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THE USE OF THERMAL METHODS TO ESTIMATE THE STATE OF HYDRATION OF CALCIUMTRISULPHOALUMINATE HYDRATE $3CaO.Al_2O_3.3CaSO_4.nH_2O$

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ABSTRACT

Calciumtrisulphoaluminate hydrate (ettringite) is found in several hydrated construction cements, however, its thermal stability has been questioned. A thermogravimetric method is described by which the stability of ettringite may be evaluated.

A synthetic hydrate was prepared and its composition verified by XRD, SEM and thermogravimetry.

The dehydration was investigated between ambient temperature and 1000°C. A stoichiometric calculation based on the mass of ettringite in the sample established a consistent value of 30-32 for 'n' in the hydrate.

The introduction of isothermal techniques enabled the identification of two distinct divisions for the loss of water molecules into 21-22 H_2O up to 70°C and 9-10 H_2O between 70°C and 1000°C. The implications of this development were explored in relation to drying of ettringite at various temperatures and relative humidities.

INTRODUCTION

Calcium trisulphoaluminate hydrate (ettringite) is found in hydrated Portland cement and is a principal constituent of several construction cements (ref.1,2). Doubts have arisen as to its thermal stability (ref.2,3) and this paper presents initial results obtained in a study of the stability of ettringite in supersulphated cement. These results have confirmed the use of the method.

The thermal methods and complementary techniques used have confirmed that the water of hydration is of two types which can be differentiated and quantitatively evaluated.

EXPERIMENTAL

A synthetic hydrate was manufactured by the mixing of stoichiometric proportions of tricalcium aluminate ($3CaO.Al_2O_3$) and anhydrous calcium sulphate in sufficient distilled, deionised water to provide a solution under-saturated with respect to $CaSO_4$. The solution was stirred for two days in a desiccator, evacuated to reduce contamination by atmospheric carbon dioxide. After filtration the material was desiccator-stored to remove excess water.

XRD analysis confirmed that the only crystalline phases present were ettringite (ASTM index No. 9-414) and calcite (ASTM No. 5-0586). SEM showed long hexagonal needle-like crystals 5-10 µm long and about 0.5 µm thick which are characteristic of ettringite.

Thermogravimetry was carried out using a Stanton Redcroft TG 760 with Universal Temperature Programmer and Balance Control Unit. DTG was obtained simultaneously from a Linseis N42 derivative unit with N31 preamplifier. Samples with initial weights between 0.5 and 3.0 mg were heated at $5°C min^{-1}$ from ambient to 1000°C in an atmosphere of flowing CO_2-free nitrogen.

RESULTS AND DISCUSSION

Figure 1 shows TG and DTG curves obtained for synthetic hydrate under the conditions stated. The small DTG peak at approximately 700°C and the corresponding weight loss are characteristic of the decomposition of $CaCO_3$ to CaO and CO_2. Calcite was also confirmed by XRD. Stoichiometric calculation from the weight loss gave a value of 2.5-4.0% for $CaCO_3$.

XRD and SEM showed no evidence of other phases or unused starting materials, therefore, the remaining weight losses and DTG peaks are considered to be the removal of hydrate water from crystalline ettringite. The DTG peaks indicate distinct stages in the dehydration which should correspond to differently bonded water molecules.

The number of water molecules 'n' was calculated from the relationship

$$\text{wt of ettringite} = \frac{\text{Dehydration wt loss} \times \text{molecular wt of } 3CaO.Al_2O_3.3CaSO_4.nH_2O}{18 \times n}$$

$$n = \frac{\text{weight loss} \times 678}{(\text{weight of ettringite} - \text{weight loss}) \times 18} \qquad (1)$$

The results of using this analysis on samples from different batches of ettringite gave a mean value of 30.7 (with a coefficient of variation of 4.6%) which is in agreement with that quoted for the mineral ettringite.

To confirm that the water loss occurred in distinct stages an isothermal mode was introduced in which the temperature was held constant at a value corresponding to the apex of the large DTG peak (Approx. 70°C) until the curve returned to the base line indicating no further weight loss.

This method divided the two dehydration stages into approximately $21H_2O$ (mean value 21.0, 4.3%CV) up to 70°C and $10H_2O$ (mean value 9.7, 8.7%CV) from 70°C - 1000°C.

In order to make the method more convenient for routine testing one further modification was introduced. At approximately 200°C the heating rate was

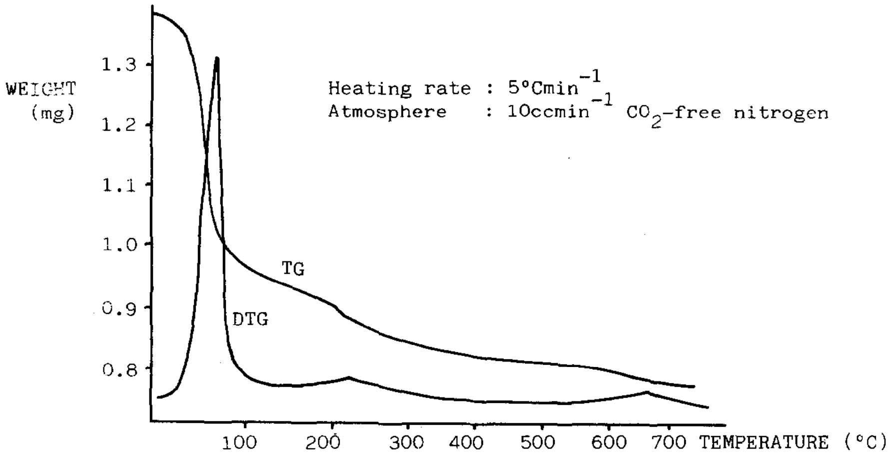

FIGURE 1: TG/DTG RESPONSE FROM SYNTHETIC ETTRINGITE

increased to 25°C min^{-1} to shorten the time for each run. This had the effect of emphasising DTG peaks above this temperature but was a necessary modification and helped define these peaks.

Results from pilot tests have shown the method to be flexible in being able to detect decomposition by different routes, particularly when used in conjunction with other identification methods.

Analysis of ettringite stored at 95°C, 11% RH (over saturated lithium chloride solution) illustrates decomposition by drying. Figure 2 shows values for total water content and the second stage water loss obtained using the semi-isothermal method, which confirms the ease of removal of the first stage water. This also shows that the semi-isothermal method will distinguish whether the removal of more closely bound water, likely to have a greater effect on the crystal structure, has occurred.

Decomposition leading to new phases can also be quantified if the nature of these is determined and they can be assumed to behave stoichiometrically. The decomposition of ettringite at 75°C, 100% RH (moist air) in the presence of a small amount of atmospheric CO_2 was monitored. Figure 3 shows the change in shape of the DTG curve at 1,9 and 28 days, obtained using the dual heating method discussed. XRD analysis identified the new phases as gypsum ($CaSO_4.2H_2O$), bayerite ($Al(OH)_3$) and aragonite ($CaCO_3$) which were related to the DTG curve as shown in Figure 3. The corresponding weight losses were then used to quantify the decomposition as illustrated in figure 4 where the ettringite is clearly seen to disappear with the formation of gypsum, aluminium hydroxide and calcium carbonate.

The initial results also have implications for the study of hydrated cements

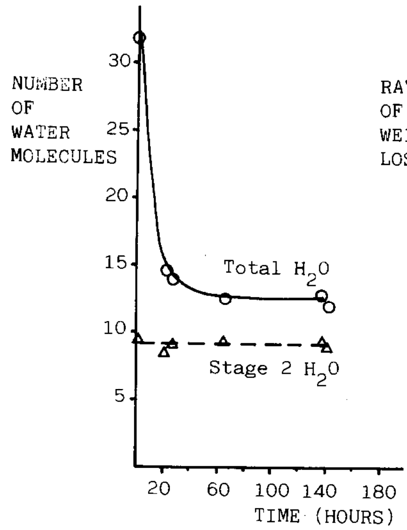

FIGURE 2: DEHYDRATION OF ETTRINGITE AT 95°C, 11% RH

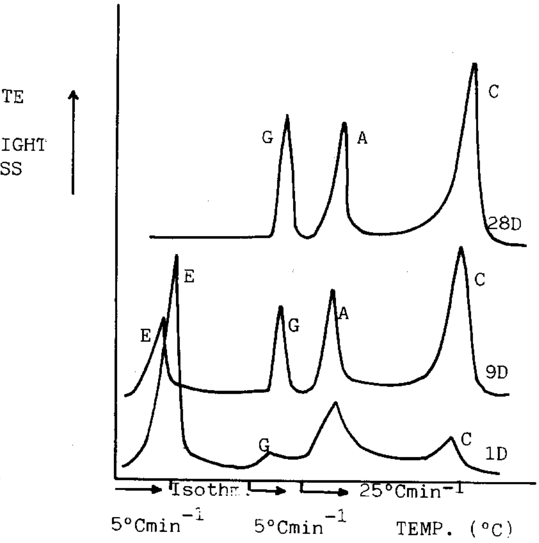

FIGURE 3: CHANGE IN DTG SHAPE AT 75°C 100% RH

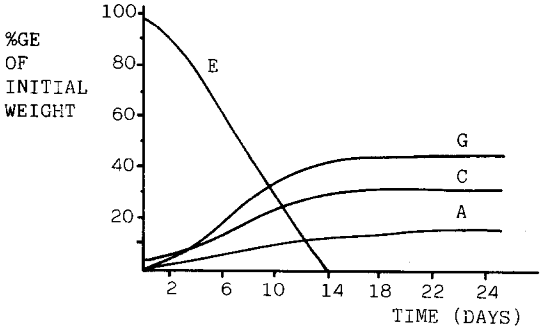

FIGURE 4: PHASE CHANGES AT 75°C, 100% RH

E = ETTRINGITE
G = GYPSUM
C = $CaCO_3$
A = $Al(OH)_3$

containing ettringite in that they highlight the need for care when drying and storing such cements in preparation for microstructural and mineralogical analyses due to the sensitivity of ettringite to such treatment.

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