

# A Time-Resolved Neutron and X-Ray Powder Diffraction Investigation of Reactions between $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ , $\text{CaCl}_2$ , $\text{CaBr}_2$ and Water

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The effect of the additives  $\text{CaCl}_2$  and  $\text{CaBr}_2$  on the reaction between  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  and water was investigated by time-resolved neutron and X-ray powder diffraction. With each of the additives a precursor phase is formed prior to formation of the stable end products  $\alpha\text{-Ca}_2\text{Al}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$  and  $\text{Ca}_2\text{Al}(\text{OH})_6\text{Br} \cdot 2\text{H}_2\text{O}$ . The consumption of  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  in the hydrolysis reaction with water is much faster when the additives  $\text{CaCl}_2$  and  $\text{CaBr}_2$  are present than in pure water.

In earlier investigations, the reactions between calcium aluminates and water have been studied by means of time-resolved powder neutron diffraction.<sup>1–3</sup> The effects of selected additives ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{D}_2\text{O}$ ,  $\text{CaSO}_4 \cdot 2\text{D}_2\text{O}$  and  $\text{CaCO}_3$ ) on the reaction rates and on the formation of crystalline products were discussed in Ref. 3. Preliminary experiments on the reaction between  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  (abbreviated  $\text{C}_{12}\text{A}_7$ ),  $\text{CaCl}_2$  and water<sup>3</sup> indicated that an intermediate phase exists over a certain time and temperature interval before the stable end product  $\alpha\text{-Ca}_2\text{Al}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$  (Friedel's salt) is formed. In this work, the reactions between  $\text{C}_{12}\text{A}_7$ ,  $\text{CaCl}_2$  or  $\text{CaBr}_2$ , and  $\text{D}_2\text{O}/\text{H}_2\text{O}$  were studied at various temperatures between 20 and 120 °C in order to obtain information on (i) the formation and crystal state of precursor phases, and (ii) effects of  $\text{CaCl}_2$  and  $\text{CaBr}_2$  as additives on the rate of reaction between  $\text{C}_{12}\text{A}_7$  and water.

## Experimental

The calcium aluminate  $\text{C}_{12}\text{A}_7$  was synthesized by zone-melting mixtures of  $\text{Al}_2\text{O}_3$  (Merck, analytical grade) and  $\text{CaO}$  (prepared as described in

Ref. 3). Water-free  $\text{CaCl}_2$  (Merck, min. 95 %  $\text{CaCl}_2$ ) and water-free  $\text{CaBr}_2$  (Merck, min. 84 %  $\text{CaBr}_2$ ) were used. The reaction medium  $\text{D}_2\text{O}$  was of 99.7 % purity.

The time-resolved powder neutron diffraction experiments were made with the D1B diffractometer at the Institut Laue-Langevin and the data reduction was performed as described previously.<sup>3</sup> Time-resolved powder X-ray diffraction measurements were made with a Stoe diffractometer with a position-sensitive detector and using  $\text{CoK}\alpha_1$  radiation ( $\lambda = 1.78897 \text{ \AA}$ ). The diffractometer was calibrated with silicon ( $a = 5.43050 \text{ \AA}$ ). The sample was a paste of  $\text{C}_{12}\text{A}_7$ ,  $\text{CaCl}_2$  and  $\text{H}_2\text{O}$ , housed in a 0.2 mm diameter glass capillary. The paste was sucked into the capillary using a syringe, by placing the capillary, open at both ends, on the syringe instead of a needle. The open ends of the capillary were closed with wax and the sample was placed on the goniometer of the diffractometer and rotated at a speed of approximately one revolution per second. Diffraction patterns were recorded at room temperature after periods of 1,2,3...24 h after mixing of the paste.

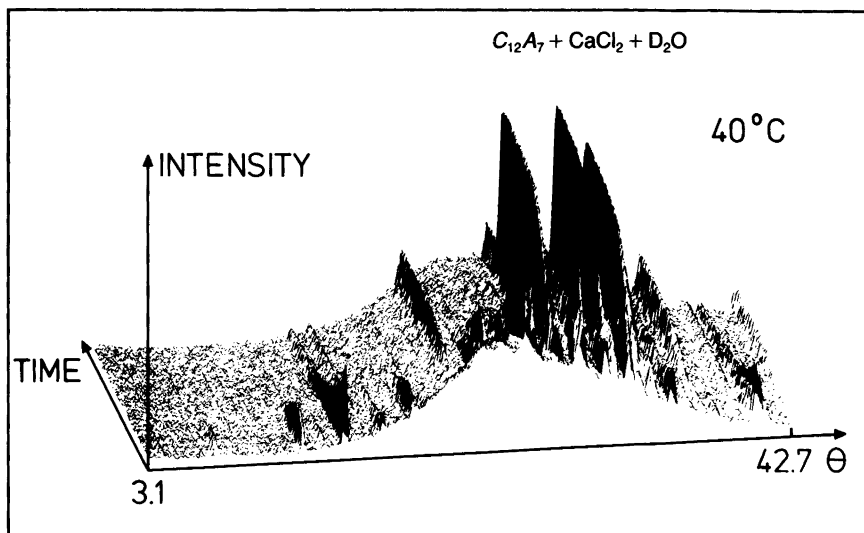


Fig. 1. Powder diffraction patterns for a  $C_{12}A_7$ - $CaCl_2$ - $D_2O$  mixture at  $40^\circ C$ , recorded at 5 min intervals. The quantity of  $C_{12}A_7$  decreases continuously, and the end product  $\alpha$ - $Ca_2Al(OD)_6Cl \cdot 2D_2O$  starts to appear when the quantity of the precursor is at a maximum.

## Results and discussion

(i). *CaCl<sub>2</sub> as additive.* A three-dimensional representation of the time evolution of the diffraction patterns of a  $C_{12}A_7$ - $CaCl_2$ - $D_2O$  mixture at

$40^\circ C$  is shown in Fig. 1. From the figure it is seen that the formation of a precursor phase as an intermediate reaction product takes place before the formation of the final reaction product  $\alpha$ - $Ca_2Al(OD)_6Cl \cdot 2D_2O$  (Friedel's salt).<sup>4</sup> The time

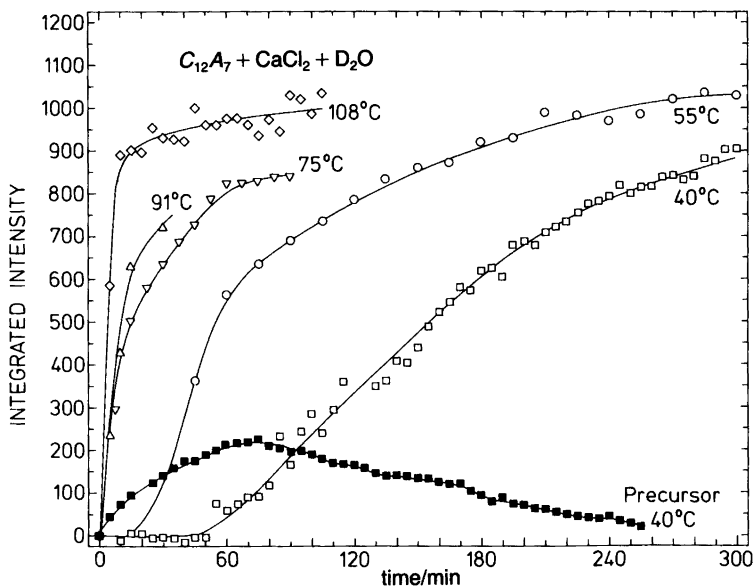


Fig. 2. Integrated intensities of solids in the reaction of  $C_{12}A_7$ - $CaCl_2$ - $D_2O$  mixtures at 40, 55, 75, 91 and  $108^\circ C$ . The solids observed are precursor (■) and  $\alpha$ - $Ca_2Al(OD)_6Cl \cdot 2D_2O$  (□, ○, ▽, △, ◇).

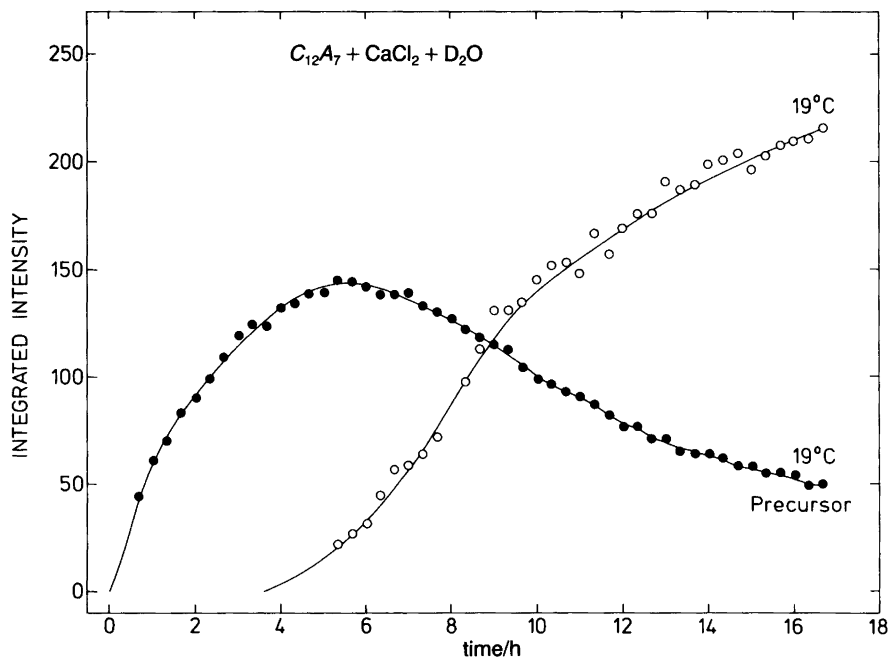


Fig. 3. Integrated intensities of precursor (●) and  $\alpha$ -Ca<sub>2</sub>Al(OD)<sub>6</sub>Cl · 2D<sub>2</sub>O (○) in a reaction at 19°C.

dependence of the amounts of  $C_{12}A_7$ , the precursor phase and  $\alpha$ -Ca<sub>2</sub>Al(OD)<sub>6</sub>Cl · 2D<sub>2</sub>O in the sample was evaluated by integration of Bragg reflections in the diffraction diagrams. The results are presented for different temperatures in Figs. 2–4.

It is clear from Fig. 4 that the formation of the precursor is temperature dependent, and it does not take place at temperatures above ca. 50°C.

At lower temperatures it is observed that  $\alpha$ -Ca<sub>2</sub>Al(OD)<sub>6</sub>Cl · 2D<sub>2</sub>O does not start to precipitate until the point when maximal amounts of the precursor are present in the samples (Figs. 2 and 3). This behaviour is quite analogous to that seen for the formation of ettringite when using calcium sulphate as additive.<sup>3</sup>

Selected  $d$ -values ascribed to the precursor phase are listed in Table 1. The time-resolved

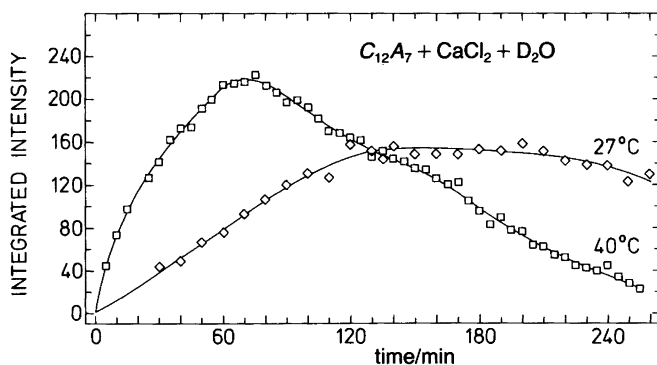


Fig. 4. Integrated intensity of precursor (□ 40°C, ◇ 27°C) in the reaction of  $C_{12}A_7$ -CaCl<sub>2</sub>-D<sub>2</sub>O mixtures. The formation of the precursor is temperature dependent.

Table 1. Interplanar distances (Å) for the intermediate phase in the  $C_{12}A_7$ - $CaCl_2$ - $D_2O/H_2O$  system.

Neutron diffraction $d$	X-Ray diffraction $d$	I/%
10.0	10.24	100
5.83		
	5.09	11
4.73	4.74	11
3.83	3.67	25
3.13		
3.00	3.00	12
2.85		
2.81		
2.68	2.68	11
2.56	2.57	22
2.54		
2.50		
2.42		
2.40		
2.33		
2.31		
2.29		
	2.19	17
	1.94	12
	1.66	11
	1.60	13

X-ray diffraction experiment also gave clear evidence for the existence of a precursor phase. The composition of this phase is unknown and its powder diffraction pattern was not found in the JCPDS index.

(ii). *CaBr<sub>2</sub> as additive.* A three-dimensional representation of the time evolution of the diffraction patterns of a  $C_{12}A_7$ - $CaBr_2$ - $D_2O$  mixture at 20°C is displayed in Fig. 5. Before the final reaction product  $Ca_2Al(OD)_6Br \cdot 2D_2O^5$  is formed, a precursor phase is observed. This phase is consumed in the same way as the precursor in the  $CaCl_2$ -containing system. Figs. 6 and 7 show integrated intensities for the precursor and the final product. It is clear that the formation of the precursor is temperature dependent, and the formation possibly does not take place at temperatures above ca. 50°C.

Time-resolved X-ray powder diffraction measurements were also made on this system using a Stoe diffractometer with  $CoK\alpha_1$  radiation. The diffraction patterns of a paste of  $C_{12}A_7$ ,  $CaBr_2$  and  $H_2O$  were recorded at room temperature as described above. This also gave clear evidence for the formation of a precursor phase.

The hydration of  $C_{12}A_7$  at room temperature has been investigated by Costa, Massazza and Testolin,<sup>6</sup> using X-ray diffraction. The first crys-

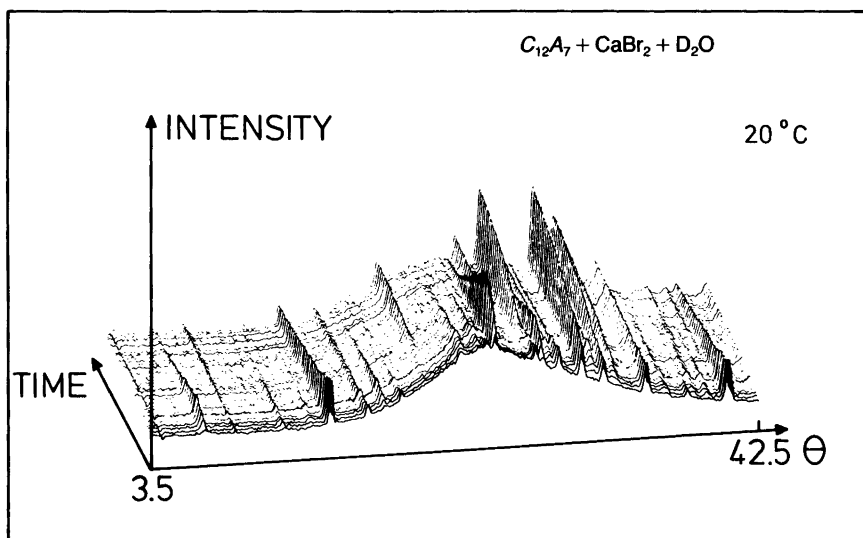


Fig. 5. Powder neutron diffraction patterns for a  $C_{12}A_7$ - $CaBr_2$ - $D_2O$  mixture at 20°C, recorded at 20 min intervals.

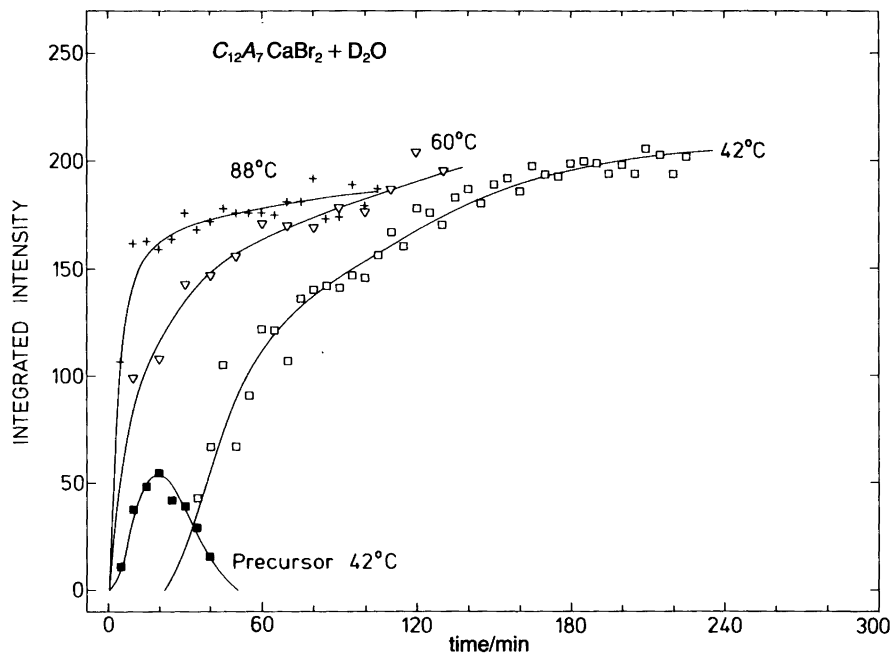


Fig. 6. Integrated intensities of solids in reactions of  $\text{C}_{12}\text{A}_7$ - $\text{CaBr}_2$ - $\text{D}_2\text{O}$  mixtures at the temperatures 42, 60 and 88°C. The solids observed are precursor (■) and the reaction product  $\text{Ca}_2\text{Al}(\text{OD})_6\text{Br} \cdot 2\text{D}_2\text{O}$  (□, ∇, +).

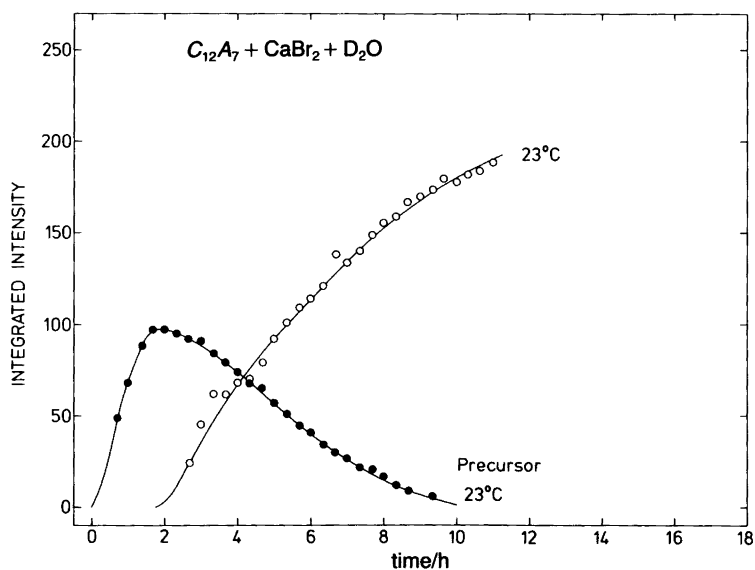


Fig. 7. Integrated intensities of precursor (●) and the product  $\text{Ca}_2\text{Al}(\text{OD})_6\text{Br} \cdot 2\text{D}_2\text{O}$  (○) in a reaction at 23°C.

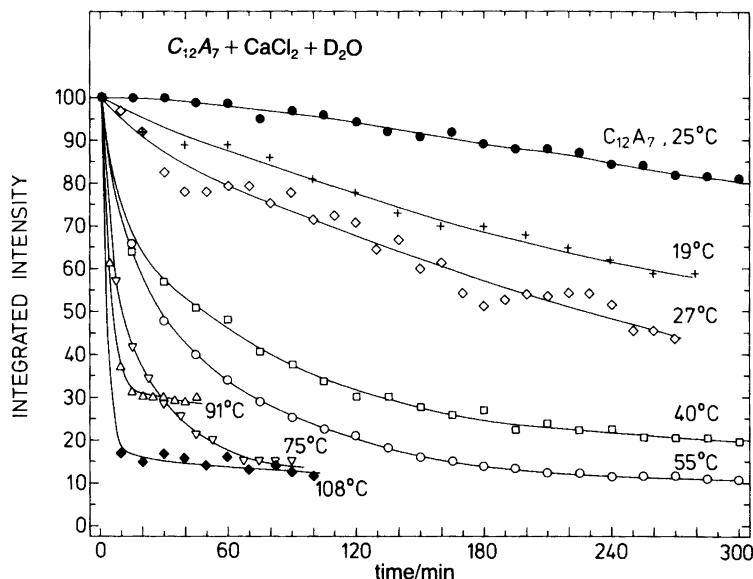


Fig. 8. Residual quantities of crystalline  $C_{12}A_7$  observed in hydrolysis experiments at different temperatures.

talline reaction product formed is the calcium aluminium hydroxide hydrate,  $Ca_2Al_2(OH)_{10} \cdot 3H_2O$ . This compound shows strong diffraction intensities for  $d$ -spacings of 10.7 and 5.35 Å, and is most likely the precursor phase in this system. The compound  $Ca_2Al_2(OH)_{10} \cdot 3H_2O$  is known to be a metastable compound and is consumed during the formation of the final end-product  $Ca_2Al(OH)_6Br \cdot 2H_2O$ ,<sup>5</sup> which is the only crystalline reaction product present after 6 h at room temperature.

### Conclusion

The consumption of  $C_{12}A_7$  in the hydrolysis reaction with  $D_2O$  is much faster when the additives  $CaCl_2$  and  $CaBr_2$  are present than in pure  $D_2O$ . Fig. 8 shows the quantity of crystalline  $C_{12}A_7$  present in seven reaction mixtures containing the additive  $CaCl_2$ , and in one reaction mixture without  $CaCl_2$ . When the additives are present, a considerable reduction in the quantity of crystalline  $C_{12}A_7$  takes place during the first few minutes after the start of the reaction. An amorphous gel is formed and the precursors grow from this gel. Later, when the precursor has been consumed but the final end-product continues to be formed,

this growth must also proceed with material from the amorphous gel, since the quantity of crystalline  $C_{12}A_7$  decreases rather slowly, possibly due to an effect of grain size or of deposits of reaction products on the surface of the  $C_{12}A_7$  grains. Similar results are found with  $CaBr_2$  as the additive. The effect of the additives in changing the rate of reactions of mortars containing calcium aluminates is thus related to the rate of the hydrolysis of the aluminate, and is related to the formation of reaction products other than  $Ca_3Al_2(OD)_{12}$  that will prevail in systems not containing the additives investigated in this and in previous work.<sup>3</sup> With the additives present,  $C_{12}A_7$  is hydrolyzed to products containing less aluminium than  $C_{12}A_7$ . The residual aluminium has not been observed as a crystalline phase in the reaction mixtures but is assumed to be present in an amorphous gel during the relatively short periods investigated.

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### References

1. Christensen, A. N. and Lehman, M. S. *J. Solid State Chem.* 51 (1984) 196.
2. Christensen, A. N., Fjellvåg, H. and Lehmann, M. S. *Acta Chem. Scand., Ser. A* 39 (1985) 593.
3. Christensen, A. N., Fjellvåg, H. and Lehmann, M. S. *Acta Chem. Scand., Ser. A* 40 (1986) 126.
4. Kuzel, H.-J. *Neues Jahrb. Mineral., Monatsh.* (1966) 193.
5. Kuzel, H.-J. *Neues Jahrb. Mineral., Monatsh.* (1971) 477.
6. Costa, U., Massazza, F. and Testolin, M. *Ind. Chim. Belg.* 39 (1974) 587.

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