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THE QUANTITATIVE DETERMINATION OF HYDRATED CALCIUM SULPHATES IN CEMENT BY DSC*

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ABSTRACT

A DSC technique has been developed which permits rapid analysis of gypsum and hemihydrate in industrial cements. Initial studies indicated that the most important factor in achieving good resolution of the endothermic peaks associated with the dehydration of gypsum and hemihydrate was the water vapour pressure over the cement sample, although sample mass and heating rate also contributed. Optimal conditions of 8 mg sample sealed in an aluminium pan with a seal gap of 0.2 mm, and a heating rate of 15 °C min^{-1}, were determined from experiment. Determination of gypsum and hemihydrate (1–5% of each) in cements gave RSD values of 3.7 and 9.1%, respectively. Standard additions of gypsum and hemihydrate to analysed cement samples were made, and the means of the measured values were within 3% of expected values for gypsum, and 5% for hemihydrate. Analysis time was approximately 20 min per sample.

INTRODUCTION

Calcium sulphate dihydrate, or gypsum, is added at about the 5% level to cement clinker as a means of decreasing the rate of setting so as to prevent flash sets. During the subsequent milling process, generated thermal energy may cause partial dehydration, so that a mixture of gypsum and hemihydrate ($CaSO_4 \cdot 0.5H_2O$) is produced. Because the presence of the hemihydrate increases the rate of setting as well as causing deleterious long-term effects on the set cement, it is of some technological importance to monitor each of these phases in the final cement product.

Since the dehydration of gypsum occurs in a two-stage process, i.e.

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 0.5H_2O \rightarrow CaSO_4$$

which involves two endothermic weight losses, both DTA [1–6] and TG [7–10] have been proposed as analytical techniques. However, in order to

* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

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achieve good separation of the two endothermic peaks or weight losses, a high partial pressure of water vapour is required above the sample. This can be realised either by using a gas flow saturated with water vapour [2] or a steam atmosphere [3], or a closed sample crucible with a large sample to provide a self-generated water vapour atmosphere [4, 7, 8, 10]. Slow heating rates of $2\,^{\circ}C\ min^{-1}$ with an isothermal hold at 90–93 °C have also been reported to be successful [9].

Most of these studies produced methods that were either time consuming and/or involved large sample masses. Only two methods, one involving TG [10] and the other DTA [11], were concerned with the determination of gypsum and hemihydrate in cement. We have investigated the parameters important in obtaining good resolution of the endothermic peaks associated with the two dehydration steps. Using optimised conditions, a rapid heat-flux DSC method has been developed which permits determination of gypsum and hemihydrate in typical commercial cement samples.

EXPERIMENTAL

Samples

Laboratory grade gypsum and hemihydrate were supplied by May and Baker Chemicals Ltd. The water loss from gypsum was 20.15%, which is 96% of the theoretical value. The hemihydrate was analysed as: combined water, 5.8% (6.2); Ca^{2+}, 29.3% (27.6); SO_4^{2-}, 63.7% (66.2); and insoluble, 0.5% (0). Theoretical values are given in parentheses.

Standard samples were prepared by weighing out quantities of gypsum, hemihydrate and a typical cement clinker and mixing gently in an agate mortar and pestle. The cement samples tested, and materials used to prepare standards, had 98% of the particles passing a 45 μm sieve.

Indium used as a calibration standard for the DSC cell was supplied by Du Pont.

Instrumentation

All DSC work was performed on a Du Pont 1090 thermal analysis system which included data acquisition and processing facilities, and a standard heat flux DSC cell. Hermetic sealing of aluminium sample pans (part no. 900-796-901) was achieved with the Du Pont encapsulating press (part no. 900733) fitted with a hermetic sealing die (part no. 900720) that could be adjusted to give differing seal tightnesses.

Procedures

Samples of standards or cements were sealed into aluminium pans and heated at a constant heating rate from ambient temperature to 260 °C. The endothermic peaks resulting from the dehydration reactions of gypsum and hemihydrate were integrated and expressed as units of joules per gram. The instrument was calibrated at not less than weekly intervals for energy and temperature using an indium standard (enthalpy of melting 28.4 J g^{-1}, melting point 156.6 °C).

RESULTS AND DISCUSSION

Investigation of experimental parameters on peak resolution

The analytical method requires that the endothermic peaks due to the dehydration of gypsum and hemihydrate be sufficiently resolved to enable unambiguous integration. The various parameters that might affect peak resolution, such as water vapour pressure, sample mass and heating rate, were systematically investigated as a first step in method development. The degree of resolution or peak separation (see S in Fig. 1a) was determined as the temperature interval between the final integration point on the first peak and the first integration point on the second peak. Figure 1b shows the DSC record for the cement clinker. It is evident that no thermal effects occur

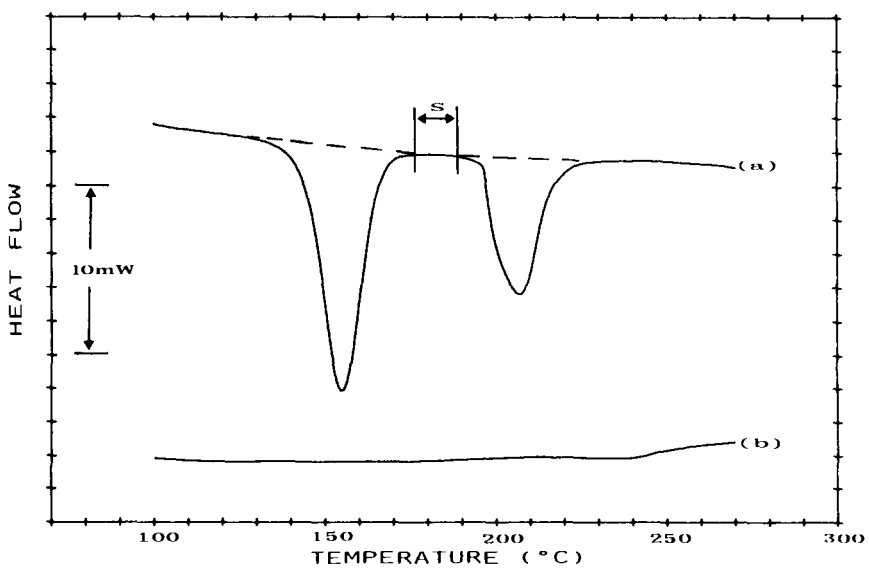

Fig. 1. DSC trace showing method of defining peak resolution.

which are likely to interfere with the gypsum–hemihydrate analysis, although this may not be true for all clinkers.

Effect of variation in water vapour pressure

One way of creating a self-generated water vapour atmosphere is to seal the sample in the sample pan. Water released during the dehydration of gypsum will remain in the pan and delay the appearance of the hemihydrate peak. The vapour pressure produced, however, will depend on the tightness of the seal on the pan. Light sealing will enable vapour to leak away at quite low internal pressures, whereas tight sealing will yield much higher internal vapour pressures.

Several experiments were performed on the effect of varying the seal tightness on the degree of resolution of the endothermic peaks. Samples of a standard synthetic cement (~ 8 mg), made by mixing known amounts of clinker, gypsum and hemihydrate, were sealed in an aluminium sample pan and heated at 15 °C min^{-1} in a DSC cell. The seal tightness was varied from 0.1 to 0.40 mm gap set on the sealing die in the encapsulating press. A 0.1 mm gap corresponds to a tight seal, and 0.40 mm to a light seal. The results are presented in Fig. 2, and show that good resolution of the two peaks can be achieved with die settings of 0.10, 0.15 and 0.20 mm, and that the resolution decreased from 25 °C for the tightest seal (0.1 mm) to 14 °C with a 0.2 mm seal. At a larger gap setting no resolution was apparent. Overlap of

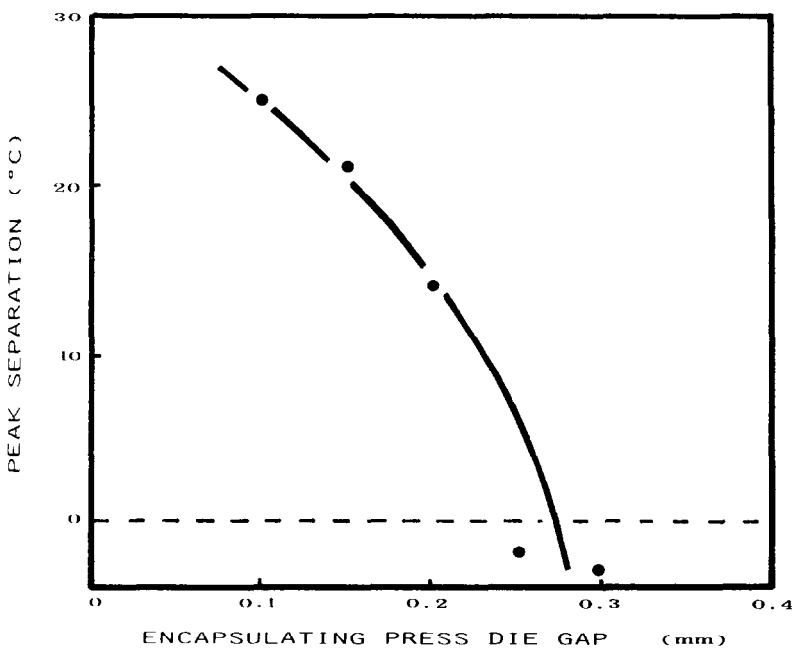

Fig. 2. Effect of sealing die setting on peak resolution.

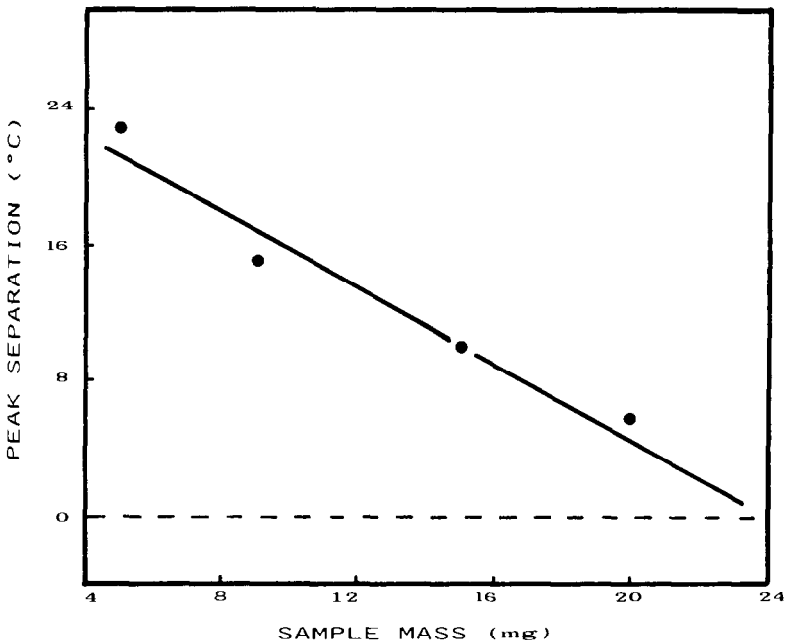

Fig. 3. Effect of sample mass on peak resolution.

the two peaks occurred at settings in excess of 0.25 mm, thus interfering with accurate peak integration. Despite the better resolution achieved with tighter seals, a problem was encountered with reopening the encapsulating press. In addition, the sample pans occasionally exploded at the tighter seal settings as the water vapour pressure exceeded the mechanical strength of the aluminium pan. A setting of 0.2 mm was chosen to give acceptable peak resolution, smooth operation of the encapsulating press and no risk of pan rupture.

Effect of sample mass

A further set of experiments was conducted in which samples were heated at 15°C min^{-1} with a sealing gap of 0.2 mm, and varying the sample mass between 5 and 35 mg. The results are presented in Fig. 3. The best peak resolution of 23°C was achieved with the lowest sample mass, and there was a steady decline in resolution as the sample mass increased. Beyond 22 mg no resolution was evident. A sample mass of 8 mg was selected for further work.

Effect of heating rate

Samples of ~ 8 mg were sealed into aluminium pans (sealing gap 0.2 mm) and heated at rates between 5 and 20°C min^{-1}. The results are presented in Fig. 4. Good resolution was achieved at all heating rates, although there was

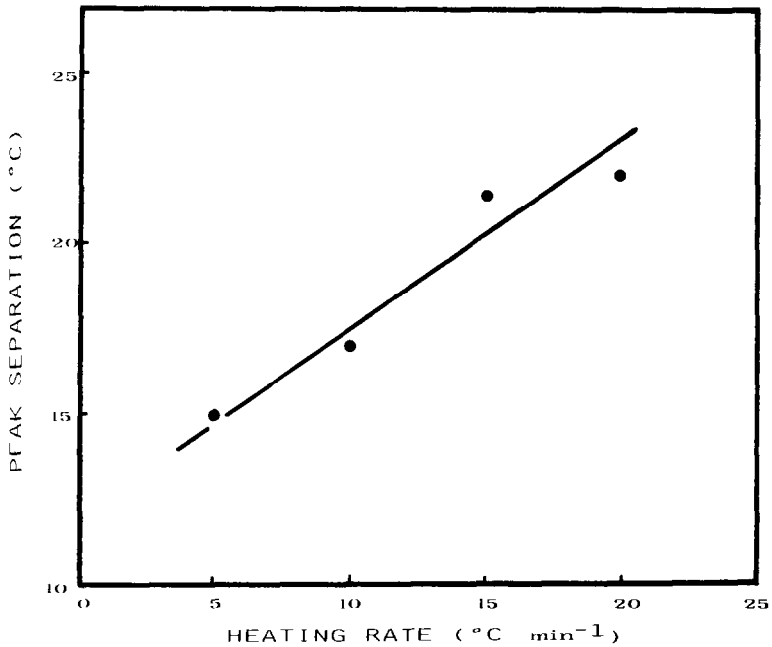

Fig. 4. Effect of heating rate on peak resolution.

a steady increase in resolution with increasing heating rate. This is related to the faster increase in water vapour pressure with heating rate, and the retardation of the appearance of the dihydrate peak. At 20 °C min^{-1}, however, the sample pan occasionally exploded through the high water vapour pressure. A heating rate of 15 °C min^{-1} was chosen to provide fast analysis time without the risk of pan rupture.

Discussion

Experimental conditions relating to sample pan sealing tightness and sample mass have major influences on the resolution of the two endothermic peaks corresponding to the dehydration reactions. Sealing effects can be related to the increase in partial pressure of water vapour as the seal is increased in tightness, and thus is related to increasing suppression of the dehydration of the hemihydrate to higher temperatures. In a typical example the peak temperature due to the gypsum dehydration occurred at 162 °C and that of the hemihydrate peak at 211 °C for a seal set at 0.1 mm. This compared to values of 153 and 182 °C for the two peaks at a seal of 0.4 mm. Hence, although a decrease in water vapour pressure caused both dehydration reactions to occur at lower temperatures, the effect was greater for the hemihydrate dehydration step relative to the gypsum reaction.

Mass effects on peak resolution can be related to two factors. Firstly, the major factor is due again to water vapour pressure, because the larger

sample masses of greater than 25 mg were difficult to seal tightly into the sample pans. Hence the seal was never very efficient, and only low internal water pressures were generated. Secondly, broadening of the two peaks with consequent loss of resolution was observed as the sample mass increased, probably due to an increase in temperature gradients within the sample. However, too small a sample size resulted in a low peak intensity which required high sensitivity and thus increased noise levels. A sample mass of ~ 8 mg was selected, giving ease of sealing in the pan and good detectability. An 8 mg sample of a typical cement may contain about 400 μg of gypsum. This quantity is easily detected by the DSC system, since it is possible to detect 0.2% gypsum in 8 mg of sample, corresponding to 16 μg of gypsum.

The effect of heating rate was relatively unimportant in terms of resolution, and 15 °C min^{-1} was chosen as the fastest safe heating rate. Hence a typical DSC trace over the temperature range 80–260 °C could be achieved in 12 min. Allowing for sample handling, a typical analysis could be obtained in about 20 min. The final values chosen for analysis were thus a sealing gap of 0.2 mm, sample mass of ~ 8 mg and a heating rate of 15 °C min^{-1}.

Analysis of gypsum and hemihydrate in cement

Using the experimental conditions reported in the previous section, the peak areas for the dehydration of gypsum and hemihydrate were determined for a series of synthetic standards covering the ranges 1–7% gypsum and 0–5% hemihydrate. These were the most likely ranges of these compounds to be found in commercial cement samples. The calibration curve for gypsum can be plotted directly as the peak area of the first peak against percentage gypsum (see Fig. 5). Each point is a mean of at least five determinations. Reproducibility tests were carried out on samples containing 4, 2 and 1% gypsum, and the results are presented in Table 1. It is evident that the RSD value increases as the peak area decreases. Although the RSD values for 4 and 2% gypsum are acceptable, there is quite a sharp increase between 2 and 1% gypsum.

TABLE 1

Reproducibility tests on synthetic cement samples containing 4, 2 and 1% gypsum

Gypsum (%)	Number of determinations, n	Mean ($J\ g^{-1}$)	SD	%RSD
4	12	14.5	0.37	2.5
2	9	6.40	0.20	3.1
1	10	3.55	0.26	7.4

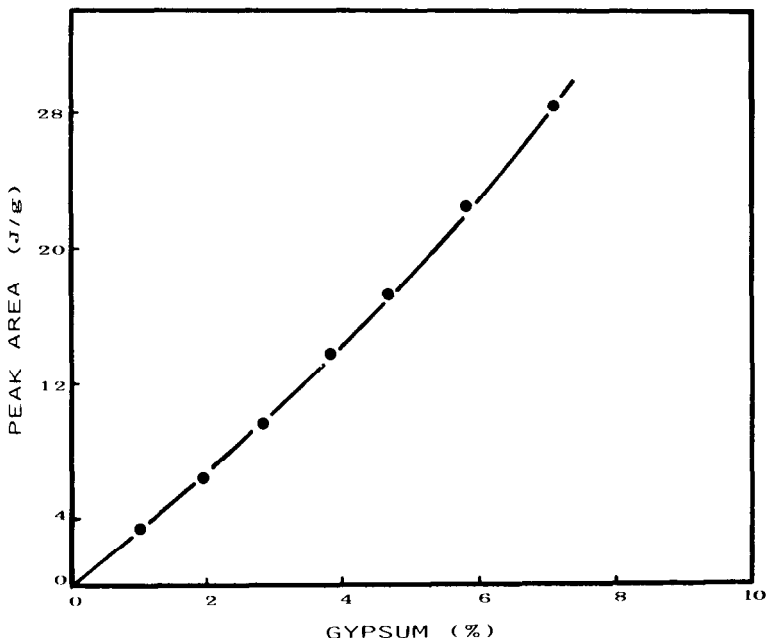

Fig. 5. Calibration curve for gypsum in cement.

The second peak at around 200 °C represents the dehydration of hemihydrate. However, this peak is the sum of the hemihydrate derived from the dehydration of gypsum plus the dehydration of any hemihydrate originally in the sample. Therefore, the area contributed by the gypsum present must be subtracted from the total peak area to determine the area arising from the original hemihydrate alone. To determine what value to subtract from the second peak, DSC traces of a sample containing gypsum only were obtained. The peak areas were determined, and the second peak area corrected for the weight loss due to the first dehydration step. The ratio of these peaks, taken as a mean from several experiments, was found to be 3.51. This factor should be determined for each DSC instrument as part of the calibration procedure, and should be checked regularly. The method of calculation of the hemihydrate value involves the following steps.

(a) The amount of gypsum in the sample is determined from the area of the first peak and the gypsum calibration curve.

(b) The area of the second peak is corrected for the weight loss due to the dehydration of gypsum to hemihydrate, i.e.

$$\text{corrected weight} = \text{weight taken} - \left(\text{weight taken} \times \frac{\%\text{gypsum}}{100} \times \frac{27.0}{172.2}\right)$$

then

$$\text{corrected area of second peak} = \text{area of second peak} \times \frac{\text{weight taken}}{\text{corrected weight}}$$

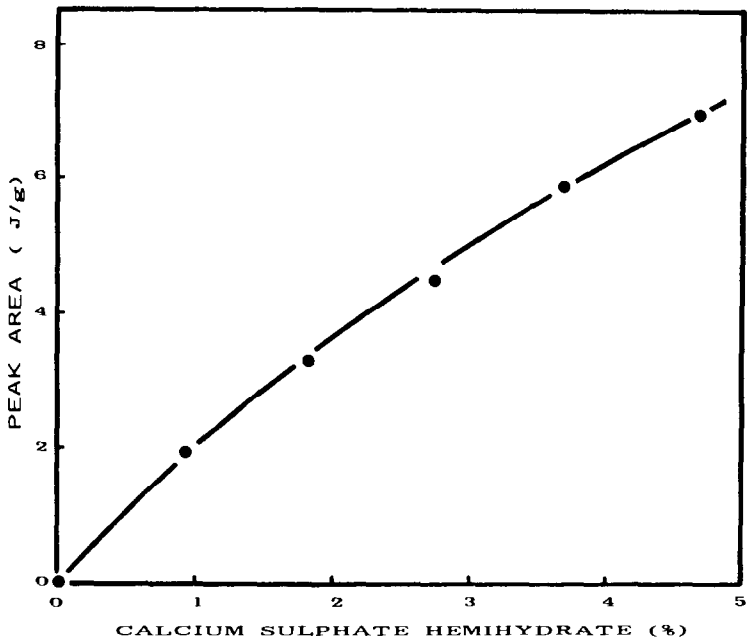

Fig. 6. Calibration curve for hemihydrate in cement.

(c) The area for the first peak is divided by 3.51, and this fraction subtracted from the corrected value for the second peak. The remainder value is now related to the quantity of hemihydrate originally in the sample.

A calibration curve was constructed for the hemihydrate concentration in the synthetic cement based on the above method, and is presented in Fig. 6. Each point is the mean of at least three determinations.

Two cement samples (6 and 7) were analysed (see Table 2) and doped with known quantities of gypsum and hemihydrate. Sample 6 had high

TABLE 2

Reproducibility tests on cements, and cements doped with known quantities of gypsum and hemihydrate

Sample	*n*	Gypsum (%)[a]		SD	%RSD	Hemihydrate (%)[a]		SD	%RSD
		Calc.	Found			Calc.	Found		
6	11	–	4.16	0.12	2.8	–	1.61	0.14	8.7
6a	10	4.12	4.19	0.22	5.1	2.49	2.37	0.23	9.7
6b	12	4.08	4.01	0.10	2.4	3.43	3.25	0.23	7.1
7	10	–	1.73	0.12	6.7	–	2.23	0.33	14.8
7a	11	3.12	3.20	0.06	1.9	2.20	2.19	0.12	5.5
7b	10	4.47	4.54	0.13	2.9	2.17	2.24	0.20	8.9

[a] The inclusion of three significant figures in these columns is for the purpose of the statistical analysis only. Quoted results would be rounded to two significant figures.

TABLE 3

Gypsum and hemihydrate values in a series of cement samples milled at various temperatures

Sample	Gypsum (%)	Hemihydrate (%)	Milling temp. (°C)
1	3.5	0.7	108
2	3.4	0.7	113
3	3.2	0.9	119
4	2.2	2.2	123
5	0.9	3.4	127

gypsum and low hemihydrate contents. Pure hemihydrate was added to bring the value to 2.49 (sample 6a) and 3.43% (sample 6b) and this dilution reduced the expected gypsum value to 4.12 and 4.08%, respectively. Samples 6a and 6b were analysed and the experimentally determined results compared to those of the expected value (see Table 2). Sample 7 was treated similarly, but since this had a low gypsum and high hemihydrate content standard additions of gypsum were made to give samples 7a and 7b. Analysis of the doped samples gave an indication of the accuracy of the method. For the four gypsum results, three values were higher than expected by an average of 2.0%, and one result was lower by 1.7%. For the four

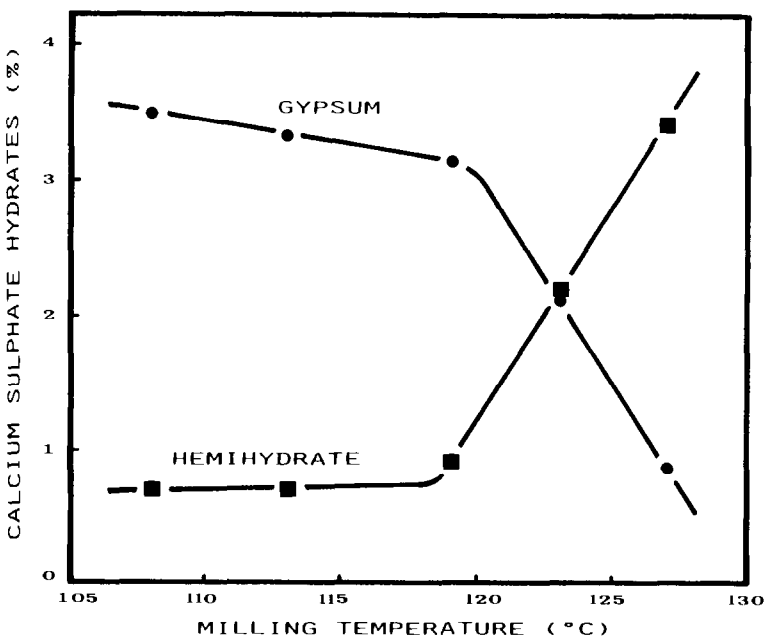

Fig. 7. Gypsum and hemihydrate values (determined by DSC) in cement as a function of milling temperature.

hemihydrate results, three values were lower than expected by an average of 3.5%, and one was higher by 3.2%

The replicate results obtained on the above six samples were analysed for reproducibility (see Table 2). It is evident that the RSD values for the gypsum determination (RSD = 3.7% average for all results) are significantly better than for the hemihydrate determinations (RSD = 9.1% average for all results). This is expected since the quantity of hemihydrate is related to the peak area difference between the total peak area and the peak area due to gypsum present in the sample. The errors are additive and hence give larger RSD values.

Cement samples obtained from a local industrial manufacturing plant were analysed by the DSC method using the calibration curves shown in Figs. 5 and 6. Some typical results for a range of gypsum–hemihydrate values are given in Table 3. These samples were taken from increasingly hotter milling environments and the gypsum and hemihydrate results are plotted against milling temperature in Fig. 7. The expected trend of decreasing gypsum concentrations and increasing hemihydrate concentrations as the milling temperature increased was observed.

CONCLUSIONS

The DSC technique can provide a fast, accurate and reliable technique for the routine analysis of gypsum and hemihydrate at the concentrations found in commercial cements.

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