

EVALUATION OF THE DEGREE OF HYDRATION  
OF TRICALCIUM SILICATE PASTES BY QUANTITATIVE  
DIFFERENTIAL THERMAL ANALYSIS\*

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The hydration kinetics of  $C_3S$  pastes can be easily evaluated by DTA using the most intense and reversible transition of  $C_3S$ . Some modifications are proposed to Ramachandran's method concerning the measurement of this effect, the weight of the sample used for each experiment and the heating rate. The results of the hydration degree versus times of  $C_3S$  agree reasonably with those reported by Ramachandran, while still better agreement is observed with those of Locher who used X-ray quantitative analysis.

The evaluation of the hydration kinetics of Portland cement constituents has been widely investigated in recent years. For tricalcium silicate, a few methods have been proposed. X-ray quantitative analysis [1] is the one most used. This method, which directly determines the amount of unreacted  $C_3S$ \*\* at different hydration times, has been criticized because of its inaccuracy, due mainly to the envelopment of unreacted particles by the hydrates. These vary their composition and crystallinity during the hydration process and render the X-ray analysis inaccurate. It may be pointed out that the numerous data reported in the literature are not comparable since the reactivity of  $C_3S$  is affected by several factors; in fact, even if the same conditions (water/solid ratio, temperature, etc.) are adopted it is difficult for different investigators to study different samples with the same characteristics.

Ramachandran [2] has proposed the estimation of the hydration of  $C_3S$  through polymorphic transformation, using the most intense and reversible transition of  $C_3S$ . During heating from room temperature to  $1000^\circ$ , four thermal effects, related to polymorphic transformations of  $C_3S$ , are observed [3]. The transition enthalpies are minute, the polymorphic forms being very similar [4]. The most intense peak, at  $\approx 925^\circ$ , exhibits a transition enthalpy of  $\approx 1$  cal/g; this amplitude can be used to estimate the anhydrous  $C_3S$  during the hydration process. The effects due to decarbonation, dehydration of the calcium silicate hydrate and recrystallization of  $\beta$ -wollastonite may interfere with the signal at  $925^\circ$ .

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\*\* The following abbreviated formulae are used: C = CaO; S = SiO<sub>2</sub>.

In this note some modifications are proposed to Ramachandran's method. They concern the measurement of the effects, the weight of the sample used for each experiment and the heating rate.

### Experimental

The chemical analysis of the sample is reported in Table 1.

Table 1

CaO (total)	73.80%
CaO (free)	0.28
SiO <sub>2</sub>	26.25
MgO	0.10

The fineness (Blaine) was 5050 cm<sup>2</sup>/g.

When this sample was mixed with water for a few minutes, in the ratio water/solid = 0.5, a disc-shaped paste was obtained. It was aged in a humid environment (R. H. = 100%) at 25°. At different times a portion of paste was ground with acetone and desiccated in vacuum for 15 hours.

The powder passing through a 150 mesh sieve was submitted to DTA, using the 900-Du Pont thermal analyzer; the reference material was ignited  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The heating and cooling cycles were performed at a rate of 30°/min, using a  $\Delta T$  sensitivity of 0.004 mV/in. A first cycle of heating at 1000° permitted elimination of the interference effects; after a cooling at  $\approx$ 700°, followed by new heating at 1000°, the peak area at 925°, due to the active fraction of C<sub>3</sub>S, was estimated.

The calibration curve for the C<sub>3</sub>S content was obtained by estimating the peak areas of C<sub>3</sub>S diluted with different amounts of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

A part of each differently-hydrated sample was submitted to TG at a heating rate of 13°/min, using a Stanton Massflow. In turn another part, weighed on the TG base, was submitted to DTA. The weights adopted in each experiment were related to the time of hydration of the sample by the formula:  $m = \frac{m_0}{1-l}$ , where  $m$  represents the weight of the differently-hydrated fraction sample,  $m_0$  the corresponding starting C<sub>3</sub>S, and  $l$  the loss of weight relative to unit weight of the hydrated samples. Thus,  $m$  increases with the hydration time as the  $l$  value increases.

### Results

Fig. 1 illustrates DTA diagrams obtained on heating of anhydrous C<sub>3</sub>S of weight  $m_0$ . Two endothermic and reversible peaks appear, of which the one at 925° has been studied. In the first heating this effect is less sharp than the corresponding peak in the second heating. This originates from the different slopes of the base

lines for the same sample in the two heating cycles (Fig. 1); nevertheless, the corresponding areas are equal. Therefore, in all the experiments the peak areas rather than the peak heights were measured [2].

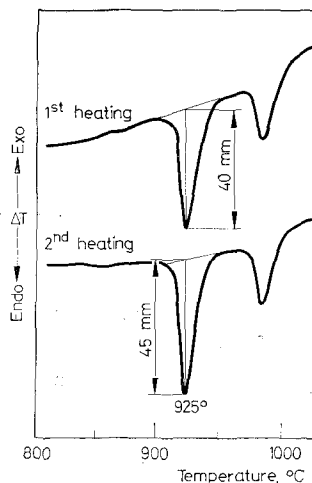


Fig. 1. Variation of peak height in the two heating cycles for anhydrous  $C_3S$

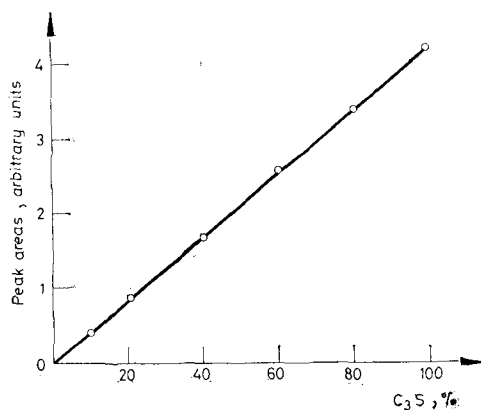


Fig. 2. Plot of peak area versus  $C_3S$  content

Since the peak at  $925^\circ$  is too far away to coalesce with the subsequent smaller peak (Fig. 1), a fast heating rate was used ( $30^\circ/\text{min}$ ) in order to obtain larger and broader peaks. This was also possible because of the high speed of the polymorphic transformation at the above-mentioned temperature.

In Fig. 2 are plotted the peak areas of the active fraction versus  $C_3S$  content,

derived from weights  $m_0$  of different percentages of  $C_3S$  in  $\alpha-Al_2O_3$  mixtures. The peak areas at  $925^\circ$  increase with  $C_3S$  content according to a linear relation.

The adoption of a variable weight,  $m$ , in experiments relating to differently-hydrated samples, depends on their different losses of weight due to the different hydration times before the signal at  $925^\circ$ . On the basis of TG, it was possible to have the same weight  $m_0$  for all the samples, in correspondence with this signal.

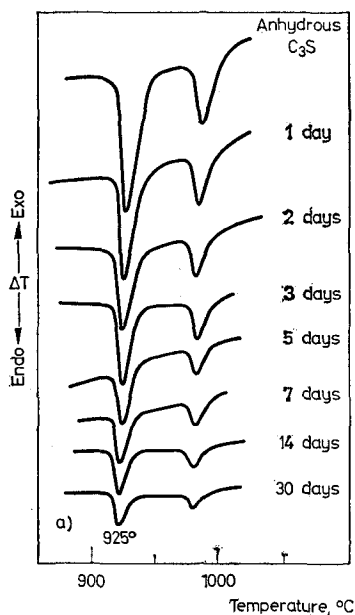


Fig. 3a. Endothermic transitions of anhydrous and hydrated  $C_3S$  for different periods

Measurement of the peak area on the second heating cycle was necessary to eliminate the above-mentioned interference phenomena. By comparing the corresponding areas of the peak at  $925^\circ$  in the first and second heating cycles, we note that the two areas are equal for samples hydrated for a short time, that is when the interference phenomena are small. This was a positive result, because it excludes secondary effects related with the heating and cooling cycles.

In Fig. 3a are reported the DTA curves of the anhydrous samples and those hydrated for 1, 2, 3, 5, 7, 14 and 30 days. The hydration degrees were determined first from the ratios between the peak areas of samples hydrated for the above times and the corresponding areas for anhydrous  $C_3S$ . They were compared with those obtained directly from the calibration curve in Fig. 2. Plotting of the data gave the curve in Fig. 3b. It can be pointed out that the degree of hydration of the examined  $C_3S$  after a short period (1 day) has a value near to 35%; after 7 days a value of 71%; and after a long period (30 days) a value slightly above

80%. In the interval 1–7 days a quite linear relation can be observed between the hydration degree and time, while in the range 7–30 days the hydration degree increases slightly up to 80%.

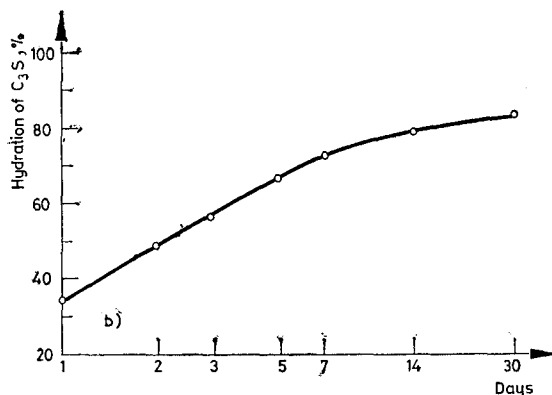


Fig. 3b. Hydration rate of C<sub>3</sub>S as measured by DTA

The degrees of hydration of the examined sample can not be compared with those from the literature because it is difficult for different investigators to have C<sub>3</sub>S samples with the same composition, distribution size, specific surface, thermal history, etc. It is better to compare the behaviour of the hydration degree versus time.

In this case the results agree reasonably with those reported by Ramachandran [2], while better agreement is observed with those of Locher [6], who used X-ray quantitative analysis.

It would be interesting for different investigators to examine a C<sub>3</sub>S sample with the same characteristics in order to make a reliable comparison of the different methods.

### References

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ZUSAMMENFASSUNG — Die Hydratisierungskinetik von  $C_3S$  Pasten kann mittels DTA leicht bewertet werden, falls der intensivste und am meisten reversible Übergang von  $C_3S$  genutzt wird. Einige Änderungen zur Methode von Ramachandran bezüglich der Messung dieses Effekts, des Gewichts der bei den einzelnen Messungen eingesetzten Proben und der Aufheizgeschwindigkeit werden vorgeschlagen. Die Ergebnisse des Hydratisierungsgrades von  $C_3S$  in Abhängigkeit von der Zeit sind in guter Übereinstimmung mit denen von Ramachandran, während eine noch bessere Übereinstimmung mit den Werten von Locher beobachtet werden kann, welcher sich jedoch der quantitativen Röntgenanalyse bediente.

Résumé — La cinétique de l'hydratation des pâtes de  $C_3S$  peut être facilement déterminée par ATD, en utilisant la transition de  $C_3S$  la plus intense, qui est réversible.

On propose des modifications à la méthode de Ramachandran, concernant la mesure du phénomène, le poids des échantillons utilisés pour chaque expérience et le choix de la vitesse de chauffage. Les résultats donnant le degré d'hydratation de  $C_3S$  en fonction du temps sont en bonne concordance avec ceux publiés par Ramachandran tandis qu'une concordance encore meilleure est observée avec les résultats de Locher obtenus par analyse quantitative aux rayons X.

Резюме — Кинетика гидратации  $C_3S$  паст может быть легко определена при помощи ДТА используя наиболее интенсивный и обратимый переход в  $C_3S$ . Предложены некоторые изменения метода Рамачандрана, относящиеся к измерению этого эффекта: вес образца, используемого в каждом эксперименте и скорость нагрева. Зависимость степени гидратации от времени хорошо согласуется с тем, что было сообщено Рамачандраном, но лучшее согласие наблюдается с данными Лохера, который использовал количественный рентгеновский анализ.