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THE SEMI-ISOTHERMAL THERMOGRAVIMETRIC TECHNIQUE AND THE DETERMINATION OF THE DEGREE OF CONVERSION OF HIGH ALUMINA CEMENT CONCRETE

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ABSTRACT

Two Standard high alumina cement (HAC) – concrete samples with known degree of conversion were used to test the applicability of the thermogravimetric technique in the determination of the degree of conversion. The results obtained indicate that simultaneous thermogravimetry (TG) and derivative thermogravimetry (DTG) under semi-isothermal conditions would be a suitable technique not only for the determination of the degree of conversion of HAC – concrete but also for the study of the phase composition of this material.

1. INTRODUCTION

The mineralogy of set high alumina cement HAC[1–4] and the problems associated with the conversion of HAC have been extensively discussed[5–7]. It is established[1–5] that HAC undergoes a conversion from the metastable compounds, mono-calcium aluminate penta-hydrate $CaO \cdot Al_2O_3 \cdot 10H_2O$ (CAH_{10}), di-calcium aluminate octa-hydrate $2CaO \cdot Al_2O_3 \cdot 8H_2O$ (C_2AH_8) and alumina gel, into the more stable compounds, tri-calcium aluminate hexa-hydrate $3CaO \cdot Al_2O_3 \cdot 6H_2O$ (C_3AH_6) and various polymorphs and polytypes[8] of $Al_2O_3 \cdot 3H_2O$ (AH_3).

The degree of conversion as a percentage has been defined[5] for the appraisal of quality of HAC concrete as

$$Dc = \frac{\text{weight of } AH_3}{\text{weight of } CAH_{10} + \text{weight of } AH_3} \times 100 \tag{1}$$

Generally, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been used for the determination of the degree of conversion, which is usually based on the peak heights of the DTA or the DSC curves as a measure of the relative amounts of CAH_{10} and AH_3 present in the test sample. The choice of AH_3 in the determination of the degree of conversion is mainly because unlike C_3AH_6 it is not subject to carbonation[5, 6].

This investigation considers the application of simultaneous thermogravimetric

(TG) and derivative thermogravimetric (DTG) techniques in the determination of the degree of conversion of HAC. Firstly, it deals with the current technique using dynamic conditions of heating and considers its limitations. Secondly, it introduces modification to the technique which allows the proportions of the phases of the conversion reaction of HAC to be determined more readily.

2. MATERIAL

Two Standard HAC-concrete samples having known degrees of conversion of 28 and 66%, were provided by courtesy of Dr. H. G. Midgley of the Building Research Establishment (BRE), Watford, U.K. The Standard samples were extracted from HAC-concrete by light crushing and sieving through a 150 μm sieve. The two concrete samples were made with a cement of the following mineral composition: CA 45, pleochroite 26, C_2AS 1, C_2S 3, $C_{12}A_7$ 3, ferrite solid solution 14, FeO 5 and CT 3%[9].

3. APPARATUS AND EXPERIMENTAL PROCEDURE

For the experiments, a TG 750 Thermobalance apparatus (Stanton Redcroft, London, U.K.) was used. The weights of the test samples were always between 10–11 mg with a counter balance weight of 10 mg, so that the weight-loss (TG) curve could be expanded to a sensitivity of 1 mg at 10 mV full scale deflection (FSD).

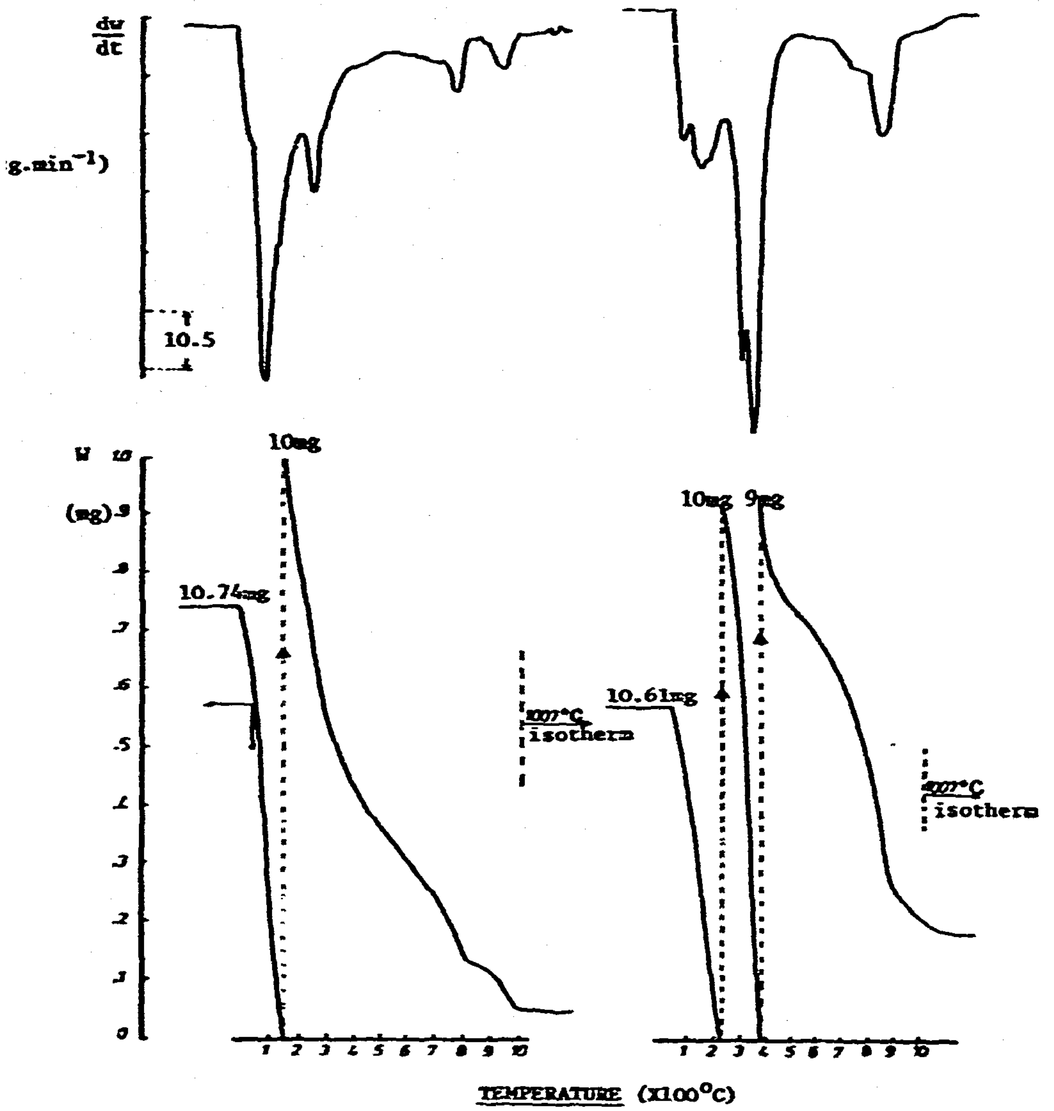
For the derivative thermogravimetric (DTG) curve, the weight-loss output signal was connected in series to a Linseis N30 μV-preamplifier and subsequently to a Linseis N42 Derivative unit. The DTG curves were recorded at approximately 1.05 $\mu g\ min^{-1}$ per division. The TG, DTG and temperature curves were simultaneously recorded on a Linseis multi-pens recorder (Linseis Messgeräte GmbH, Selb, W. Germany; type L1040).

All experiments were carried out at a heating rate of 15°C min^{-1}, chart speed of 100 mm h^{-1} and in a static atmosphere of dry and CO_2 free nitrogen. All the curves that will be referred to are direct tracings from the recorder charts.

4. DYNAMIC THERMOGRAVIMETRIC MEASUREMENTS OF THE STANDARD HAC-CONCRETE SAMPLES

Simultaneous dynamic thermogravimetric (TG) and derivative thermogravimetric (DTG) measurements were made on each of the Standard HAC-concrete samples and the results are shown in Fig. 1.

The dynamic technique employs a continuous constant heating rate giving for both samples a corresponding continuous loss of weight as recorded in the TG curves. Evidently to differentiate between the components of the conversion reaction of both samples from their respective TG curves is not possible. This is due to the absence of plateaux or points of inflection in the TG curves. This is particularly true in the



(a) (b)

Fig. 1. Simultaneous dynamic TG–DTG measurements of two standard HAC concretes having a degree of conversion of (a) 28% and (b) 66%, respectively.

lower part of the temperature range (up to 550°C) within which the degree of conversion of HAC is determined[6]. The corresponding DTG curves (see Fig. 1) give a more clearly identified resolution through their peaks which relate to the individual components of the conversion reaction, but it is difficult to determine the points of inflection that straddle any particular peak. In addition the troughs between peaks are far removed from the DTG baseline indicating a considerable rate of weight change at those points.

Thus, it is evident that overlapping reactions are being recorded. The degree of overlap is evidently greater in the lower part of the temperature range and it is

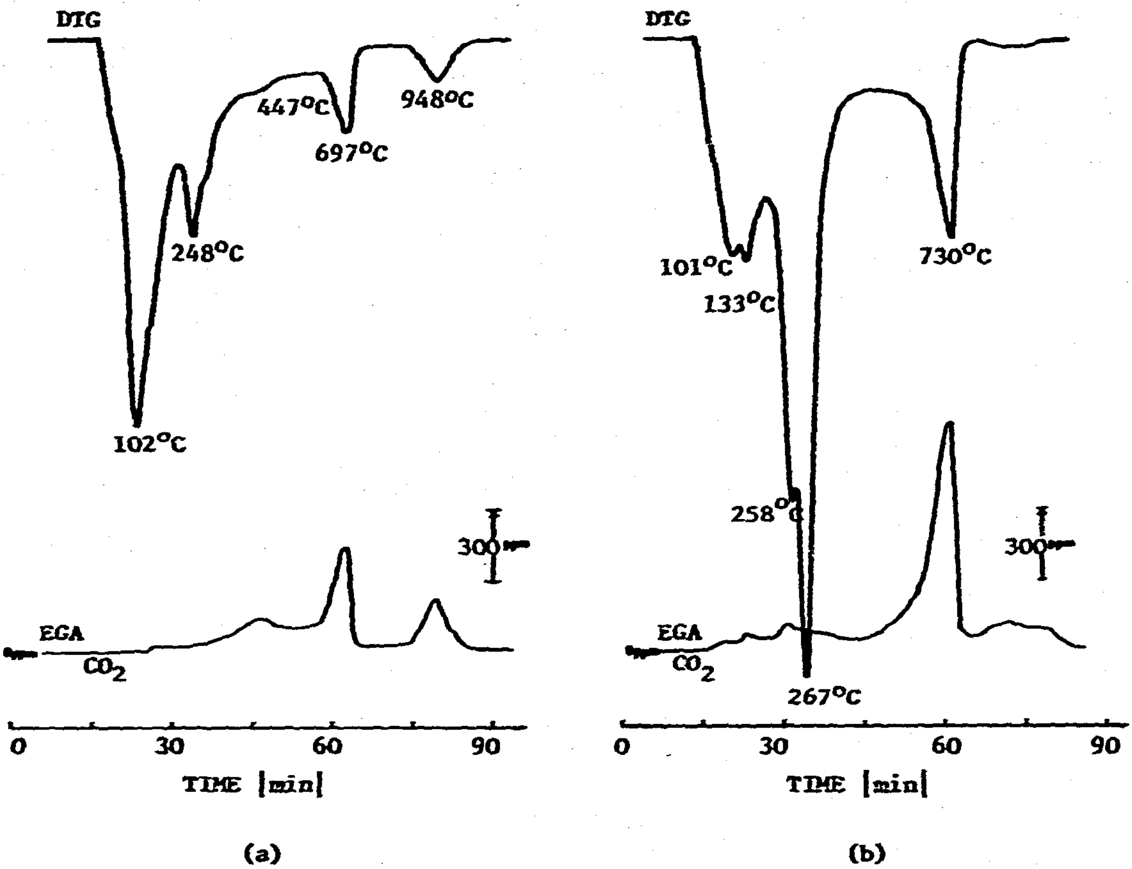


Fig. 2. Simultaneous dynamic DTG–EGA measurements of standard HAC concrete samples having a degree of conversion of (a) 28% and (b) 66%, respectively.
Heating rate 15°C min^{-1}, chart speed 100 mm h^{-1}, and dynamic atmosphere of CO_2 free nitrogen with flow-rate of 25 mh min^{-1}.

clear that there are considerable difficulties in making quantitative estimates from the dynamic curve. However, this does not exclude the possibility of making a broad division of the DTG curves into increments representing the constituents of the conversion reaction.

Thus, the first major peak includes CAH_{10} and the second major peak includes both AH_3 and C_3AH_6. The peaks above the 550°C include carbonates of these concretes, as verified by CO_2-IR evolved gas analysis (EGA) as shown in Fig. 2. The major peaks of the conversion reactions in the DTG curves are essentially similar to the endothermic peaks of the DTA curves reported for the conversion reactions of HAC (see refs. 5 and 6).

5. THE SEMI-ISOTHERMAL THERMOGRAVIMETRIC TECHNIQUE

The intention of the semi-isothermal method is to avoid the disadvantages of the dynamic method. That is, the attempt is made to eliminate the overlapping of peaks so that individual features of the thermogravimetric pattern may be isolated and readily quantified. Advances in morphological interpretation may also follow if the individual features can be associated with particular compounds.

The essential features of the semi-isothermal technique are as follows:

As the rate of weight change reaches a maximum (at a peak) and starts to decrease, the temperature programmer is switched from dynamic heating to the isothermal condition for 30 min. The isotherm temperature is usually 2–5°C higher than the peak temperature. At the end of the 30-min isotherm the temperature programme is again switched to dynamic heating until the next peak is reached. The procedure is repeated at each peak of the DTG curve up to the required temperature, i.e., up to 550°C in accordance with the recommendation of ref. 6.

6. SEMI-ISOTHERMAL THERMOGRAVIMETRIC DETERMINATION OF THE DEGREE OF CONVERSION OF HIGH ALUMINA CEMENT CONCRETE

In order to determine the degree of conversion (Dc) six semi-isothermal tests were carried out with each of the 28% and 66% Dc standard samples. Figures 3 and 4 show the characteristic TG–DTG curves of this technique for these samples.

The DTG curve of the 28% Dc standard sample (Fig. 3) shows four main peaks up to the 550°C temperature region. The first peak at the 101°C isotherm is related to CAH_{10}. The second peak at the 171°C isotherm is likely to be related to C_2AH_8 or C_4AH_{13} or both corresponding to the endothermic peak at 175°C that has been reported[10] for either C_2AH_8 or C_4AH_{13} or both. The third peak at the 264°C isotherm is related to AH_3. The fourth peak under continuous heating is related to C_3AH_6 with a peak temperature of 363°C.

The DTG curve of 66% Dc standard sample (Fig. 4) is unlike the 28% Dc sample in that it shows three main peaks up to the 550°C temperature region. The first peak at the 123°C isotherm is related to CAH_{10}. The second peak at the 271°C isotherm is related to AH_3, and the third peak under dynamic heating conditions is related to C_3AH_6 with a peak temperature of 350°C. Further dynamic heating up to 1007°C isotherm again shows the decarbonation peak at 794°C.

It is worth noting that in the semi-isothermal determination of the components of the conversion reactions for both Standard samples, the 66°C peak was included within the CAH_{10} DTG peak but it was excluded from the semi-isothermal procedure. For both samples the separation of the 66°C peak from the main CAH_{10} peak proved to be erroneous in relation to the determination of Dc, since this peak is part of the dehydration stages of CAH_{10} and is dependent on the humidity conditions of the sample[5].

In contrast to the dynamic procedure (Fig. 1), it can be seen from Figs. 3 and 4 that the rate of weight-loss during each of the 30 min isotherms decreases rapidly with time. This is emphasised by the levelling off of the TG curves to a semi-plateau state at the end of each isotherm, and consequently the approach of DTG curve to

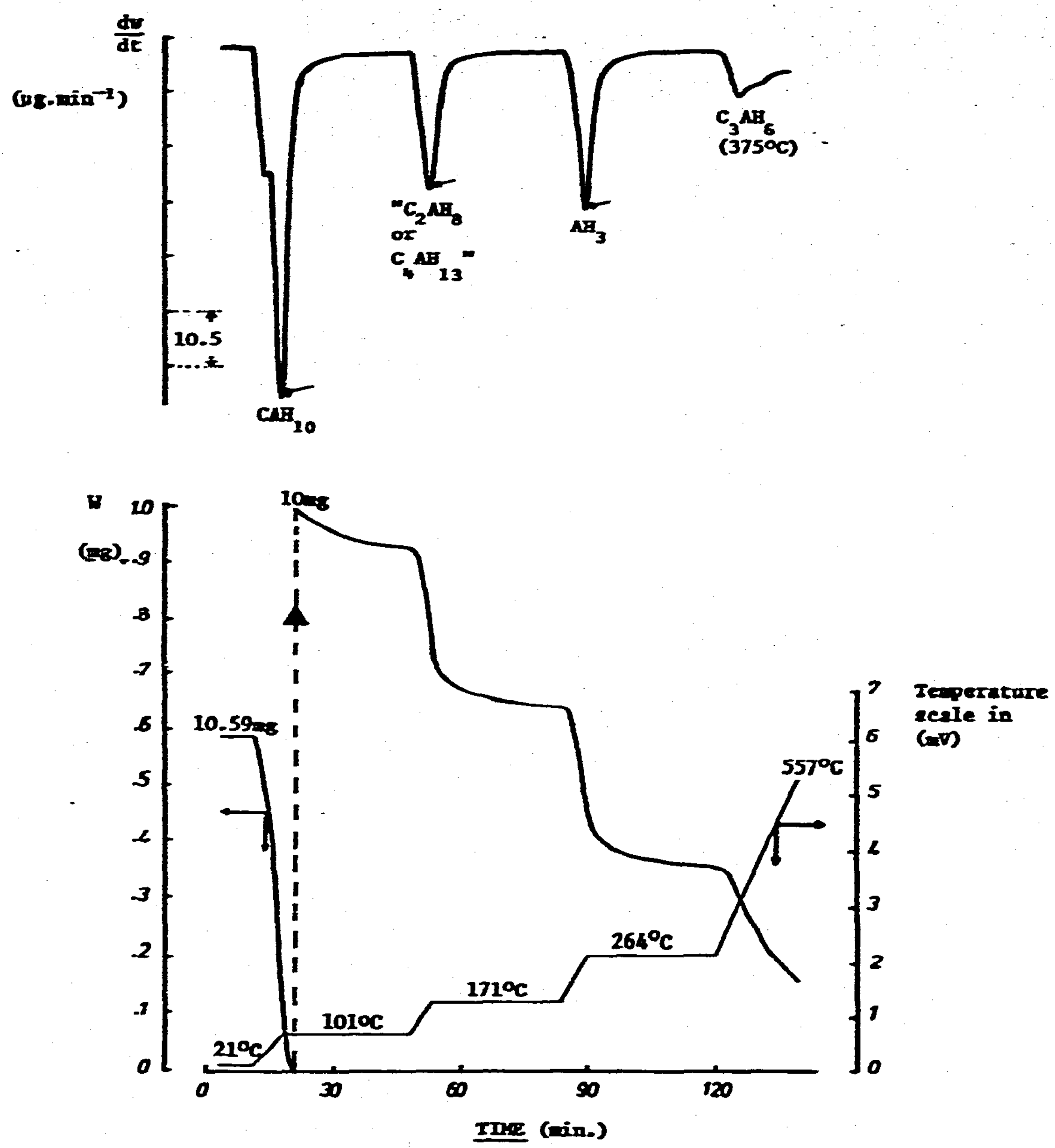


Fig. 3. Simultaneous semi-isothermal TG and DTG measurements for a standard HAC-concrete sample having a degree of conversion of 28%.

its baseline. With the consecutive isotherm–dynamic steps, three pronounced features in the TG–DTG curves merit mention:

(i) the separation of the overlapping of the different hydrates, especially those of the conversion reactions,

(ii) better representation of the different compounds or groups of compounds,

(iii) a more clearly defined weight-loss curve in relation to each compound or group of compounds.

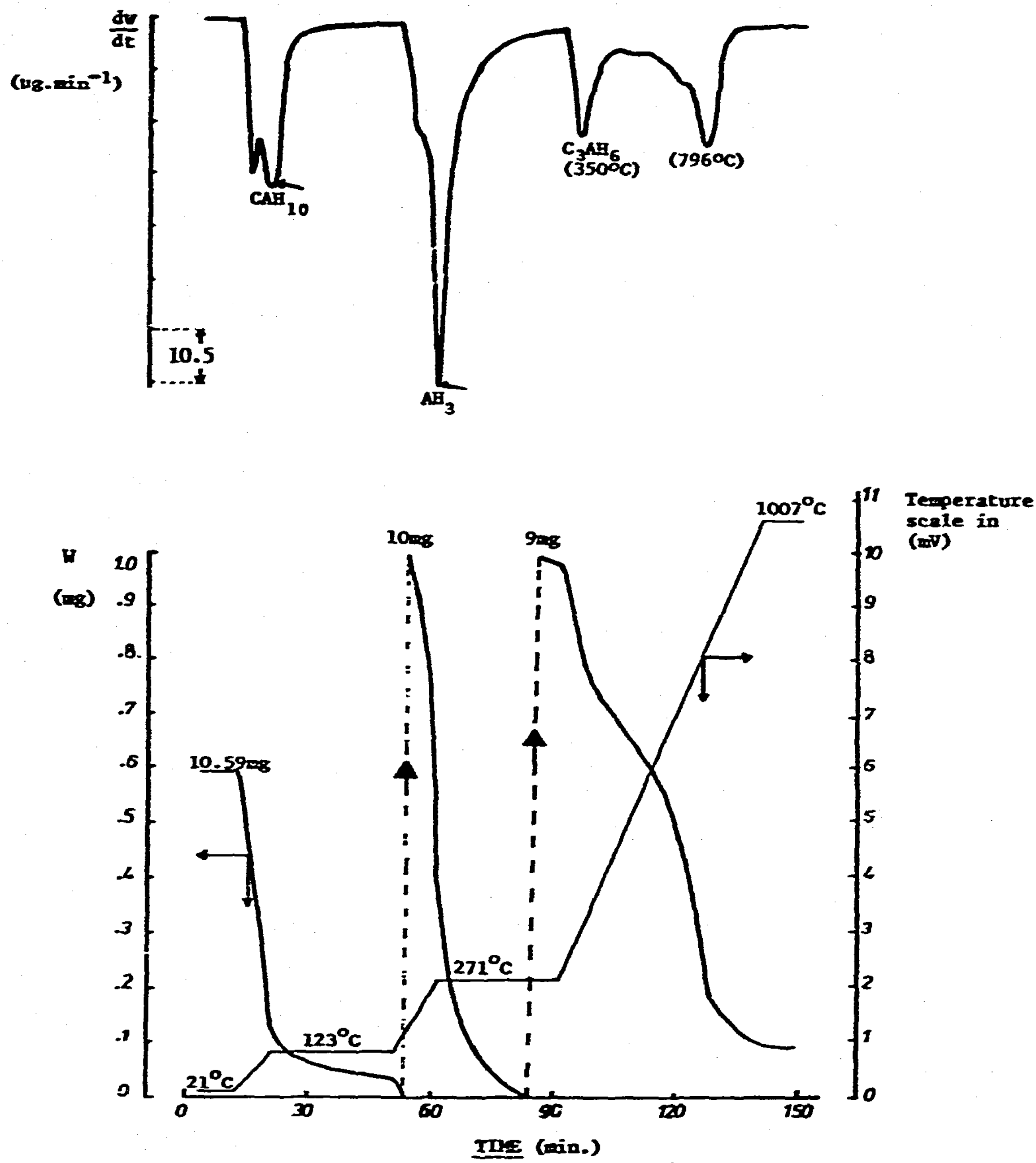


Fig. 4. Simultaneous semi-isothermal TG and DTG measurements for a standard HAC concrete sample having a degree of conversion of 66%.

The weight losses due to the thermal dehydration $\Delta W_{CAH_{10}}$ and ΔW_{AH_3} are simply calculated by the weight difference between the initial weight of the sample before the dehydration process of the particular hydrate and its weight at the end of the 30 min isotherm. Thus using $\Delta W_{CAH_{10}}$ and ΔW_{AH_3} it is a simple matter to determine the degree of conversion (Dc) according to eqn (1) which could be re-written as

$$Dc(\%) = \frac{\Delta W_{AH_3}}{\Delta W_{CAH_{10}} + \Delta W_{AH_3}} \times 100$$

5.1 RESULTS

The results of the six semi-isothermal thermogravimetric determinations of the Dc for the 28% standard sample are given in Table 1.

TABLE 1

SEMI-ISOTHERMAL THERMOGRAVIMETRIC DETERMINATION OF THE DEGREE OF CONVERSION OF THE 28% DC STANDARD HAC CONCRETE SAMPLE

Expt. No.	*Sample weight (mg)*	*Initial sample temp. (°C)*	*Temp. of isotherms of (°C)*		*ΔW at the end of each isotherm*		*Dc (%)*
			CAH_{10}	*AH_3*	*CAH_{10}*	*AH_3*	
1	10.59	12	101	264	0.66	0.28	30
2	10.92	15	101	262	0.66	0.28	30
3	10.62	15	101	261	0.65	0.28	30
4	10.75	12	103	267	0.62	0.24	28
5	10.82	12	105	266	0.61	0.24	28
6	10.63	12	103	264	0.61	0.25	29

As can be seen from the experimental results in Table 1 the degree of conversion ranges from 28 to 30% with a mean of 29% and a standard deviation of less than 1%. Thus the individual results deviate from the BRE 28% degree of conversion Standard sample by differences ranging from 0 to + 2% but the mean of these results deviates by only + 1%.

The results of the degree of conversion by the semi-isothermal technique obtained from six tests on the 66% Standard HAC concrete sample are summarized in Table 2.

TABLE 2

SEMI-ISOTHERMAL THERMOGRAVIMETRIC DETERMINATION OF THE DEGREE OF CONVERSION OF THE 66% DC STANDARD HAC CONCRETE SAMPLE

Expt. No.	*Sample weight (mg)*	*Initial sample temp. (°C)*	*Temp. (°C) of isotherms of*		*ΔW at the end of each isotherm*		*Dc (%)*
			CAH_{10}	*AH_3*	*CAH_{10}*	*AH_3*	
1	10.43	12	120	267	0.51	1.12	69
2	10.65	18	120	266	0.47	1.03	69
3	10.74	22	120	269	0.52	1.05	67
4	10.51	12	120	258	0.55	1.03	65
5	10.59	21	123	271	0.56	1.05	65
6	10.60	21	120	267	0.50	1.03	67

As can be seen from Table 2 the degree of conversion ranges from 65 to 69% with a mean of 67% and a standard deviation of less than 2%. Thus the individual results deviate from the BRE 66% degree of conversion Standard sample by differences from − 1% to + 2% but the mean of these results deviates by only + 1%.

6. CONCLUSIONS

The semi-isothermal technique, in contrast to the dynamic techniques, provides a better possibility of separation between overlapping components, and also enabling a better identification of the individual phases, that are associated with weight losses during the thermal treatment. This is demonstrated by the separation of the C_2AH_8 (or C_4AH_{13}) from the main components of the 28% Standard sample, and also by the separation of C_3AH_6 from AH_3. This separation makes it possible to determine the relative weights of such components in HAC concrete.

The results obtained for the degree of conversion (Tables 1 and 2) indicate a satisfactory accuracy and reproducibility for the semi-isothermal method, noting that the quoted figures of 28 and 66% degrees of conversion for the BRE Standard samples can be taken to vary by ± 1%[8].

It is reasonable to suggest that the semi-isothermal thermogravimetric technique could be used for not only the determination of the degree of conversion but also for the determination of the phase composition of HAC concrete.

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