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Determination of $Ca(OH)_2$ in hydrated cement paste by differential scanning calorimetry

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Abstract

The use of differential scanning calorimetry (DSC) for the determination of calcium hydroxide in hydrated cement paste is discussed. The statistical analysis performed on the calibration data indicates the causes of errors, the suitability of linear regression and the validity of the assumptions made. The accuracy of the prediction of calcium hydroxide in hydrated cement paste from thermograms is also assessed. The different factors which may affect the DSC curves are also examined.

INTRODUCTION

Calcium hydroxide is produced during cement hydration. It is the result of the reaction between the calcium silicates and water

$$3CaO \cdot SiO_2 + H_2O \rightarrow xCaO \cdot ySiO_2 \cdot zH_2O + Ca(OH)_2$$

$$2CaO \cdot SiO_2 + H_2O \rightarrow xCaO \cdot ySiO_2 \cdot zH_2O + Ca(OH)_2$$

The ratio x/y typically varies from 1.2 to 1.7 depending upon the type of cement used. The amount of $Ca(OH)_2$ is often determined and used to track the kinetics of cement hydration. It also serves to measure the reactivity of pozzolanic materials. Additionally, calcium hydroxide affects the mechanical and durability properties of cement based materials.

Different methods have been used for the determination of calcium hydroxide formed during hydration of Portland cement, namely chemical extraction, quantitative X-ray diffraction (QXRD) and thermal analysis methods [1,2]. The chemical extraction method is tedious and time consuming, and there is concern that the cement constituents and other hydration compounds may be attacked by the solvents. Quantitative X-ray diffraction measures only crystalline materials and has been found of limited value because of the change in morphology that the hydration products sometimes undergo. Thermogravimetric analysis (TGA) seems to be limited by the fact that other hydrated compounds may lose water at the same temperature as calcium hydroxide. Differential thermal analysis (DTA) is

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affected by the heating rate, the size of the sample and the sample packing, and this limits its use for quantitative analysis.

There is another thermal analysis method which has not been used extensively, differential scanning calorimetry (DSC). It differs from DTA in its principles and is considered to present numerous advantages. In this paper, differential scanning calorimetry is described and its application for the determination of calcium hydroxide in hydrated cement paste is examined.

DIFFERENTIAL SCANNING CALORIMETRY

In differential thermal analysis the decomposition reaction of $Ca(OH)_2$ to $CaO + H_2O$ is observed by measuring the deviation of the sample temperature from the temperature of a reference material. However, this deviation causes thermal fluxes and this complicates the theoretical description of the DTA curves and decreases the sensitivity of the method [3]. It appears to be advantageous to keep the sample and the reference at the same temperature, and to measure the rate of heat flow into each that is necessary to maintain the constant temperature. This is achieved by placing separate heating elements in the sample and reference chambers; the rate of heating by these elements can be controlled and measured as desired. This is the basis of differential scanning calorimetry.

The heat flow necessary to maintain both the samples at the same temperature is usually expressed as a function of temperature. The temperature corresponding to a peak of the heat flow curves is known as the peak temperature, and serves as an identifying value. The area under the peak is directly proportional to the heat evolved or absorbed by the reaction. Since the heat involved in the decomposition reaction is proportional to the amount of the compound being studied, the peak area is also proportional to the amount of the compound being studied. The proportionality coefficient is an electrical conversion factor in DSC, whereas a similar constant in DTA depends on the sample characteristics [3]. In DSC the proportionality coefficient is also independent of temperature, and this is a major advantage of DSC over DTA. The major factors that affect the shape and

TABLE 1
Common factors influencing DTA heating curves [4]

Factor	Effect
Heating rate	Changes in peak size and position
Sample size	Changes in peak size and position
Sample packing	Irreproducible curves

size of the DTA curves, as summarized in Table 1, are considered to have minimal effects on DSC curves [3,4]. In particular, quantitative determination of any compound from the total area under the curves is expected not to be affected.

EXPERIMENTAL

To generate the calibration curve, peak areas versus $Ca(OH)_2$ content, different mixtures of unhydrated Type I cement with reagent grade calcium hydroxide were prepared at 2.5%, 5%, 8%, 15%, 20%, 25% and 30% by weight. Samples were prepared in triplicate and the mixtures were ground to pass through a 63 μm sieve after mixing.

To illustrate the application of DSC to hydrated cement paste, a test sample of the same cement (C) was prepared with distilled water (W) at $W/C = 0.40$. The cement paste was hand mixed, cured for one day under moist cloth in the laboratory atmosphere, and cured for 28 days in lime saturated water. At 1, 7 and 28 days, broken pieces of the sample were washed in alcohol to stop the hydration. They were then dried under vacuum for 24 h, ground to pass through a 63 μm sieve and subsequently examined on the DSC to determine the calcium hydroxide content using the calibration curve generated previously. To give some confidence to the results obtained, quantitative X-ray diffraction was performed on $3CaO \cdot SiO_2$ ($2\theta = 41.4°$) using KBr ($2\theta = 27°$) as an internal standard. The percent reacted $3CaO \cdot SiO_2$ was then compared with the simultaneous formation of $Ca(OH)_2$. In this experimental series samples were also prepared in triplicate. The cement used in this study had the following composition expressed in percent: SiO_2 21.5, Al_2O_3 3.9, Fe_2O_3 2.6, CaO 63.7, MgO 3.3, SO_3 2.6, Na_2O 0.16, K_2O 0.6.

Differential scanning calorimetry was performed with a DuPont 990 thermal analysis apparatus. The samples used to generate the calibration data and those from the hydrated cement paste were heated from room temperature to 600 ° C. In these two series of experiments the heating rate was 10 ° C min^{-1}, as in general practice, and the sample size varied from 20–25 mg.

In the last series of experiments, the effects of heating rate, sample fineness and sample size on the peak size and position were determined using the 28 day cured samples. The effect of heating rate was determined by heating two sets of samples at 5 ° C min^{-1} and 2 ° C min^{-1} respectively. To assess the effect of fineness on the DSC, unground 2 mm samples were run and the results were compared with those for the 63 μm ground samples. Here also, 20–25 mg samples were used. To assess the effect of sample size, approximately 10 mg of ground material were heated at 10 ° C min^{-1} and the results were compared with those for 20 mg samples.

RESULTS AND DISCUSSION

Calibration data

The calibration data are shown in Table 2 in terms of the peak area measured as a function of the amount of calcium hydroxide in the samples. Each of those values were measured three times and the average standard deviation was calculated to be 0.88 J g^{-1}. In the calibration process, the $Ca(OH)_2$ content was taken as the independent variable and the peak area as the predicted value.

Peak area (J g^{-1}) $= 1118.251 \times$ wt% of $Ca(OH)_2$ with $r^2 = 0.997$.

The high correlation obtained with the regression equation given above indicates that the total variation in peak area can be accounted for by this equation in 99.5% of cases. The above relationship can reasonably be used to represent the effect of $Ca(OH)_2$ content in a sample on the peak area. Since no other compound in the hydrated cement exhibits thermal effects in the range 440–550 °C, interference effects are not expected. However, in the actual use of DSC for $Ca(OH)_2$ determination in hydrated cement samples, the peak area will be measured and the $Ca(OH)_2$ content will be predicted.

Calcium hydroxide in hydrated cement paste

The DSC curves generated by the decomposition of calcium hydroxide in hydrated cement paste were broadly the same as for the samples containing reagent grade calcium hydroxide and used for calibration. Figure 1 shows typical differential scanning calorimetry peaks for calcium hydroxide at 1 day, 7 days and 28 days. Table 3 gives the average values of the peak area measured at different ages and the corresponding calcium hydroxide content predicted from the calibration equation, with the respective standard deviation.

It appears that the standard deviation (SD) attached to the peak measured is high at early ages, but more or less stabilizes beyond 7 days. The standard deviation of the peak area and subsequently that of the predicted calcium hydroxide contents are, on the average, consistent with the standard deviation of single measurements generated from the calibration data [0.88 J g^{-1} for the peak area and 0.23% for the predicted $Ca(OH)_2$]. The

TABLE 2
Calibration data for $Ca(OH)_2$

$Ca(OH)_2$ (%)	2.5	5.0	8.0	15.0	20.0	25.0	30.0
Area (J g^{-1})	28.74	50.84	87.75	157.60	220.30	289.30	335.9

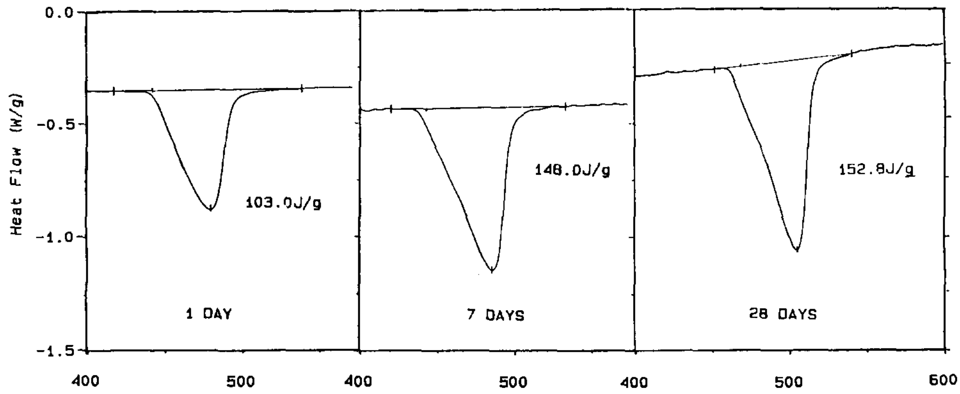

Fig. 1. Typical DSC curves for calcium hydroxide in a W/C = 0.40 cement paste at 1, 7 and 28 days.

TABLE 3
Average peak area and $Ca(OH)_2$ content in cement paste

Age (days)	Average peak area (J g^{-1})	Standard deviation (J g^{-1})	Predicted $Ca(OH)_2$ content (%)	Standard deviation (%)
1	104.9	8.1	9.4	0.7
7	147.3	0.6	13.1	0.05
28	153.8	2.0	13.7	0.19

change in $Ca(OH)_2$ content as hydration proceeds was compared with the percentage of Alite ($3CaO \cdot SiO_2$) reacted during hydration. Figure 2 indicates that the production of $Ca(OH)_2$ within the cement matrix is

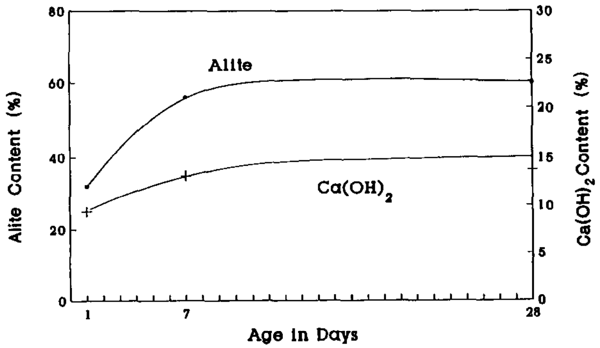

Fig. 2. Amount of reacted $3CaO \cdot SiO_2$ during cement hydration compared with the production of $Ca(OH)_2$.

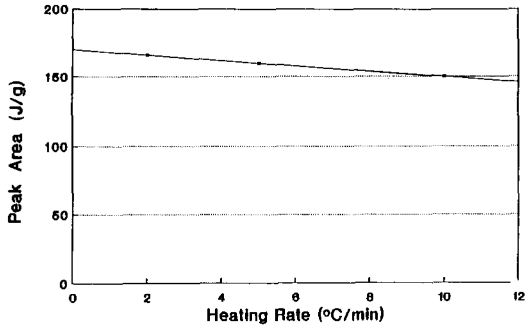

Fig. 3. Effect of heating rate on the peak area.

consistent with the reduction in $3CaO \cdot SiO_2$ content during cement hydration.

The effects of heating rate on the peak area are shown in Fig. 3. It appears that the heating rate affects only slightly the peak temperature, which tends to increase with the heating rate. It can also be observed that, as the heating rate is increased, the average peak area decreases. It can be suggested that the heating rate, within the range examined in the study, has a minimal effect on the predicted calcium hydroxide at 28 days. It is usually accepted that in DTA the heating rate affects the peak height and the peak width, and that for a decomposition reaction like $Ca(OH)_2 \rightarrow CaO + H_2O$ it affects the peak temperature [1,4]. It has been suggested that in DTA working with the curves of $\delta T/T$ (change in temperature versus temperature) does not affect the peak area [4]. The general effect of slow heating rates is to produce sharp small peaks, and fast rates give large broad peaks. The results of this study with DSC seem to indicate that these effects are minimal within the range of heating rates investigated.

The fineness of the sample being examined was observed to affect the peak area. The average peak area measured with the unground 2 mm samples was higher than with the 63 μm ground sample (171.8 J g^{-1} against 153.8 J g^{-1}) with a higher standard deviation (10.1 J g^{-1} against 2.0 J g^{-1}).

On average, the peak temperature measured with the 2 mm unground samples was slightly higher (512.6°C, SD 5°C) than with the 63 μm ground samples (452.1°C, SD 5°C). The sample size (from 10–30 mg) was found not to affect the peak height, the peak temperature or the peak area.

In general, it has been observed with DTA that the effect of particle size for a decomposition reaction such as $Ca(OH)_2 \rightarrow CaO + H_2O$ is greater on the peak temperature and the peak shape than on the peak area [4]. As far as the sample size is concerned, small samples usually yield smaller, but narrower, peaks with DTA. For decomposition reactions, the peak temperatures are also markedly affected.

CONCLUSIONS

Differential scanning calorimetry is a useful tool for the determination of $Ca(OH)_2$ in cementitious systems. It is possible to predict calcium hydroxide in cement paste within an accuracy of less than 1%. The statistical analysis of the calibration data indicated that this error was mainly attributable to the preparation of samples for calibration data. It may be the result of systematic errors, random errors or the combination of both. In hydrated cement paste, error could also be associated with the inhomogeneity of the sample, in the case of calcium hydroxide particularly at early age.

Factors such as heating rate and sample size, which have detrimental effects on DTA curves, appear to have minimal effect on DSC curves. In particular, measurements of the peak area and, consequently, the predicted calcium hydroxide content are affected negligibly by the heating rate and not at all by the sample size, within the ranges examined in this study. The use of unground coarse particles leads to a much higher value of both the peak area and the standard deviation associated to it.

No firm recommendation can be made as to optimum particle size, except that this should be known for each sample so that results may be correctly interpreted. In practice with thermal analysis, finely ground powders are commonly used. In comparative studies it is important to employ powders of similar particle size. Most current commercial instruments are designed for use of up to 20–35 mg of ground hydrated cement paste. In any case, for an efficient use of DSC, it is recommended to grind the samples and perform the determination of calcium hydroxide under the same conditions that were used to collect the calibration data.

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