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Differential scanning calorimetry study of hydrated ground granulated blast-furnace slag

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Abstract

The present work involves using differential scanning calorimetry (DSC) in an investigation of the thermal behaviour of hydration products in ground granulated blast-furnace slag (ggbs). The two-step loss of water from calcium silicate hydrates and dehydroxylation of calcium hydroxide ($Ca(OH)_2$) contribute, respectively, to the two major peaks in the DSC curves. Peaks due to the formation of ettringite and Fe_2O_3 solid solution were also found. The crystallisation peaks from amorphous phases in the ggbs are also significant in the DSC thermograms. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hydration; Characterisation; Hydration products; Thermal analysis; Granulated blast-furnace slag

1. Introduction

Granulated blast-furnace slag is a waste product in the manufacture of pig iron, the amounts of iron and slag obtained being of the same order. The slag is a mixture of lime, silica, and alumina, the same oxides that make up Portland cement, but not in the same proportion [1]. In combinations of the Portland cement and slag, the cement component hydrates in the normal manner and it appears that the calcium hydroxide ($Ca(OH)_2$) thus liberated gives the correct alkalinity needed to provide a "starter" for the hydration of the granulated slag.

In a recent work in the authors' research group, differential scanning calorimetry (DSC) was used to characterise the hydration products and the hydration process in ordinary Portland cement (opc) paste [2]. Various hydration product phases were identified corresponding to the peaks in the DSC curves. In this paper, this work is continued, extending to the study of the hydration products of ground granulated blast-furnace slag (ggbs).

2. Methods

Ground granulated blast furnace slag was obtained locally in Northern Ireland. It was mixed with equal weight of Blue Circle opc (i.e. 50% cement replacement), at the water/solid ratio of 1:3. The total mix was small, weighing about 5 kg. A 100-mm cube was made and kept cured under water, which was maintained at 20°C. Samples were chiselled off from the cube and taken to be tested in the DSC at different ages. Each time when a DSC sample was taken, the first 4–5 mm of the local surface on the cube was removed. Once the sample was obtained the cube was returned to the water tank.

A heat flux DSC404 calorimeter was used. Two alumina crucibles were used with lid for each. One crucible was used to carry the sample and the other one was used to carry a reference material. Each empty crucible weighed at approximately 240 mg with the lid. Alumina powder was used as the reference material in the DSC runs, its total heat capacity approximately balancing that of the ggbs sample's by weighing them in calculated proportions. In each experiment, the weight of the ggbs sample was 80 mg and the weight of the alumina powder reference was 74 mg.

All experiments in the DSC were carried out at a heating rate of 10°C/min in helium with a flow rate of 30 ml/min through the enclosed heating chamber. Some

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further information about the DSC experimentation can be found in a previous publication [2]. The DSC data analysis software gives graphs of heat flow between sample and reference crucibles versus temperature.

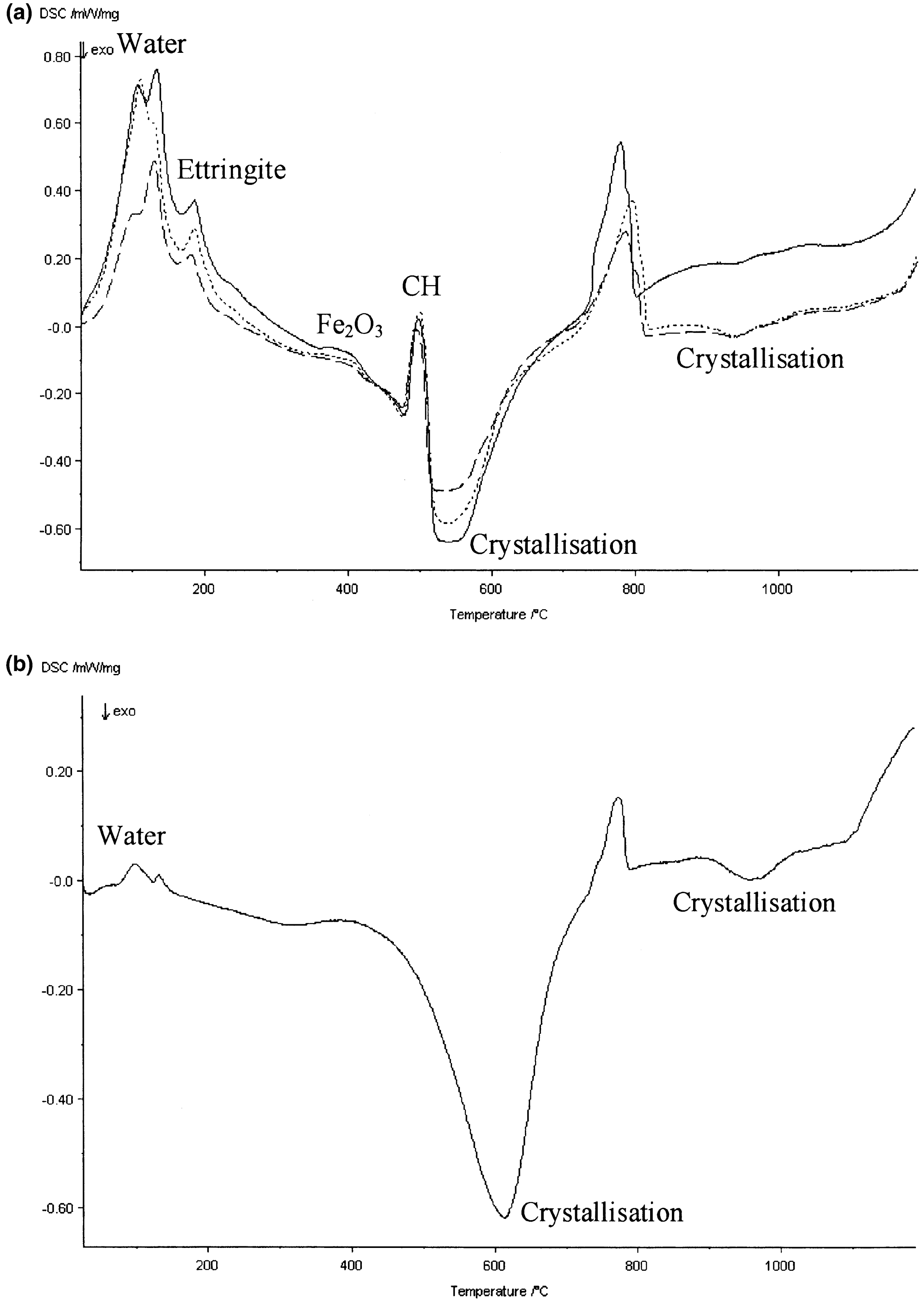

Fig. 1. DSC curves of ggbs: (a) hydrated at the ages of 26 (solid line), 29 (long dashed line), and 35 (short dashed line) days; (b) powder (not hydrated).

3. Results and discussion

From DSC experiment results, it was found that there is large heterogeneity in the mix. A total of seven runs were made. The DSC curves of four runs appear similar to each other, and they are as if from a pure opc mix. The shape of these four curves is the same as the published DSC curves for opc paste [2]. The other three experiments, however, gave completely different results (Fig. 1a). Comparing with DSC runs from pure ggbs powder before mixing (Fig. 1b) [3], these three were certainly from the part of the mix containing ggbs.

It was concluded therefore that there was inadequate mixing between ggbs and opc due to the small quantity of the mix and the probable improper use of the mixing procedures for such a small quantity. The limitation of the small crucible size in the DSC signifies this problem. However, this does give us an opportunity of studying the hydration products from an almost pure ggbs mix. As stated earlier, ggbs itself has some hydration capability, especially in the presence of hydroxyl ions released during the hydration of opc.

There are a number of peaks in the DSC curves, as shown in Fig. 1a. The peak temperatures and enthalpy values are summarised in Table 1. Most of the peaks also appear in DSC curves from opc paste [2], thus their identifications are assumed to be the same. Although the three experiments were conducted at three different ages, 26, 29, and 35 days, the curves are very similar as can be seen from Fig. 1a, with no sign of significant progressive development with increasing age. Therefore, in Table 1, the values are the averages from the three runs at the three different ages.

The most significant reaction from the presence of ggbs in the mix is the large exothermic peak at around 537°C. This peak was also found in unmixed ggbs powder, and was identified as from the crystallisation of an amorphous phase in ggbs [3]. There is an overlap between the peak corresponding to the dehydroxylation of $Ca(OH)_2$ and the crystallisation peak, which are in opposite directions as the former reaction absorbs heat while the latter releases heat. The overlap was taken into account when calculating the enthalpy for crystallisation. There is a second crystallisation peak at a higher temperature, around 938°C, which may be due to a different amorphous phase. This peak is also present in the DSC curve of ggbs powder samples [3]. Peaks in similar positions are also found in DSC runs of fly ash and metakaolin powders [3,4], which were also thought to be from the crystallisation of amorphous phases.

The quantity of $Ca(OH)_2$ can be quantified using the heat of dehydroxylation of $Ca(OH)_2$, which is 1021 J/g as estimated from published calorimetric data [5]. This is similar to the value of 856 J/g calculated from the Gibbs energy of formation of $Ca(OH)_2$, CaO, and H_2O [6]. Therefore, a measured enthalpy of 59 J/g of the original DSC sample gives a total heat of $59 \times 0.08 = 4.72$ J, which corresponds to the decomposition of 4.6 mg of $Ca(OH)_2$. If assuming that the initial DSC sample was a mixture of only water and ggbs in the ratio of 1:3, there was 60-mg ggbs in the sample. Therefore, the percentage of $Ca(OH)_2$ is 7.7% of the ggbs originally present. This is below the level from the hydration of normal opc mixes. There is quite possibly some contribution from the hydration of opc from elsewhere in the mix as a result of migration, thus the level of $Ca(OH)_2$ generated by hydration of ggbs should be even lower.

There is a large peak at 786 ± 8°C in all three DSC curves, with an enthalpy (absorption of heat) of 102 ± 13 J/g of the entire DSC sample. The temperature range of this peak is not much above the limit for that for the decarbonation of $CaCO_3$, but its size is much larger than what would be expected from the residual $CaCO_3$ in the system [2]. The identification of this peak is not clear at present.

Table 1
Peak temperatures and enthalpy in differential scanning calorimeter curves

Peak	Temperature (°C)	Enthalpy (J/g of sample)
First water loss from calcium silicate hydrates	106 ± 4	–
Second water loss from calcium silicate hydrates	129 ± 4	–
Ettringite	183 ± 3	13 ± 2
Fe_2O_3 solid solution	368 ± 20	–
Dehydroxylation of $Ca(OH)_2$	496 ± 2	59 ± 12
Crystallisation (low temperature)	537 ± 3	414 ± 80
Crystallisation (high temperature)	938 ± 2	15 ± 11

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