INVESTIGATIONS BY THERMOGRAVIMETRY INTO THE HYDRATION PROCESSES IN TRICALCIUM ALUMINATE AND TRICALCIUM ALUMINATE–GYPSUM MIXTURES

By

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Introduction

Those familiar with cement chemistry are aware of the importance of tricalcium aluminate and of its effect on the setting and hardening of cements.

Because of their great practical importance the hydration processes and products of tricalcium aluminate and of tricalcium aluminate—gypsum mixtures have been the subject of many investigations involving, among others, thermal methods, primarily differential thermoanalysis (DTA), but thermogravimetric (TG) and differential thermogravimetric (DTG) data have also been published. These publications, however, are mostly restricted to recorded curves, while an accurate description of the experimental conditions is often lacking.

The extension of knowledge on thermal tests has — besides of qualitative descriptions — made it timely to proceed to a deeper analysis of the complex phenomena tested. The exact description of test conditions is necessary also if determination of thermal peaks is aimed at. The shape of the curves and the peak temperatures are significantly influenced by test conditions, especially by the quantity of the specimen, the rate of heating and the shape of the crucible. Data reported else than according to Recommendations of the Standardization Committee of ICTA [1] will be practically worthless for other researchers. The importance of accurately defining the test conditions is obvious from the study on the dissociation of calcium carbonate [2] which is generally known to have a single thermal peak, but was proved by our measurements to display two peaks in different test conditions [3].

The kinetic constants of the processes are less affected by the conditions of thermal tests than are peak temperatures [3]. The kinetic constants were preferred to the peak temperature for characterizing the various thermal processes.

When DTA curves are used for the kinetic analysis of thermal processes [4, 5] a certain difficulty is encountered in the determination of the base line and of the changes in specific heat and heat conduction during the measurement. Therefore, thermogravimetric measurements were considered as more suitable to kinetic analysis. VAN KREVELEN et al. [6] were the first to carry out calculations of this kind. The actual calculation methods are based on or may be deduced from the differential equation (1) also applied by these authors [7, 8]:

$$-\frac{dX}{dt} = kX^{\nu} \tag{1}$$

where

$-\frac{dX}{dt}$	decomposition rate of the tested component,
X	quantity of the tested component still unchanged,
k	Arrhenius rate constant,
ν	order of reaction.

The rate constant k is temperature dependent (2)

$$k = Ze^{-\frac{E^*}{RT}} \tag{2}$$

where

Z	a pre-exponential factor,
e	base of natural logarithm,
E^*	activation energy,
R	universal gas constant,
T	absolute temperature.

FREEMAN and CARROLL [9] developed the initiative by VAN KREVELEN et al. They too started from Eq. (1) and worked out a graphic method by which they determined the order of reaction. As this method furnishes the most reliable results [8], it was applied to our calculations too, with the difference that the graphic differentiation of the TG curve could be omitted, since this operation was performed automatically by the instrument named Derivatograph we applied [10].

In the case of "simple" peaks which may be characterized by a single overall main process, such as the evaporation of water or the decomposition of calcium carbonate under the usual conditions, the method of FREEMAN and CARROLL was found to be quite satisfactory [3, 11], but careful analysis was required in the case of several different, partly overlapping main processes, such as that of the analysis of lubricating oils with several additives of simultaneous volatilization and thermal decomposition resulting in hardly identifiable products.

Methodically, the tricalcium aluminate hydrate system investigated is a transition between the "simple" and "highly complex" systems, for though the main processes overlap, only thermal decomposition is possible and the substance leaving the system is water. From the aspect of kinetical analysis the substances investigated may be considered model substances.

Many questions remain unanswered from the data of thermal investigations alone. In our case the complementary X-ray diffraction measurements proved to be highly useful.

Materials

Tricalcium aluminate was prepared from calcium carbonate of 99.0% and of aluminium oxide of 99.8% purity. Stoichiometric mixture of the two substances was pelletized with some water and calcined at 1400 °C in an electric oven, ground and hydrated. Calcination and hydration were repeated till the free calcium oxide content of the product was less than 0.1%. This product was used in the experiments, after being ground to a specific surface of 3000 cm^2/g as determinered in the Blaine apparatus.

The mixture containing gypsum was of a composition corresponding to ettringite ($C_3A \cdot 3CaSO_4 \cdot 31H_2O$) made from ground tricalcium aluminate and gypsum. Both tricalcium aluminate and the gypsum mixture were hydrated with water added in a ratio 1 : 1 (paste).

The samples* were stored at 20 °C and the hydration process was interrupted by the addition of alcohol at ages of 30 minutes, 2, 5 and 24 hours and 7, 14 and 28 days from the addition of hydration water.

After dehydration with alcohol, the samples were tested by derivatograph [10]; some samples also by X-ray diffractometry in the Müller Mikro 111 X-ray diffractometer. Thermal tests involved the measurement of the temperature within the sample. Temperature was raised at a rate of 15 °C/minute. Weighing was done at 500 mg sensitivity on a balance with 20 mg base sensitivity. The quantity of the sample was always 1000 mg.

Simultaneously to recording the curves of thermogravimetric (TG) and of that of the rate of weight change (DTG curve) the DTA curve of the same sample was also plotted. (Aluminium oxide calcined at 1500 °C was used as the inert substance.) Because of the identical character of the DTG and DTA curves and since the DTG and TG curves were used in the calculations, the DTA curves will not be included in this report.

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* The samples were prepared in the Department of Building Materials, while the measurements were carried out in the Department of Chemical Technology (Technical University, Budapest).

Investigation of the hydration products of tricalcium aluminate

The published DTA curves of the hydrates formed in the tricalcium aluminate—water system show in general three, exceptionally four dehydration stages. The most important conclusions may be summed up as follows [12]:

The first endothermic effect is the cleavage of water from C_2AH_7 and C_4AH_{13} which begins at about 80 °C.

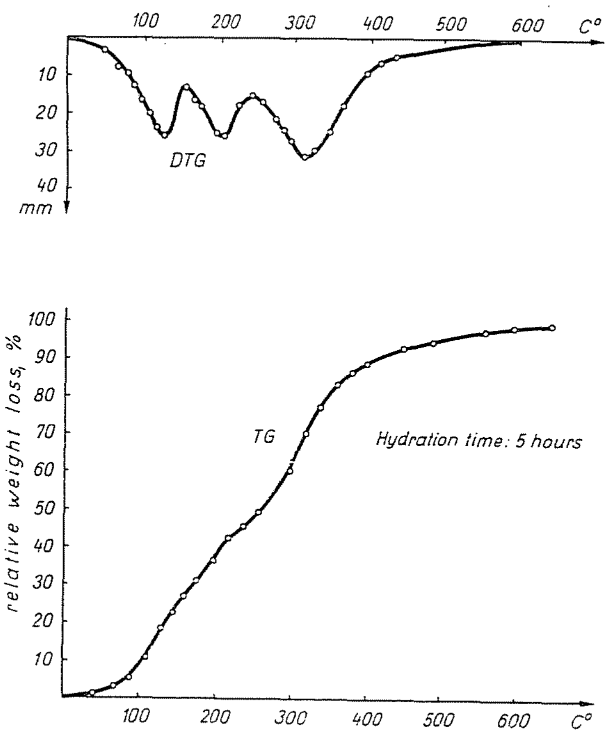

Fig. 1. Derivatogram of the hydrates of C_3A

The second endothermic effect is the second stage in the loss of water of C_2AH_7 and C_4AH_{13} which takes place between 150° and 250 °C.

The third endothermic effect is the loss of water of C_3AH_6 between 280° and 400 °C.

The fourth endothermic peak indicates the loss of water of calcium hydroxide between 500° and 600 °C.

Because of the reasons outlined in the Introduction, the DTA curves of different authors are difficult to compare and it may be said in general that the published curves are not suitable for calculations.

Figures 1 and 2 show the derivatograms of the samples hydrated for 5 hours and for 28 days which we considered the most significant; while DTG curves of all samples are presented in Fig. 3.

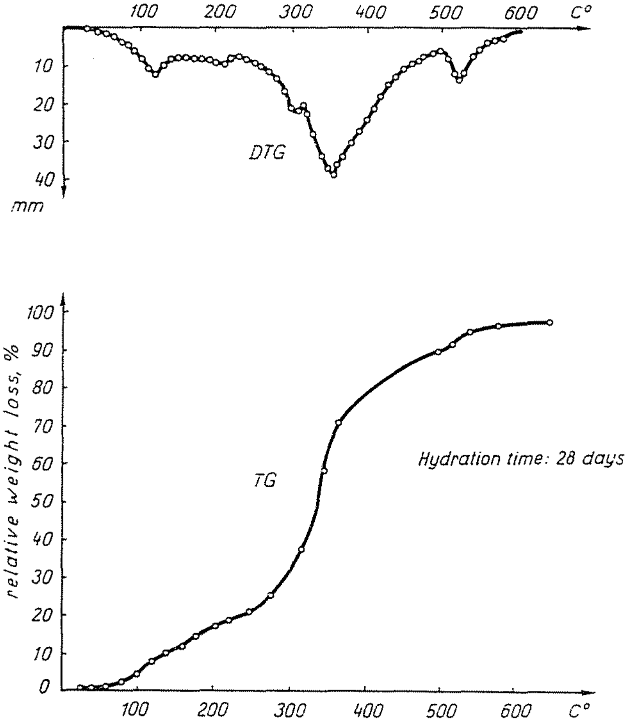

Fig. 2. Derivatogram of the hydrates of C_3A

From these figures, complementing and modifying the literature data, calculation in the temperature range as in Table 1 seems to be fully justified.

Table 1

Typical temperature ranges of water losses of the hydrates (pastes) prepared from C_3A

Temperature of water loss		Symbol of water position	Assumed compounds according to	
literature data [12] DTA, °C	own tests		literature data [12]	own tests
80—150	25—150	1	C_2AH_7 1st step C_4AH_{13}	C_4AH_{13}; CAH_{10} C_2AH_8
150—250	150—250	2	C_2AH_7 2nd step C_4AH_{13}	C_4AH_{13}; CAH_{10} C_2AH_8; C_4AH_x
280—400	250—320	3	C_3AH_6	C_3AH_6; AH_3
	320—480	4		C_3AH_6; AH_3
500—600	480—650	5	$Ca(OH)_2$	$Ca(OH)_2$

Thus the loss of water due to thermal treatment of hydrates prepared from tricalcium aluminate can be divided into five main stages instead of three (or four). It seems highly probable that at least some of the peaks are envelope curves of several processes.

Among the five processes, only three can be distinguished on the DTG curves up to the age of 5 hours. The 24-hour sample already indicates the fourth process which can be identified as the loss of water by calcium hydroxide. In the 7-day sample the fifth process appears quite definitely.

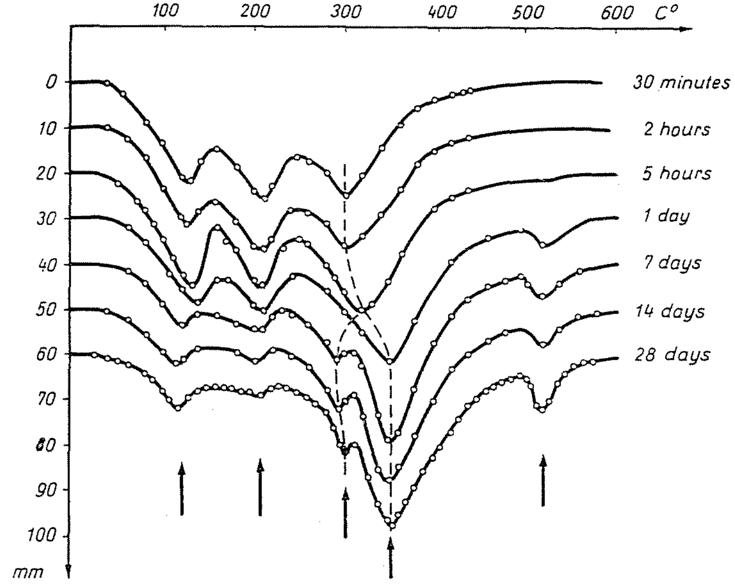

Fig. 3. DTG curves of the hydrates of C_3A

It should be mentioned here that peak temperatures in the vicinity of 125°, 210° and 525 °C do not change with changes in the period of treatment, while the peak which has appeared first at 300 °C divides into two in the manner shown in Fig. 3 and the temperature shifts. This latter phenomenon may be interpreted by assuming that the peak corresponding to the loss of water at 300 °C of the sample hydrated for 30 minutes is the resultant of the water cleavage process of at least two different substances. The quantity of the substance responsible for the peak at 300 °C does not change significantly as hydration proceeds, while the quantity of the substance responsible for the peak at 355 °C at 28 days greatly increases and the decomposition of the 7, 14 and 28-day samples, producing a peak at 300 °C is superimposed on the other water loss.

The various peaks correspond to different water bond strengths. From Fig. 3 waters in five different positions may be distinguished.

The identification of compounds with different water bond strengths is a hypothetical one, it is believed therefore to be more correct to designate water positions in our calculations rather than the above mentioned compounds.

The water quantities pertaining to the various positions were calculated from the TG curves with the help of the DTG curves. The quantity of water lost up to 650 °C was considered as the total bound water. The processes more or less overlap, so that the water quantities calculated for the various positions can only be considered as approximate values though the tendencies are quite definite. The results of the calculations are shown in Fig. 4.

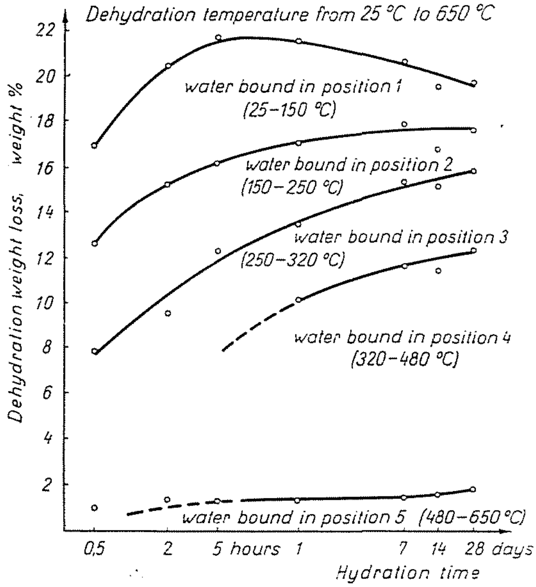

Fig. 4. Changes in the quantities of water of different bond strengths during the hydration of C_3A *vs.* hydration time

It appears from Fig. 4 that tricalcium aluminate binds 78.8% of the maximum hydrate water in the first 30 minutes.

The maximum of the hydrate water quantity is bound in the hydration interval from 5 to 24 hours after which the hydrate water content decreases.

The quantity of water in position 1 increases up to the age of 5 hours, after which it begins to decrease. The quantity of water in position 2 gradually decreases, the quantities in positions 3 + 4, that is in position 4, gradually increase.

The quantity of water in position 4 increases at the expense of the water in positions 1 and 2 due to internal rearrangement which is probably related to the appearance of calcium hydroxide. At the beginning of hydrolysis a major quantity of the loosely bound water passes gradually into a more strongly bound state. Figure 5 shows the water percentages with different bond strengths.

Changes in the quantities of water in positions 1 and 2 are not parallel which is in contradiction to the assumption cited from the literature (Table 1), namely that the second peak on the DTA curves corresponds to the second

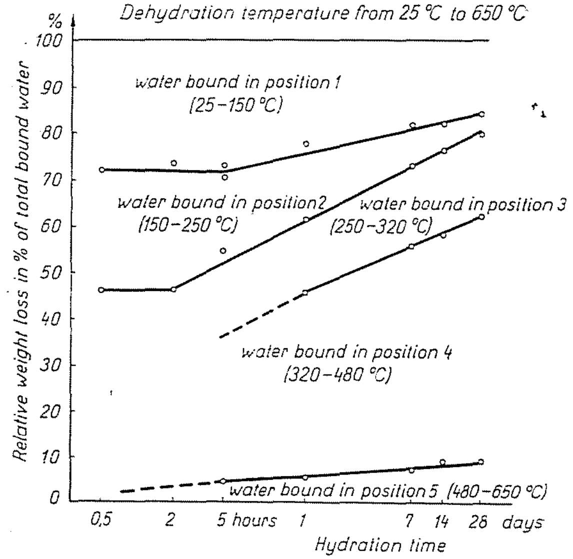

Fig. 5. Changes in the relative quantities of water of different bond strengths during the hydration of C_3A *vs.* hydration time

dehydration step of compounds which had been partially dehydrated in the vicinity of the first peak temperature.

The results of the X-ray diffraction measurements are shown in Table 2.

The products of short hydration periods indicate the presence of several compounds. The diagram of the 28-day sample includes fewer reflections and its evaluation is more unambiguous.

In the initial period of hydration the presence of compounds with more than six mols of crystal water was detected, just as the presence of cubic and hexagonal C_3AH_6 and possibly of C_2AH_8.

In the 1-day sample hexagonal C_3AH_6 was quite unequivocally detected, though cubic, and to a lesser degree C_2AH_8 reflections were also observed. The compound containing more calcium oxide could only be identified with C_4AH_x according to the ASTM2-0072 X-ray chart. C_3A reflection was also observed and the reflection of $Ca(OH)_2$ appeared too. Contrary to the patterns of the 30-minute and 28-day samples, the pattern of the 1-day sample indicated the presence of colloids.

Table 2

Identified hydration products of C_3A

Hydration time		
30 minutes	1 day	28 days
C_3A	C_3A	—
C_3AH_6 (cubic)	C_3AH_6 (cubic)	C_3AH_6 (cubic)
C_3AH_6 (hexagonal)	C_3AH_6 (hexagonal)	C_3AH_6 (hexagonal)
C_4AH_{13}	—	—
C_2AH_8	C_2AH_6	—
—	C_4AH_X	C_4AH_X
—	CAH_{10}	—
—	$Ca(OH)_2$	$Ca(OH)_2$
—	—	AH_3

From the definite, fewer reflections of the sample hydrated for 28 days, the presence of C_3AH_6 (hexagonal), gibsite and $Ca(OH)_2$ was ascertained and there was a great probability of the presence of C_4AH_X.

The results of the X-ray diffraction studies seem to support the assumption that the peaks on the DTG curves are envelope curves of several dehydration processes.

The kinetic analysis of the dehydration process of the hydrated products was performed according to the principles outlined in the Introduction.

The loss of the water in position 1 was studied on the derivatograms of samples hydrated either for 5 hours or for 28 days, and of water in positions 2 and 3 and in positions 4 and 5 on samples treated for 5 hours, and for 28 days, respectively. Data needed for the determination of the order of reaction based on the diagram proposed by FREEMAN and CARROLL [9] are given in Figs 6, 7 and 8, while the function log k vs. $1/T$ calculated from determined order of reaction is plotted in Figs 9, 10 and 11.

The order of reaction of the dehydration process involving water in position 1 seems independent of the hydration period (Fig. 6), but there appears quite clearly an increase in the bond strength (Fig. 9, slope of the straight-line log k vs. $1/T$). Thus not only part of the water in positions 1 and 2 is transferred into the more stable position 4, but there is a certain stabilization within position 1 itself.

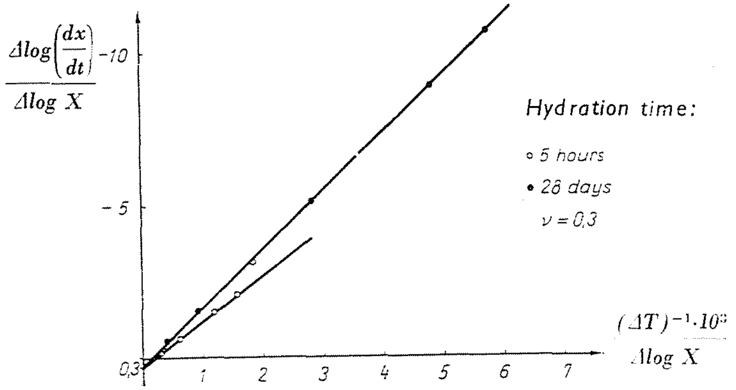

Fig. 6. Hydration products of C_3A. Order of reaction of the loss of water in position 1

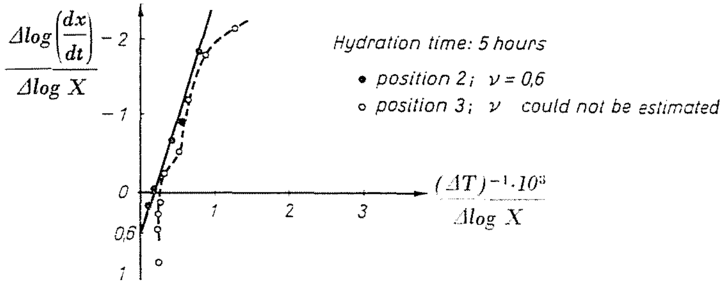

Fig. 7. Hydration products of C_3A. Order of reaction of the loss of water in positions 2 and 3

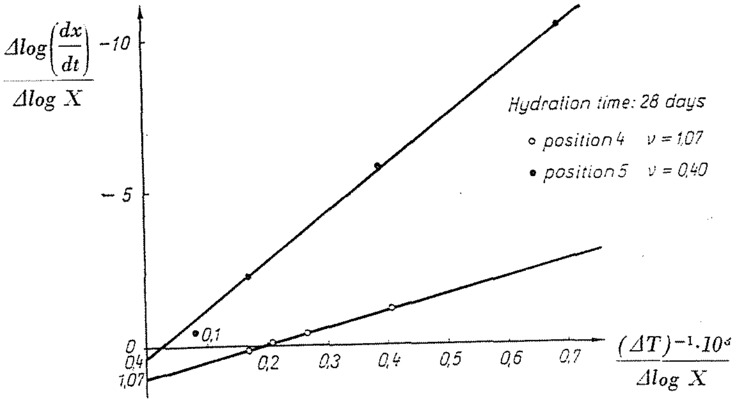

Fig. 8. Hydration products of C_3A. Order of reaction of the loss of water in positions 4 and 5

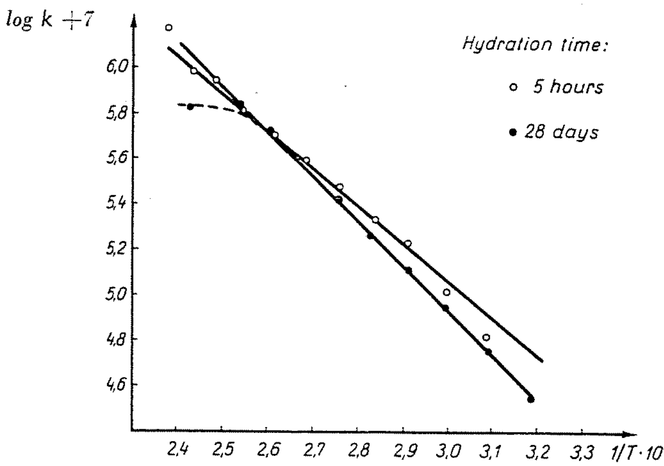

Fig. 9. Dehydration rate constant in position 1

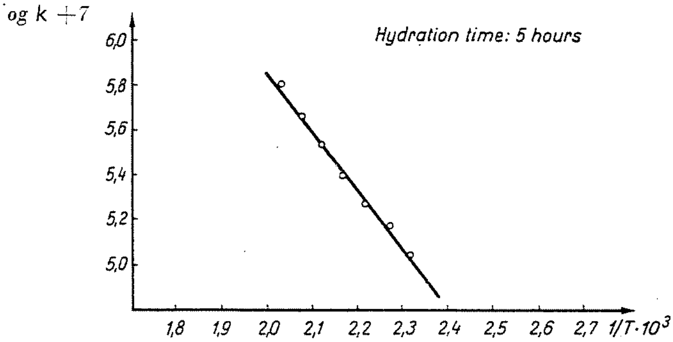

Fig. 10. Dehydration rate constant in position 2

Overlappings interfere to a lesser degree with the analysis of position 2·

Attempts to determine the order of reaction of position 3 (5-hour sample, Fig. 7) failed. Though the third peak on the DTG curve appears to be due to a single process, it is obvious that here, as already mentioned, at least two processes completely overlap.

A uniform process was expected from the Freeman—Carroll diagram for position 4, but the function log k vs. $1/T$ was composed of two straight sections. The inflection was where 2/3 of the water in position 4 were lost, indicating a change in the activation energy of dehydration at this point.

The results of the calculations are given in Table 3. This Table indicates the many unanswered questions in this field.

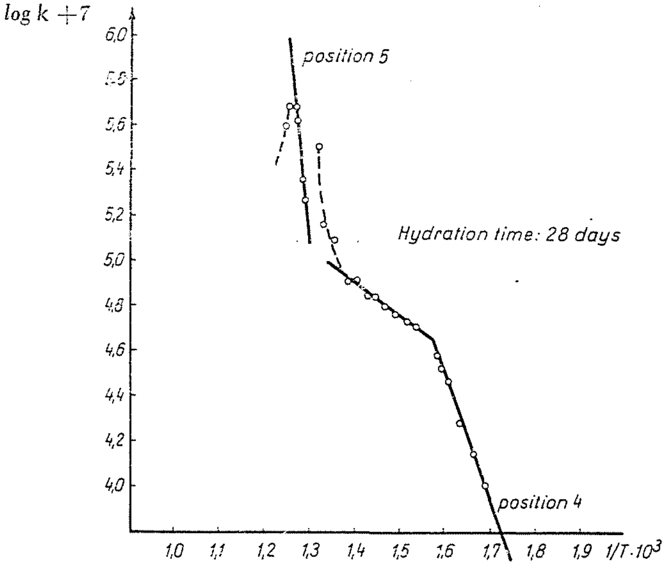

Fig. 11. Dehydration rate constant in positions 4 and 5

Table 3

Kinetic constants of the process of losing waters in different positions due to thermal effect

Paste composition	C_3A + water; 1 : 1				
Symbol of water position	1	2	3	4	5
Order of reaction	0.30	0.60	?	1.07	0.40
Activation energy kcal/mol H_2O	$7.5_{(1)}$ $8.5_{(2)}$	12.1	?	$26.8_{(3)}$ $7.1_{(4)}$	69.9
Substance losing water	? C_4AH_{13} CAH_{10} C_2AH_8	? C_4AH_{13} CAH_{10} C_2AH_8 C_4AH_x		? C_3AH_6 AH_3	$Ca(OH)_2$

(1) 5-hour sample
(2) 28-day sample
(3) for 2/3 of the water
(4) for 1/3 of the water

Investigation of the hydration products of the tricalcium aluminate—gypsum mixture

The principle of the investigations was the same as outlined in the preceding chapter.

Figure 12 shows the derivatogram of a tricalcium aluminate—gypsum mixture with a composition corresponding to that of ettringite. The Figure includes the data of products hydrated for 30 minutes, 5 hours and 28 days, respectively. On the DTA diagram by the ratio 2 : 1 of C_3A to gypsum four thermal effects appear [12], while on our own diagrams three processes can be distinguished which proceed according to the DTG curve approximately in the range 40° to 130°, 130° to 260° and 260° to 450 °C, but greatly overlap.

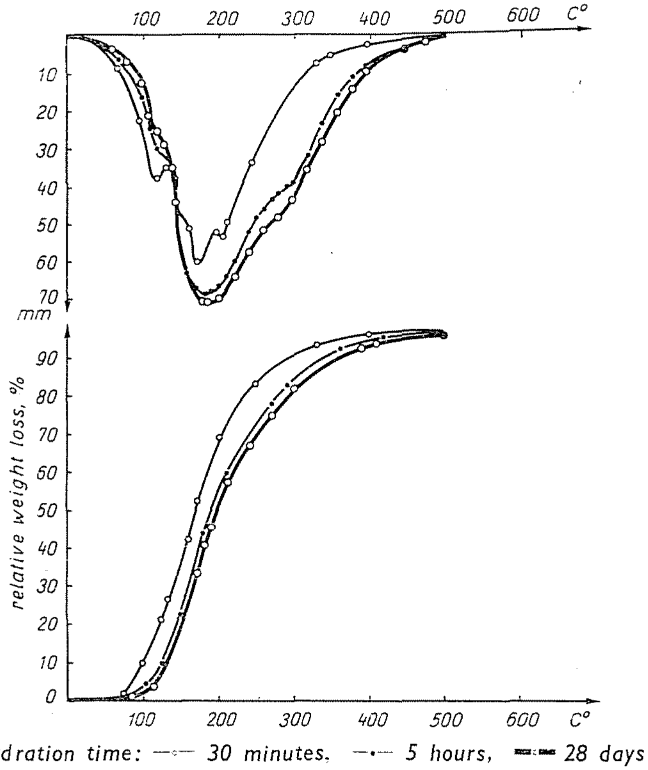

Fig. 12. Derivatogram of the hydrates of the C_3A—gypsum mixture

All three processes appear already on the diagram of the product hydrated for 30 minutes. From the age of a few hours the inflection temperatures are invariable, thus no conclusions can be drawn from thermal measurements on the qualitative changes in the substance as hydration proceeds.

Weight losses up to 650 °C, the water quantities pertaining to each process and the proportions of the water percentages in various positions are shown in Fig. 13 and Fig. 14 respectively. It appears from these Figures that water bounding is continuous and at the age of 30 minutes it is 75%, at 5 hours 96%, of that of 28-day samples. As to Figs 13 and 14, it should be noted that the classification of the bound water into these groups is adequate to express the trends, but for the time being it cannot be applied to the determination of the

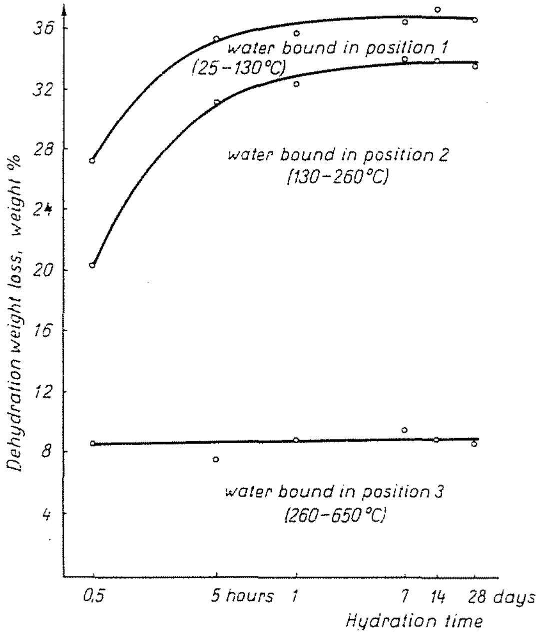

Fig. 13. Changes in the quantities of waters of different bond strengths during the hydration of the C_3A—gypsum mixture *vs.* hydration time. Dehydration temperature ranges from 25 °C to 650 °C

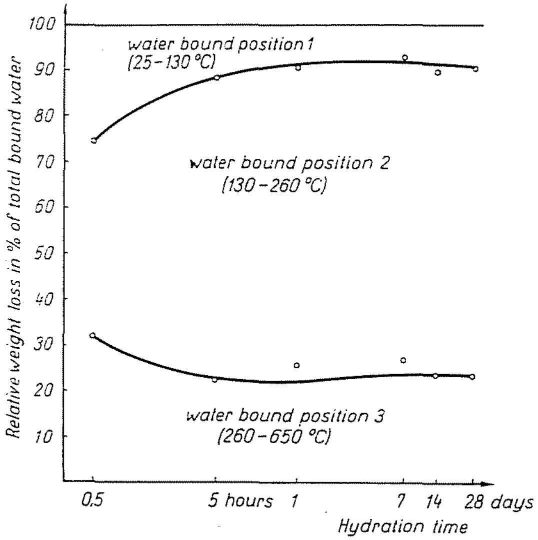

Fig. 14. Changes in the quantities of water of different bond strengths during the hydration of the C_3A—gypsum mixture *vs.* hydration time. Dehydration temperature ranges from 25 °C to 650 °C

quantities of the various hydrates or hydrate groups as the processes tend to overlap.

As a function of hydration time, the quantity of water bound in position 1 decreases, in position 2 greatly increases and in position 3 does not change noticeably. No calcium hydroxide was detected in the product.

The results of the X-ray diffractometry are shown in Table 4.

Table 4

Identified hydration products of the C_3A—gypsum mixture

Hydration time		
30 minutes	1 day	28 days
$C_3A \cdot 3CaSO_4 \cdot 31H_2O$	$C_3A \cdot 3CaSO_4 \cdot 31H_2O$	$C_3A \cdot 3CaSO_4 \cdot 31H_2O$
$C_3A \cdot CaSO_4 \cdot 13H_2O$	$C_3A \cdot CaSO_4 \cdot 13H_2O$	$C_3A \cdot CaSO_4 \cdot 13H_2O$
$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
C_3AH_6	C_3AH_6	C_3AH_6?
CAH_{10}	CAH_{10}	
C_2AH_8	C_4AH_x	

According to X-ray diffraction tests, the components of the hydrated product vs. time undergo also a qualitative change. This has led to the assumption that the peaks on the DTG (and DTA) curves are envelope curves. The X-ray diffraction tests confirm the decrease in the quantity of water in position 1 which latter originates mainly from the water content of gypsum.

The quantity increase of water in position 2 can primarily be attributed to the transformation of monosulphate into ettringite.

From the investigation of other substances it seemed that the second peak at 240 °C (water position 2) might be a suitable basis for kinetical calculations, nevertheless the order of reaction could not be determined because of the unusual scatter of the points on the FREEMAN—CARROLL diagram [9]. Satisfactory results were obtained, however, by assuming that the first and third processes were completely superimposed on the second.

Starting from this assumption, iteration gave 1.6 for the order of reaction of dehydration suiting to describe the process up to 360 °C.

Figure 15 shows the temperature dependence of the rate constant calculated with an order of reaction of 1.6. Accordingly, the dehydration of calcium sulphoaluminates beginning at 40 to 45 °C can be characterized by an order of reaction of 1.6 up to 360 °C, that is this order of reaction describes the loss of 94—95% of the bound water. The Figure partly confirms the correctness of the supposition involved in our calculations, while on the other hand, in agreement with the X-ray diffraction patterns, it proves the peaks and inflections on the DTG curve to be the resultants of several processes.

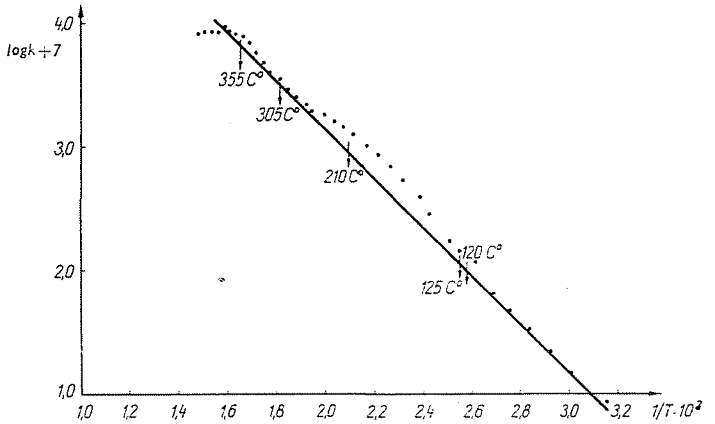

Fig. 15. Dehydration rate constant (hydrates of the C_3A—gypsum mixture) for position 2

The results of kinetical analysis indicate that in the product hydrated for 28 days, and containing even free gypsum, the same hydrates of C_3A appear as those formed without the addition of gypsum. At the temperatures indicated in Fig. 15 it was possible to detect, beside gypsum, the hydration products of C_3A which may be characterized by positions 1, 2 and 4, and the presence of water in position 3 is also probable.

It follows from the measurements that in the system C_3A—gypsum—water (similarly to the hydration of C_3A) primarily the reaction C_3A + water takes place, after which the calcium sulphoaluminates are formed whose dehydration can be observed along the entire temperature interval.

The activation energy of this dehydration is 7.7 kcal/mol H_2O.

In agreement with the X-ray diffraction tests, the compound containing water in position 3 was identified as C_3AH_6 .

Summary

The hydration processes of C_3A and of a C_3A—gypsum mixture were investigated by means of the derivatograph and by X-ray diffractometry. From thermogravimetric measurements five positions (bond strengths) of the bound water may be observed as hydration time proceeds. The appearance of water in the fifth position [$Ca(OH)_2$] is related to the process by

which the water more loosely bound is transferred into a more stable position. This process results primarily in an increase of the C_3AH_6 quantity. During thermal dehydration C_3AH_6 loses its water content in two steps in the ratio 2/3 : 1/3 with a simultaneous change in the activation energy of the process.

When gypsum is added in a quantity calculated for the stoichiometric composition of ettringite, the water bound in the hydrates of C_3A will apparently assume three different positions. Kinetical analysis of the thermogravimetric determinations revealed the presence of a gypsum free hydrate, C_3A, in the product, thus the number of water positions is greater than three. Up to the age of 28 days there was no decrease but rather an increase in the quantity of calcium sulphoaluminates.

The identification and kinetical analysis of the thermal processes are summed up in tables. The identification of the compounds pertaining to the various water positions will be the subject of further investigations.

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