THERMAL SOLUTIONS

DETERMINATION OF CALCIUM SULFATE HYDRATES IN CEMENT BY DSC

PROBLEM

An essential process in the manufacture of Portland cement is the addition of around 5% gypsum ($CaSO_4$•$2H_2O$) to control (reduce) the rate of setting. The gypsum is added to the fused clinker during processing, and the two are subsequently milled to obtain uniform mixing and the required particle size. During this milling process the thermal energy generated may cause partial dehydration of the gypsum to hemihydrate ($CaSO_4$•$0.5H_2O$) which adversely affects (increases) the rate of setting as well as the long-term properties of the set cement. Hence, it is of importance to monitor the amounts of both of these hydrates in the final cement. However, neither chemical nor X-ray diffraction techniques are able to provide quantitation at the levels required.

SOLUTION

On the other hand, differential scanning calorimetry (DSC), which measures the heat flows and temperatures associated with transitions in materials, does provide a convenient method for quantifying the amounts of gypsum and hemihydrate present based on the fact that the dehydration of gypsum occurs as a two-stage endothermic process:

$$CaSO_4 \bullet 2H_2O \longrightarrow CaSO_4 \bullet 0.5\,H_2O \longrightarrow CaSO_4$$

Figure 1 shows the DSC results for a typical cement evaluated using an open aluminum pan. In this arrangement, the two endothermic peaks associated with the successive dehydration stages are not sufficiently resolved to allow quantitation. By encapsulating the cement in a hermetically sealed DSC pan with a pinhole in the lid*,however, these two peaks can be resolved. This improved resolution results because the atmosphere of water vapor generated by the first step retards the onset of the second dehydration and moves the peak to a higher temperature. (Figure 2). Studies at the Curtin University of Technology (Perth, Australia) [1,2] indicate that the best resolution is obtained using 5-8mg samples in aluminum hermetic pans at 15^{o}C/minute heating rate.

*DSC hermetic pan lids with 75µm pinhole (TA Instruments PN 900860-901).

Figure 1: CEMENT ANALYSIS - UNSEALED PAN

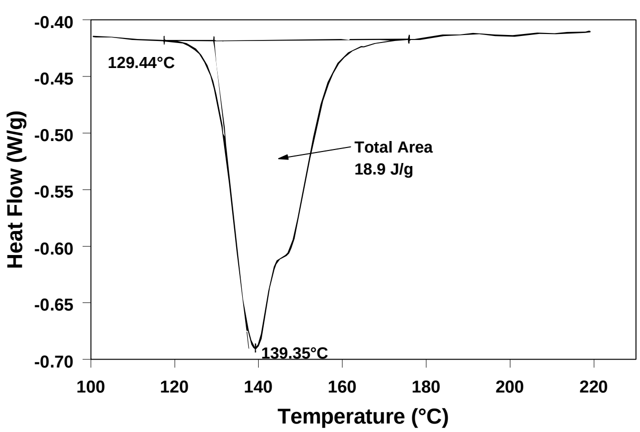
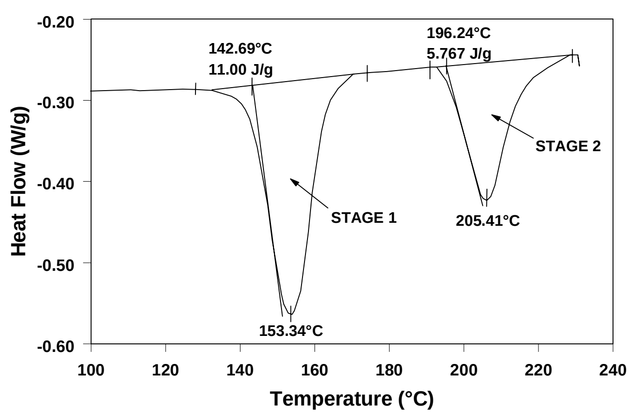


Figure 2: CEMENT ANALYSIS - HERMETIC PAN



The calculations used to quantify the amounts of gypsum and hemihydrate initially present from the resolved DSC peaks in Figure 2 are summarized below:

1) The area associated with the low temperature DSC endotherm is measured. Using a calibration curve constructed from similar experiments on pure gypsum (Figure 3), the % gypsum present in the cement is then determined.

2) Using the peak area ratio for the two stage dehydration of pure gypsum (found to be 3.3), the amount of heat in the second stage of the cement dehydration associated with the gypsum initially present is determined. Subtracting this value from the total area of the second stage for the cement yields the heat (area) associated with hemihyrate initially present.

3) Using a calibration curve constructed from evaluations on pure hemihydrate (Figure 4), the % hemihydrate present in the cement is then determined.

REFERENCES

1. J. Dunn, K. Oliver, G. Nguyen and I. Sills, *Thermochimica Acta*, 121 (1987) 181-191.
2. J. G. Dunn, K. Oliver and I. Sills, *Thermochimica Acta*, 155 (1989) 93-104.

Figure 3: GYPSUM CALIBRATION

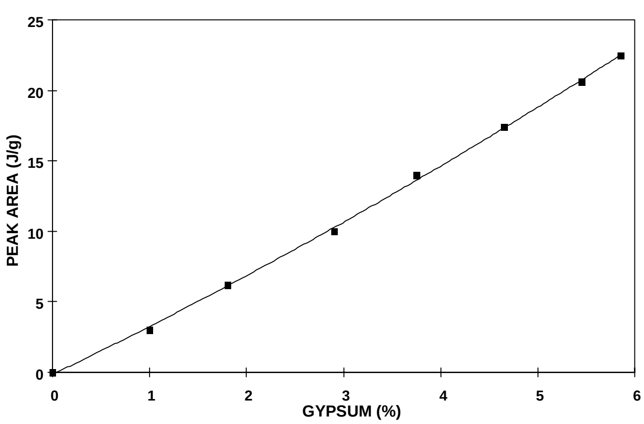
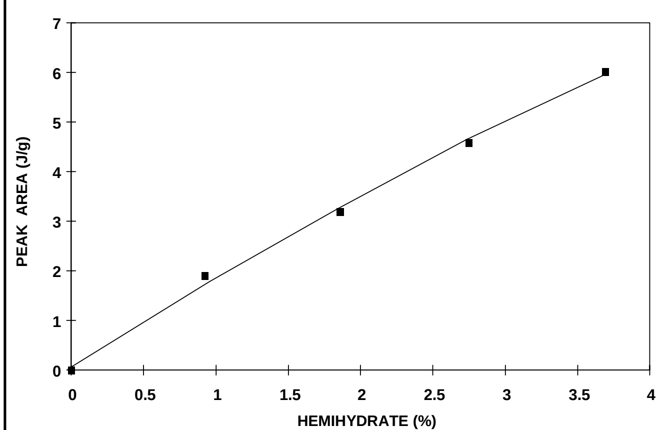


Figure 4: HEMIHYDRATE CALIBRATION



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