

## THE INFLUENCE OF BASIC CALCIUM CHLORIDE NUCLEI ON THE HYDRATION OF CALCIUM CHLORIDESILICATE

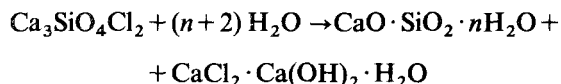
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The influence of  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  nuclei on the hydration of  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  was studied by means of calorimetry, X-ray diffraction, simultaneous DTA-TG and chemical analysis of the liquid phase.

Calcium chloridesilicate  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  is readily produced at  $600^\circ$  in some industrial processes [1, 2]. Its occurrence was first reported by Le Chatelier in 1883, but the interesting hydration properties have been known for only a few years [3-6].

$\text{Ca}_3\text{SiO}_4\text{Cl}_2$  reacts quickly with water at room temperature according to the equation:



In an earlier paper, the influence of gel-like  $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$  phase on the hydration of  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  was reported [7]. Interesting results have now been obtained using  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  (the second hydration product) as a nucleating agent in the reaction of  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  with water.

### Experimental

#### *Materials*

$\text{Ca}_3\text{SiO}_4\text{Cl}_2$  was synthesized from a mixture of  $\text{CaCO}_3$ , amorphous  $\text{SiO}_2$  and  $\text{CaCl}_2$  in 2:1:1 molar ratio by heating at  $800^\circ$  for 2 h. The product was then ground to a specific surface area of  $3000 \text{ cm}^2 \text{ g}^{-1}$  (Blaine).

Basic calcium chloride  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  was synthesized from  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ca}(\text{OH})_2$ . The hot, saturated  $\text{CaCl}_2$  solution was mixed in appropriate quantity with lime water, shaken for 7 days and then dried in a vacuum

drier at 40°. The product thus obtained contained over 90%  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , together with some  $\text{CaCl}_2$  and  $\text{Ca}(\text{OH})_2$ , was revealed by X-ray diffraction.

### Methods

The hydration of  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  was investigated by using a Bioflux differential calorimeter (RWTH, Aachen). The  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  pastes were analysed by means of X-ray diffraction (TUR diffractometer) or simultaneous DTA-TG, using a Mettler thermoanalyser. The liquid-phase composition was determined as follows:  $\text{Ca}^{2+}$  with sodium versenate solution;  $\text{Cl}^-$  by Volhard's method;  $\text{SiO}_2$  colorimerically, as a complex with ammonium molybdate.

### Results

The calorimetric data (Fig. 1) reveal that a 1% admixture  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  led to an increase in the induction period and retarded the hydration of  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$ . The addition of 5%  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  to the hydrating  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  caused a further 20-min increase in the induction period. However, this admixture did not change the phase composition of the hydration products in the paste of water and with a solid mass ratio initially equal to 1. A similar retarding effect was observed in the suspension of water and solid with a mass ratio of 10. The liquid-phase composition (Fig. 2) shows that  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  lowered the

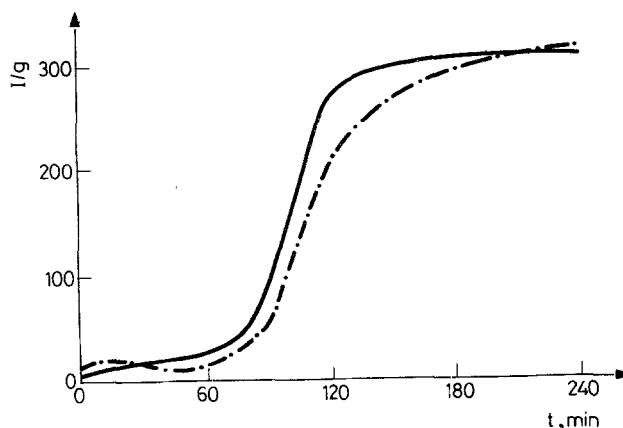


Fig. 1 Heat evolution curve during  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  hydration with  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  addition.  $\text{H}_2\text{O}/\text{solid} = 1$ , temperature: 25°. —  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$ ; - · -  $\text{Ca}_3\text{SiO}_4\text{Cl}_2 + 5\% \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$

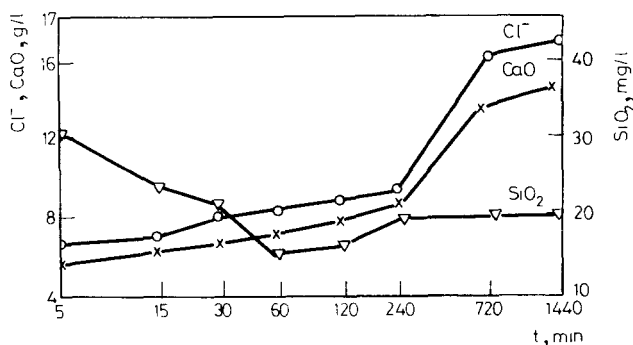


Fig. 2 Liquid phase composition in the suspension  $\text{Ca}_3\text{SiO}_4\text{Cl}_2 + 5\% \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$ .  $\text{H}_2\text{O}/\text{solid} = 10$ , temperature:  $25^\circ$

$\text{SiO}_2$  concentration in the solution to a lesser degree than observed on silica or  $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$  addition [4]. On the other hand, the increases in  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  concentrations refer to the rapid dissolution of  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  in water. As demonstrated in earlier studies, in suspensions (water to solid mass ratio = 10), this compound is not stable and decomposes quickly. The  $\text{Ca}(\text{OH})_2$  thus liberated reacts quickly with  $\text{CO}_2$  to give vaterite. The liquid-phase analysis confirmed the above findings: the  $\text{Cl}^-$  to  $\text{Ca}^{2+}$  concentration ratio corresponded to  $\text{CaCl}_2$ .

The hydration products detectable by X-ray diffraction after reaction for 2.5 h were  $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$  and  $\text{Ca}(\text{OH})_2$ . The  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  admixture lowered the  $\text{Ca}(\text{OH})_2$  content in the paste in comparison with the sample hydrating without any admixture. After hydration for 24 h, the  $\text{Ca}(\text{OH})_2$  contents were 10% and 15%, respectively. The hydration of samples with and without  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  was almost complete after 24 h. It can be further be concluded that the CaO to  $\text{SiO}_2$  ratio in the pastes without additive is lower. The

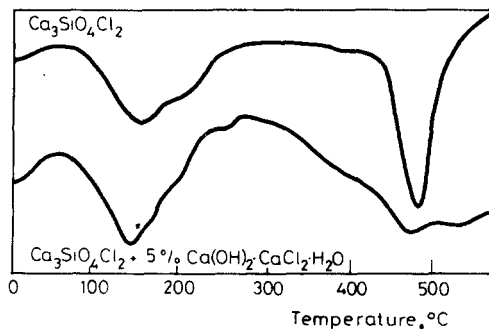


Fig. 3 DTA curves of (a)  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  and (b)  $\text{Ca}_3\text{SiO}_4\text{Cl}_2 + 5\% \text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$  hydrated mixtures after 24 hours hydration.  $\text{H}_2\text{O}/\text{solid} = 10$ , temperature:  $25^\circ$

DTA peak corresponding to the decomposition of  $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$  gel did not change (Fig. 3) and the total water contents were almost the same in samples without and with  $\text{CaCl}(\text{OH})_2 \cdot \text{H}_2\text{O}$  (23.6% and 24.0%, respectively).

### Conclusions

$\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  nuclei, in contrast with  $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$  nuclei, retard the reaction of  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  with water. Addition of  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  causes an increase in the CaO to  $\text{SiO}_2$  ratio in the gel-like hydration product  $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ .

### References

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**Zusammenfassung** — Der Einfluss von  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ -Zusätzen auf die Hydratation von Calciumchlorid-silicat  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  wurde durch Kalorimetrie, Röntgenbeugung, simultane TG-DTA und chemische Analyse der flüssigen Phase untersucht.

**Резюме** — Влияние зародышей кристаллов  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2$  на гидратацию  $\text{Ca}_3\text{SiO}_4\text{Cl}_2$  было изучено методом calorimetрии и дифракции рентгеновых лучей, совмещенных с химическим анализом жидкой фазы.