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THERMOANALYTICAL STUDIES ON HYDRATED TRICALCIUM SILICATE

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ABSTRACT

The thermal decomposition of the hydration products of tricalcium silicate has been studied by TG, DTG and DTA. The thermal decomposition characteristics of the CSH-phase formed changed, as the hydration progressed. The heat requirement for thermal decomposition of the calcium hydroxide formed in the hydration process was lower than the one of a pure crystalline material.

INTRODUCTION

In the hydration of tricalcium silicate (Ca_3SiO_5, abbr. C_3S), the main component of portland cement, an ill crystallized calcium silicate hydrate phase, the CSH-phase, and calcium hydroxide are formed. The structure, and stoichiometric composition of the CSH-phase are not exactly defined and may vary depending on the conditions of hydration. The thermal decomposition of this phase and loss of water take place contineously, in a wide temperature range, rather then at a defined temperature. As to the calcium hydroxide formed in C_3S hydration, it is known, that it contains significant amounts of silica and may be formed partially in an amorphous, non crystalline, form. It decomposes to calcium oxide and water, in a narrow temperature range at a temperature of about 450 °C. Within the work reported, the thermal decomposition of the two hydration products of C_3S was studied. In the case of the CSH-phase it was investigated, whether the thermal decomposition characteristics of this material differ at different degrees of hydration. In the case of the calcium hydroxide it was studied, whether the thermal decomposition characteristics of calcium hydroxide formed in C_3S hydration differ from those of a pure crystalline material.

EXPERIMENTAL

Pure C_3S ground to a specific surface area of 3000 cm^2/g (Blaine) was mixed with water (water-solid ratio = 0.7) and was allowed to hydrate at 20 °C for different periods of time. To prevent carbonization from air the pastes were kept sealed in small polyethylene bags. To stop hydration and to remove excessive water the pastes were dried by the D-drying method (ref. 1) to a constant weight.

After free water removal the thermal decomposition of the pastes was studied by a Netzsch modell STA 429 apparatus (heating up rate 5 °C/min, N_2 atmosphere). The construction of the apparatus allowed a simultaneous determination of TG, DTG and DTA curves on a single sample. To determine the amount of C_3S used up by hydration the non reacted fraction was determined by quantitative XRD using quarz as internal standard. In a separate series of tests pure crystalline calcium hydroxide (BET_{N_2} = 7.8 m^2/g) added in different amounts to preburned clay as inert material was studied and the results obtained were compared with those found with calcium hydroxide formed in C_3S hydration.

RESULTS

In Fig. 1 typical TG, DTG and DTA curves of a D-dried hydrated C_3S paste are

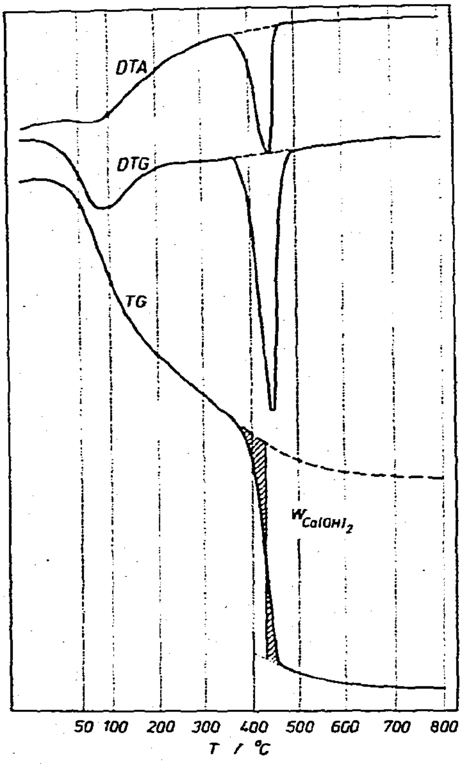

Fig. 1. Typical TG, DTG and DTA curves of a hydrated tricalcium silicate paste.

shown . The dashed lines refer to the same material after removal of calcium hydroxide by extraction with a solvent containing acetate ethyl ester and isopropanol (3 : 20). As it can be seen, in the temperature range 300 - 500 °C calcium hydroxide and the CSH-phase are decomposed simultaneously, while at temperatures below and above, just the CSH-phase alone is decomposed. Thus to obtain the amount of combined water belonging to the CSH-phase liberated in the temperature range 300 - 500 °C, the amount belonging to calcium hydroxide ($W_{Ca(OH)_2}$ in Fig. 1) has to be substracted from the total weight loss.

In Fig. 2 the fractions of the total water combined in the CSH-phase, liberated at three different temperature ranges are shown. As it can be seen, the temperature decomposition characteristics of the CSH-phase formed became altered as the hydration of tricalcium silicate progressed. Up to a hydration time of 4 hours the whole fraction of water bound within the CSH-phase was liberated at temperatures above 500 °C. On the other hand in older pastes the predominant part of the combined water escaped already at temperatures below 300 °C.

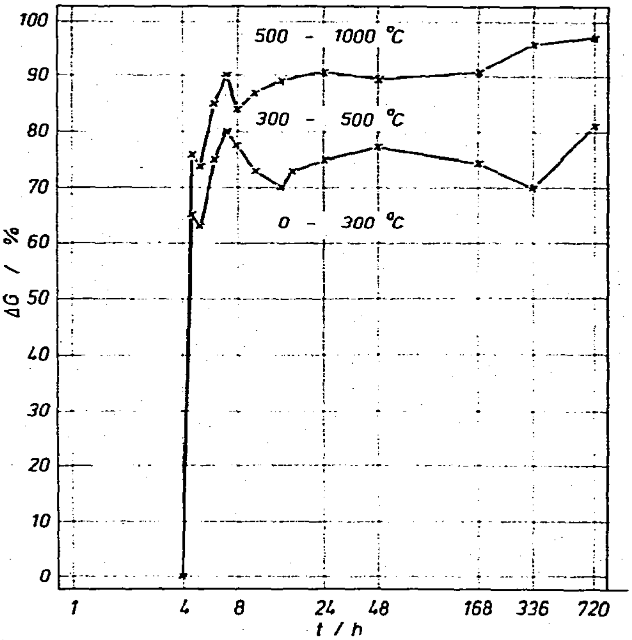

Fig. 2. Fractions of water bound within the CSH-phase liberated at temperatures below 300 °C, between 300 and 500 °C and above 500 °C, as function of hydration time.

The calcium hydroxide, unlike the CSH-phase, could be determined in the pastes, in addition to TG, also by DTG and DTA. In both cases the amount of calcium hydroxide was determined by planimetration of the peak belonging to this compound. (The CSH-phase present did not interfere with the determination,as it just lowered somewhat the baseline of the curve, but did not affect the intensity of the peak).

In Fig. 3 the DTA peak area (relative values) against the weight loss belonging to calcium hydroxide (mg/g), determined from the TG curve, is plotted. The two separate lines belong to calcium hydroxide present in the hydrated tricalcium silicate paste and to a pure crystalline material. As it can be seen in both cases, as expected, a linear plot crossing the origin point was obtained. However, the two plots were characterized by different slopes, whereby the found difference was statistically highly significant. As it can be seen from Fig. 4, similar results were found when the DTA peak areas (relative values) were plotted against the ones found by DTG. These findings imply that the heat requirement for the decomposition of calcium hydroxide formed in C_3S hydration lied below the one of a pure crystalline material.

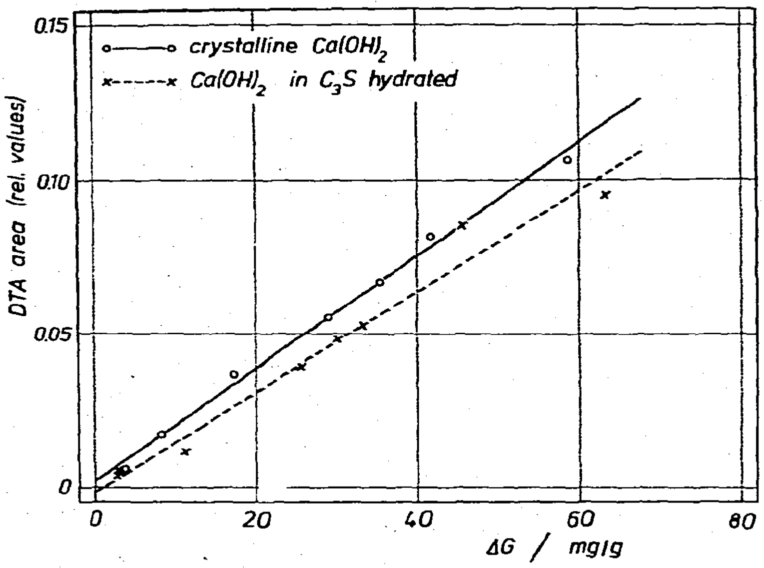

Fig. 3. Area of the DTA peak as function of the weight loss found in the thermal decomposition of pure crystalline calcium hydroxide, and calcium hydroxide formed in C_3S hydration

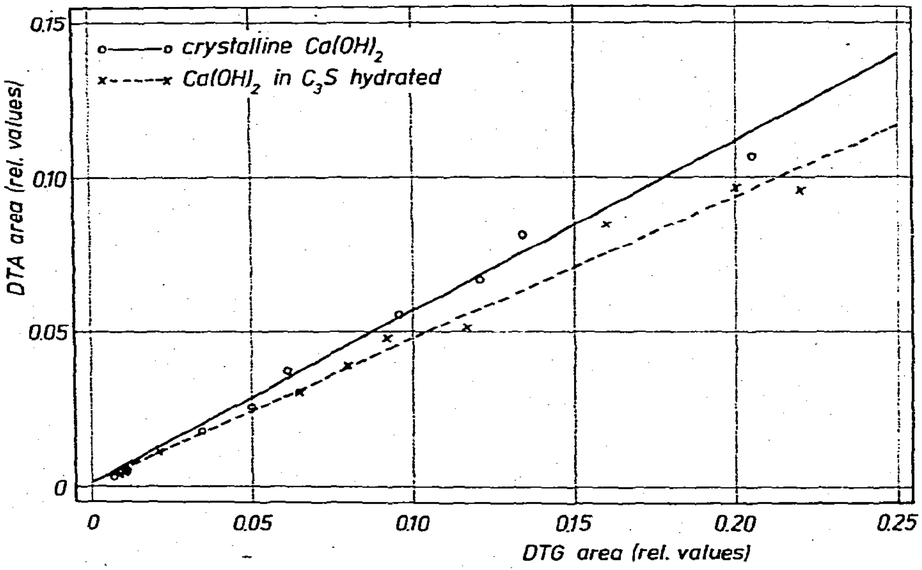

Fig. 4. Area of the DTA peak as function of the area of the DTG peak found in the thermal decomposition of pure calcium hydroxide and calcium hydroxide formed in C_3S hydration.

DISCUSSION

The results obtained revealed changes in the thermal decomposition properties of the CSH-phase formed in C_3S hydration related to the progress of hydration. The CSH-phase formed at the very beginning of the hydration process, i.e. within the first four hours, exhibited diametrically different thermal decomposition properties than the one formed later on. Thus it appears that two qualitatively different hydration products are formed in the course of tricalcium silicate paste hydration. The time at which the formation of the "first" hydrate is succeeded by the formation of the "second" hydrate coincides with the end of the "induction period" i.e. a period in which after an initial fast hydration, no noticeable other hydration takes place for several hours.

The lowered heat requirement found in the thermal decomposition of calcium hydroxide formed in C_3S hydration indicates a difference in the thermodynamical state of this phase, as compared to a pure crystalline material. We believe that, due to the presence of crystal lattice defects, the free enthalpy content of the calcium hydroxide formed in C_3S hydration was higher and thus the thermal decomposition heat requirement lower than that of the pure crystalline material. In line with this assumption is the observation that the calcium hydroxide formed in C_3S hydration is only partially detectable by XRD, due to its poor crystallinity.

CONCLUSIONS

In the paste hydration of tricalcium silicate at room temperature two different CSH-phases are formed which differ in their thermal decomposition characteristics. The CSH-phase formed at the beginning of the hydration process decomposes thermally at relatively high temperatures, i.e. above 500 ^{o}C. On the other hand the CSH-phase formed in the later course of hydration, i.e. after the induction period, looses the greatest part of its combined water already at temperatures below 300 ^{o}C. The thermal decomposition characteristics of the latter products as well as its total water content remain constant when the C_3S hydration progresses.

As to the calcium hydroxide formed in C_3S hydration, there are indications, that the thermodynamic properties of this phase (free enthalpy content) are somewhat different of those of a pure crystalline material.

ACKNOWLEDGEMENTS

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REFERENCES

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