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ESTIMATION OF TRICALCIUM SILICATE THROUGH POLYMORPHIC TRANSFORMATION

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Tricalcium silicate characteristically exhibits the most intense reversible transition at a temperature of about 915°. The intensity of this effect can be used to estimate the amount of C_3S in mixtures and to calculate the degree of hydration of C_3S. Low sensitivity for ΔT up to 800° and higher sensitivity between 800° and 1000° enable estimation of both $Ca(OH)_2$ and C_3S. Interference effects at higher temperatures owing to decarbonation, recrystallization to β-wollastonite, and dehydration of the calcium silicate hydrate can be overcome by heating to 1000°, cooling to 800°, and reheating. A determination of the degree of hydration of C_3S obtained at different periods by DTA correlates well with that using the X-ray method.

Portland cement is a complex mixture of several phases. Study of the hydration of individual phases is essential for a basic understanding of the hydration o portland cement itself, and should have an important bearing on resolving the setting phenomenon, dimensional change, strength development, durability of concrete, etc. The silicate phases, tricalcium silicate (C_3S) and dicalcium silicate (C_2S) together, are present in portland cement to a value of 70 to 80%, and in pastes their hydrolyzed products predominate and dictate many of the properties of the concrete.

The progress of hydration of C_3S may be followed by several methods, viz. by estimation of the amount of non-evaporable water or calcium hydroxide, or by estimation of the strength or amount of heat developed. These are indirect methods; they assume that the products of hydrolysis of C_3S have a constant chemical composition throughout the course of hydration. It is known, however, that the calcium silicate hydrate product has a variable composition in terms of CaO/SiO_2 ratio during the course of hydration. A simple and convenient way to follow the rate of hydration of C_3S or C_2S is to determine the amount of silicate hydrated at different times.

In the direct method of following hydration of C_3S, X-ray quantitative analysis is most widely applied [1]. The techniques of differential thermal analysis (DTA), dynamic differential calorimetry, and thermogravimetric analysis have been widely used to estimate the $Ca(OH)_2$ content in hydrating C_3S or C_2S. These are, however, indirect methods of following hydration. In the TG method of estimation of C_3S suggested by Longuet [2], especially in clinkers, the free lime is extracted and the sample is heated in an atmosphere of CO_2 at 880° for 12 hrs. The following reaction takes place: $C_3S + CO_2 \rightarrow CaCO_3 + C_2S$. The TG curve gives losses due to decarbonation and from these the C_3S content is estimated. The values thus obtained approximate those calculated by Bogue's method or by microscopy. The method is somewhat tedious and it is doubtful whether the reaction between C_3S and CO_2 goes to completion. Complications arise when the method is applied to cement pastes.

Tricalcium silicate heated from ambient temperature to about 1000° shows at least four reversible thermal transformations at approximately 585, 915, 975 and 990° [3]. The transformations leading to the development of these peaks are still not resolved, but it is well recognized that the transition at about 915° involves absorption of the maximum amount of heat; in other words, of the endothermal effects, that near 915° has the maximum amplitude (Table 1). The amplitude of this effect can be used to estimate the C_3S content in hydrating C_3S. In fact, heats of transitions of such materials as quartz and potassium sulphate have been used in the calibration of heats of reaction in DTA.

Table 1

Characteristics of the reversible transitions of C_3S

Approximate characteristic temp. of transformation, °C [3]	Nature of the endotherm	ASSIGNMENT			Heat of transformation, Cal/g [8]
		Regourd [5]	Miyabe and Roy [6]	Jeffery [7]	
585 ± 5	broad valley	Triclinic I $\rightleftharpoons$ Triclinic II	$\alpha \rightleftharpoons \beta$ transition	—	—
917 ± 3	sharp and most intense	Triclinic II $\rightleftharpoons$ Triclinic III	Triclinic $\rightleftharpoons$ Monoclinic	Triclinic $\rightleftharpoons$ Monoclinic	1.0
975 ± 3	sharp, less intense	Triclinic III $\rightleftharpoons$ Monoclinic	Monoclinic $\rightleftharpoons$ Trigonal	Monoclinic $\rightleftharpoons$ Trigonal	0.5
990 ± 2	very small peak (detectable only with high resolution DTA) [4]	Monoclinic $\rightleftharpoons$ Orthorhombic	—	—	0.05

Few attempts have been made to use the heat of polymorphic transition of C_3S for estimating it in hydrating systems. One of the reasons is that in the usual hydration experiments low sensitivities are used; otherwise the peak due to $Ca(OH)_2$ will be too intense to be accommodated in the recording paper. Under such conditions the endothermic effects due to transitions in C_3S become too feeble to be detected in the curve. A second reason why the DTA method has not been employed for estimating C_3S is that as hydration progresses the carbonated product, the C–S–H phase, and crystallization of the dehydrated C–S–H all produce effects that tend to interfere or completely mask the endothermic effect due to crystallization transitions in C_3S.

In the present paper a method is proposed for estimating the amount of C_3S during hydration by endothermic transition at about 915°. By way of a typical example C_3S is hydrated for different periods and the degree of hydration determined by DTA technique is compared with that obtained by X-ray quantitative analysis.

Experimental

Materials

The sample of tricalcium silicate used in this work was made available by the Portland Cement Association, U.S.A., and had the following composition expressed as a percentage ignited basis.

Chemical: CaO, 73.88; SiO_2, 26.17; Al_2O_3, 0.08; free CaO (ASTM), 0.18; free CaO (Franke), 0.46. *Mineralogical:* C_3S, 99.33; C_2S, 0.00; C_3A, 0.21; CaO (Franke), 0.46. Fineness: Blaine 3310 cm^2/g.

Hydration of C_3S was carried out by mixing it with double-distilled water at a water : silicate ratio of 0.5. After mixing the solid with water, the paste was transferred to a tightly-covered polyethylene container and rotated continuously for 24 hrs. At intervals of 1, 3, 7, 14 and 28 days each sample was ground and placed in a desiccator, and was continuously evacuated for 24 hrs using liquid air in the trap. Care was taken to prevent contamination with CO_2.

Method

Differential thermal measurements were obtained by the 900-Du Pont thermal analyser. The unit consists of a furnace capable of attaining a temperature of 1200°, platinum cups for housing both sample and reference material, platinum versus platinum-rhodium thermocouples for measuring sample temperature and differential temperature, heating and cooling modes of operation, a variable ΔT sensitivity with 0.004 mV/in. as the upper limit.

In each experiment a constant quantity of the sample passing through a 100-mesh sieve was placed in the platinum cup with a moderate pressure. Ignited α-Al_2O_3 was used as a reference material. DTA curves were obtained at a heating rate of 20°/min. The cold junction was maintained at 0° with crushed ice.

DTA curves are presented with the temperature on the X-axis and the differential temperature as millivolts at a sensitivity of 0.02 or 0.004 mV/in. In calibration experiments the mixture containing a weighed amount of C_3S and α-Al_2O_3

was thoroughly mixed manually with agate and mortar and finally with the Wig-*l*-bug vibrator.

Thermogravimetric analysis of the hydrated calcium silicates was conducted with a Cahn R. H. electrobalance under vacuum at a heating rate of 10°/min.

Results and discussion

Tricalcium silicate exhibits several endothermic effects representing polymorphic transformations, which are reversible. Of these transformations, that occurring at a characteristic temperature of about 915° is not only sharp but also associated with the maximum amount of heat energy. An attempt has therefore been made to estimate C_3S by measuring the intensity of this effect. The reversibility of the two most intense endothermic peaks of C_3S is shown in Fig. 1. In the cooling cycle the peaks reappear but have shifted and are less sharp, with slightly decreased amplitude. The areas enclosed by these exothermic peaks would be of the same magnitude as the endothermic peak areas occurring during the heating cycle.

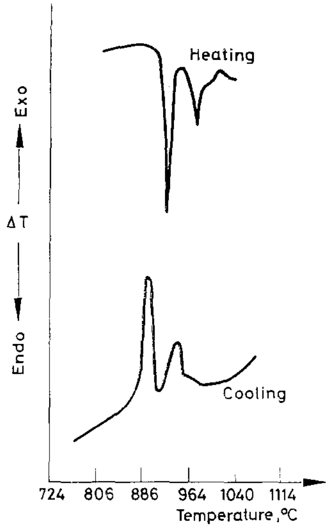

Fig. 1. Reversible endothermic transitions in C_3S

Proper standardization is a prerequisite of any estimation by DTA. This was accomplished by mixing C_3S with different amounts of ignited α-Al_2O_3 to obtain mixtures containing 10 to 80% C_3S. DTA curves of these mixtures and of pure C_3S (ΔT, 0.004 mV/in.) indicate an intense endothermic peak at about 940° for C_3S, decreasing with decrease in C_3S (Fig. 2). As the thermal effect is sufficiently sharp, it was decided that the peak height rather than the thermal peak area would be more direct and accurate for quantitative estimations.

Some endotherms showed a base line shift. In such cases the peak height was obtained as illustrated for 100% C_3S in Fig. 2. Point K, representing the beginning of the endotherm, and point L, at which the curve ends, were joined. A perpen-

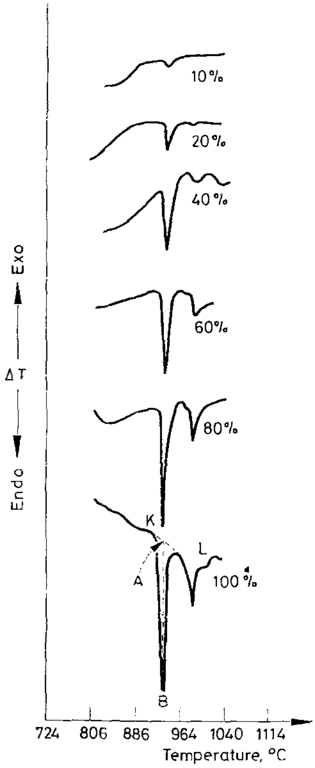

Fig. 2. Variation of endothermic peak amplitude with C_3S content

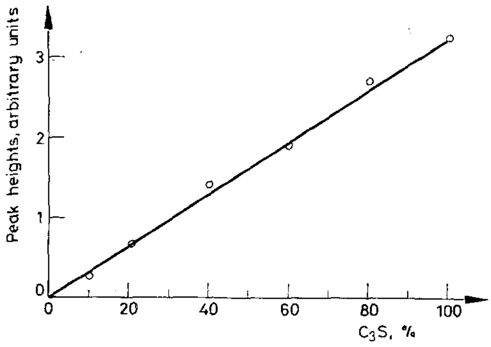

Fig. 3. Plot of peak height versus C_3S content

dicular line (with respect to the temperature axis) was drawn from the apex of the peak (B) to meet the line KL at A. The length AB is designated as peak height or amplitude and was used for calibration purposes.

In Fig. 3 are plotted the peak heights of the endothermic transformation realized for different percentages of C_3S in the (C_3S + Al_2O_3) mixtures. A linear relation is evident. This calibration curve was used to estimate the amounts of unhydrated C_3S in samples of C_3S hydrated for different periods.

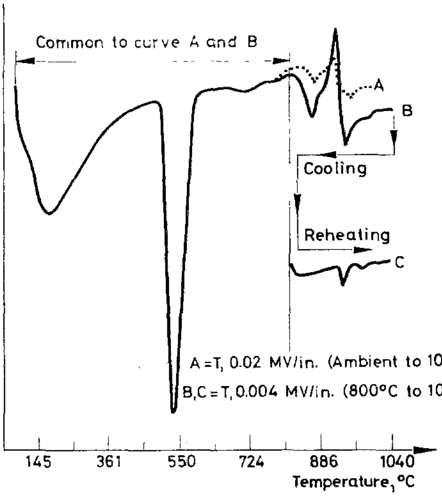

Fig. 4. Elimination of interfering effects in hydrated C_3S

A direct application of this procedure presents certain problems. In most reported work a low sensitivity for ΔT has been used throughout the course of heating to estimate $Ca(OH)_2$ from its endothermic effect [9]. At such a low sensitivity the effects due to C_3S transitions were either not registered at all or were of too low an amplitude. Figure 4 illustrates this aspect more clearly for a hydrated C_3S sample. Curve A refers to a low sensitivity setting wherein a large peak due to $Ca(OH)_2$ is evident. Beyond 900°, however, the endothermic curve for the C_3S transitions is barely registered and is not suitable for a quantitative estimation. A distinct peak due to endothermic transition could be obtained along with a measurable peak for $Ca(OH)_2$ by carrying out DTA at two different sensitivities, i.e., at a low sensitivity up to about 800° and then switching over to a higher sensitivity up to 1000°. By such a simple manipulation curve B results. Curve B refers to a hydrated C_3S with ΔT sensitivity of 0.02 mV/in. up to about 800°, and with 0.004 mV/in. sensitivity beyond this temperature. This curve shows three endothermic and one exothermic effect. The exothermic effect partly interferes with endothermic transition in C_3S; this may become more pronounced at longer periods of hydration.

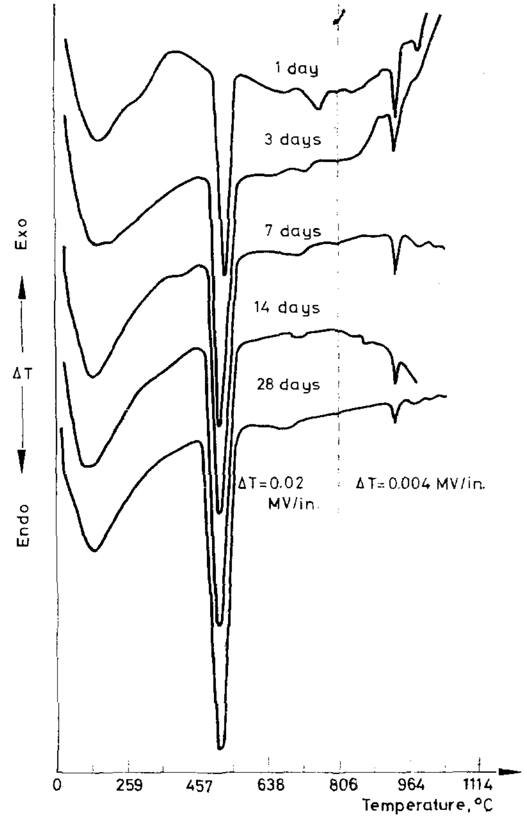

Fig. 5. DTA curves of C_3S hydrated for different periods

The interfering effects may be due to decarbonation, crystallization of β-Wollastonite and the dehydration effect of calcium silicate hydrate. A method was discovered to annul these interfering effects. As already described the material was heated to a temperature of about 800° at a low sensitivity, heated to 1000° at a higher sensitivity, cooled to 800°, and reheated to a temperature of 1000°, as shown below.

$$\begin{array}{c}\text{Hydrated } C_3S\\ \text{(Ambient temperature)}\end{array} \xrightarrow[\text{Ca(OH)}_2\text{ peak}]{\text{Heat } (\Delta T = 0.02 \text{ mV/in.})} 800^\circ \xrightarrow[\begin{array}{c}\text{Endothermic}\\ C_3S \text{ transitions} +\\ \text{interfering effects}\end{array}]{\text{Heat } (\Delta T = 0.004 \text{ mV/in.})} 1000^\circ$$

$$800^\circ \xleftarrow[\text{Exothermic (reversible) } C_3S \text{ transitions}]{\text{Cool } (\Delta T = 0.004 \text{ mV/in.})}$$

$$\xrightarrow[\begin{array}{c}\text{Endothermic } C_3S \text{ transitions minus}\\ \text{interfering effects}\end{array}]{\text{Heat } (\Delta T = 0.004 \text{ mV/in.})} 1000^\circ$$

Under such a heating schedule the interfering effects can be overcome because they are not reversible. In Fig. 4 curve C represents a curve free of interference effects.

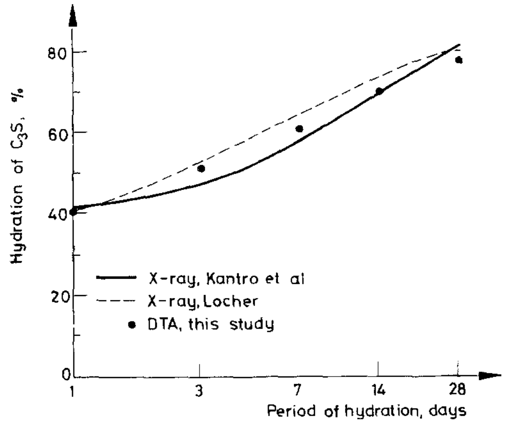

Fig. 6. Comparison of rate of hydration of C_3S by DTA and X-ray methods

This method was used to determine the amounts of unhydrated C_3S remaining in C_3S hydrated for different periods (Fig. 5). In curves for 14 and 28 days of hydration the interference effects have been eliminated by the reheating method. Duplicate determinations of the heights of the peaks attested to its reliability. The degree of hydration of C_3S could then be calculated, on ignited basis, by obtaining ignition loss values through thermogravimetric analysis.

The percentage of C_3S hydrated at different periods, determined by DTA, are plotted in Fig. 6. A comparison is made by extrapolating the results obtained through quantitative X-ray analysis by Kantro et al. [10] and Locher [11]. Considering the possible variability in the starting material, hydration procedure and determination, the correlation between DTA and X-ray determinations is very good.

Conclusions

By adopting a calibration standard, a high sensitivity and manipulation of the heating schedule DTA may advantageously be applied to estimate amounts of C_3S and $Ca(OH)_2$. This method should be particularly applicable to a determination of the rate of hydration of C_3S or portland cement in the presence of admixtures and additives. The method can be extended to the estimation of β-C_2S, which also exhibits reversible transitions. Caution should be exercised if the polymorphic transition in C_3S is affected by the presence of another component.

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Résumé — Le silicate tricalcique montre une transition réversible, intense et caractéristique à 915° environ. On peut utiliser l'intensité de cet effet pour estimer la teneur en C_3S des mélanges et pour calculer le taux d'hydratation. La sensibilité du signal ΔT, faible jusqu'à 800° et plus élevée entre 800 et 1000° permet d'estimer à la fois $Ca(OH)_2$ et C_3S. Les effets d'interférence aux températures élevées dus à la décarbonatation, à la recristallisation en β-wollastonite, et à la déshydratation du silicate calcium hydraté peuvent être évités par chauffage à 1000°, refroidissement à 800° et nouvel échauffement. La détermination du taux d'hydratation de C_3S par ATD recoupe bien les résultats de l'étude aux rayons X.

Zusammenfassung — Trikalziumsilikat zeigt einen charakteristischen Übergang bei einer Temperatur von ungefähr 915°. Die Intensität dieses Effektes kann zur Bestimmung der Mengen von C_3S in Gemischen und zur Errechnung seines Hydratationsgrades herangezogen werden. Die niedrige Empfindlichkeit für ΔT bis 800° und die höhere zwischen 800—1000° ermöglicht die Bestimmung von $Ca(OH)_2$ und C_3S. Interferenzeffekte bei höherer Temperatur, verursacht durch Entkohlung, Rekristallisation von β-Wollastonit und Dehydratation von Kalziumsilikathydrat, können durch Glühen auf 1000°, Abkühlen auf 800° und erneutes Glühen behoben werden. Die durch DTA erhaltenen Hydratationswerte von C_3S stimmten gut mit den röntgenographisch erhaltenen Ergebnissen überein.

Резюме — Для трикальцийсиликата характерно проявление наиболее интенсивного превращения при температуре около 915°. Интенсивность этого эффекта может быть использована для оценки количества C_3S в смеси и расчета степени гидратации C_3S. Низкая чувствительность ΔT до 800° и более высокая чувствительность между 800 и 1000° дают возможность оценить как $Ca(OH)_2$, так и C_3S. Эффекты, мешающие при более высоких температурах и обусловленные декарбонизацией, рекристаллизацией до β-волластонита и дегидратацией гидрата силиката кальция, могут быть преодолены путем нагревания до 1000°, охлаждения до 800° и повторного нагревания. Степень гидратации C_3S, определяемая при различных периодах методом ДТА, хорошо коррелируется с данными, полученными при использовании метода рентгеноструктурного анализа.