Thermochimica Acta, 135 (1988)347–352
Elsevier Science Publishers B.V., Amsterdam

CARBONATION OF ETTRINGITE BY ATMOSPHERIC CARBON DIOXIDE

T GROUNDS, H G MIDGLEY AND D V NOWELL
Divisions of Civil Engineering and Chemical Sciences
Hatfield Polytechnic
Hatfield
Herts
AL10 9AB
U.K.

The mineral name ettringite is used to refer to the calcium trisulphoaluminate hydrate found in several hydrated construction cements. During a programme to study its longer term stability, the extreme sensitivity of synthetic ettringite to attack by atmospheric CO_2 was confirmed.

Using a TG/DTG method synthetic ettringite, samples were shown to have decomposed by carbonation at 25°, 50°, 75° and 95°C in moist atmospheres despite attempts to reduce the exposure to atmospheric CO_2. The decomposition products were identified using XRD techniques and quantified by the TG/DTG method. The data suggested a two-stage decomposition mechanism essentially accelerated by increasing temperature. The two-stage process was found to fit a number of established kinetic equations for solid decomposition and these are discussed in relation to the crystal structure.

Elimination of CO_2 from the moist atmosphere effectively prevented similar decomposition although at 95°C ettringite becomes thermally unstable.

INTRODUCTION

Ettringite is found in several hydrated construction cements and is a principal constituent of supersulphated cement (SSC). Its stability has been questioned and this is discussed in relation to the sensitivity of synthetic ettringite to carbonation.

EXPERIMENTAL

Preparation and verification of the synthetic hydrate has been previously described along with details of the TG/DTG method developed to estimate the proportion of ettringite contained within a sample [1]. Powder X-ray diffractometry (XRD) was used as a complementary technique.

Samples of synthetic ettringite were stored in sealed containers at 25°, 50°, 75° and 95°C at approximately 100% RH (over-water). Each series was designated by its temperature and humidity eg. E75-100 corresponds to 75°C and 100% RH. A quantity of soda lime was included within each container in an attempt to minimise the presence of atmospheric CO_2.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

RESULTS AND DISCUSSION

At all of the temperatures chosen the ettringite showed complete decomposition to other phases within two months of storage. XRD traces and TG/DTG curves showed similar changes for the four temperatures but occurring at different rates. Figure 1 shows the change in shape of the DTG curves using E75-100 as an example. Examination of XRD peaks confirmed the principal decomposition products as calcium sulphate dihydrate (Gypsum), calcium carbonate and aluminium hydroxide. These products are consistent with the decomposition of ettringite through attack by atmospheric CO_2, which has been discussed by previous authors (2,3).

The following simplified decomposition reaction has been suggested:

$$3CaO.Al_2O_3.3CaSO_4.32H_2O \text{ ----- } 3CaSO_4.2H_2O + 3CaCO_3 + 2Al(OH)_3 + 23H_2O$$

The fact that decomposition had occurred in this study despite attempts to minimise the CO_2 present, indicates great sensitivity of ettringite to such attack.

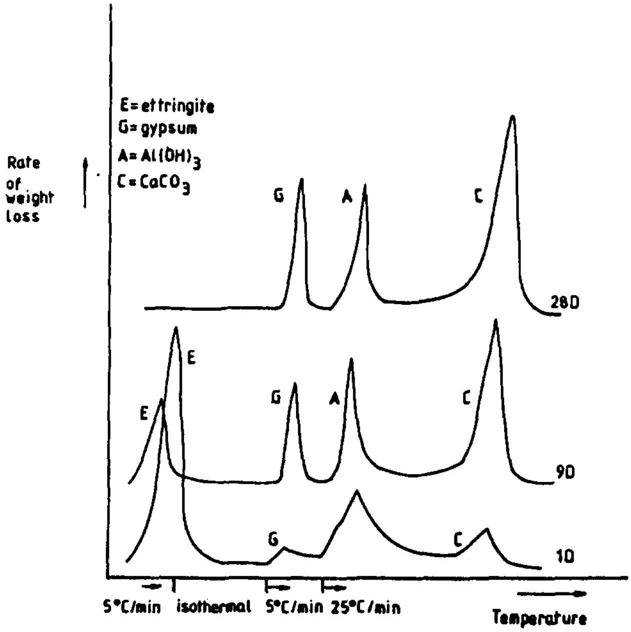


FIGURE 1 : CHANGE IN SHAPE OF DTG CURVE DURING DECOMPOSITION OF E75-100.

To obtain further data concerning the carbonation reaction the TG/DTG and XRD traces were quantified. Only the results from TG/DTG are discussed here, however, XRD consistently confirmed the trends in the reaction. Quantification of the TG/DTG curves was carried out by calibration of responses from pure compounds allowing stoichiometric calculation of the proportions of decomposition products. Figure 2 shows the results of this quantification for E25-100. Similar curves were obtained at each of the four temperatures and Figure 3 illustrates the reduction in the proportion of ettringite with time.

Calculated weight ratios of the three main decomposition products were consistent with the suggested simplified reaction. However, mass balance calculations which accounted for up to 95% of the products suggested further, unidentified material, which could not be definitely characterised by either XRD or TG/DTG. It is suggested that 'missing' material could be related to (i) adsorption of water produced onto the surfaces of other products, (ii) stabilised sections of columnar material from the ettringite crystal and (iii) the possible presence of 'plazolite' $3CaO.Al_2O_3.2(SiO_2CO_2).2H_2O$.

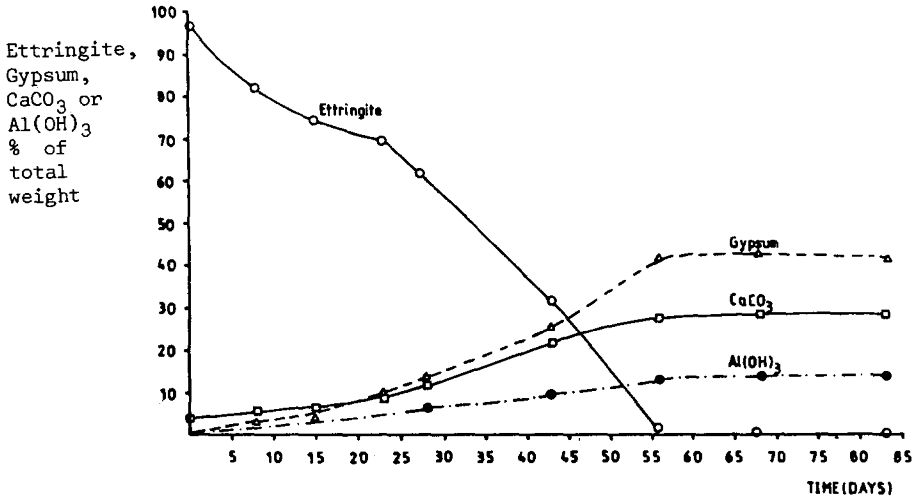


FIGURE 2 : COMPOSITIONAL CHANGES DURING CARBONATION OF E25-100 DETERMINED BY TG.

The TG/DTG results showed a two-stage reaction confirmed by X-ray data. The TG data for E50-100 showed this less clearly but XRD confirmed the presence of both stages. Examination of Figure 3 shows that the rate of decomposition was influenced by temperature and that, in terms of time taken to achieve complete decomposition, 25° > 50° > 95° > 75°C. This would suggest that the 95°C result was out of sequence, however, at 95°C other data showed ettringite to be inherently unstable even in the absence of CO_2, which may have influenced these results due to competitive reactions [4].

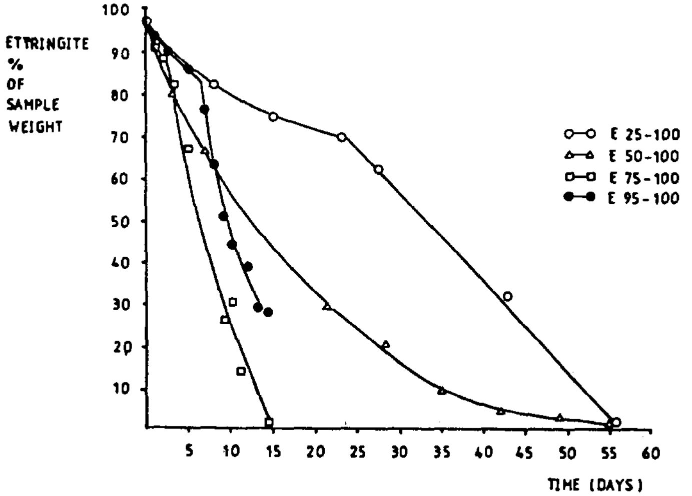


FIGURE 3 : COMPARISON OF THE DECOMPOSITION CURVES FOR ETTRINGITE STORED AT 100% RH AS DETERMINED BY TG.

A kinetic explanation of these trends through analysis of the experimental data has been attempted in order to try to explain the reaction mechanism. Care is needed in this respect since the data was obtained from experiments not designed to closely control atmospheric conditions or the particle size distribution.

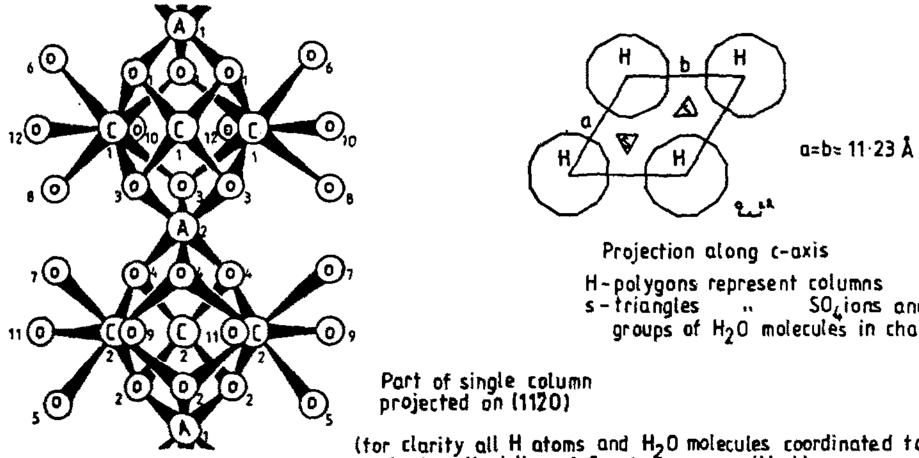
The data was first expressed in terms of α, the proportion of ettringite decomposed and time, t. Using established techniques [5] the values of α and t were compared to theoretical rate equations developed for kinetic studies of solid state reactions depending upon the rate contolling factors. Values from both TG/DTG and XRD were examined.

Data from the first stage consistently agreed with the relationship $\alpha^2=kt$ which relates to a deceleratory reaction contolled by one-dimensional diffusion. Data from the second stage could be fitted to several types of rate equation but overall the most consistent agreement was with the relationship $1-(1-\alpha)^{1/2}=kt$. This describes a deceleratory reaction controlled by reducing area of the reaction interface or reducing volume in cylindrical or lath-like structures [5]. Table 1 shows the relationships obtained for the two stages (no relationship attempted for the first stage of E50-100). The coefficients of determination were found from linear regression of α against $t^{1/2}$ and $1-(1-\alpha)^{1/2}$ against t and indicate reasonable correlation with the theoretical curves. The second stage values also show good agreement between TG/DTG and XRD.

TABLE 1. Rate Equations for 2-Stage Carbonation of Ettringite with Temperature

Designation	First Stage	Coeff. of Determination	Second Stage	Coeff. of Determination
E25-100 TG	$\alpha=0.06t^{1/2}$	0.997	$1-(1-\alpha)^{1/2}=0.02t-0.48$	0.95
E50-100 TG			$1-(1-\alpha)^{1/2}=0.018t-0.04$	0.99
XRD			$1-(1-\alpha)^{1/2}=0.016t-0.08$	0.97
E75-100 TG	$\alpha=0.063t^{1/2}$	0.99	$1-(1-\alpha)^{1/2}=0.07t-0.17$	0.97
XRD			$1-(1-\alpha)^{1/2}=0.07t-0.175$	0.88
E95-100 TG	$\alpha=0.05t^{1/2}$	0.97	$1-(1-\alpha)^{1/2}=0.05t-0.19$	0.96
XRD			$1-(1-\alpha)^{1/2}=0.04t-0.035$	0.95

The following reaction mechanism is suggested. The ettringite crystal structure [6] comprises columns of calcium and aluminium atoms co-ordinated to hydroxyl and water molecules, these columns being held as hexagonal shaped needle crystals by sulphate ions and water molecules effectively in channels between the columns (Fig. 4). It is suggested that the first stage corresponds to CO_2 gas diffusion along the channels, interference with the charge balance at the column surface and competition between SO_4^{2-} and CO_3^{2-} ions. This could cause the ettringite crystallites to split and initiate further reaction at defects in the column structure. The second stage would then involve more rapid decomposition as the reaction interface penetrates into and along the column material causing disruption of the main structure with rapid formation of calcium sulphate, calcium carbonate and aluminium hydroxide.



Projection along c-axis
H-polygons represent columns
s-triangles " SO_4 ions and
groups of H_2O molecules in channels

Part of single column
projected on (11$\bar{2}$0)

(for clarity all H atoms and H_2O molecules coordinated to
central vertical line of Ca atoms are omitted)

FIGURE 4 : THE MAIN FEATURES OF THE ETTRINGITE CRYSTAL STRUCTURE (MOORE AND TAYLOR 1970)

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ACKNOWLEDGEMENT

The authors wish to acknowledge the financial support of the SERC for this work.