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Differential scanning calorimetry study of ordinary Portland cement

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Abstract

The present work involves using differential scanning calorimeter (DSC) in an investigation of the thermal behaviour of hydration products in ordinary Portland cement as a function of age. The two-step loss of water from calcium silicate hydrate, dehydroxylation of calcium hydroxide, and decarbonation of calcium carbonate contribute respectively to the three major endothermic peaks in the DSC curves. Peaks due to the formation of ettringite and iron-substituted ettringite, C_4AH_{13} and Fe_2O_3 solid solution, were also found. Some DSC observations were supplemented by X-ray diffraction analysis.

Keywords: Hydration; Characterisation; Hydration products; Thermal analysis; Cement paste

1. Introduction

In ordinary Portland cement (OPC), there are four major compounds: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). Both C_3S and C_2S react with water (H) to form calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) as their principal hydration products [1,2] in the following manner: $2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$ and $2C_2S + 4H \rightarrow C_3S_2H_3 + CH$.

The formula of $C_3S_2H_3$ is a rough approximation and more than one form of this hydrate is possible.

In the presence of gypsum, as in the case of OPC, C_3A undergoes a rapid reaction to form C_4AH_{13}, which reacts with calcium sulphate in gypsum to form ettringite. The fourth compound, C_4AF, reacts with gypsum to form iron-substituted ettringite [2].

Thermal analyses with differential thermal analysis (DTA), thermogravimetry (TG), and differential thermogravimetry (DTG) have been used in various studies of cement hydration for a number of years [2–5]. In the present work, this is further extended to using high temperature heat flux differential scanning calorimeter (DSC). X-ray diffraction (XRD) was also used for phase identification in samples studied with DSC.

2. Methods

An ordinary Portland cement cube was made with a water:cement ratio of 0.33. The cube was stored constantly under water at 20°C. Before each collection of DSC samples from the cube, the first 4–5 mm of the surface was removed by either grinding or filing. The sample was obtained from the surface then showing, either by chipping or filing enough to approximately half fill the DSC sample holder (giving a sample weight of ~40 mg), and tested immediately in the DSC. Such a procedure helps to avoid surface moisture due to underwater storage. A Netzsch DSC404 calorimeter (Netzsch-Gerätebau GmbH, Selb/Bavaria, Germany) was used with a computer-controlled furnace that heats a measuring head containing the sample. Further details of this technique and the equipment can be found in previous publications [6,7]. All experiments were conducted at a heating rate of 10°C/min up to 1000°C in a dynamic helium atmosphere.

XRD analyses were carried out on some DSC samples heated to certain temperatures (unheated, and up to 325 and 635°C) for phase identification.

3. Results and discussion

The DSC data analysis software gives graphs of heat flow between sample and reference crucibles vs. temperature. Upward peaks show endothermic reactions and downward peaks show exothermic reactions. In this paper, only DSC curves obtained during heating are considered. No obvious pattern was observed in cooling curves.

A number of peaks were observed in DSC curves consistently, albeit they do not appear at all ages. The identifica-

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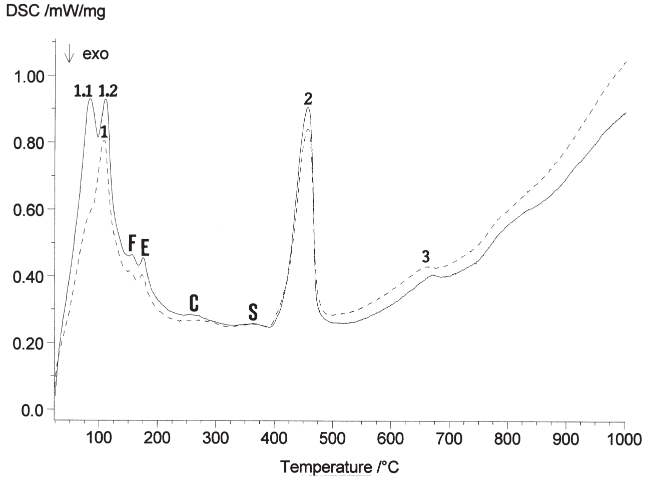

Fig. 1. DSC curves of hydrated ordinary Portland cement at the ages of 10 (solid line) and 16 (dashed line) days. C = C_4AH_{13}; E = ettringite; F = iron-substituted ettringite; S = Fe_2O_3 solid solution.

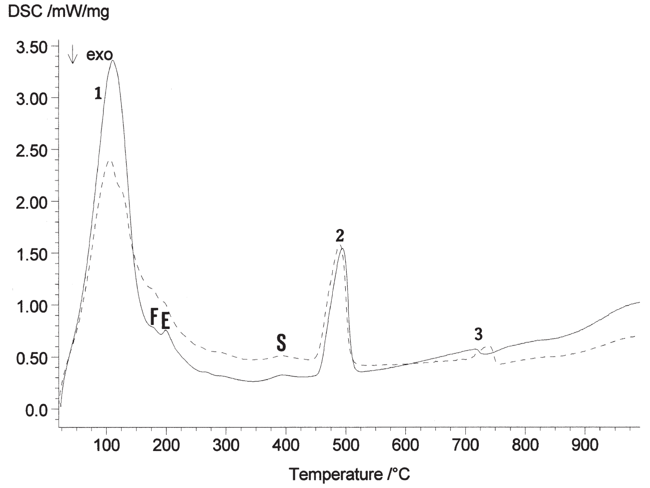

Fig. 2. DSC curves of hydrated ordinary Portland cement at the ages of 17 (solid line) and 45 (dashed line) days. E = ettringite; F = iron-substituted ettringite; S = Fe_2O_3 solid solution.

tion of these peaks are given in Figs. 1 and 2. There are three major peaks (peaks 1, 2, and 3), the peak temperatures of which are shown in Fig. 3. The first endothermic peak, peak 1, is the result of dehydration reactions due to the loss of water from C-S-H. For cement in early ages (up to 15 days), there is a stepwise loss of two types of molecules of water, giving two subpeaks, which is clearly shown by the solid line in Fig. 1. It was found that the relative sizes of the two subpeaks are similar in general but can have variations in their exact proportions from sample to sample. However, as the cement ages to over 15 days, the first subpeak diminishes and there remains one predominant peak (Figs. 1 and 2). The remaining peak can have shoulders, however, usually at its left side at earlier ages (dashed line in Fig. 1), moving to the right side after prolonged aging. There is an increase in the size of the peak, which may be partly attributed to the desorption of capillary water from the silica-lime gel with time [8]. It may also be due to some degree to the absorption of water from under water storage.

The second major peak, peak 2, corresponds to the dehydroxylation of $Ca(OH)_2$, another hydration product. X-ray analysis showed the absence of $Ca(OH)_2$ in DSC samples heated to 635°C, confirming this reaction. The third peak, peak 3, corresponds to the decarbonation of calcium carbonate, together with possible solid-solid phase transformations [2].

Four smaller peaks were also found in DSC curves, corresponding to the hydration products from C_3A and C_4AF (Fig. 4). The endothermic peaks in the 165–205 and 255–300°C ranges are respectively attributed to ettringite and C_4AH_{13} (and possibly C_3AH_6), which are both reaction products from C_3A. The peaks at 155 and 390°C are due to the presence of high iron-substituted ettringite and the formation of Fe_2O_3 solid solution, which are both products from C_4AF. Details of the reactions leading to these compounds can be found in the paper by Bhatty [2].

The results mentioned above are supported by a parallel study using DTA [9].

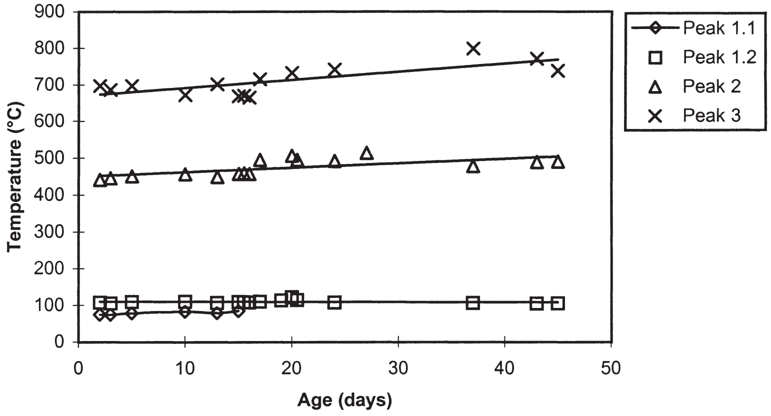

Fig. 3. Peak temperatures of the three major DSC peaks.

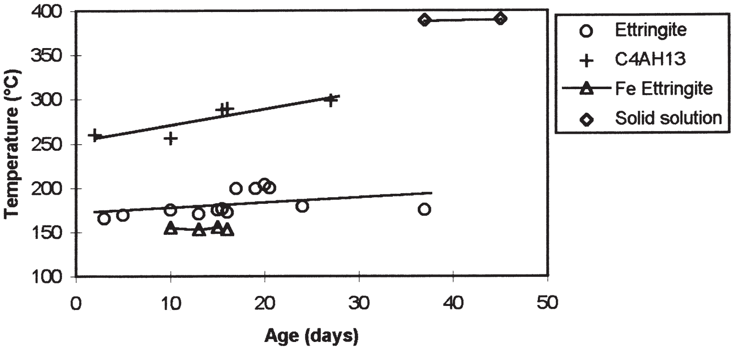

Fig. 4. Peak temperatures of the four minor DSC peaks.

A DSC analysis of cement powder that was not mixed with water was also carried out (Fig. 5). There had been limited hydration in this cement powder during storage, as shown by the presence of C-S-H dehydration peaks (82 and 112°C). However, the sizes of these peaks are substantially smaller than the corresponding peaks in hydrated cement (see Figs. 1 and 2). The peak at 385°C is due to the formation of Fe_2O_3 solution, which is a product from C_4AF. Because C_4AF is present in full amount in the anhydrous Portland cement, this peak is much higher than those in Figs. 1 and 2. The peak at 648°C corresponds to the decarbonation of calcium carbonate.

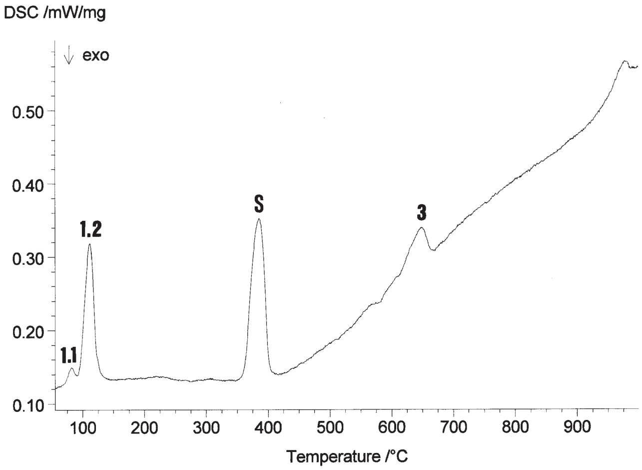

Fig. 5. DSC curve of ordinary Portland cement powder. S=Fe_2O_3 solution.

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