Journal of Thermal Analysis, Vol. 29 (1984) 1005—1008

STUDIES ON THE HYDRATION OF CALCIUM ALUMINATES

M. Gawlicki, W. Nocuń-Wczelik and *M. Pyzalski*

INSTITUTE OF BUILDING AND REFRACTORY MATERIALS, UNIVERSITY OF MINING AND METALLURGY, CRACOW, POLAND

The hydration reactions of calcium aluminate in water and in Na_2CO_3 solution have been investigated using calorimetric, DTA, DTG and XRD methods.

The calcium aluminates, which are of special importance in the setting and hardening of several binders, occur in the system $CaO-Al_2O_3$. Their chemical formulae correspond to C_3A, $C_{12}A_7$, CA, CA_2 and CA_6, respectively [1], where C means CaO and A means Al_2O_3, as commonly used in the chemistry of cement. Three of these salts, tricalcium aluminate C_3A, monocalcium aluminate CA and the compound $C_{12}O_7$, react with water rapidly and the courses of their hydration are relatively well established despite of the difficulties involved in the methods of investigation. On the other hand, the number of published works relating to calcium aluminate hydration in solutions of alkali metal salts is not significant. Studies on the hydration of calcium aluminates in solutions of alkalies would therefore be interesting from both theoretical and practical points of view (cement hydration, Al_2O_3 lixiviation from calcium aluminates).

Elucidation of the course of reaction of C_3A, CA and $C_{12}A_7$ in dilute solutions of Na_2CO_3, and comparison with those in water, was the purpose of the present investigation. The reactions in the former systems are complex processes following or overlapping each other [2].

In the present paper the reaction kinetics have been established through the use of a microcalorimeter, and the reaction products have been analysed by DTA, TG, DTG and XRD. The chemical composition of the liquid phase has also been determined.

Experimental

The starting materials used were the calcium aluminates C_3A, $C_{12}A_7$ and CA, röntgenographically pure and ground to a fineness of 3500±50 cm^2/g (Blaine). Hydration was carried out using redistilled water or 6% Na_2CO_3 solution with a solid: liquid ratio of 1 : 10. The starting temperature was kept constant at 25±0.005°.

Results

Calorimetric curves obtained with a differential microcalorimeter type BMR are presented in Fig. 1. The concentrations of aluminate and calcium ions in the liquid phase, calculated as Al_2O_3 and CaO concentrations, were determined simultaneously; the results for Al_2O_3 are presented in Table 1.

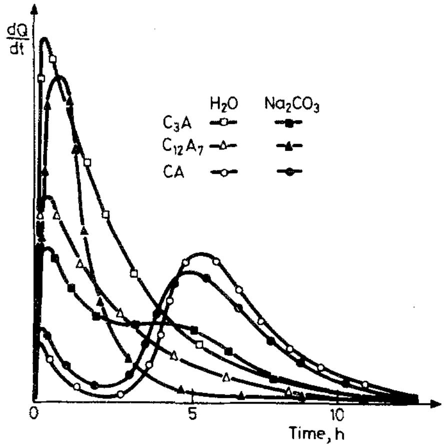

Fig. 1 Calorimetric curves of aluminate samples hydrated with H_2O or with Na_2CO_3 solution

Solid phase precipitated during the hydration process was separated from solution, washed with acetone and ether (in order to stop hydration and remove the rest of the liquid), and analysed by DTA, TG, DTG and XRD. The DTA curves obtained with a derivatograph for samples hydrated for 24 h in H_2O and in Na_2CO_3 solution are presented in Fig. 2. The results of phase composition analysis are presented in Table 2. These data relate to hydration for 1 h and 24 h after initiation of the reaction. The formulae of compounds are given using the following abbreviations: $A = Al_2O_3$, $C = CaO$, $\bar{C} = CO_2$, $H = H_2O$.

Na_2CO_3 introduced into the calcium aluminates–water mixtures gives rise to considerable alternations in the decomposition rate and in the nature and amount of products formed. Sodium carbonate accelerates the decomposition of CA, despite the fact that the calorimetric curves run closely to each other, with two heat evolution peaks and a "dormant period" between them. The phase composition and liquid phase composition suggest that the delayed nucleation of CAH_{10} takes place and influences the reaction rate. After 3 h, the hydration reaction in H_2O accelerates owing to the crystallization of hydrates CAH_{10}, C_2AH_8 and AH_3. In Na_2CO_3 solutions calcium carbonate is present as a precipitate from the beginning of the reaction, coexisting with CAH_{10}. After hydration for 3 h, the CAH_{10} content decreases, while the quantities of $CaCO_3$, calcium aluminate carbonate hydrate and aluminium hydroxide tend to increase. Na_2CO_3 in solution influences the decomposition of $C_{12}A_7$,

Table 1 Al_2O_3 fractions lixiviated from calcium aluminates as a function of liquid medium and reaction time (solid : liquid = 1 : 10)

Starting material	Liquid medium	Al_2O_3 fraction in solution after hydration time							
		5′	10′	30′	1 h	2 h	3 h	8 h	24 h
C_3A	H_2O	0.03	0.05	0.05	0.06	0.05	0.01	0.01	0.01
	Na_2CO_3	0.26	0.27	0.28	0.30	0.34	0.38	0.40	0.49
CA	H_2O	0.06	0.06	0.09	0.10	0.10	0.07	0.04	0.04
	Na_2CO_3	0.05	0.13	0.25	0.28	0.54	0.48	0.54	0.51
$C_{12}A_7$	H_2O	0.10	0.11	0.14	0.15	0.13	0.07	0.05	0.05
	Na_2CO_3	0.11	0.14	0.36	0.54	0.68	0.78	0.82	0.72

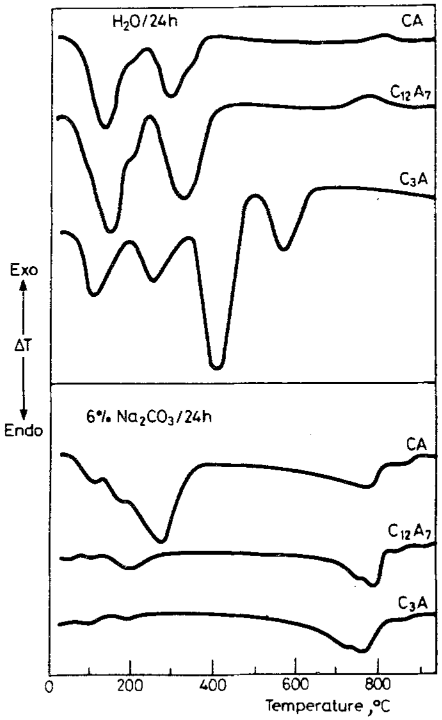

Fig. 2 DTA of aluminate samples after hydration for 24 h with H_2O or with Na_2CO_3 solution

strongly accelerating this process. In thermokinetic curves obtained for the samples $C_{12}A_7 + H_2O$ and $C_{12}A_7 + H_2O + Na_2CO_3$, only one high effect, without any dormant period, can be observed, thus indicating the rapid, exothermic reaction. At the beginning of the $C_{12}A_7$–water reaction, the hexagonal calcium aluminate hydrates are present. in which the CaO to Al_2O_3 ratio is greater than in $C_{12}A_7$, together with a certain amount of AH_3. After hydration for 24 h, the phase compo-

Table 2 Solid-phase composition as a function of hydration time and hydration medium

Starting material	Liquid medium	Phase composition of precipitates after reaction time	
		1 h	24 h
C_3A	H_2O	C_3A, C_3AH_6, C_4AH_{13-19}	C_3AH_6, C_2AH_8*, C_4AH_{13}
	Na_2CO_3	C_3A, $C\bar{C}$, $C_3AC\bar{C}H_{12}$	$C\bar{C}$, $C_3AC\bar{C}H_{12}$, C_3A
CA	H_2O	CA, CAH_{10}*	C_2AH_8, CAH_{10}, AH_3, CA
	Na_2CO_3	CA, $C\bar{C}$, CAH_{10}	$C\bar{C}$, $C_3AC\bar{C}H_{12}$, AH_3
$C_{12}A_7$	H_2O	$C_{12}A_7$, C_2AH_8, AH_3, C_4AH_{13}	C_2AH_8, C_4AH_{13}, CAH_{10}, AH_3
	Na_2CO_3	$C_{12}A_7$, $C\bar{C}$, $C_3AC\bar{C}H_{12}$	$C\bar{C}$, $C_3AC\bar{C}H_{12}$, $C_{12}A_7$*

* = traces.

sition of the precipitate is closely similar to that after the CA–water reaction for 24 h. The DTA curves of the CA and $C_{12}A_7$ hydration products show only the difference of peak areas relating to varying amounts of particular hydrates. The decomposition of $C_{12}A_7$ in Na_2CO_3 solution proceeds very fast. At first, besides $CaCO_3$ and calcium aluminate carbonate hydrate, C_4AH_{13} can be observed. Later, the amount of the latter hydrate decreases. After hydration for 24 h, the solid product consists mainly of $CaCO_3$, while about 80% Al_2O_3 occurs in the liquid phase. In Na_2CO_3 solution the decomposition of C_3A proceeds more slowly than in water. The calorimetric curve reveals the induction period and the second heat evolution peak. Even after a very short hydration time, the thermodynamically stable product, the regular hydrate C_3AH_6, appears, and its amount gradually increases, while the contents of the hexagonal hydrates, C_4AH_{13} and C_4AH_{19}, decrease. After hydration for 24 h, only traces of hexagonal hydrates are present and the DTA curve practically corresponds to that of C_3AH_6 dehydration. The solid products formed in the system $C_3A–Na_2CO_3–H_2O$ are calcium carbonate and calcium aluminate carbonate hydrate. The great amount of $C_3AC\bar{C}H_{12}$ probably relates the induction period of the reaction. The role of this product in the described process is presumably analogous to that of calcium trisulfate aluminate hydrate (ettryngite) during portland cement hydration, forming an impermeable layer surrounding the C_3A grains, thereby inhibiting the reaction.

References

1 E. M. Lea, The Chemistry of Cement and Concrete, Chemical Publ. Comp., New York, 1971.

2 Proceedings of the 7th Inter. Congr. on the Chemistry of Cements, Paris, 1980.

Zusammenfassung — Die Hydratisierung von Calciumaluminate in Wasser und Na_2CO_3-Lösungen wurde mittels kalorimetrischer, DTA, DTG und XRD untersucht.

Резюме — Используя калориметрический метод, ДТА, ДТГ и рентгено-дифракционный метод, были исследованы реакции гидратации алюмината кальция в воде и в растворе карбоната натрия.