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Differential scanning calorimetry study of ordinary Portland cement paste containing metakaolin and theoretical approach of metakaolin activity

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Abstract

This paper aims to investigate the hydration and pozzolanic reactions in cement pastes with different levels of metakaolin replacement, using differential scanning calorimetry (DSC) and theoretical analysis based on reaction stoichiometry. It was found that the DSC technique could follow the hydration process quantitatively by measuring the peak temperature and enthalpy corresponding to decomposition of hydration products, as functions of age. The pozzolanic process can also be followed from the measurements of the changes in the amount and the nature of amorphous material in the paste and the change of the amount of calcium hydroxide. In addition, it was confirmed that a theoretical approach using reaction stoichiometry could give a good estimation of the concentration of calcium hydroxide in a metakaolin concrete. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Calorimetry; Hydration products; Thermal analysis; Blended cement; $Ca(OH)_2$; Metakaolin; Portland cement; Pozzolan; Modelling

1. Introduction

Ordinary Portland cements (OPC) can be combined with other materials to produce a range of cementing materials [1]. In such combinations, the normal Portland cement hydration reactions take place but other chemical reactions also occur. The hydroxyl ions (OH^-) in pore water, produced during the Portland cement hydration, increase the pH of the system. If pozzolanas, essentially minerals containing amorphous silica, are added, reactions take place with the $Ca(OH)_2$ (*CH*) generated by the cement hydration. As a consequence, extra calcium-silicate-hydrate (C–S–H or CSH) is produced and the amount of calcium hydroxide (Portlandite, *CH*) is reduced in the hardened paste. This is beneficial because

- more strength-giving material is produced
- less Portlandite can be leached out during chemical attack, and thus porosity is decreased.

Metakaolin, $Al_2Si_2O_7$, is one such pozzolanic material.

The cement and concrete industry is the largest consumer of natural materials in the world and a major contributor to greenhouse gases that are responsible for global warming and climate change. The key to a successful strategy for the sustainable development of the construction industry is the conservation of concrete-making materials. This can be achieved by substituting both the normal Portland cement and the natural aggregates in concrete with industrial by-products. The replacement of normal Portland cement with pulverised fuel ash (PFA), ground granulated blast furnace slag (GGBS), micro silica and metakaolin has widely been investigated in the context of engineering properties of concrete. However, procedures for the design of concrete mixes incorporating these materials differ due to insufficient understanding of the phase changes and the microstructural development of the hydrated cement although some studies exist on the subject. Such change and development influence the physical and mechanical properties of the finished product. As a consequence, concrete incorporating these materials could perform differently in different service environments, which needs to be modelled in order to design concrete mixes for different service conditions.

To date, although microstructural characterisation exists for cement with replacement materials, there has been no systematic thermal analysis work covering all

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ranges of cement replacements. Thermal analysis has proved to be a valuable technique in the study of cement hydration [2–4,6].

The aim of this research is to characterise and understand the microstructural evolution during hydration of combinations of OPC and metakaolin, as a function of replacement level and age. The research follows the preliminary differential scanning calorimetry (DSC) work by Sha et al. on OPC paste [6].

2. Experimental procedure

10-cm cement paste cubes were made, at a water solid ratio of 0.45, with 20% or 30% metakaolin replacing cement. OPC was used, made by Blue Circle. Imerys (formerly ECC International) supplied Metastar 500 metakaolin powder, which is completely amorphous except for impurities. The chemical compositions of cement and metakaolin are shown in Table 1 [6].

Detailed sample collection and DSC experimentation were given in a previous paper [5], and will not be repeated here, apart from the following that is particular to the present work only. Two types of DSC experiments were conducted. The first type is isothermal holding of the wet paste immediately after mixing, at 25°C for 24 h, in air. The second type, similar to the experiments conducted in [6], involved heating the samples up at a constant heating rate of 10°C per minute, to 1100–1200°C, in a dynamic helium atmosphere. The samples used weighted around 65 mg. For this type of experiment, the samples were collected from cubes stored under water at about 20°C from approximately 24 h after mixing. Unfortunately, for the early periods, up to 52 days for the 20% metakaolin cube and 16 days for the 30% metakaolin cube, respectively, the curing temperature was not maintained constant and ranged between 13°C and 21°C. For the first 24 h after mixing, the cubes were kept in air in steel moulds to set.

Table 1
Chemical compositions (percentage) of cement and metakaolin

Compound	Ordinary Portland cement	Metakaolin
SiO_2	21.8	54.8
Al_2O_3	4.2	41.2
Fe_2O_3	2.5	0.57
CaO	65.1	0.02
MgO	–	0.31
Na_2O	0.13	0.04
K_2O	0.72	2.27
TiO_2	–	0.01
SO_3	2.4	–

Although the DSC analysis is capable of obtaining peak start, maximum or minimum and end temperatures, in the result presentation part of this paper, all peak temperatures refer to the maximum or minimum points. In all DSC curves presented in the following, downward peaks indicate release of heat from the sample during heating up, and upward peaks indicate absorption of heat. Except for metakaolin powder runs, where three experiments were conducted, only one experiment was carried out for each condition with mixed pastes. It should be noted that the relation between peak size and enthalpy is not simply linear, but also depends on the temperature at which the peak occurs. This is because the sensitivity of the enthalpy measurement of the DSC decreases with increasing temperature.

3. Experimental results and discussion

3.1. Metakaolin powder

Fig. 1 shows a DSC thermogram of pure, dry metakaolin powder, without mixing with cement or water. The only peak is at 992 ± 3°C, averaged over three separate runs. The enthalpy for the peak was measured, averaged at 98 ± 5 J/g. This peak should correspond to the crystallisation of the amorphous metakaolin. The nature of the products has been identified some years ago: Al_2O_3 (γ) and mullite. The enthalpy value is of the same order of magnitude for crystallisation in metallic systems e.g. [7]. The crystallisation temperature is similar to those of metal-metalloid glasses such as $Ta_{80}Si_{10}B_{10}$ (952°C) and $W_{40}Re_{40}B_{20}$ (1027°C) [8].

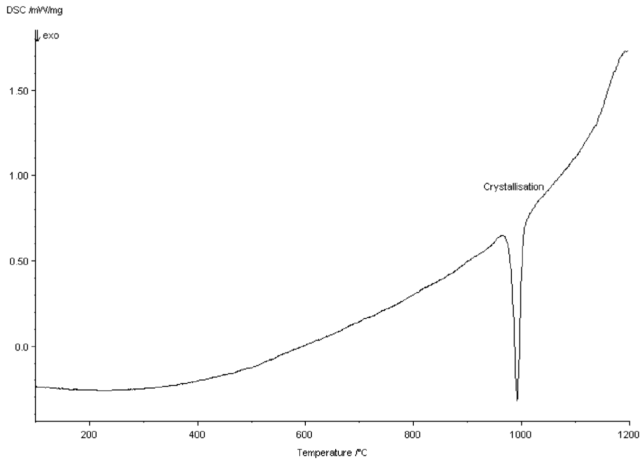

Fig. 1. DSC thermogram from metakaolin powder.

3.2. Isothermal experiments in the first 24 h after mixing

Isothermal holding of the wet pastes in DSC was used in an attempt to follow the evolving heat in the first 24 h of hydration. However, it was found that due to the DSC furnace set-up and the constraint in the volume of paste that could be accommodated by the small crucible (up to 175 mg wet paste weight), the technique could not trace the heat evolution accurately. The total hydration heat that can be detected is small and comparable with background noise of the equipment. After isothermal holding at 25°C for 24 h, the samples were found to be 20% lighter. Initially, there was 31% water in weight in the wet paste, corresponding to the water solid ratio of 0.45. Therefore, about two thirds of the water evaporated during the holding, due to the very small volume of the paste in the crucible leading to a large surface area for evaporation.

The above finding is despite the acceleration effect of metakaolin on cement hydration, with increased heat release. The following results are all based on constant rate heating experiment of hydrated pastes at different ages.

3.3. 20% metakaolin

Fig. 2 shows three DSC thermograms from hardened paste containing 20% metakaolin replacement at three distinct ages, 1 day, 28 days and 109 days. There are a number of peaks, in addition to the crystallisation peak of the metakaolin that is always present, even after 109 days into hydration. The size of this crystallisation peak decreases with increasing age, indicating a reduction of the amorphous material as a result of the pozzolanic reaction with calcium hydroxide. The identification of the other peaks is the same as that presented in the earlier paper [5]. The peak temperatures are summarised in Fig. 3. Readers should refer to [6] for detailed discussion about these peaks.

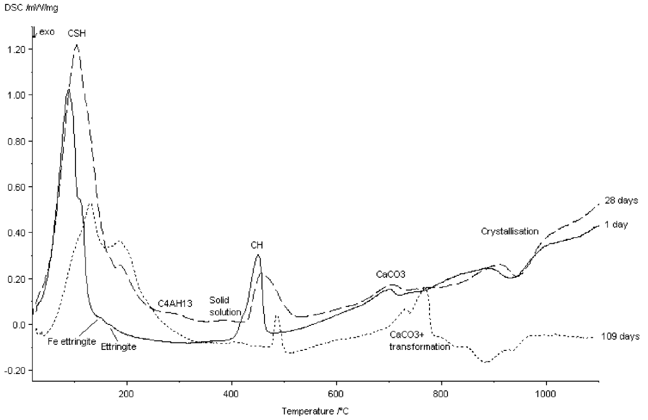

Fig. 2. DSC thermograms from hardened paste containing 20% metakaolin replacement at 1 day (solid line), 28 days (long dashed line) and 109 days (short dashed line).

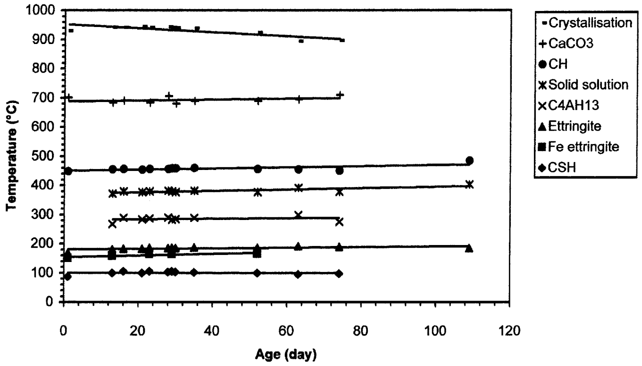

Fig. 3. DSC peak temperatures from the mix with 20% metakaolin replacement.

The amount of the various phases present in the hardened paste can be monitored through the mea-

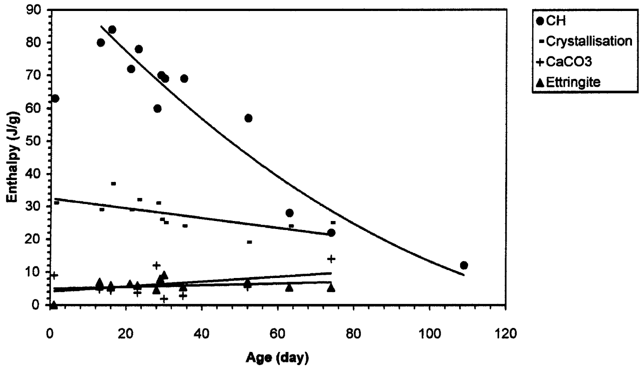

Fig. 4. DSC peak enthalpy from the mix with 20% metakaolin replacement, for peaks attributed to, dehydroxylation of $Ca(OH)_2$ (*CH*), crystallisation of amorphous metakaolin, decarbonation of calcium carbonate, and ettringite.

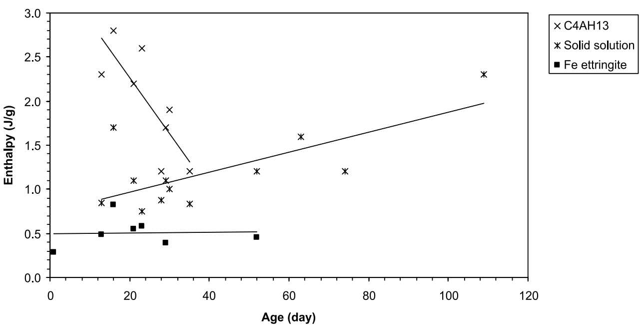

Fig. 5. DSC peak enthalpy from the mix with 20% metakaolin replacement, for peaks due to C_4AH_{13} (and possibly C_3AH_6), the formation of Fe_2O_3 solid solution, and the presence of high iron-substituted ettringite.

surement of the enthalpy under the corresponding peaks. The result of this measurement is given in Figs. 4 and 5. The peaks for Fig. 5 are due to C_4AH_{13} (and possibly C_3AH_6), reaction products from C_3A, and the formation of Fe_2O_3 solid solution and the presence of high iron-substituted ettringite, both products from C_4AF. As these peaks are small (Fig. 2), there are large errors in the enthalpy values determined, resulting in the large scatter of the data points in Fig. 5. The general trends may be used to monitor the hydration process. Further understanding of cement hydration chemistry is required however to draw a quantitative conclusion. The same may be said for the enthalpy variation for the two peaks due to the decarbonation of calcium carbonate together with possible solid–solid phase transformation, and ettringite, a reaction product from C_3A, respectively (Fig. 4). In addition, it is thought that the heterogeneous distribution of calcium carbonate, a residual phase in OPC, contributes to the large apparent variation of the amount of this phase as indicated from the enthalpy measurement from its decomposition. In some experiments, the sizes of these peaks are too small to allow for accurate measurement of their positions and, in particular, enthalpy. Thus there is no data point in the graphs (Figs. 3–5) for some ages. This is particularly true for samples at longer ages.

Of more interest are the changes of the amount of $Ca(OH)_2$ in conjunction with the size of the crystallisation peak, the latter associated with the amount of amorphous metakaolin remaining in the mix. It can be seen from Fig. 4 that, after an initial increase between 1 and 16 days, the amount of $Ca(OH)_2$ drops continuously with increasing age. This shows quantitatively, albeit with experimental error in the enthalpy measurement and sample-to-sample variation due to the small sample volume, the progress of pozzolanic reactions with age. The peaks corresponding to the crystallisation of metakaolin in cement paste are not in exactly the same position as in runs for pure metakaolin powder prior to mixing (Fig. 3). The peak temperatures are lower, and drop slightly with increasing age. This should be due to the influence of modified chemistry after mixing and the possible influence of the surrounding environment on the crystallisation behaviour. The size of this crystallisation peak decreases with increasing age, showing a reduction of amorphous metakaolin as a result of its reaction with calcium hydroxide.

The trend of variation of the amount of calcium hydroxide with age (Fig. 4) compares well qualitatively with a pore solution chemistry study by Coleman and Page [9], but the latter data need to be converted into $Ca(OH)_2$ concentration before quantitative comparison can be attempted.

As the age proceeds beyond 35 days, the shape of the crystallisation peak starts to change, from a single peak as in Fig. 2 for 1 day and 28 days, to starting to separate, as in Fig. 6 for 52 days, until complete separation into two peaks at 74 days. The peak temperatures and enthalpy values given in Figs. 3 and 4 are for the peak at higher temperature among the two separate peaks in the crystallisation temperature range. It is not clear at present what contributes to the additional peak at the slightly lower temperature. It is most likely a crystallisation peak of a different amorphous structure, derived after the pozzolanic reaction becomes significant. In $Al_2Si_2O_7$ (metakaolin), Al_2O_3 and SiO_2 parts should react with $Ca(OH)_2$ at significantly different rates and extents, with different mechanisms, and the preferentially retained Al_2O_3 or SiO_2 may crystallise at the slightly different temperature. The occurrence of the two peaks adds some error in the enthalpy evaluation, especially for the stages when the separation is incomplete. Further development occurs between 74 and 109 days, as shown by the large change of peak shape at the latter age (Fig. 2).

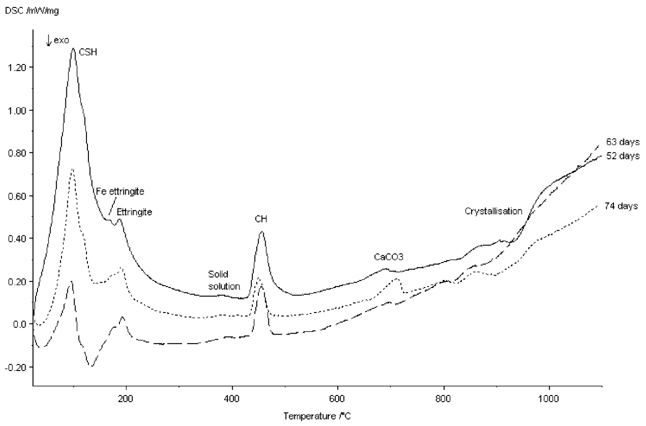

Fig. 6. DSC thermograms from hardened paste containing 20% metakaolin replacement at 52 days (solid line), 63 days (long dashed line) and 74 days (short dashed line).

It may be noted that the enthalpy from crystallisation of metakaolin is consistently higher than what would be predicted from the proportion of the metakaolin in the mix, i.e. $\approx 0.2/1.45 = 14\%$ of the crystallisation enthalpy of the pure metakaolin powder. At 1 day after mixing, the crystallisation enthalpy is 31 J per gram of the entire sample weight, converting approximately to an enthalpy of 225 J per gram of metakaolin, more than twice as large as that obtained from pure metakaolin runs, 98 J/g. It is thought that this may be due to changes in the composition and structure of the amorphous material.

Using data from a DSC and thermogravimetry (TG) analysis of cement mortar [10], the heat of dehydroxylation of $Ca(OH)_2$ was estimated at 1021 J/g. This agrees reasonably well with the value of 856 J/g derived from the Gibbs energy of formation of $Ca(OH)_2$, CaO and H_2O [11]. Using the former data, multiplying the enthalpy value, in J/g, for the peak for dehydroxylation of $Ca(OH)_2$ by 0.175 will give the amount of the $Ca(OH)_2$ phase in percentage of OPC in the original mix. The values obtained this way from Fig. 4 agree well with data found in other work [12]. Similarly, the heat of decarbonation of $CaCO_3$ is estimated at 1791 J/g, from the Gibbs energy of formation of $CaCO_3$, CaO and CO_2 [11]. The amount of $CaCO_3$ in the mix can thus be derived from data presented in Fig. 4. It may be noted that at 109 days, when the metakaolin has had strong pozzolanic reaction, $CaCO_3$ peak becomes strong and has two sub-peaks (Fig. 2). For this reason, no temperature and enthalpy information about the peak at this age are included in Figs. 3 and 4. This phenomenon may be connected with pozzolanic products.

Some samples were re-weighted after DSC runs. It was found that the weight loss is on average 32% of the original sample weight before heating up. This corresponds well with the water content in the mix, 31%. As the cubes were stored under water constantly before testing, the water content in the cubes should have remained almost constant as from the mixing stage. However, there are also contributions to weight loss from dehydroxylation of $Ca(OH)_2$ and decarbonation of $CaCO_3$. Therefore the weight analysis can only be treated as qualitative.

3.4. 30% metakaolin

With 10% more metakaolin replacing OPC in the mix, the paste with 30% metakaolin exhibits significant acceleration of the speed and expansion of the scale of the pozzolanic reaction. Fig. 7 shows DSC thermograms for pastes at the ages of 2, 24 and 73 days, respectively. Now, the separation of the crystallisation peak is complete after 38 days (Fig. 8), half of the age for this in the paste with 20% metakaolin. Also, the peak corresponding to the decarbonation of $CaCO_3$ now starts to grow large at an earlier age. There is an overlap of peaks at this region, with possible additional contribution from solid–solid transformations [2]. Therefore, the obvious dual peak phenomenon in this temperature range may be attributed to this transformation. Also, it is interesting to note the significant peaks corresponding to ettringite and iron-substituted ettringite, at 24 days (Fig. 7). These continue to increase with longer age (Fig. 8), overlapping to cause the large peak in the curve for 73 days (Fig. 7). As ettringite is a hydration product from C_3A, this difference from the behaviour of 20% metakaolin paste could provide information on the effect of metakaolin on hydration process. Figs. 9 and 10 show the variation of peak temperature and enthalpy as a function of age.

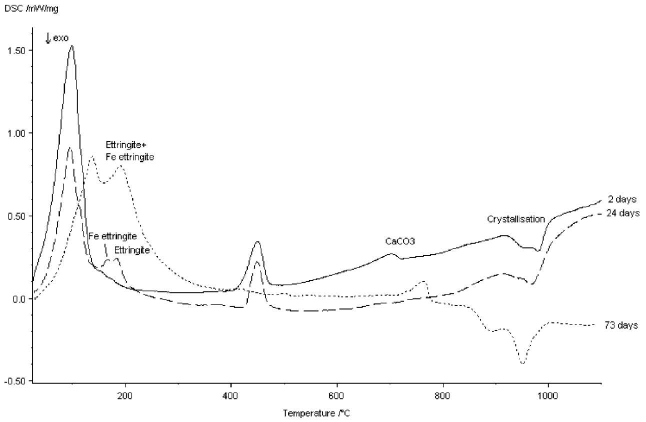

Fig. 7. DSC thermograms from hardened paste containing 30% metakaolin replacement at 2 days (solid line), 24 days (long dashed line) and 73 days (short dashed line).

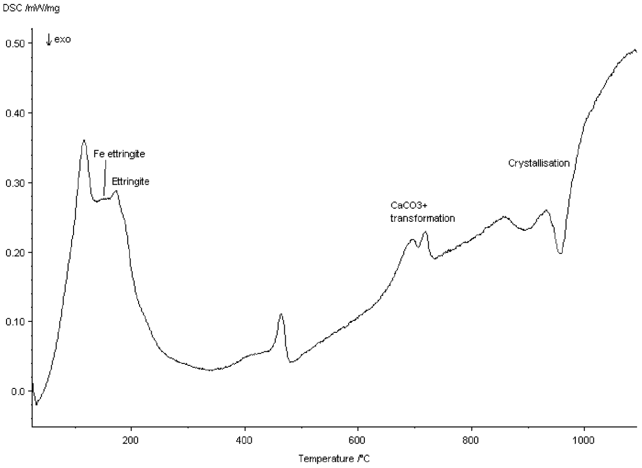

Fig. 8. DSC thermogram from hardened paste containing 30% metakaolin replacement at 38 days.

3.5. Samples after one day hydration in air in DSC

The samples after isothermal experiment were heated up to 1200°C at 10°C/min in the DSC, with the resulting

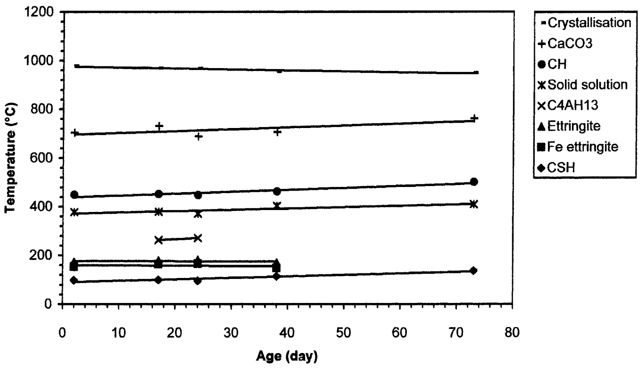

Fig. 9. DSC peak temperatures from the mix with 30% metakaolin replacement.

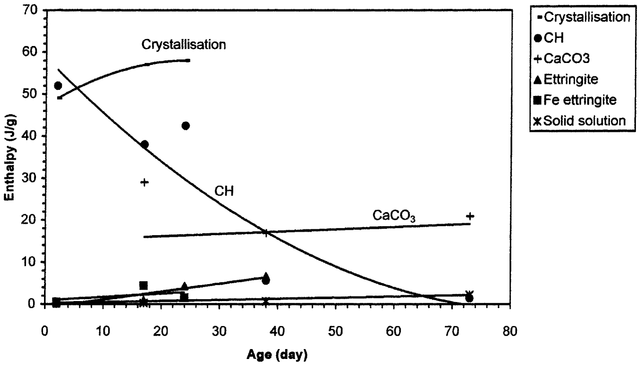

Fig. 10. DSC peak enthalpy from the mix with 30% metakaolin replacement.

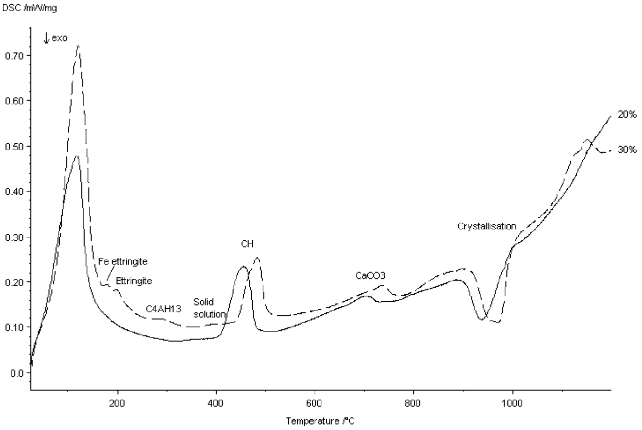

Fig. 11. DSC thermograms from cement paste with 20% (solid line) and 30% (dashed line) metakaolin, after isothermal holding at 25°C in DSC for 24 h.

thermograms shown in Fig. 11. For the paste with 20% metakaolin, in comparison with Fig. 2, it can be seen that ettringite and iron-substituted ettringite have not developed, due to the lower degree of hydration as a result of the small sample in air. For the paste containing 30% metakaolin, these, and C_4AH_{13}, have developed, however, possibly due to the reported hydration accelerating effect of metakaolin in the very early stages [13]. The peak temperatures and enthalpy are summarised in Table 2. From this comparison, it is easy to see the pozzolanic effect of metakaolin even at this very early stage of hydration. The amount of calcium hydroxide drops by 25% when the level of replacement increases from 20% to 30%. With this increase of metakaolin replacement, the amount of OPC drops by 14%. Also, the size of the crystallisation peak increases by 24%, much less than expected from the 50% increase of the amount of metakaolin.

Table 2
DSC peak temperatures and enthalpy in constant heating runs for samples hydrated for 24 h in air in DSC

Peak	20% Metakaolin		30% Metakaolin	
	T (°C)	J/g	*T* (°C)	J/g
C–S–H	118	–	120	–
Fe ettringite	No peak	–	177	0.4
Ettringite	No peak	–	198	0.9
C_4AH_{13}	No peak	–	291	1.2
Solid solution	No peak	–	393	0.3
CH	455	40	482	30
$CaCO_3$	705	2.4	737	1.8
Crystallisation	935	42	968	52

For the sample with 30% metakaolin, it was found that there is a weight loss of 20% after heating to 1200°C. This, and the water loss during isothermal DSC, adds approximately to the total water content of the mix.

4. Theoretical approach of metakaolin activity in Portland cement systems

Papadakis recently presented an excellent model for the theoretical analysis of pozzolanic activity in Portland cement systems, and successfully applied it to cement with PFA replacement [14]. In the present work, this approach was used to calculate the equilibrium $Ca(OH)_2$ content in hydration fully completed and pozzolanic reaction fully developed cement with different levels of metakaolin, based on the OPC and metakaolin compositions given in Table 1 in [12]. Four mix proportions in Table 3 in [11] were used for the calculations, corresponding to metakaolin replacement levels of 0%, 5%, 10% and 15%. This method can be used for mixes used in the above DSC work in the present experimental programme.

The calculations are based in 1 m^3 of concrete or mortar, which contains C and P kg of Portland cement and pozzolan (metakaolin). The Portland cement and the metakaolin can be analysed in terms of oxides: CaO (C), SiO_2 (S), Al_2O_3 (A), Fe_2O_3 (F) and SO_3 ($\overline{S}$). Let us denote as $f_{i,c}$ and $f_{i,p}$ the weight fractions of the constituent i ($i = C, S, A, F$ and $\overline{S}$) in the cement and pozzolan, respectively. It was confirmed with the ma-

Table 3
Final *CH* content as a fraction of OPC for mixes containing different levels of metakaolin replacement

% Metakaolin	0	5	10	15
Gypsum higher than required	Yes	No	No	No
CH/OPC	32.3	21.6	9	0

terial supplier (Imerys, formerly ECC International) that the metakaolin used in the present work is 100% amorphous except for impurities. Therefore, it was assumed that 100% of the SiO_2 (S) and Al_2O_3 (A) in the metakaolin contribute to pozzolanic reactions. There are two equations for calculating the final $Ca(OH)_2$ content in hydrated cement when pozzolanic reaction also takes place between metakaolin and calcium hydroxide. For their derivation, [14] should be consulted:

$$CH = \{1.321(f_{C,c} - 0.7f_{\overline{S},c}) - (1.851f_{S,c} + 2.182f_{A,c} + 1.392f_{F,c})\}C - (1.851f_{S,p} + 2.182f_{A,p})P, \tag{1}$$

$$CH = (1.321f_{C,c} - 1.851f_{S,c} - 2.907f_{A,c} - 0.928f_{F,c})C - (1.851f_{S,p} + 2.907f_{A,p})P, \tag{2}$$

where CH is the amount of $Ca(OH)_2$ in kg/m^3.

Eq. (1) applies if the gypsum content is higher than that required for full hydration of the cement and complete pozzolanic reaction of metakaolin:

$$f_{\overline{S},c} > 0.785f_{A,c} - 0.501f_{F,c} + 0.785f_{A,p}(\mathrm{P/C}) \tag{3}$$

and Eq. (2) applies if the gypsum content is lower than that required for cement hydration and for complete pozzolanic reaction of the active part of Al_2O_3 in metakaolin (100% in the present calculation), i.e. if Eq. (3) is not satisfied.

Using these equations, the final CH contents were calculated and the results are summarised in Table 3. For comparison, experimentally, the amount of CH is 8.6% of OPC for the mix with 15% metakaolin replacement, after one-year curing [12]. Theoretically, there should be no CH remaining in the equilibrium, final state. This indicates that the hydration rate is greater than the pozzolanic rate. The amount of CH is 11.6% of OPC for the mix with 5% metakaolin replacement, smaller than the theoretical value of 21.6%. This indicates that at this replacement value, the pozzolanic rate is greater than the hydration rate. Such are common with the phenomenon that dilute solutions are more effective per unit material used. For the control mix without metakaolin, the experimental CH value is far smaller than the theoretical one, but this is reasonable as in practice, in OPC concrete, the full extent of alkalinity is never reached due to incomplete hydration.

For mixes used in the experimental programme described in this paper, with 20% and 30% metakaolin replacement, it is expected that, eventually, all CH should be used up by the pozzolanic reaction. This is proved in the case of 30% replacement, shown by the diminishing peak from CH in DSC thermograms after long ages.

5. Concluding remarks

The present work has demonstrated that DSC analysis can be used to trace the hydration process of cement with metakaolin replacement. The pozzolanic reaction of metakaolin and its effect on cement hydration can be monitored. The technique, combined with theoretical analysis based on reaction stoichiometry, can contribute to the understanding of these processes.

Acknowledgements

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