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A CRITICAL ANALYSIS OF THE APPLICATION OF DERIVATIVE THERMOGRAVIMETRY TO THE DETERMINATION OF THE DEGREE OF CONVERSION OF HIGH ALUMINA CEMENT*

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ABSTRACT

Derivative thermogravimetry is shown to be a precise method for evaluating the degree of conversion of high alumina cement. The effects of heating rate and sample size on the degree of conversion, the calibration constant of the method and on DTG peak temperatures are measured and discussed.

INTRODUCTION

High alumina cement (HAC) is a widely used material which can suffer, under some circumstances, a severe loss in strength. The structural properties of HAC are thought to be related to the rate of the so-called conversion process and hence the measurement of the degree of conversion is of considerable importance[1]. While X-ray powder diffractrometry is in some ways a superior method, differential thermoanalytical techniques have assumed a major role following their recommendation by Midgley and the publication of details of their application to this problem[2]. In addition to these works, there have been reports, with a limited circulation, produced by a number of organisations. However, little, if any critical assessment of the use of thermoanalytical methods in the determination of the degree of conversion of HAC has been published.

Although an extremely complex multi-component material[1], HAC can be regarded, for the purpose of determining the degree of conversion, as a mixture of $CaO \cdot Al_2O_3 \cdot 10\ H_2O$, ($CaH_{10}$), $Al_2O_3 \cdot 3\ H_2O$, (AH_3) and $3\ CaO \cdot Al_2O_3 \cdot 6\ H_2O$, ($C_3AH_6$). On hydration of the main constituent of HAC, $CaO \cdot Al_2O_3$, (CA), the decahydrate CAH_{10} is produced at low temperatures in the form of needle-like hexagonal crystals which give rise to the high early strength of the material. Un-

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fortunately CAH_{10} is metastable and converts into the more dense cubic hexahydrate C_3AH_6 as shown by the equation

$$3\,CAH_{10} \rightarrow C_3AH_6 + 2\,AH_3 + 18\,H$$

It is thought that the resulting volume contraction contributes to the loss in strength. The degree of conversion is defined[2] as:

$$\frac{\text{amount of } C_3AH_6}{\text{amount of } C_3AH_6 + \text{amount of } CAH_{10}}$$

In normal use the C_3AH_6 is subject to carbonation, thus reducing the apparent amount as indicated by DTA. This leads to an erroneous value for the degree of conversion and hence it is customary to use the amount of AH_3 present instead[2]. This is valid as CAH_{10} is converted into almost equal amounts of C_3AH_6 and AH_3.

The equipment is calibrated with standard cement samples supplied by the Building Research Establishment and, in practice, it is usual to employ a calibration constant, *B*, defined in the equation:

$$\text{Degree of conversion} = \frac{B \times \text{peak height due to } AH_3}{B \times \text{peak height due to } AH_3 + \text{peak height due to } CAH_{10}}$$

It will be seen that peak heights are used rather than the more usual peak areas, because better reproducibility is obtained[3].

Although both DTA and derivative thermogravimetry have been used to determine the degree of conversion of HAC, the latter possesses the great advantage of having a baseline which is horizontal (Fig. 1). Apart from any instrumental variation, the baseline position in DTA will reflect the changing heat capacity of the sample as it undergoes chemical and/or physical processes. Clearly with DTG, the baseline position depends only on the rate of change of weight and, provided buoyancy effects are negligible, it will remain sensibly constant. For this reason, the quantitative aspects of the analysis were examined using DTG.

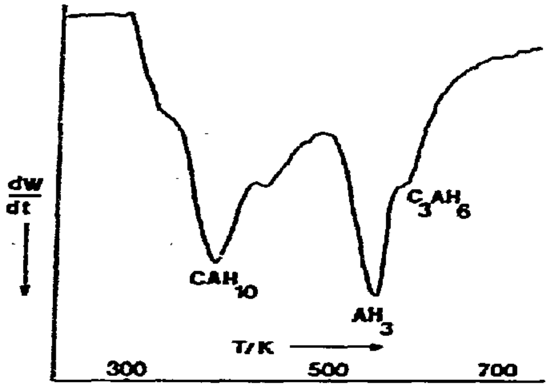

Fig. 1. A DTG curve for a sample of HAC (55% converted) illustrating the horizontal baseline and the main dehydrations observed. Sample weight, 8.0 mg; heating rate, 20 K min^{-1}; atmosphere, static air.

In any analytical procedure, one needs to know the reproducibility and accuracy of the method. In addition, with thermoanalytical techniques, the experimental conditions greatly influence the results and a knowledge of the effects of heating rate and sample size on the degree of conversion is essential. Further, the temperatures at which the various dehydrations occur are used for identification and it is widely known that these are greatly affected by operating conditions.

This paper reports a study of the effect of these parameters on the measured degree of conversion.

EXPERIMENTAL

A Stanton Redcroft TG750 thermobalance was used together with a Cahn time derivative unit to give derivative thermogravimetric curves. A Philips twin channel potentiometric recorder was used to record the DTG curve simultaneously with the sample temperature as measured by a thermocouple approximately 0.5 mm distant from the platinum sample-crucible. Samples were weighed on a microbalance reading to ± 1 μg.

RESULTS

In order to determine the reproducibility of the DTG method ten determinations were made on one sample under constant experimental conditions. A heating rate of 20 K min^{-1}, a sample weight of 8.0(0) mg and an atmosphere of static air were chosen as typical values.

An absolute measure of the degree of conversion of the sample is irrelevant for this test but it is known to be approximately 80% for the material used.

Of the ten results, one appeared to be invalid [$(x - \bar{x}/x) \times 100\% = 2.66\%$) and, on applying the t (0.95) test, it was rejected. The remainder passed the t (0.95) test and gave a coefficient of variation of 0.71%, with a mean value of 81.(0)%.

In order to assess the influence of the heating rate on the calibration constant B, and hence on the degree of conversion, twenty-five experiments were made using conditions as before except that the heating rate was varied from 5 to 100 K min^{-1}.

Figure 2 shows a plot of the apparent value of the constant B at the heating rates chosen, i.e., 5, 10, 20, 50 and 100 K min^{-1}. The equipment was calibrated at 20 K min^{-1} and the result for this heating rate represents the "true" value.

The effect of sample size was investigated in a further nineteen experiments at a constant heating rate of 20 K min^{-1}, using a range of weights from 5 to 50 mg, the latter representing the maximum capacity of the sample container used. The results are also illustrated in Fig. 2 where the mean values for each sample weight are plotted against the apparent value of the constant B. The sample weight used in the standardisation was 8.0(0) mg and hence the "correct" values are obtained at this weight. The effect of the variation in the value of B on the degree of conversion is also illustrated in Fig. 2.

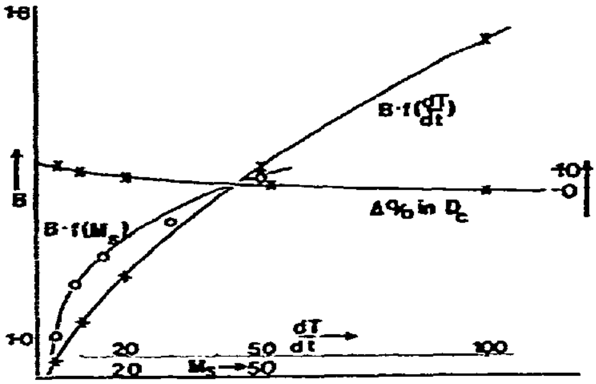

Fig. 2. The effect of heating rate and sample weight on the calibration constant B and the apparent degree of conversion of HAC, D_c, expressed as a percentage change, $\Delta\%$ in D_c.

TABLE 1

VARIATION OF THE DTG PEAK TEMPERATURE WITH HEATING RATE FOR THE DEHYDRATION OF CAH_{10} AND AH_3 IN THE DETERMINATION OF THE DEGREE OF CONVERSION HAC

Heating rate (*K min*$^{-1}$)	*Peak temp. for* CAH_{10}/*K*	*Peak temp. for* AH_3/*K*
20	369	539
50	389	575
100	436	581

The dependence of the DTG peak temperature on heating rate for the two important dehydration processes is shown in Table 1. In all cases, a constant sample weight of 8.0(0) mg was used to eliminate the effect of variations in this quantity. The results are mean values taken from a total of twenty-five separate experiments.

DISCUSSION

It is recognised that the construction industry does not require a precision of better than ± 5% in the measurement of the degree of conversion of HAC. Nevertheless, the precision of available methods should be established to ensure that these limits are not exceeded in practice. Further, the results illustrate the magnitude of variations which can be expected in derivative thermogravimetry in general. Naturally, equipment of different design will not yield identical results as temperature gradients and furnace atmosphere conditions will vary. Nevertheless, similar trends would be expected.

It is clear that the technique of DTG is capable of yielding results of high precision. The absolute accuracy of the method in this case depends on the substandards used and the results indicate that it is the uncertainty in these which is the limiting factor. In addition, the Building Research Establishment point out that these materials continue to undergo conversion although when stored under refrigerated conditions the process is considerably retarded. An important consideration which contributes to the high reproducibility of the results is the fact that the method uses ratios of peak heights. Thus the possibility of any long-term variation influencing the result is minimised.

The variation of the calibration constant B with heating rate is very marked (Fig. 2). Over the range of heating rates used the value of B changed by a factor of two. Fortunately, this caused a change in the measured degree of conversion of the order of only 10%. The reason for this lies in the form of the equation. As the degree of conversion tends to 100%, the height of the CAH_{10} peak tends to zero and the effect of the magnitude of B is minimised. Conversely, if the degree of conversion is low, i.e., $[CAH_{10}] > [B \cdot AH_3]$ the effect of variations in B becomes more serious.

Similar considerations apply to the dependence of B and the degree of conversion on the weight of sample used. In this case, the upper weight was limited by the capacity of the sample container and the lower value by the need to obtain peaks of a usefully measurable size.

The broad similarity of the curves shown in Fig. 2 suggests that the overall controlling factor is the temperature gradient established across the sample and its container.

The most readily located portion of a DTG curve is that of the peak height. Clearly, apart from indicating the position of maximum rate of weight loss, it has no significance as it varies with the heating rate, sample size and the atmosphere around the sample. Nevertheless, it is reproducible with a given set of experimental conditions. The results presented in Table 1 show that in order to be able to make use of the peak temperature to identify CAH_{10} and AH_3 the experimental conditions must be carefully controlled. In practice, there is usually no difficulty found in distinguishing between these two materials, but confusion can arise when other constituents, for example ettringite, may be present.

REFERENCES

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