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POTENTIAL ERRORS IN THE QUANTITATIVE DETERMINATION OF HYDRATED CALCIUM SULPHATES IN CEMENT BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Gypsum and hemihydrate can be quantitatively determined in cement samples by DSC. However, difficulties have been found with this method, related to the properties of the cement sample and the use of synthetic cement standards to produce the calibration curve.

In the present work, a number of cement samples were found to give a very distorted endothermic peak associated with the first dehydration step, in which gypsum is converted to hemihydrate. The determined gypsum values were lower than expected. The low results were found to occur when the clinker used was more reactive than is usual for cement clinkers. An explanation for this behaviour is proposed, and information is given to allow assessment of the reliability of results obtained. Ways of minimizing errors are also suggested.

The effect of humidity on stored samples and standards was investigated, and recommendations for storage conditions are made.

Synthetic standard cements were prepared by mixing clinker with either (a) gypsum and hemihydrate, or (b) gypsum that had been partially dehydrated to a mixture of gypsum and hemihydrate. The former method is recommended.

INTRODUCTION

It is of some importance to the cement industry to have a rapid method available for determining the calcium sulphate dihydrate (gypsum) and the calcium sulphate hemihydrate content of cement. These compounds affect the rate of setting of the cement, and also have long-term effects on the set cement.

We have recently reported a rapid and sensitive heat-flux DSC method for the determination of these components in cement [1]. It became apparent after a short period of application that the method was not as universally applicable as we had originally expected, and some cement samples gave results that were clearly in significant error. In the present work, the reasons for these errors are explained.

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In addition, problems were encountered in reproducing results over a time span of some months, and this was particularly apparent in the value of the conversion factor used to calculate the hemihydrate content generated from the decomposition of the gypsum. (A full explanation of this calculation is given below.) The present work investigates these variations and relates them to the storage environment of cement samples and of synthetic standard cements.

We also investigate the use of partially dehydrated gypsum for the preparation of the synthetic standard cements, as advocated by St. John [2]. St. John has claimed that the results obtained using these standards are different from those obtained when clinker is mixed with gypsum and hemihydrate, and that the response of the real sample is closer to that of the partially dehydrated standards. In the present work, results obtained using the two kinds of standard are compared.

EXPERIMENTAL

Samples

May and Baker L.R. grade calcium sulphate dihydrate and calcium sulphate hemihydrate were used as previously [1]. Cement clinker samples were kindly donated by Cockburn Cement Ltd. (W.A.) and Swan Portland Cement Ltd. (W.A.).

Standards were prepared by two methods: (a) by weighing out quantities of gypsum, hemihydrate and a cement clinker, all of which had been ground to pass through a 45 μm sieve, and blending until homogeneous using an agate mortar and pestle; and (b) by weighing out quantities of clinker and partially dehydrated gypsum samples, which had been ground to pass through a 45 μm sieve, and again blending until homogeneous using an agate mortar and pestle.

Unless otherwise specified, the standards were stored in sealed glass containers in a desiccator containing silica gel.

Partially dehydrated gypsum samples were prepared by accurately weighing 4 g samples of gypsum into small screw-top jars and then heating the opened jars at 92 °C for periods of time of between 30 and 160 min. Full dehydration of one gypsum sample required heating for 480 min at 92 °C. These samples were then cooled in air for 24 h so that any anhydrite formed could rehydrate to hemihydrate [2]. The samples were accurately weighed and placed in desiccators over phosphorous pentoxide or silica gel for 4 to 5 days. They were then reweighed to determine the weight of water adsorbed onto each sample.

Instrumentation

All DSC work was performed using a Du Pont 1090 thermal analysis system, which included data acquisition and processing facilities and a standard heat-flux DSC cell.

Micrographs were obtained using a Jeol JSM 35 scanning electron microscope.

Procedures

DSC experiments were carried out using 8 mg samples of cement contained in sealed aluminium pans and heated at 15 °C min^{-1} from 70 to 260 °C, as previously described [1].

The instrument was calibrated at regular intervals using an indium standard.

Calculations

The peak ratio factor is obtained by heating a standard cement containing gypsum, but no hemihydrate, in a sealed pan. The second endothermic peak produced is fully attributable to the dehydration of the hemihydrate produced by the partial dehydration of the gypsum

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

The computed energy value of the first peak is divided by the computed energy value of the second peak to given the peak ratio factor.

For the most accurate results, it is necessary to correct the value of the second peak for the change in weight resulting from loss of water in the conversion of gypsum to hemihydrate [1].

RESULTS AND DISCUSSION

Reactivity of clinkers

If a sample of cement containing gypsum and hemihydrate is heated in partly sealed pans, two well-resolved endotherms are observed. The first endotherm is associated with the dehydration of gypsum to hemihydrate, and the second with the dehydration of hemihydrate to anhydrite. The area under the peaks can be used to quantify the two forms of calcium sulphate hydrates. A typical DSC trace for a Portland cement is shown in Fig. 1. Both endothermic peaks are well defined, with extrapolated onset temperatures of 148 and 196 °C, respectively. However, some cement samples and standards produced traces in which the first endothermic effect was atypical (Fig. 2).

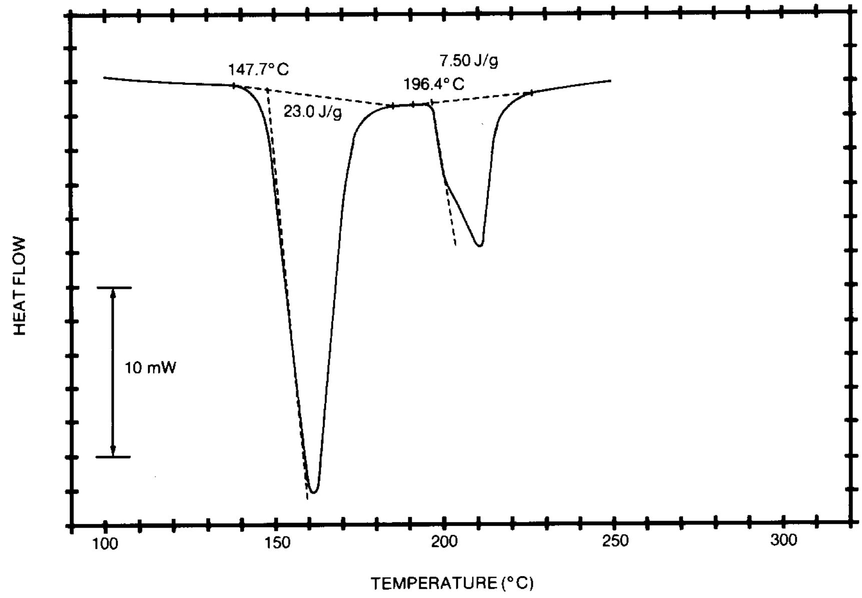

Fig. 1. A typical DSC record for a cement.

These atypical peaks were smaller than would be expected given the gypsum content of the cement, and were characterized by a low initial onset temperature, as low as 128° C. In addition, doublets were sometimes observed, and in all cases the peak tended to be broad and shallow instead of narrow and deep.

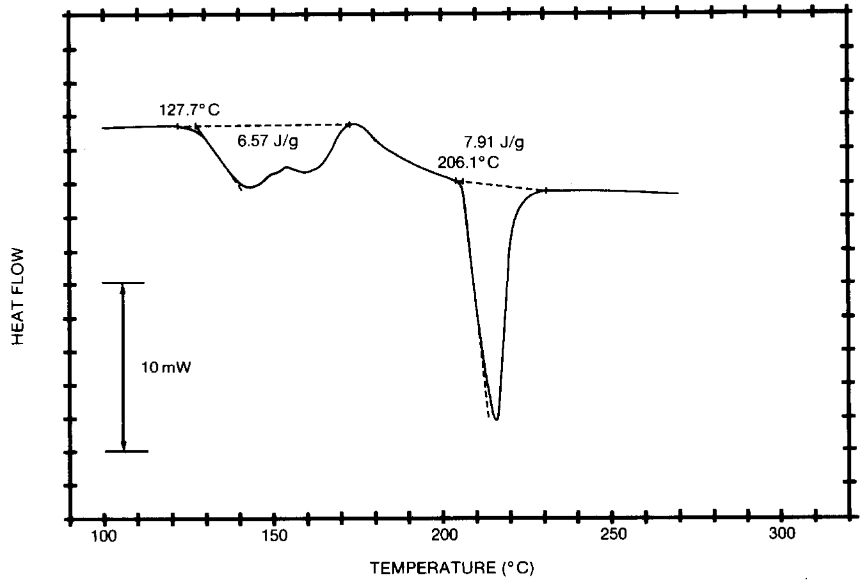

Fig. 2. A DSC record for a cement made from a reactive clinker.

This effect was only observed when a certain off-white clinker was present, and then only when the clinker was ground to < 45 μm. (The grinding step was necessary in order to match the standards prepared from gypsum, hemihydrate and clinker to the particle size characteristics of the commercial cement.) This was demonstrated by mixing known amounts of gypsum and hemihydrate with three different freshly ground clinkers. Two clinkers produced the usual DSC curves, but the third produced an atypical first endotherm. In standards containing gypsum only, the calculated value of the peak ratio factor is usually about 3.3. When a similar standard was prepared from the atypical clinker, the first peak was smaller than the second, giving a peak ratio factor of < 1 (see Fig. 2).

The clinker causing the atypical first peak did not interfere with the second peak. However, an atypical first peak affects the estimation of both the gypsum and the hemihydrate in a cement sample. In addition to the low value obtained for gypsum, it causes an error in the calculation of the hemihydrate, giving a high result. In a standard containing only hemihydrate, for which no first peak was obtained, the second peak was atypical.

The clinker causing the problem was quite reactive, and adsorbed water vapour readily from the atmosphere. When the ground clinker was stored for 48 h in a desiccator at a relative humidity of 45% and standards containing gypsum and hemihydrate were made up and tested, the DSC records were normal. The values obtained for gypsum and hemihydrate were as expected. Commercial cements with atypical first peaks treated in a similar manner also produced a normal DSC curve. Peak area integrations and the calculated gypsum and hemihydrate values for some commercial cements before and after exposure to 45% relative humidity are given in Table 1.

Samples A and B were tested when received and again after being exposed to 45% relative humidity for 2 days. There is a large increase in the area of the first peak, giving much higher gypsum values and much lower hemihydrate values. The calculated negative value for hemihydrate in sample B, exposed to 45% relative humidity for 2 days is because of the

TABLE 1

The effect of storage at 45% relative humidity for 2 days on commercial cement samples made from a reactive clinker

Sample	Storage time (days)	First peak (J g^{-1})	Second peak (J g^{-1})	Gypsum found (%)	Hemihydrate found (%)
A	0	2.38	5.81	0.7	2.8
	2	7.98	5.27	2.2	1.4
B	0	4.40	4.85	1.3	1.8
	2	13.60	4.41	3.5	−0.2

TABLE 2

The effect of 14 days of storage on a 6.38% gypsum standard prepared in a < 45 μm alumina matrix [a]

Storage environment	First peak (J g^{-1})	Second peak (J g^{-1})	Corrected second peak (J g^{-1})	Peak ratio factor
Desiccator	28.4	9.83	9.93	2.86
(Silica gel)	27.2	9.71	9.81	2.77
45% humidity	27.7	9.97	10.07	2.75
(Saturated K_2CO_3)	28.3	10.5	10.61	2.67

[a] Results are given in duplicate.

uncertainty in the value of the peak ratio factor used to calculate the hemihydrate.

Storage under normal laboratory conditions returned the sample to the expected behaviour, but this took a considerable time. When a standard prepared from gypsum and clinker was stored in intermittently opened sealed jars, the first peak took 32 days to change from being atypical (Fig. 2) to being normal (Fig. 1).

As a further test, gypsum and hemihydrate standards were made up in an inert matrix of < 45 μm alumina, and stored for 14 days in either a desiccator containing silica gel or a sealed container at 45% humidity. The samples were analysed in duplicate by the DSC method (see Table 2). The results showed no great variation, and were within experimental error. Since the gypsum and hemihydrate values were unaffected, this experiment further supports the suggestion that it is the reactivity of the clinker that causes errors in the determinations.

The DSC record provides a visual method for the detection of samples that will give gross errors in the determination of the two sulphate components in the cement. However, samples that give normal DSC records and hence appear to contain unreactive clinkers may be affected to a lesser degree by initial exposure to humidity. A standard prepared from a clinker freshly ground in a disc mill to < 45 μm and exposed for a time to 45% humidity produced an increase in the size of the first peak, while the second peak remained roughly constant. This results in changes to both the gypsum and hemihydrate values calculated for cements as well as introducing changes to the value of the peak ratio factor. A standard prepared from 5.6% by weight gypsum in an apparently unreactive clinker and placed in different storage environments illustrates this effect. DSC analysis of a subsample of a standard which had been stored for 2 weeks over silica gel in a desiccator gave a gypsum value of 5.3%, which increased within a week to 6.0% on storage in a 45% relative humidity environment. Another subsample placed directly into a 45% humidity environment for 2 weeks attained a gypsum value of 6.0%, which was not reduced on exposure to silica gel. This suggests that the clinker adsorbs water relatively easily, but that the reaction is not readily reversed. Thus the two extremes of storage can produce an error of $\approx 6\%$ in the calculated gypsum value.

The above experiments stress the need to make standards from inert clinkers. Before we were aware of this problem, values of the peak ratio factor varied from 2.8 to 3.5, which we can now attribute to variation in the reactivity of the clinker. The importance of using a correct peak ratio factor can be illustrated by inserting these two extreme peak ratio factors into the calculation. This produced hemihydrate values of 1.0 and 1.5%, respectively, for a typical cement.

Despite the above problems, standards prepared from three different clinkers, including the very reactive one, gave identical or very similar results after the elapse of enough time for the reactive clinker to mature. The > 45 and < 45 μm fractions gave the same results, showing that once the reactivity of these clinkers had been quenched, the particle size distribution did not affect the results obtained.

The most likely explanation for the formation of the atypical peaks is that when the reactive clinker containing gypsum is sealed in a pan and heated, the tendency of the clinker to acquire water reduces the temperature at which the first dehydration step occurs. Under pressurized conditions the water vapour evolved reacts exothermically with the clinker, and this reduces the area of the first endothermic peak. This explanation accounts for the reduction in temperature of the first endotherm, the reduction in peak area, and the splitting of the peak into a doublet.

Preparation of standard cements

The preparation of standard cements can be achieved by adding mixtures of gypsum and hemihydrate to ground clinker in known proportions [1]. Similarly, standard additions of gypsum or hemihydrate can be used to produce a suitable spiked sample. It is simple to make standards of any desired value. The calibration curves produced from such mixtures are highly reproducible. St. John [2] used a DTA technique to investigate standards prepared from mixing known quantities of clinker, gypsum and hemihydrate. He also made standards by mixing partially dehydrated gypsum, prepared by heating in an oven at 90–95 °C for various periods of time, with clinker. In this case the gypsum and hemihydrate contents were estimated from the loss on ignition. He then compared the curves obtained by plotting the ratios of the first and second endothermic peak (A_1/A_2) for the various standards against per cent hemihydrate, and found that the curves were different for the standards prepared by the two methods. While the standards prepared from gypsum and hemihydrate mixtures produced an essentially linear plot, standards prepared with the partially dehydrated

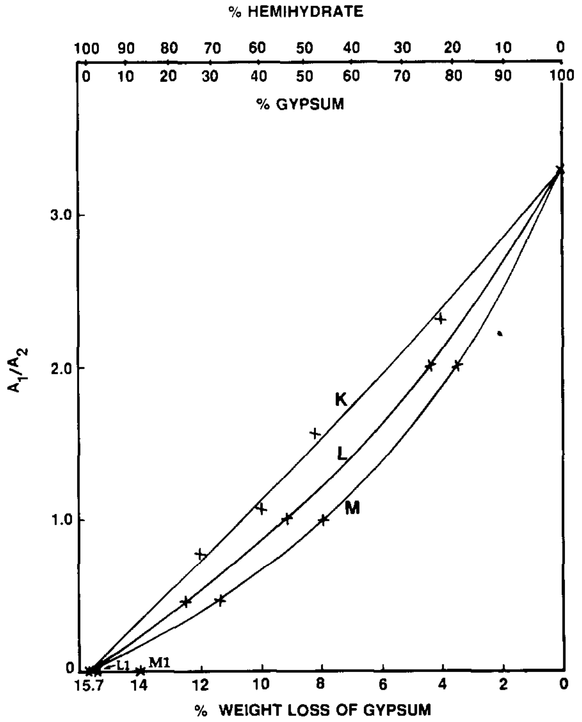

Fig. 3. Variation in peak area ratio for cement standards prepared from a mixture of clinker and: M, partially dehydrated gypsum; L, partially dehydrated gypsum exposed to P_2O_5; K, gypsum and hemihydrate.

gypsum produced a curved plot convex to the per cent hemihydrate axis. The latter samples were considered to be closer to the real cement samples, as it was assumed that the cement consisted of partially dehydrated particles containing both gypsum and hemihydrate phases. Thus, it was argued that standards of this kind should be used to construct calibration curves.

To investigate this apparent difference between standards prepared from partially dehydrated gypsum and from gypsum and hemihydrate mixtures, standards were prepared and analysed using the method reported by St. John [2]. This involved heating gypsum in an oven at 92° C for various periods of time, and then exposing the samples to the laboratory atmosphere for 24 h. The purpose of this step was to convert any anhydrite formed back to hemihydrate through interaction with atmospheric water vapour. Figure 3 shows the results obtained. Curve M represents the results obtained when cement standards prepared from partially dehydrated gypsum and clinker were analysed. This displays the marked curvature observed by St. John [2]. The hemihydrate sample produced by heating gypsum for 480 min at 92° C, followed by 24 h exposure in air, showed no evidence of gypsum, but had a weight loss of 14.0% instead of the expected 15.7% (see point M1 in Fig. 3).

St. John had a similar point off the curve in his graph, which he attributed to some instrumental effect [2].

Curve K shows the results obtained when mixtures of gypsum and hemihydrate were used to make the standards. This curve is much more linear than the curve obtained from the partially dehydrated samples.

Samples of the partially dehydrated gypsum were exposed to the laboratory environment for 24 h, then stored over phosphorus pentoxide in a desiccator for 4 days, with exposure to the laboratory atmosphere daily during the weighing procedure, and then made into standards by mixing with clinker. Curve L shows the results obtained from this set of standards. The degree of curvature is much less marked than for the standards made from the partially dehydrated samples not exposed to phosphorus pentoxide. Point L1 has a weight loss of 15.4%, which is much closer to the theoretical value of 15.7% for the dehydration of gypsum to hemihydrate.

The deviant point, M1, which our work suggests is a real result and not as a result of an instrumental effect [2], coupled with the more linear curve achieved when the partially dehydrated samples were dried, indicates that the curvature may be due to adsorption of surface water during the 24 h exposure to the atmosphere. If all the samples showed this effect, a high value would be obtained in the calculation for the calcium sulphate phases, resulting in a deviation from the expected result.

To test this idea, samples of the partially dehydrated gypsum were prepared. In Table 3 the period of time for which the gypsum samples were heated at 92 ° C is shown in the first column, with the corresponding weight lost after heating and exposure to the atmosphere for 24 h being given in the second column. These samples were placed in a desiccator for 5 days over P_2O_5, and then reweighed. The weight lost by these samples is shown in the third column, calculated as a percentage of the partially dehydrated gypsum produced after the varying amount of oven drying. This can be assumed to

TABLE 3

Adsorbed water content of partially dehydrated gypsum samples after 24 h exposure to the environment

Period of heating at 92 ° C (min)	Weight lost after heating and 24 h exposure (%)	Further weight lost after 5 days over P_2O_5 (%)
0 (Gypsum)	−0.01	0.02
80	6.36	0.94
120	8.20	1.13
155	10.06	1.34
480	13.87	1.82
0 (Hemi-hydrate)	−0.4	1.63

be adsorbed water gained during the equilibration for 24 h. The gypsum sample which was simply exposed to the atmosphere for 24 h showed essentially no change in weight. However, the amount of adsorbed water did increase with increasing degree of gypsum dehydration, from 0.02% for the gypsum (time = 0 min) to 1.82% for the gypsum which lost 13.87% during oven drying (time = 480 min). In other words, during exposure to the laboratory atmosphere, the percentage of water adsorbed increased as the proportion of hemihydrate increased. For comparison, a sample of hemihydrate (time = 0 min) lost 1.63% over P_2O_5. An examination of particles of fully and partially dehydrated gypsum by scanning electron microscopy revealed cracking of the particles that had been subjected to dehydration. The cracking increased as the degree of dehydration increased, and this leads to the conclusion that the proportion of adsorbed water was related to the surface area of the particles. The sample of commercial hemihydrate also displayed a similar cracked surface and a similar hygroscopic nature.

As the ratio of gypsum to hemihydrate in a partially dehydrated gypsum must be calculated from either the weight lost during the initial heating or the weight lost during subsequent total dehydration of the sample, any adsorbed water must be removed prior to estimating the weight after equilibration with the laboratory atmosphere. It is therefore important to know how much time in a desiccator is needed to completely remove the adsorbed water. Samples were placed in desiccators containing either silica gel or P_2O_5, and the weight was monitored at intervals.

The results obtained for samples stored over P_2O_5 are plotted in Fig. 4. Three samples were tested: gypsum, gypsum that had been partially dehydrated, and gypsum dehydrated to hemihydrate. The weight changes shown by the samples on the first day are those obtained after exposure for 24 h to the room atmosphere. The partially dehydrated gypsum (curve B) and the hemihydrate (curve C) lost weight continuously until fully dehydrated to anhydrous calcium sulphate. This took over 200 days. The gypsum underwent a much smaller weight loss for the first 20 days (curve A), but thereafter lost weight at an increasing rate to achieve complete dehydration at 470 days.

These samples maintained over silica gel behaved differently from those maintained over phosphorous pentoxide. Figure 5 shows that while the partially dehydrated gypsum lost weight from the first day (curve B), and gypsum only after 50 days (curve A), their rates of dehydration were much less than those of samples kept over P_2O_5. In contrast, the hemihydrate appeared to reach a stable weight sometime before day 5 (curve C). The total weight loss then corresponded to the loss of the 1.5 H_2O required to produce hemihydrate.

When using standards containing partially dehydrated gypsum, it is necessary to remove the adsorbed water in order to determine the precise amount of hemihydrate formed during oven dehydration. As the partially

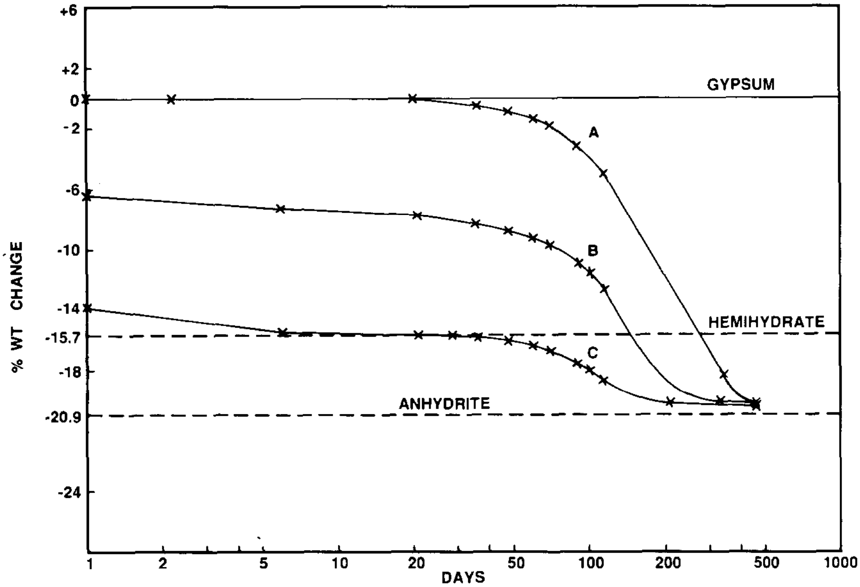

Fig. 4. Dehydration of gypsum and partially dehydrated gypsums by P_2O_5. The dotted lines represent the theoretical weight losses for the conversion of gypsum to hemihydrate and anhydrite.

dehydrated gypsum continues to lose weight in a desiccator containing either P_2O_5 or silica gel, there is some uncertainty about the time needed to completely remove adsorbed water without also removing some of the

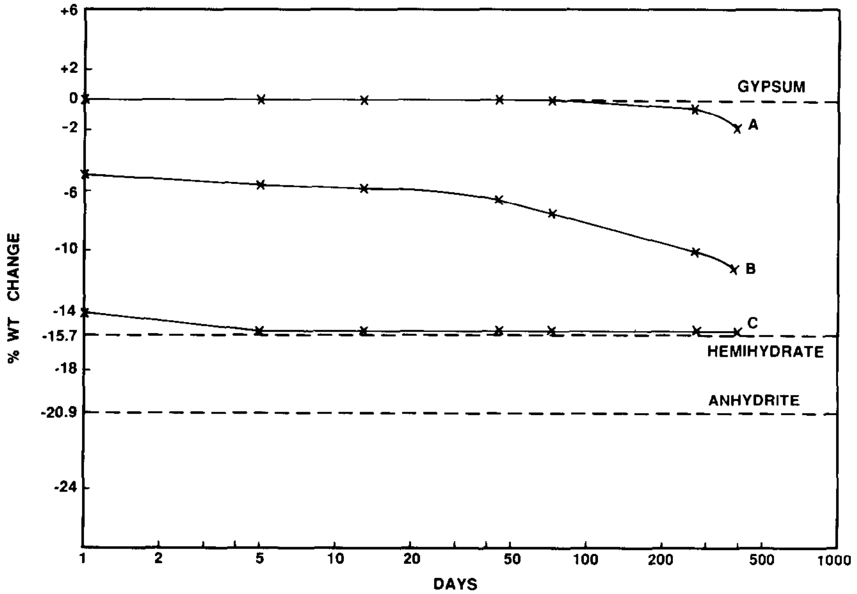

Fig. 5. Dehydration of gypsum and partially dehydrated gypsums by silica gel.

structural water. This is likely to lead to errors in the calculation of the components of the standards.

CONCLUSIONS

The recently published method for estimation of the gypsum and hemihydrate content of cement [1] is valid if used with precautions. Low results for gypsum, and consequently high results for hemihydrate will be obtained if the cement clinker is reactive. A highly reactive cement clinker can be detected by monitoring the DSC results for signs of abnormal behaviour in the endotherms associated with the dehydration of gypsum or hemihydrate. If a highly reactive clinker is present, then, for the cements that we have analysed, exposure to 45% humidity for 48 h restores the dehydration endotherms to their usual shape and temperature range. The analytical values obtained for the two calcium sulphate phases are then much more accurate. Less reactive clinkers can be similarly deactivated. Since there is likely to be variation in the rate of deactivation from clinker to clinker, it is recommended that the conditions for deactivation be established on an individual cement basis.

The method of using mixtures of gypsum, hemihydrate and cement clinkers to prepare standard cements for the calibration of the calorimeter is simple, reproducible and effective. Standards stored in sealed jars in a desiccator over silica gel appear to remain valid for at least 2 years. However, the use of partially dehydrated gypsum to prepare standards in cement clinker is not recommended. The partially dehydrated samples adsorb moisture from the atmosphere, and are difficult to dry to a known composition. Consequently the use of partially dehydrated gypsum is likely to lead to errors in analytical results.

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