geometrical characteristics of the T, S and h values of DTA diagrams confirms the absence of reliable connections. The rank correlation coefficients are determined according to Spearman. Non-linear programming is formulated to obtain the kinetic dependencies of the process of hydration of cement studied by DTA.

The inherent properties of cement pastes (the multiplicity of components, the variegated morphological properties and dimensions of separate particles and formations, the presence of faults, etc.) lead to certain difficulties in the interpretation of the results of their differential thermal analysis (DTA). Much trouble is caused by the possibility of superposition of thermal effects of different origins and intensities on the DTA diagrams. For instance, in the temperature range between 100 and 300°, apart from the partial dehydration of ettringite-like and hydrosilicates, many calcium hydroaluminates evolve their crystallization water. At 200–400° hydration products of $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ are decomposed. Heating from 500° to 600° in most cases causes decomposition of $Ca(OH)_2$. The endothermal effect at 700–900° is due to the decomposition of calcium hydrosilicates and of $CaCO_3$. It is also possible that "false" effects of substances not present under usual circumstances, but formed during the heating as a result of chemical interaction of the primary phases, may appear on the diagrams.

The errors of DTA are of purely occasional origin and depend upon a large number of factors connected not only with the non-homogeneity of the material under analysis, but also with specific properties of the given instrument.

To increase the reliability of data obtained by means of DTA (detection of correlations between separate elements of DTA diagrams and choice of necessary indications) we have statistically analysed the results of studies of cement stones with different periods of hardening.

Experimental results and discussion

An FPK-55 pyrometer was used. The reference sample was Al_2O_3, the thermocouple was made of platinum and platinum–rhodium, the sample weight was

0.3 g and the rate of heating 18° per minute. While preparing samples special attention was paid to their granulometric constancy and dehydration (cleaning off moisture water).

Fig. 1 shows DTA diagrams of cement samples hydrated for different times at 20 ± 1° (cement composition: SiO_2 – 23.4%; Al_2O_3 – 5.0%; Fe_2O_3 – 6.2%; CaO – 61.3%; MgO – 0.9%; SO_3 – 1.5%). As defining indications we chose

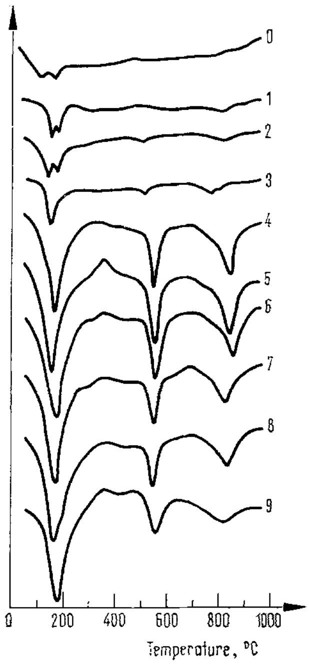

Fig. 1. DTA diagrams of cement (0) and cement stone with time of hydration 2 hours (1), 7 hours (2), 12 hours (3), 1 day (4), 2 days (5), 3 days (6), 7 days (7), 14 days (8), 28 days (9)

areas of the three main endothermal effects S_I, S_{II}, S_{III}, their depths h_I, h_{II}, h_{II} and the temperatures of extreme points T_I, T_{II}, T_{III}, defined according to [1, 2] and given in Table 1. The average areas of S are given together with their average square deviations (σ).

From the graph of $S = f(\tau)$, we can trace the change of the gross minarel composition of the cement stone in the hardening process during three pfriods (Fig. 2). The first period (0–24 hours) is characterized by intense hydratef ormation; the second one (1–7 days) by slower hydration; S_{II} and S_{III} attain maximum values in the third period (7–28 days).

Judging from the change of S_I, an intense build-up of hydrate phases takes place. As to the change of S_{II}, we can suppose either crystallo-chemical transformation or carbonation of $Ca(OH)_2$. The importance of the latter is unlikely to be large, as the value of S_{III} also decreases with time.

It is known that the areas of given thermal effects under otherwise identical circumstances are proportional to the amount of decomposing substance. Therefore, the study of the kinetics of the hydration of cement by DTA is of some interest; for quantitative estimation it is expedient to define the shape and parameters of empirical equations describing the change of $S = f(\tau)$.

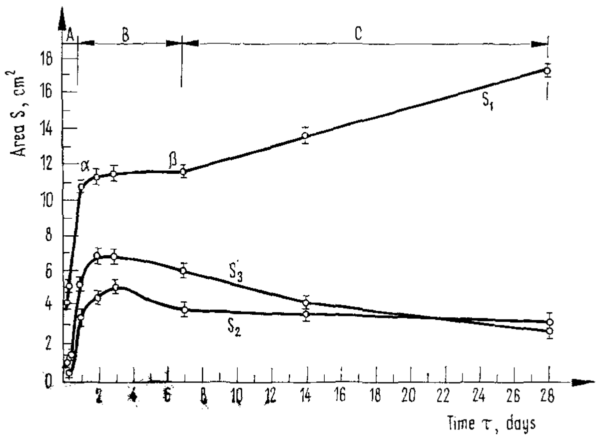

Fig. 2. Change of areas of the first (S_I), second (S_{II}) and third (S_{III}) endothermal effects as a function of time

The degree of the approximating polynomial is defined by the orthogonal contrast method [3, 4]. The result of the analysis shows that the elements of the curve are approximated by a polynomial of not higher than the second bower. The empirical equations for segments of $S_I = f(\tau)$ are:

$$S_A = a_{1A}\tau_A + a_{0A} \tag{1}$$

$$S_B = a_{1B}\tau_B^2 + a_{2B}\tau_B + a_{0B} \tag{2}$$

$$S_C = a_{1C}\tau_C^2 + a_{2C}\tau_C + a_{0C} \tag{3}$$

where S_A, S_B, S_C, are values of the function $S = f(\tau)$ in the segments A, B and C (Fig. 2); a_1, a_0 are empirical constants in the segments defined by the second index.

To realize the congruency of the values of S calculated from equations (1), (2) and (3), in the points α and β (Fig. 2), the following non-linear programming task is formulated. The function L is described as

$$L = \sum [a_{1A}\tau_A + a_{0A} - S_A]^2 + \sum [a_{1B}\tau_B^2 + a_{2B}\tau_B + a_{0B} - S_B]^2 + \\ + \sum [a_{1C}\tau_C^2 + a_{2C}\tau_C + a_{0C} - S_C]^2 \to \min \tag{4}$$

by limitations

$$a_{1A}\tau_\alpha + a_{0A} = a_{1B}\tau_\alpha^2 + a_{2B}\tau_\alpha + a_{0B} \tag{5}$$

$$a_{1B}\tau_\beta^2 + a_{2B}\tau_\beta + a_{0B} = a_{1C}\tau_\beta^2 + a_{2C}\tau_\beta + a_{0C}, \tag{6}$$

where τ_α, τ_β are the values of τ in the points α and β.

The solution of this is obtained by the method of feasible direction [5, 6].

For S_{II} and S_{III} similar models are constructed. To obtain statistical interdependencies between the endothermal effects I, II, III in time, pair correlative analysis was conducted in which the rank correlation coefficient was calculated according to Spearman [7]:

$$\rho_S = 1 - \frac{6\sum_{i=1}^{n} d^2}{n(n^2-1)}, \tag{7}$$

where d = difference between ranks,
n = number of pairs.

The non-parametric method of defining ρ is chosen because the data of the kind of distributive law of the values under study are inaccessible to us.

The results of calculations (Fig. 3) show that only ρ_{II-III} is considerable (at the level 0.95). The values of ρ_{I-II} and ρ_{I-III} are less than the tolerable 0.714 and 0.609, respectively.

The size of ρ_{II-III} gives evidence of the connection between the second and the third effects on the DTA diagram of cement stone. Indeed, the products of the

Table 1

Characteristic indications of DTA diagrams

DTA diagram	Values of S, h and T for effects											
	I				II				III			
	$\bar{S}$, cm²	σ, cm²	$\bar{h}$, mm	$\bar{T}$, °C	$\bar{S}$, cm²	σ, cm²	$\bar{h}$, mm	$\bar{T}$, °C	$\bar{S}$, cm²	σ, cm²	$\bar{h}$, mm	$\bar{T}$, °C
0		—	14; 14	105; 152	—	—	—	—	—	—	5	780
1	4.23	0.10	34; 27	152; 176	—	—	—	—	0.62	0.02	8	804
2	5.12	0.09	23; 16	140; 164	0.13	0.01	5	496	0.83	0.02	7	804
3	5.10	0.12	30	152	0.63	0.01	10	504	1.01	0.02	13	764
4	10.84	0.17	82	164	3.63	0.08	58	552	5.30	0.15	46	840
5	11.13	0.45	84	156	3.78	0.06	56	552	6.82	0.15	41	840
6	11.36	0.25	89	164	5.09	0.01	54	552	6.60	0.16	47	852
7	11.32	0.30	89	162	4.14	0.16	41	540	6.23	0.10	34	824
8	14.22	0.26	78	152	3.98	0.03	39	536	4.41	0.18	34	824
9	17.49	0.47	94	170	3.38	0.09	36	544	2.98	0.03	15	812

hydration reactions of the main cement-building minerals ($3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$) are crystalline $Ca(OH)_2$ and so-called "hydrosilicate gel" of variable composition which constitute up to 80% of the hydrate formations.

These are the formations which define the second and the third effects respectively on the DTA diagrams. Some lessening of S_{II} and S_{III} (Fig. 1, Table 1) gives evidence of the close connection of the crystallochemical transformations taking place in the hardening of calcium silicates with time. The very low values of ρ_{I-II} and ρ_{I-III} confirm the existing opinion that the hydroaluminate and hydrosulfoaluminate formations are completely decomposed by heating up to 200–300° and in spite of low gross composition in the cement stone they make a large contribution to the formation of the first endothermal effect.

To choose the inherent indications for constructing discriminative functions of (8) the main geometrical characteristics of DTA diagrams were analysed. The rank correlative coefficients ρ_{S-h}, ρ_{S-T}, ρ_{T-h} were calculated for effects I, II and III. As some ranks appeared to be interconnected the rank correlative coefficients of Spearman were defined according to

$$\rho_S = \frac{\frac{n^3-n}{6} - (T_x + T_y) - \sum_{i=1}^{n} d^2}{\sqrt{\left(\frac{n^3-n}{6} - 2T_x\right)\left(\frac{n^3-n}{6} - 2T_y\right)}} \qquad (8)$$

at $T = \sum_{r=1}^{k} \frac{t_r^3 - t_r}{12}$,

where k = the number of equal rank groups;
t = the number of elements in an equal rank group;
x,y = indications of inherency of T in one of the groups under comparison.

The results of calculations are given in Fig. 3 (b, c, d). The following values appeared significant: ρ_{S-h} for the first effect, ρ_{T-h} for the third effect; no signifi-

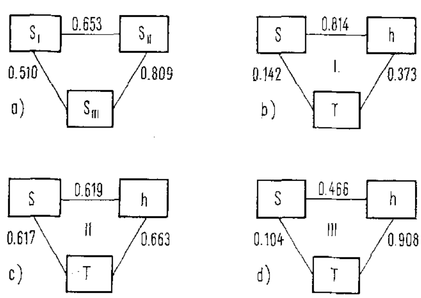

Fig. 3. Graph of correlation connection with thermal effects on the DTA diagrams (a), and geometrical characteristics of the I- (b), II- (c) and III-effects (d)

cant connection was found for the second effect. The importance of the deviation from zero was estimated according to tables [7].

Therefore, all the chosen characteristics of the effects of DTA diagrams are necessary for the estimation of the results obtained, and neglecting any of them may cause the loss of information.

Conclusions

The method of pair rank correlation was used according to Spearman for the statistical evaluation of interconnections between thermal effects of DTA diagrams and their separate elements (area of the effect, its height, peak temperature). A significant connection was found between the second and the third endothermal effect. An analysis of the geometrical characteristics of DTA diagrams showed the absence of reliable connections from one effect to another. To obtain the kinetic dependencies of the hydration process of cement studied by DTA, a method is described of constructing an empirical equation which is a result of the solution of a non-linear programming task.

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RÉSUMÉ — On décrit les résultats de l'analyse statistique des courbes d'ATD. On a trouvé une connexion entre le second et troisième effet endothermiques. L'analyse des caractéristiques géométriques des effets des valeurs *T*, *S* et *h* qui apparaissent sur les courbes d'ATD confirme l'absence de connexions sûres. On a déterminé les coefficients de la corrélation de rang suivant Spearman. On propose un programme non linéaire pour obtenir les dépendances cinétiques du processus d'hydratation du ciment étudié par ATD.

ZUSAMMENFASSUNG — Es wurden die Ergebnisse von statistischen Analysen der DTA Kurven besprochen, und ein Zusammenhang zwischen dem zweiten und dritten endothermischen Effekt gefunden. Durch Untersuchung der geometrischen Kennzeichen der T, S und h Werte der DTA Diagramme konnten keine verläßlichen Zusammenhänge festgestellt werden. Die Koeffizienten der Rangkorrelation wurden nach Spearman bestimmt. Zur Klärung der kinetischen Zusammenhänge der Zementhydratation durch DTA wurde eine nichtlineare Programmaufgabe formuliert.

Резюме — Статья описывает результаты статистического анализа диаграмм ДТА. Найдена связь между вторым и третьим эндотермическими эффектами. Проанализированные геометрические характеристики T, S и h эффектов диаграмм ДТА устанавливают отсутствие существенных связей. Коэффициенты корреляции определены по Спирмену. Для получения кинетических зависимостей процесса гидратации цемента, изучаемого с изпользованием метода ДТА сформулирована задача нелинейного программирования.