

# PHASE TRANSFORMATIONS DURING HYDROTHERMAL HEATING OF TRICALCIUM ALUMINATE IN LIQUID WATER

VLADIMÍR ŠATAVA

*Institute of the Chemistry of Glass and Ceramic Materials, Czechoslovak Academy of Sciences,  
Sokolská 38, 120 00 Prague 2*

Received 23. 3. 1992

*Hydration of the paste of powder  $C_3A^*$  in liquid water was studied by the method of differential hydrothermal analysis over the temperature range of 0–350 °C. The process takes place in two stages. During the first, at temperatures of up to 40 °C, a continuous layer of  $C_4AH_{13-19}$  is formed on the surface of  $C_3A$  grains, and a layer of the more stable  $C_3AH_6$  at up to 80 °C. At 100 °C, the rate of the reactions falls virtually to zero as a result of slow water diffusion through the layer of the product. The second stage starts at 180 °C, producing non-crystalline calcium hydroaluminate with the approximate composition  $C_{12}A_7H_x$ , and the process proceeds up to 300 °C until the  $C_3A$  has been spent. The share of hydroaluminates formed during the first stage increases with increasing specific surface area of the initial  $C_3A$ . The hexagonal aluminates are converted at 130 °C to cubic  $C_3AH_6$  which is then decomposed to  $C_4A_3H_3$  and  $CH$  on attaining the temperature of 250 °C.*

## 1. INTRODUCTION

The processes taking place during hydration of tricalcium aluminate under various conditions, significant in particular with respect to the role it plays in the hardening of cement pastes, mortars and concrete, was studied by a number of authors [1]. They were mostly concerned with processes occurring at normal temperature, either from the standpoint of the equilibria to which they proceed [2, 3], or from that of kinetics and the mechanism [4–8]. Only equilibria in the system  $CaO-Al_2O_3-H_2O$  were investigated at elevated temperatures, and the results obtained by Majumdar [9], Pepler [10] and Warning [11] clearly show that attainment of equilibria is a matter of very long periods of time, of the order of up to hundreds of hours. Under the conditions employed in the technology of accelerating the hardening of mortars and concrete by curing at elevated temperatures, the equilibria in the system  $C_3A-H$  just cannot be attained. It was deemed desirable to learn the sequence of transformations taking place at the heating rate comparable to the conditions used in technological practice, rather than to deal with the equilibria. As shown in previous papers [12, 13], information on the sequential reactions can be provided by the method of differential hydrothermal analysis (DHA) which allows, at a chosen constant rate of heating, the sequence of processes taking place in the given system to be studied continuously.

\*The abbreviations  $C = CaO$ ,  $A = Al_2O_3$  and  $H = H_2O$  are used throughout this study.

## 2. EXPERIMENTAL

### 2.1 Materials

The  $C_3A$  was prepared from  $CaCO_3$  and  $Al(OH)_3$  of A.R. purity, mixed by joint grinding and fired three times at 1400 °C. The product, identified by X-ray diffraction as a single phase, was ground into three fractions with the respective specific surface areas of  $0.02 \text{ m}^2\text{g}^{-1}$ ,  $0.5 \text{ m}^2\text{g}^{-1}$  and  $5.1 \text{ m}^2\text{g}^{-1}$ . The specific surface area was determined by Nelsen-Eggertsen's method [14].

The  $C_3AH_6$  was prepared by hydrating  $C_3A$  in aqueous suspension in the autoclave at 150 °C.  $C_4AH_{19}$  was prepared after Dosch [15] and likewise identified by means of DTA and X-ray diffraction.

### 2.2 The methods

#### Differential hydrothermal analysis (DHA)

The apparatus records processes taking place in the sample during its heating up in the medium of liquid water under saturated water vapour pressure. The design of the autoclave and the measuring equipment was described in an earlier paper [12]. The vessel in the DHA block was filled with the powdered sample, saturated with distilled water and sealed in the autoclave, which contained just the amount of water providing free space for the vapour phase. All reactions thus took place under saturated vapour pressure, corresponding to the temperature in the autoclave. Powdered graphite was used as standard sample. The constant heating rate of  $10^\circ\text{C min}^{-1}$  was automatically controlled, and a highly sensitive line recorder was employed for recording the DHA curves.

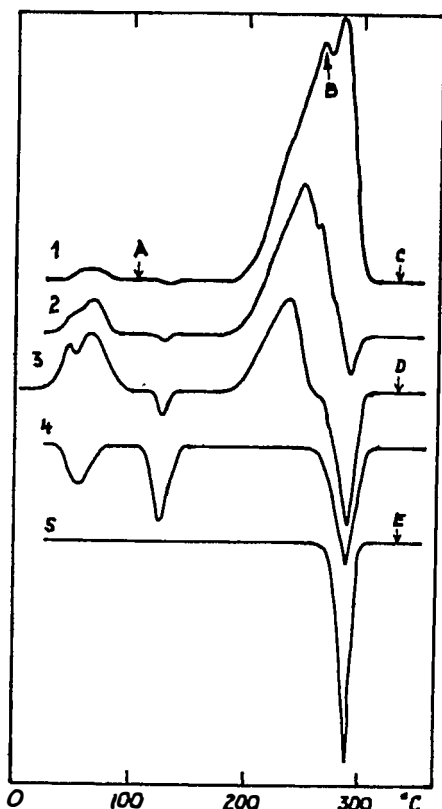


Fig. 1. DHA curves:

- 1)  $C_3A$  suspension – specific surface area  $0.02 \text{ m}^2 \text{ g}^{-1}$ ;
- 2)  $C_3A$  suspension – specific surface area  $0.5 \text{ m}^2 \text{ g}^{-1}$ ;
- 3)  $C_3A$  suspension – specific surface area  $5 \text{ m}^2 \text{ g}^{-1}$ ;
- 4)  $C_4AH_{19}$  suspension;
- 5)  $C_3AH_6$  suspensions.

#### Isolation of the reaction products

The course of DHA had been kept undisturbed until the required temperature was attained; then the autoclave was cooled by removing it quickly from the kiln and immersing in cold water. The product removed immediately from the autoclave was dispersed in alcohol, filtered, dried and kept at room temperature in a desiccator with natron lime.

#### Identification of the products

By means of X-ray diffraction ( $\text{CuK}\alpha$  radiation), DTA, electron microprobe (EMPA), EDAX and scanning electron microscopy (SEM).

### 3. RESULTS AND THEIR DISCUSSION

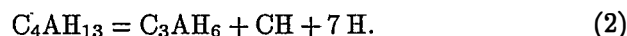
The sequence of reactions which took place under DHA conditions in  $C_3A$  paste with a specific surface area of  $0.02 \text{ m}^2 \text{ g}^{-1}$  is shown by curve 1 in Fig. 1. The product formed up to  $90^\circ\text{C}$  (point A) and separated by the abrupt cooling method, was found to contain a small proportion of  $C_3AH_6$  apart from unreacted  $C_3A$  (by X-ray diffraction and DTA). The

next stage of heating up to the point designated B on the DHA curve yielded a new phase in the product, characterized by a distinct diffusion band in the diffraction pattern. According to EMPA and EDAX chemical analyses the composition of the phase varied between  $C_{12}A_{6.9}H_x$  and  $C_{12}A_{7.1}H_x$ . A phase of similar composition and with a cubic structure was identified by Kuzel [16] and Bartl [17] in the products of thermal decomposition of  $C_3AH_6$  in the presence of water vapour over the temperature range of  $300\text{--}500^\circ\text{C}$ . The authors assume that the compound is produced by the reaction



According to X-ray diffraction, the product isolated at  $350^\circ\text{C}$  (designated C on the curve) contained calcium hydroxide and  $C_4A_3H_3$  (for diffraction data refer to [17]), beside a small amount of  $C_{12}A_7H_x$  amorphous phase.

DHA curves 2 and 3 in Fig. 1 show the sequence of processes when the initial  $C_3A$  had a specific surface area of  $0.5$  and  $5.0 \text{ m}^2 \text{ g}^{-1}$  respectively. The curves indicate that the intensity of reactions in the first stage of hydration increases with increasing specific surface area of  $C_3A$ , as does the endothermal peak at  $130^\circ\text{C}$ . This corresponds, as found out (compare to DHA curve 4), to the transformation



Curve 3 was obtained by first cooling the autoclave, sample and water down to  $0^\circ\text{C}$  and starting the heating at max.  $5^\circ\text{C}$ . The curve shows that the first stage of hydration proceeded in two steps, and it may be assumed that the first peak (at  $45^\circ\text{C}$ ) corresponds to the decomposition of hexagonal aluminates, and the other (at  $80^\circ\text{C}$ ) to that of  $C_3AH_6$ . At  $180^\circ\text{C}$  there follows formation of an amorphous hydroaluminate phase, and a pronounced endothermal peak appears at  $260^\circ\text{C}$ . A comparison with the DHA curve of  $C_3AH_6$  (cf. curve 5 in Fig. 1) indicates that the peak may represent the reaction



This is also indicated by the composition of the product identified at point D (cf. curve 3) in which X-ray diffraction, similarly to product E (cf. curve 5), revealed the presence of  $C_4A_3H_3$  and CH. The crystalline character of the products is also well demonstrated by the EMPA micrographs in Fig. 2 where one can see the orthorhombic crystals of  $C_4A_3H_3$  and the finer hexagonal crystals of CH. The orthorhombic prisms of  $C_4A_3H_3$  are more distinctly visible in Fig. 3.

The temperature of the peak on curve 5 decreases with decreasing heating rate, and extrapolation to zero heating rate allows the equilibrium of reaction (3) to be established: it amounts to  $210^\circ\text{C}$ , which is

in good agreement with the results obtained by Pepppler [9] and Majumdar [10].

It can be concluded that the mechanism of hydration of  $C_3A$  is similar in both stages in that a non-crystalline product is formed as first on the surface of  $C_3A$  grains. In the first stage, its stoichiometry approaches the composition  $C_4AH_x$ , in the second stage  $C_{12}A_7H_x$ . In both cases, diffusion of water through the layer of the product is the most probable controlling process, in view of the width of both exothermal peaks on the DHA curve.

#### Acknowledgement

The author thanks to doc. Ing. Václav Hulínský, CSc, and Ing. Martin Maryška, CSc, from the Department of Glass and Ceramics at the Institute of Chemical Technology in Prague, for their friendly help in studying the products by electron microscopy and with the electron microprobe.

#### References

- [1] Taylor H.F.W. (editor): *The Chemistry of Cements*. Academic Press, New York 1964.
- [2] D'Ans J., Eick H.: *Zement-Kalk-Gips* 6, 197 (1953).
- [3] Brown P.W.: The Implication of Phase Equilibria on Hydration in the  $C_3S-H_2O$  and  $C_3S-C\bar{S}H_2-H_2O$  Systems, in Proc 8th International Symposium on the Chemistry of Cement, Vol. III, p. 237, Rio de Janeiro 1986.
- [4] Pommersheim J., Chang J.: *Chem. Concr. Res.* 16, 440 (1986).
- [5] Stein H.N.: *J. Appl. Chem.* 13, 228 (1963).
- [6] Feldman R.F.: *J. Am. Cer. Soc.* 49, 268 (1966).
- [7] Breval E.: *Cem. Concr. Res.* 6, 129 (1976).
- [8] Breval E.: *Cem. Concr. Res.* 7, 297 (1977).
- [9] Pepppler R.B., Wells L.S.: *J. Res. Nat. Bur. Standards* 52, 75 (1954).
- [10] Majumdar A.J., Roy R.: *J. Am. Cer. Soc.* 39, 434 (1956).
- [11] Waring J.L., Roth R.S., Brower W.S., Harding C.A.: *J. Res. Nat. Bur. Standards* 82, 167 (1977).
- [12] Šatava V., Vepřek O.: *J. Am. Cer. Soc.* 58, 357 (1975).
- [13] Šatava V.: *Ceramics – Silikáty* 36, 105 (1992).
- [14] Nelsen F.H., Eggertsen F.T.: *Anal. Chem.* 30, 1387 (1958).
- [15] Dosch W., zur Strassen H.: *Zement-Kalk-Gips* 5, 233 (1965).
- [16] Kuzel H.J.: *N. Jb. Miner. Mh.* 26, 397 (1969).
- [17] Bartl H.: *N. Jb. Miner. Mh.* 26, 404 (1969).
- [18] Percival A., Taylor H.F.W.: *Acta Cryst.* 14, 324 (1961).

Translated by K. Němeček

#### FÁZOVÉ PŘEMĚNY PŘI HYDROTERMÁLNÍM OHŘEVU TRIKALCIUMALUMINÁTU V KAPALNÉ VODĚ

VLADIMÍR ŠATAVA

Ústav chemie skelných a keramických materiálů ČSAV,  
Sokolská 38, 120 00 Praha 2

Hydratace pasty práškového  $C_3A^*$  v kapalně vodě byla studována metodou diferenční hydrotermální analýzy v intervalu teplot 0–350°C. Proces probíhá ve dvou etapách. V první, do teploty 40°C, vzniká na povrchu zrn  $C_3A$  souvislá vrstva  $C_4AH_{13-19}$ , do 80°C pak stálejšího  $C_3AH_6$ . Při 100°C klesne rychlost těchto reakcí prakticky k nule v důsledku pomalé difúze vody vrstvou produktu. Druhá etapa začíná při 180°C, tvoří se nekrytalický hydroaluminát vápenatý přibližného složení  $C_{12}A_7H_x$  a proces probíhá do vyčerpání  $C_3A$  až do teploty 300°C. S rostoucím měrným povrchem výchozího  $C_3A$  roste podíl hydroaluminátů vytvořených v první etapě. Hexagonální alumináty se přeměňují při teplotě 130°C na kubický  $C_3AH_6$ , který se pak při dosažení teploty 250°C rozkládá na  $C_4A_3H_3$  a  $CH$ .

#### Obr. 1. Křivky DHA:

- 1) Suspenze  $C_3A$  – měrný povrch 0,02 m<sup>2</sup>.g<sup>-1</sup>;
- 2) Suspenze  $C_3A$  – měrný povrch 0,5 m<sup>2</sup>.g<sup>-1</sup>;
- 3) Suspenze  $C_3A$  – měrný povrch 5 m<sup>2</sup>.g<sup>-1</sup>;
- 4) Suspenze  $C_4AH_{19}$ ;
- 5) Suspenze  $C_3AH_6$ .

#### Obr. 2. Produkt hydratace $C_3A$ při teplotě 250°C (bod B) – snímek EMPA.

- a) obraz v odražených elektronech;
- b) rozložení hliníku.

#### Obr. 3. Krystaly $C_4A_3H_3$ – SEM.

\*) V práci je použito zkratk: C ... CaO, A ... Al<sub>2</sub>O<sub>3</sub> a H ... H<sub>2</sub>O.

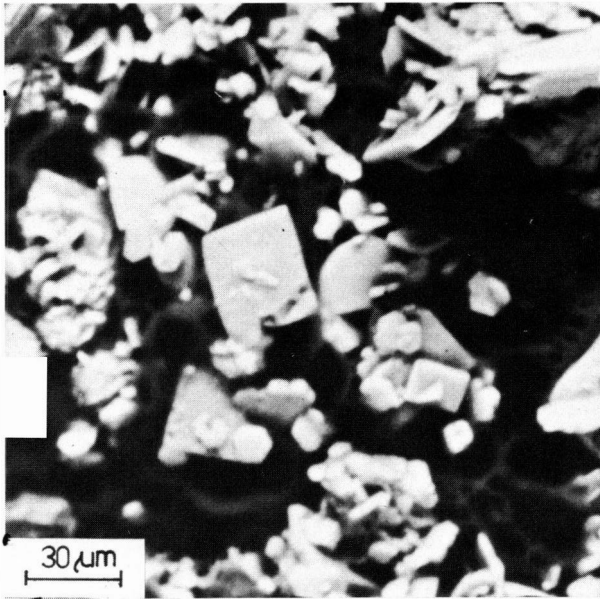
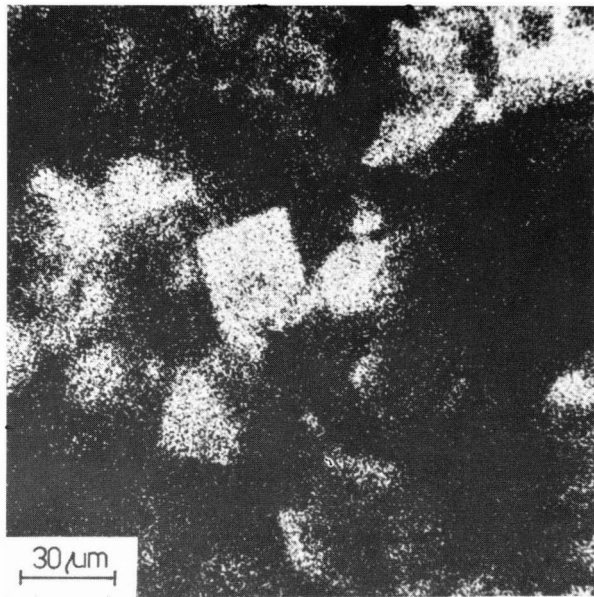


Fig. 2. The product of hydration of  $C_3A$  at  $250^\circ C$  (point B) – EMPA micrograph.  
a) reflected electron image;



Fig. 3. Crystals of  $C_4A_3H_3$  – SEM.



b) distribution of aluminium.