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THE TRICALCIUM SILICATE HYDRATION - - CALCIUM HYDROXIDE DETERMINATION

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ABSTRACT

The DTA and TG techniques have been utilised to investigate the calcium hydroxide crystallisation in the pastes composed of the tricalcium silicate, silica and water. The results show, that SiO_2 can accelerate $Ca/OH/_2$ crystallisation.

INTRODUCTION

The tricalcium silicate $/Ca_3SiO_5/$ is the main constituent of portland cement and during the reaction with water it forms the calcium hydroxide and so-called calcium silicate hydrated phase of varying composition and poorly crystallized /1/. In the presence of certain admixtures introduced to the hydrating paste the hydration products formation process can be altered considerably. Taking into account the data concerning the "poisoning" of calcium hydroxide nuclei by silicate ions in the liquid phase /2/ as well as the results obtained in the previous work /3/, the problem was thought to be elaborated and clarified. In order to resolve this problem the series of suspensions produced in Ca_3SiO_5 hydration process have been investigated. The DTA and TG measurements were carried out to determine the calcium hydroxide content. The chemical analysis of liquid phase coexisting with the hydrating material were made to establish the factors influencing the amount of $Ca/OH/_2$ crystallized from the solution as a function of hydration time and temperature as well as the admixture content. The amount of unhydrated Ca_3SiO_5 /so-called hydration degree/was also determined in the samples, after liquid phase filtration, using the quantitative X-Ray diffraction.

EXPERIMENTAL

The tricalcium silicate has been synthesized from the $CaCO_3$ and silica-gel pre-calcined mixture at 1550°C and then ground to the specific surface of 3000 cm^2/g. SiO_2 - "Aerosil"/Degussa/ has been used as an admixture. The series of mixtures containing Ca_3SiO_5 with 0.1; 0.5; 1; 2; 5; 10% SiO_2 has been prepared. The suspensions with

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water to Ca_3SiO_5 ratio equal to 10 were shaken in poliethylene containers using shaking apparatus. After the time in the range from 5' to 24hrs the suspensions were filtered through the miliporous G4 filter and the precipitates were washed with acetone and ether to stop the hydration process. The DTA and TG measurements were carried out using the Mettler thermoanalytical equipment to determine $Ca/OH/_2$ content in the samples as a function of time and admixture content. The unhydrated Ca_3SiO_5 determinations were made using Philips diffractometer. The Ca^{2+} ions concentration in the liquid phase was determined by EDTA solution.

RESULTS

The DTA curves of the samples are shown in FIG.1, the results of $/CaOH/_2$ determination - in TABLE 1.

TABLE 1

Calcium hydroxide content in the pastes $Ca_3SiO_5 + SiO_2$.

Sample	$Ca/OH/_2$ content after hydration time /g/		
	3hrs	7hrs	24hrs
C_3S^x	1.2	2.4	10.0
C_3S+0.1S	1.2	3.2	10.4
C_3S+0.5S	1.6	2.8	11.2
C_3S+ 1S	2.4	5.6	12.4
C_3S+ 5S	2.4	6.4	12.8
C_3S+ 10S	4.0	7.6	16.8

x - C=CaO, S=SiO_2

As it can be seen in FIG.1, the shape and the surface of peaks corresponding to the hydration products change in relation to the hydration time and SiO_2 content. With the increasing SiO_2 content in the samples, the $Ca/OH/_2$ increase as well as the calcium silicate hydrated phase content increase can be easily observed. It can be noticed also, that the "amorphous" $Ca/OH/_2$ transforms into the more ordered phase of higher decomposition temperature. The series of measurements for 7hrs hydrating samples illustrates the co-existence of both $Ca/OH/_2$ forms and the predominance of more ordered $Ca/OH/_2$ form in the samples containing more than 1%SiO_2. During the 3hrs hydration the co-existence of these two forms is not detected

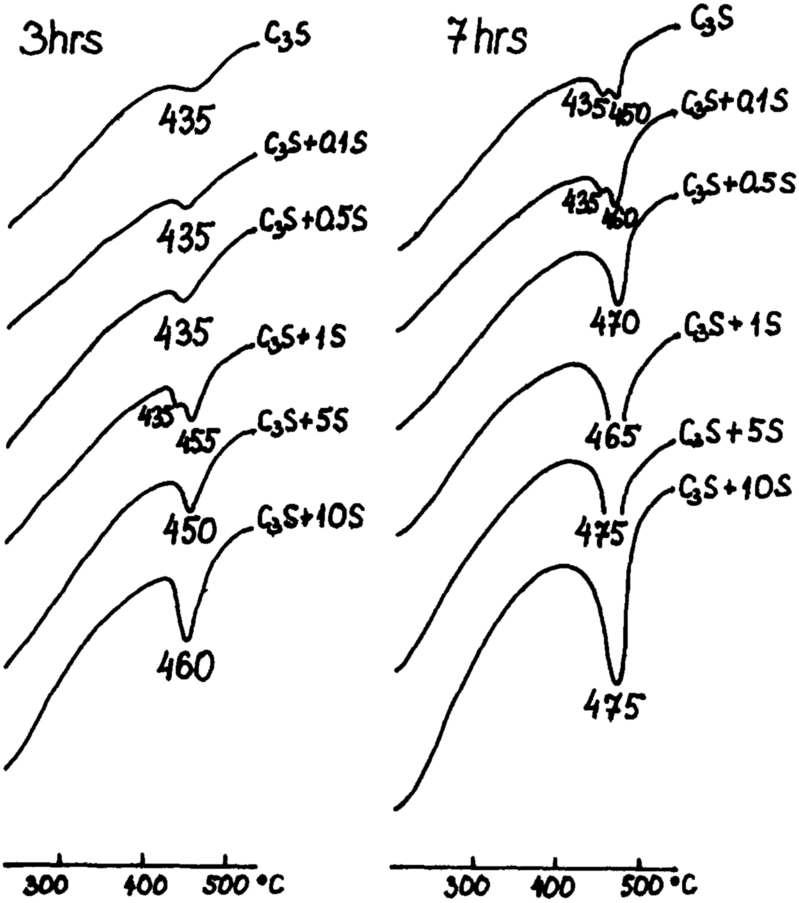

FIGURE 1

DTA curves of Ca_3SiO_5 samples hydrated 3hrs and 7hrs.

but only the shift of the peak maxima towards the higher temperature in the "disordered" form decomposition temperature area can be observed. After 24hrs hydration all the samples reveal only the ordered $Ca/OH/_2$ phase and the differences in $Ca/OH/_2$ amount, significant in the initial stage of reaction, relatively decrease.

The liquid phase analysis indicate, that for the Ca_3SiO_5 sample the

Ca^{2+} ions liberation into the solution occurs typically, with the maximum after ~7hrs, corresponding to the considerable supersaturation in relation to $Ca/OH/_2$. The concentration of Ca^{2+} ions proceeds similarly for the samples with 0.1%SiO_2 and 0.5%SiO_2 attaining a little higher supersaturation value. In the samples with 1-10% SiO_2 addition the Ca^{2+} concentration in the liquid phase increases faster and its maximum can be observed after ~5hrs.

QXRD measurements prove that the unhydrated Ca_3SiO_5 content decrease depends closely on the increasing SiO_2 content.

CONCLUSIONS

SiO_2 introduced into the hydrating Ca_3SiO_5 suspension accelerates the Ca_3SiO_5 decomposition. SiO_2 combines the Ca^{2+} ions and thus favours the calcium silicate hydrated phase as well as the calcium hydroxide amount increase. $Ca/OH/_2$ crystallizes from the highly supersaturated solution. It seems, that there is no hindering effect of SiO_2 on $Ca/OH/_2$ in the presence of small SiO_2 amount. As it results from the presented data - SiO_2 in the mixture Ca_3SiO_5 - H_2O - SiO_2 can stimulate the $Ca/OH/_2$ nucleation and growth due to the intermediate liquid phase supersaturation with calcium ions. On the other hand it should be completely understood, that when the SiO_2 admixture is high, the calcium silicate hydrated phase forms rapidly and this process prevails over the calcium hydroxide crystallisation /4/.

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