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THE USE OF THERMAL ANALYSIS METHODS IN ASSESSING THE QUALITY OF HIGH ALUMINA CEMENT CONCRETE

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High alumina cement (HAC) concrete undergoes with ageing a change in mineral constitution known as conversion which may be accompanied by a loss in strength. The amount by which this change in composition has gone, measured by the ratio of $CaO \cdot Al_2O_3 \cdot 10\,H_2O$ to $Al_2O_3 \cdot 3\,H_2O$ is known as the degree of conversion (D_c). The faster the conversion goes the greater the loss in strength.

High alumina cement (HAC) concrete undergoes a chemical change where metastable components change to more stable compounds, this has been called conversion [1]. Although the reactions are complicated this change may be represented by a simplified equation:

$$3CAH_{10} = C_3AH_6 + 2AH_3 + 18H^*$$

The rate at which the conversion takes place influences the amount of loss of strength which HAC concrete may suffer. The degree of conversion, D_c, has been defined [1] as the ratio of the main constituents CAH_{10} and AH_3:

$$D_c = \frac{100}{1 + \dfrac{\text{Amount of } CAH_{10}}{\text{Amount of } AH_3}}$$

The author in earlier papers [1, 2] discussed the conversion reaction in relation to laboratory cured specimens, this report extends the study of the conversion reaction to HAC concretes in structures and especially to HAC concrete beams from buildings.

Thermoanalytical techniques including differential thermal analysis (DTA), calorimetric differential thermal analysis, differential scanning calorimetry (DSC) and derivative thermogravimetry (DTG) have all been used successfully. The estimated standard deviation of the mean of D_c due to the instruments used is about 0.5%. Sampling an apparently homogeneous concrete gave a standard deviation of 5%, while various methods of sampling the inside of an HAC concrete member did not

* Cement chemists shorthand notation used throughout. $C = CaO$, $A = Al_2O_3$, $H = H_2O$. So $CAH_{10} = CaO \cdot Al_2O_3 \cdot 10\,H_2O$.

introduce a standard deviation greater than 5%. Inter-laboratory correlation on standard samples gave a standard deviation of 7.7%.

Conversion is a chemical reaction and so the rate at which it proceeds will be affected by a number of factors. Midgley and Midgley [1] have enumerated in order of importance those factors known to affect the rate of the conversion reaction: temperature, water cement ratio, pressure and chemical environment.

When HAC undergoes conversion there may be a loss of strength and the amount of the loss of strength depends on the rate at which the conversion takes place; the faster the conversion the greater the loss in strength.

Rapid conversion also increases the porosity of the HAC concrete and so the permeability. This increase in porosity on conversion is due to the difference in volume of the products; specific gravity (s.g.) of CAH_{10} is 1.72, C_3AH_6 has an s. g of 2.52 and for AH_3 it is 2.4. For HAC pastes the density of unconverted HAC is 2.11 and converted 2.64, a decrease in volume of 20%. From the information on the behaviour of HAC concrete in the laboratory it is inferred that the quality of concrete in structures could be assessed if the rate of conversion could be determined. To do this the degree of conversion and age of the concrete is required. As the degree of conversion is determined from the ratio of the amounts of CAH_{10} and AH_3 some means of determining this ratio is required.

Two analytical techniques were considered possible; differential thermal techniques and quantitative X-ray diffraction. This paper presents the data on investigation into the use of thermal analysis techniques for the determination of degree of conversion.

Experimental

Use of thermal analysis techniques to determine the degree of conversion of HAC

The degree of conversion D_c of high alumina cement has been defined [3] as the ratio of the amounts of the minerals CAH_{10} and AH_3 present. Most thermal analysis techniques are suitable to determine this ratio for by calibrating the apparatus with known mixtures of the minerals the method may be made quantitative. Figure 1 shows DTA curves obtained from two HAC samples of different D_c and and the peaks that are to be used are sufficiently clear. Figure 2 shows the calibration curves used in Midgley [2], where pure synthetic minerals were diluted with α Al_2O_3 and relates peak height to weight of mineral.

The method using intermediate standards of HAC concretes with known D_c was investigated by the Thermal Methods Group of the Analytical Division of the Chemical Society and a report has been issued [3].

The thermal analysis peaks used in measuring the amounts of CAH_{10} and AH_3 in HAC concrete may be ill defined so for most work peak heights have been used instead of the more usual peak area. To investigate the validity of using peak height the reproducibility of the determination has been carried out. Six people measured both peak height and peak area on six different DTA curves, all were allowed to use any method of measurement they chose. The results are given in Tables 1 and 2.

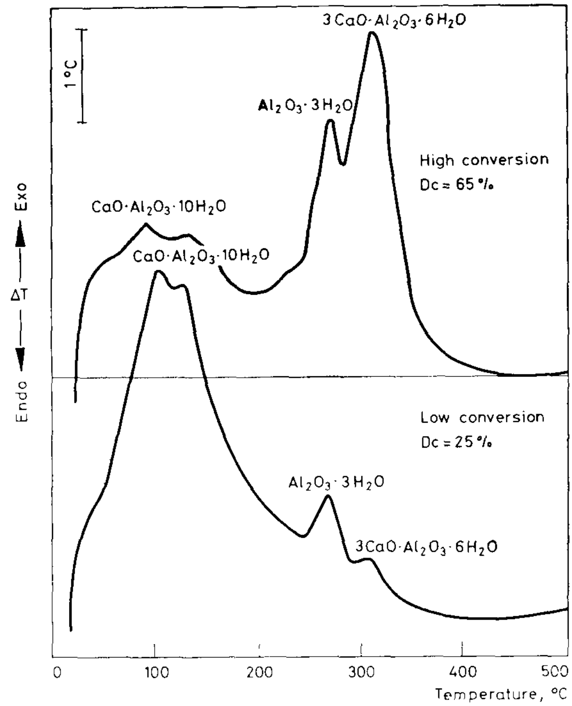

Fig. 1. DTA curves for high alumina cements of different degrees of conversion. Heating rate: 20°/min

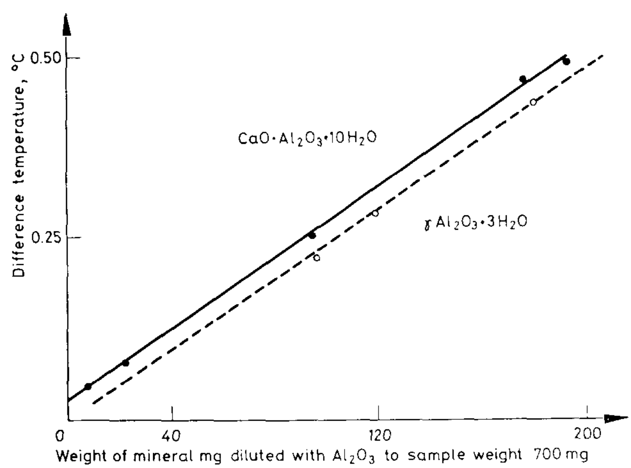

Fig. 2. Calibration curves relating peak height to weight of synthetic mineral present in mixture

Using standard deviation as a measure of reliability there is little to choose between measuring peak height and peak area; the average standard deviations for the respective measurements (Tables 1 and 2) were 2.4 and 2.5. However the standard deviations for the degrees of conversion were different, for peak height measurement 1.3 and for peak area measurement 4.1. It should be noted that for the peak height measurement the standard deviation of the measurement were highly influenced by the determinations on cement No 1 (Table 1). If this cement were ignored then the average standard deviation of the measurement would be 1.4. Cement No 1 was a highly converted cement and analyst *D* clearly had difficulty in establishing the base line. However the results of degree of conversion were not adversely affected.

Table 1

Measurement of peak heights (mm) of CAH_{10} and AH_3

Analyst / Cement	A	B	C	D	E	F	Av	SD*
				(CAH_{10})				
1	10	16	16	0	0	16	9.6	7.2
2	5	5	4	0	0	4	3	2.1
3	86	87	86	85	86	86	86	2.1
4	42	43	42	42	42	42	42	0.4
5	38	39	39	39	38.5	38	39	0.5
6	46	47	46	46	46	46	46	0.4
				(AH_3)				
1	113	114	113	86	113	113	109	10.0
2	160	160	160	156	160	159	159	1.4
3	63	64	63	64	63	63	60	0.2
4	34	35	35	34	34.5	34	34	0.4
5	22	23.5	23	23	22.5	23	23	2.4
6	56	57	57	53	56.5	57	56	2.1
				(D_c)			Average	2.4
1	92	88	88	100	100	88	93	5.4
2	97	97	97	100	100	98	98	1.3
3	42	42	42	42	42	42	42	0.0
4	45	45	45	45	45	45	45	0.0
5	37	37	37	37	37	38	37	0.4
6	55	55	55	54	55	55	55	0.4
							Average	1.3

* SD Standard Deviation from mean

The accuracy of various thermoanalytical techniques was investigated by the repeated determination of the degree of conversion by four methods; differential thermal analysis (DTA), calorimetric differential thermal analysis, differential scanning calorimetry (DSC) and derivative thermogravimetry (DTG). The analyses were carried out by four different analysts. The results are given in Table 3.

Table 2

Measurement of peak area of CAH_{10} and AH_3, cm^2 and D_c

Analyst / Cement	A	B	C	D	E	F	Av	SD
				(CAH_{10})				
1	2.0	1.8	0	0	0	0	0.6	0.9
2	1.0	< 1	0	0	0	0	0.3	1.1
3	17.2	32.4	31.5	30.5	38.5	30.4	30.0	6.3
4	8.4	8.6	9.0	9.1	12.6	9.3	9.5	1.4
5	7.6	8.4	8.4	8.9	13.5	4.8	8.6	2.6
6	9.2	11	10.8	10.3	17.2	11.3	11.6	2.6
				(AH_3)				
1	22.6	22.1	18.7	12.1	21.1	18.2	19.1	3.5
2	32.0	24.7	23.0	24.7	25.3	26.5	26.0	2.8
3	12.6	9.7	9.0	9.0	12.1	11.9	10.7	1.5
4	6.8	4.2	5.0	5.9	5.4	5.4	5.3	0.9
5	4.4	3.5	3.0	3.7	8.4	1.4	3.6	1.2
6	11.2	8.5	8.2	9.1	14.6	11.6	10.5	2.2
				(D_c)			Average	2.5
1	92	92	100	100	100	100	97	1.5
2	97	96	100	100	100	100	99	1.7
3	42	23	22	23	24	28	26	7.0
4	45	33	32	35	32	47	37	6.2
5	37	29	26	29	29	23	29	4.3
6	55	44	43	48	46	51	48	4.0
							Average	4.1

The results indicate that the errors introduced by the apparatus when used in a correct manner is small.

The results so far discussed refer to results obtained in laboratories with which the author is closely involved. It is to be expected that inter-laboratory errors would be greater and so two well homogenized samples of HAC from concrete beams CT 73 HO, Dc 20 and CTAG, Dc 70 were circulated to 50 laboratories who were asked to carry out the 'DTA' test on the samples and return the results. Thirty nine laboratories replied and a summary of the results is given in Table 4. Since the 'DTA method' of analyzing HAC concretes is not absolute but depends on calibration undertaken at the BRE the initial calibration value is given as well as the mean in Table 4. The conclusion from the results from the co-operating laboratories (Table 4) is that there is a 95% confidence of a result obtained from a test house being between $\pm 15.4\%$ of the mean value of the degree of conversion.

Table 3

Repeated determination of degree of conversion of one sample of HAC (Degree of conversion, per cent)

Method	DTA	Calorimetric DTA	DSC		DTG
	70.9	69.3	71.7	68.8	72.7
	69.8	69.0	69.3	70.8	70.8
	71.5	67.0	69.2	71.4	71.1
	71.0	69.0	68.5	70.1	70.5
	71.1	67.0	68.5	72.7	71.1
	72.8	65.9	70.0	70.3	70.0
	72.4	68.7	71.8	73.6	69.9
	72.3	69.8	71.4	68.6	72.0
	72.4	67.5	69.6	70.4	70.7
Mean	71.6	69.2	70.3		71.0
Standard Dev.	0.9	0.4	1.4		0.9

No pattern could be found for the errors; type of apparatus, heating rate, weight of sample, familiarity of operator with the technique, familiarity of operator with cement mineralogy were all considered. Some of the errors were simple; three laboratories measured the wrong peaks, one laboratory measured the incorrect base line, one laboratory had a spurious instrumental peak, one laboratory had mixed up the samples and one laboratory used a very high heating rate (64°/minute). However none of the results indicated that any laboratory would have classified an HAC concrete as 'good' according to the Department of the Environment Circular BRA/1068/2(4) when it was 'highly converted' or vice versa, although a sample in the intermediate region could have given results in the two outer regions.

Table 4

Results obtained by 38 test Laboratories for the degree of conversion (%) of two test samples

Lab No	Sample mark	
	CT 73 HO	CTAG
1	7.5	65
2	25	80
3	19	69
4	27	67
5	23	65
6	15	77
7	21	70
8	24	72
9	32	65
10	28	64
11	22	57
12	33	67
13	15	63
14	25	70
15	20	70
16	30	68
17	17	71
18	25	66
19	27	67
20	16	75
21	17	56
22	10	45
23	14	71
24	24	52
25	19	65
26	30	72
27	12	53
28	25	68
29	24	82
30	20	75
31	39	68
32	39	68
33	22	69
34	35	66
35	10	72
36	22	71
37	—	65
38	22	68
Average	22	68
Standard Dev	7.7	7.7
Calibration value	20	70

Results and discussion

The thermal analysis techniques are capable of giving the degree of conversion of an HAC concrete to an accuracy of $\pm 1.0\%$ (DTG, Table 3). Other thermo-analytical techniques at 95% confidence limits gave values of $\pm 1\%$ for DTA, $\pm 0.8\%$ for calorimetric DTA and $\pm 2.8\%$ for DSC.

An inter-laboratory investigation showed that the standard deviation of the mean for the degree of conversion of two samples of HAC concrete was 7.7%, which would suggest that the results obtained by analysts are meaningful at 95% confidence limits of $\pm 15.4\%$.

Sample collection

The degree of conversion of HAC concrete is affected by its environment, for example in a drying atmosphere the apparent degree of conversion of the first 5 mm or skin may be considerably less than the interior [2] or in thoroughly wet conditions it may be greater. To appraise the degree of conversion of a structural member it is necessary to collect a sample from the inside. Various methods of sample collection have been advocated; some destroying part of the member. To investigate the relative merits of sample collection three methods were investigated; 1 drilling, 2 chipping from surface, 3 crusting a sample from inside a beam. It must be emphasized that method 3 is only possible if the beam is destroyed.

Table 5 gives the results of two series of tests using different drilling techniques viz. rotary (1 – 14) and rotary percussion (15 – 28) drilling inch masonry type drills. Since these tests were carried out on laboratory beams it was possible to obtain

Table 5

Comparison of degree of conversion (%) on HAC concretes obtained by different sampling techniques

No	Drilled	Crushed	Difference	No	Drilled	Crushed	Difference
1	15	10	+ 5	15	45	42	+ 3
2	32	41	− 9	16	27	17	+10
3	58	59	− 1	17	88	71	+17
4	70	70	0	18	84	80	+ 4
5	85	75	+10	19	17	10	+ 7
6	80	85	− 5	20	33	23	+10
7	83	89	− 6	21	36	27	+ 9
8	80	90	−10	22	39	28	+10
9	80	90	−10	23	41	45	− 4
10	70	90	−10	24	67	69	− 2
11	85	90	− 5	25	24	29	− 5
12	15	17	− 2	26	77	92	−15
13	15	12	+ 3	28	77	81	− 4
14	39	85	− 6	28	86	92	− 6

crushed samples for inside the beam. In the pooled series the distribution is such that there are about the same number of examples where the drilled sample is less than the crushed sample as there are when the drilled sample is greater. The average difference between drilled and crushed is about 7% D_c.

A comparison has also been made between samples obtained by drilling using 'good practice' and surface chipping. It will be seen, Table 6, that the 'chipped' samples were lower than the results obtained by drilling. The difference which is large is considered to be due to the dehydration of the skin which gives anomalous results.

Table 6

Comparison of estimated degree of conversion (%) of HAC concrete samples obtained by chipping and drilling techniques

Drilled	Chipped
80	40
79	40
77	36

This emphasises the need to follow the recommendations to drill samples that is given in the Department of the Environment Circular BRS/1068/2 of 20 July 1974(4). Sampling by chipping (contrary to these recommendations) could lead to a serious underestimate of the degree of conversion as can be seen from Table 6.

Variation of degree of conversion in HAC concrete beams

The variation along and through beams has been investigated. Samples were taken using the drilling technique, the first 10 mm being discarded along the length of two beams. The beams had an average D_c of 85 and 28%; in the highly converted beam the variation along the beam, on 13 samples, as measured by standard deviation was 3.8%. On the low conversion beam, on 10 samples, the variation was as standard deviation 4.7%.

Samples taken through the thickness of two beams were investigated. If the first 4 mm were discarded then on a sample with a high D_c, 80%, the standard deviation of the mean was 2.2%; and on a low D_c 34, the standard deviation was 3.3%.

The results discussed above refer to homogeneous beams but if there has been localised heating due for example to central heating pipes, flue ducts, or electrical heating then large variations in D_c will occur. One such beam with a central heating pipe gave a D_c near to the pipe of 75% and away from the pipe 46%.

Anomalous results may also occur if there have been additions to the concrete; for example sodium silicate additions increased the D_c from 33% to 95%.

Conclusions

It is concluded that differential thermal analysis methods using small samples taken from any part of a beam give a reasonable estimate of the degree of conversion to an accuracy of not greater than $\pm 5\%$. It is recommended that if the beam is not to be destroyed that the sample is collected by drilling, using good masonry practice, discarding the first 5 mm.

The degree of conversion as measured on one sample will only represent the degree of conversion of the whole beam or of a suite of beams if there have been no special circumstances in manufacture or environment. Examples of special circumstances are segregation of the concrete, localized heating or subsequent chemical attack.

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Résumé — Le béton à haute teneur en alumine subit, au cours du vieillissement, un changement de constitution minérale. Ce phénomène, connu sous le nom de conversion, peut être accompagné d'une perte de résistance. La définition quantitative de ce changement, mesurée par le rapport $CaO \cdot Al_2O_3 \cdot 10\,H_2O/Al_2O_3 \cdot 3\,H_2O$, est connue sous le nom de degré de conversion (D_c). Plus la conversion est rapide, plus les pertes de résistance sont notables.

Zusammenfassung — Beim Altern von Zement mit hohem Aluminiumoxidgehalt (HAC) treten Änderungen in der Mineralienkonstitution auf. Diese als Konversion bekannte Erscheinung kann mit Festigkeitsverlusten verbunden sein. Der Umfang dieser Veränderungen der Zusammensetzung wird an dem Verhältnis von $CaO \cdot Al_2O_3 \cdot 10\,H_2O$ zu $Al_2O_3 \cdot 3\,H_2O$ gemessen und Konversionsgrad (D_c) genannt. Je schneller die Konversion, umso grösser die Verluste an Festigkeit.

Резюме — Бетон высоко глиноземистого цемента при старении изменяется в минеральном составе, что известно как превращение, сопровождающееся потерей прочности. Степень, на которую протекало изменение состава, измерялось отношением $CaO \cdot Al_2O_3 \cdot 10H_2O$ к $Al_2O_3 \cdot 3H_2O$, которое известно как степень превращения ($Д_c$). Более быстрое превращение приводит к большей потере прочности.