Journal of Thermal Analysis, Vol. 32 (1987) 1731–1734

THE INFLUENCE OF CSH* PHASE NUCLEI ON $Ca_3SiO_4Cl_2$ HYDRATION

K. Miśkiewicz

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

The influence of CSH phase nuclei on calcium chlorosilicate hydration has been studied by means of calorimetry, QXRD, DTA and TG methods.

Calcium chlorosilicate, $Ca_2SiO_4Cl_2$, is synthesized at about 600° in the system $CaO—SiO_2—CaCl_2$ [1–5]. This compound, first produced in 1883 from CaO, SiO_2 and $CaCl_2$ by Le Chatelier, forms readily in some industrial processes. Its hydration has not been investigated till now. Our studies [8, 9] proved that calcium chlorosilicate reacts intensively with water. This process reveals an induction period, typical for calcium silicate hydration. Calcium silicate hydrate (CSH phase) and basic calcium chloride $CaCl_2 \cdot Ca(OH)_2 \cdot H_2O$ form as the hydration products at room temperature, with the anhydrous sample to water ratio equal to 1. The role of CSH phase nucleation as a decisive factor in $Ca_3SiO_4Cl_2$ hydration has been studied and the results are listed below.

Experimental

Materials

Calcium chlorosilicate, $Ca_3SiO_4Cl_2$, was synthesized from $CaCO_3$, amorphous SiO_2 and $CaCl_2$ mixed together in a 2 : 1 : 1 molar ratio and heated at 800° for 2 hours. The product was ground to a specific surface of 3000 cm^2/g. The CSH phase with $CaO/SiO_2 = 0.5$ was synthesized during shaking of amorphous silica with calcium hydroxide-saturated water solution for 10 days. Depending on the further sample preparation, the CSH phase was filtered or not from the suspension.

---

* $C = CaO$, $S = SiO_2$, $H = H_2O$

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Methods

Calcium chlorosilicate hydration was examined by differential calorimetry. The hydrated pastes were analysed by X-ray diffraction (TUR diffractometer) and by DTA + TG using a derivatograph thermoanalyser. The liquid phase composition was also determined as follow:

Ca^{2+} — with sodium versanate solution,
Cl^- — by Volhard's method,
SiO_2 — calorimetrically as a complex with ammonium molybdate.

Results

The calorimetric measurements during $Ca_3SiO_4Cl_2$ hydration with the filtered CSH phase addition (water to chlorosilicate ratio = 1) confirmed the significant influence of this additive on the hydration rate, as can be seen in Fig. 1. The acceleration of the hydration process in the presence of the CSH phase at low CaO/SiO_2 ratio is attributed to the nucleation effect. The X-ray diffraction measurements confirmed that the hydration products form earlier than without the CSH phase nuclei, and their phase composition does not change; the CSH phase seems to reveal a better ordered structure. Similar results have been obtained with an excess of water (water to solid ratio equal to 10). The induction period in the microcalorimetric curve disappeared for $CSH/Ca_3SiO_4Cl_2 \geq 1$. To explain the influence of the CSH phase on calcium chlorosilicate hydration, liquid phase analyses were also made. It was found that the CSH phase lowers the SiO_2 concentration in the liquid phase simultaneously accelerating the migration of

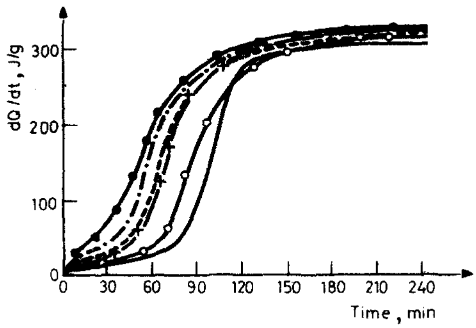

Fig. 1 Heat evolution during $Ca_3SiO_4Cl_2$ hydration with CSH addition. $H_2O/Ca_3SiO_4Cl_2 + CSH = 1$. ——— 0% CSH, —o— 0.05% CSH, —+—0.1% CSH, - - - 0.1% CSH, —·— 5.0% CSH, — ● —10.0% CSH

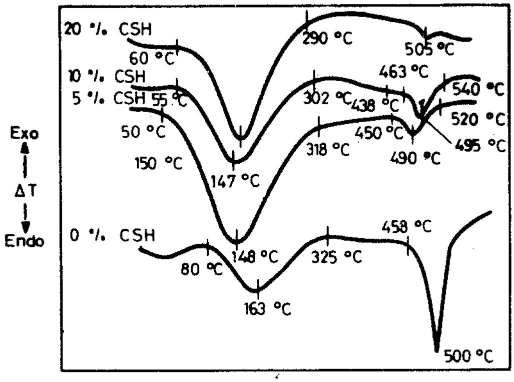

Fig. 2 DTA curves of $Ca_3SiO_4Cl_2 + CSH$ hydrated mixtures after 24 hours hydration. Water : solid = 10

Ca^{2+} and Cl^- to the solution. Just after 5 minutes, their concentrations are 15–20 times greater than without CSH addition. During the first 12 hours, the ratio of Ca^{2+} and Cl^- concentrations approaches the $CaCl_2$ solution composition, and after 24 hours the Ca^{2-} to Cl^- concentration ratios as a function of the CSH phase addition are as follows:

CSH, %	0	5	10	20
Cl_2/CaO in liquid phase	1.01	1.06	1.13	1.22

The DTA measurements proved the CSH content increase and $Ca(OH)_2$ content decrease in the pastes with CSH addition (Fig. 2). The bound water content in the paste also increases, as shown in Table 1.

Table 1 $Ca(OH)_2$ and H_2O contents in $Ca_3SiO_4Cl_2$ hydration products with CSH phase addition after 24 hours. $H_2O/Ca_3SiO_4Cl_2 = 10$

CSH addition, %	$Ca(OH)_2$ content, %	H_2O content, %
0	15	24
5	8.2	24
10	7.3	24.5
20	4.8	29.3

To summarize the results it can be stated that CSH phase addition accelerates $Ca_3SiO_4Cl_2$ hydration in the early stages. This relates to calcium chlorosilicate dissolution as well as to the formation of hydration products.

References

1 W. G. Czułchaczew, Dokł. Ak. Nauk SSSR, 246 (5) (1979) 1188.

2 W. Kurdowski, Cement, Wapno Gips, 3 (1962) 506.

3 W. Kurdowski, Silicates Industriels, 30 (1965) 500.

4 J. M. Butt, W. W. Timaszew and A. P. Osokin, Proc. of the 6th Int. Congress on the Chemistry of Cements, Moscow, 1974, Vol. 1, pp. 132–153.

5 M. Regourd and A. Guinier, Proc. of the 6th Int. Congress on the Chemistry of Cements, Moscow, 1974, Vol. 1, pp. 25–71.

6 A. Winkler and W. Wieker, Chemie 22 (1982) 52.

7 H. Lafuma, Proc. of the 3rd Int. Congress on the Chemistry of Cements, London, 1952, p. 583.

8 W. Kurdowski and K. Miśkiewicz, Cement and Concrete Research, 15 (1985) 785.

9 W. Kurdowski, W. Nocuń-Wczelik and K. Miśkiewicz, Bijing Int. Symp. on Cem. and Concr., China Academic Publ., 45–46, 1085 (abstract).

Zusammenfassung — Mittels kalorimetrischen, QXRD-, DTA- und TG-Verfahren wurde der Einfluß von CSH Phasenkörpern auf die Hydratierung von Kalziumchlorosilikat untersucht.

Резюме — Методом ДТА, ТГ, калориметрии и оптической рентгенографии изучено влияние зародышей фазы гидрата силиката кальция на гидратацию хлоросиликата кальция.