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THE REACTION OF CALCIUM ALUMINATES WITH SOME BASIC SOLUTIONS

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ABSTRACT

The calcium aluminates hydration in water and Na_2CO_3 solutions have been studied using the microcalorimetry, DTA, TG and XRD methods. The composition of the liquid and solid phase products have been thereby established.

INTRODUCTION

The calcium aluminate reactions with water and with different salts solutions are of important role in hardening of several binders, such as portland cement,aluminous cements and slag cements. The investigations of these reactions allow to controll the process in practice and to explain the phenomena accompanying the concrete corrosion. The reaction of aluminates with alkaline solutions occurs also in the leaching of alumina from aluminates in some basic methods of the Al_2O_3 production.

There are five compounds in the system $CaO-Al_2O_3$, which correspond to the following formulae: C_3A, $C_{12}A_7$, CA, CA_2, CA_6 /1-2/. We apply the abbreviations used in the chemistry of cements, where C=CaO, $A=Al_2O_3$, $H=H_2O$, $\bar{C}=CO_2$. C_3A, CA and $C_{12}A_7$ react rapidly with water. The most of authors is of the opinion that these reactions start with the congruent dissolution and then, the metastable hexagonal hydrates precipitate from the supersaturated solution and transform finally to the cubic C_3AH_6 /1-4/.This hydrate is the only thermodynamicaly stable compound in the system $CaO-Al_2O_3-H_2O$. When $C_{12}A_7$ and CA react with water, the aluminium hydroxide forms also as the hydration product. The introducing of $CaSO_4$, Na_2CO_3 and the other salts into the hydrating mixture results in the considerable change of hydration rate and the formation of hydrated double salts containing SO_4^{2-}, CO_3^{2-} and other anions /4-7/.

The aim of the present paper was to investigate the C_3A, $C_{12}A_7$ and CA reactions with Na_2CO_3 solutions in relation to the reactions of these compounds with water. The systems examined are dynamic and they not attin the equilibrium during the observation time. That is the reason, that the calorimetry has been used as a basic investigation method. These results have been supplemented with the liquid phase chemical analysis and solid phase analysis by DTA, TG and XRD methods.

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EXPERIMENTAL

The calcium aluminates rentgenographically pure: C_3A, $C_{12}A_7$ and CA have been used as the initial materials. They were synthesized as a result $CaCO_3$ and $Al/OH/_3$ mixtures sintering process at 1350°C /after the precalcination at 1100°C/ and then ground to the specific surface of $3500 \pm 50 cm^2/g$ /Blaine method/.

The hydration was carrird out in the redistilled water or in the 6% Na_2CO_3 solution with solid to liquid ratio equal to 1:10. The starting temperatures were 65°C and 25°C. The calorimetric measurements were carried out in the polish differential microcalorimeter, which allow to initiate the reaction when the reagents are in thermal equilibrium. The sample, which is outgassed and sealed in special glass container, can be wetted immediately with water when the containeris crushed. The results thus obtained are presented in figure 1. The liquid phase analysis was carried out using 0.05m EDTA solution. The phase composition analysis of materials hydrated in water correlates well with the data obtained by chemical method and reveals, that the hexagonal hydrated aluminates form as an initial products. The CaO to Al_2O_3 ratio in these hydrates depends on the CaO to Al_2O_3 in the unhydrous aluminate. Namely, after 1 hour hydration in the CA hydration products the CAH_{10} is the predominant phase. In the $C_{12}A_7$ hydrating suspension - C_2AH_8 with small amount of C_4AH_{13} and the aluminium hydroxide. In the tricalcium aluminate hydration products - C_4AH_{13} and C_3AH_6 can be detected. After the 24 hours hydration the metastable products transform into the stable C_3AH_6 phase as it can be seen from the DTA and TG mrasurements. When CA and $C_{12}A_7$ react with water, the metastable C_2AH_8 and C_4AH_{13} do not transform to the C_3AH_6. When the hydration occurs at 65°C - C_3AH_6 appears as the primary product.

Na_2CO_3 introduced to the investigated system alters the hydration products phase composition radically. After 1 hour hydration of C_3A and $C_{12}A_7$ only the calcium carbonate and carbonated calcium aluminate hydrate - - $C_3A \cdot C\bar{C} \cdot H_{12}$ can be detected. In the case of CA the process results in the formation of calcium carbonate and CAH_{10}. Later, the aluminium hydroxide is also present in the reaction products.

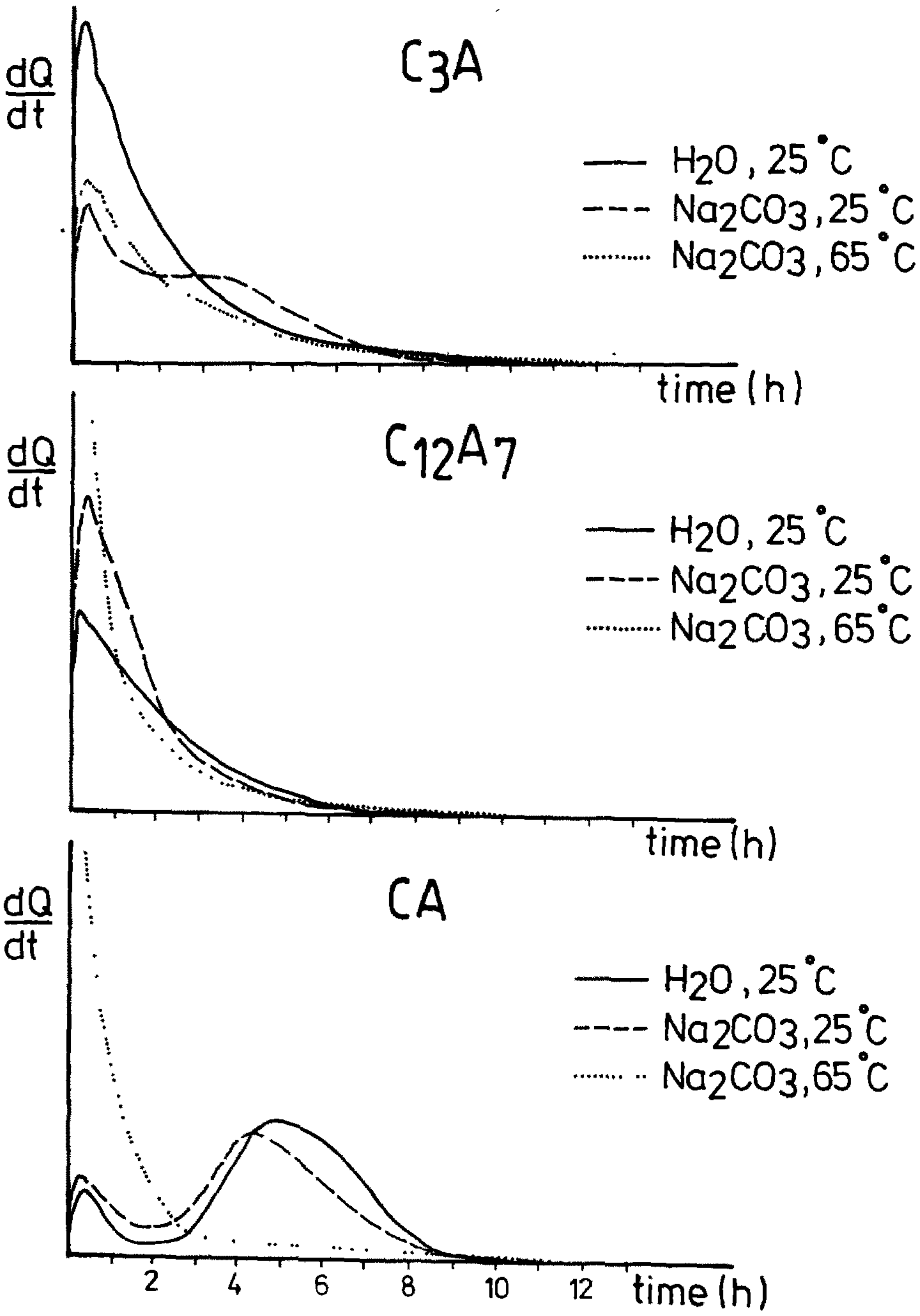

FIG 1. Heat evolution curves for C_3A, $C_{12}A_7$ and CA.

DISCUSSION

The change in the reaction medium as a result of Na_2CO_3 addition brings on the substantial alterations concerning to the calcium aluminate decomposition rate as well as the phase composition of the reaction prodocts and the ions concentrations in the liquid phase. The temperature also influences strongly the course of the reactions mentioned above. The reaction progress as a function of temperature and Na_2CO_3 admixture is clearly visible form the microcalorimetric curves for all the compounds examined.

C_3A reacts rapidly with water. Na_2CO_3 seems to retard the C_3A decoposition - the induction period appears probably as a result of the hydration products impermeable layer surrounding the C_3A grain. When the temperature increases, C_3A reacts quickly with Na_2CO_3 solution. The microcalorimetric curves of $C_{12}A_7$ samples do not reveal any dormant period - the reactions proceed quicly in water as well as in the Na_2CO_3 solution. The tigh Al_2O_3 content in the system $C_{12}A_7-H_2O-Na_2CO_3$ should be underlined. The reactions in the system $CA-H_2O-Na_2CO_3$ are relatively slower. The influence of increasing temperature is practicularly strongly expressed - the effect on microcalorimetric curve is the highest among the effects observed in the present work. This result correlates well with the Al_2O_3 determination and phase analysis data indicating, that the CAH_{10} delayed nucleation barrier disappears with the increasing temperature.

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