

REACTIVITY OF FLY ASH IN CEMENT PASTE STUDIED BY MEANS OF THERMOGRAVIMETRY AND ISOTHERMAL CALORIMETRY

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Four paste mixtures with varying replacement level of the cement content by fly ash have been studied. Due to fly ash, the acceleration period decreased and a third hydration peak was noticed with isothermal calorimetry. The total heat after 7 days increased with increasing fly ash content. From 1 to 7 days, thermogravimetry showed a higher chemically bound water and Ca(OH)₂-content for the pastes with fly ash. Between 7 and 14 days the calcium hydroxide started to be depleted due to the pozzolanic reaction. A unique relation was found between calcium hydroxide and total heat development.

Keywords: cement hydration, fly ash cement paste, pozzolanic reaction

Introduction

The hydration of fly ash–cement binders includes two interrelated processes: the hydration of cement clinker and the pozzolanic reaction of fly ash. Ca(OH)₂ is released during the hydration of cement clinker and activates the pozzolanic reaction of fly ash, where it will be absorbed. Besides the pozzolanic reaction, fly ash has the ability to promote the cement hydration [1]. The hydrolysis of clinker minerals is accelerated by alkalis, which are present in fly ash [2].

Unique correlations were found between the amount of chemically bound water and the hydration heat of a binder, between the chemically bound water and the Ca(OH)₂-content and between the reactivity degree of a fly ash with its soluble silica content and its fineness [3]. According to [4], the effects of fly ash incorporation into portland cements on hydration reactions, correspond to a delayed appearance of the second peak, caused by the clinker reaction, on calorimetric curves and a reduced intensity of the heat dissipation rate compared to the plain portland cement. However, in the first hours immediately after mixing, the total amount of heat evolved was greater than for the plain portland cement. In some cements, there is also a third peak attributed to transformations in aluminates' hydrated phase. It can be generally attributed to some excess of tricalcium aluminate and replacement of tricalcium sulphoaluminate phase (AFt) by monosulphoaluminate (AFm) or renewed formation of this former one [5].

During its reaction the glassy, aluminosilicate phase, being the main constituent of fly ash transforms into calcium silicate hydrate and ettringite, as a result of the so-called pozzolanic reaction with calcium ions [2].

These calcium ions are released into the solution from the calcium silicate clinker minerals. The pozzolanic reaction starts after one week or more [6]. An explanation of this delay could be that the glass material in fly ash is only broken down when the pH value of the pore water is at least 13.2 [6]. The increase in the alkalinity of the pore water requires that a certain amount of hydration of the portland cement in the mix has taken place. Also the temperature influences the rate of pozzolanic reaction: the rate of solubility of the glass network is dependent on the temperature and so is the rate of the pH development. In the incubation period particles of fly ash behave as crystallization centers of hydration products precipitation for Ca(OH)₂ and (needle-like) reaction products originating from the cement hydration (C–S–H). The fly ash surfaces act as thermodynamically favourable areas of nucleus formation [7]. In this study thermogravimetry and isothermal calorimetry are both performed on fly ash–cement pastes to determine when fly ash starts to react and also what its influence is on as well the initial as the later hydration of cement, and more specifically on the chemically bound water and heat release. To stop the hydration at the desired test ages, a methanol replacement technique has been applied. The possible influence of this technique on the final outcome has also been investigated.

Experimental

Materials and mixture compositions

An ordinary Portland cement CEM I 51.5 N, complying with EN 197-1 (2000) was used in all paste mixtures as hydraulic binder. A low calcium fly ash with

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Table 1 Chemical analysis of cement according to EN 196-2 and of fly ash according to prEN 196-2.2

	CEM I 52.5 N	Fly ash
SiO ₂ /%	19.6	53.31
Al ₂ O ₃ /%	4.9	26.43
CaO/%	63.6	4.46
Fe ₂ O ₃ /%	3.1	7.53
MgO/%	0.9	2.45
SO ₃ /%	3.3	0.9*
Na ₂ O	not available	1.15
K ₂ O	not available	3.58
Free CaO/%	not available	0.02
LOI	1.65	4.00
C ₃ S/%	66.8	–
C ₂ S/%	6.9	–
C ₃ A/%	5.6	–
C ₄ AF/%	10.7	–

*determined according to NBN EN 196-2 (2005)

Table 2 Mix proportions of the cement–fly ash pastes

Mixture	C(I)/ CM	FA(I)/ CM	W/ CM	W/ C(I)
C(I)100FA(I)0W40	1.00	0.00	0.40	0.40
C(I)65FA(I)35W40	0.65	0.35	0.40	0.67
C(I)50FA(I)50W40	0.50	0.50	0.40	0.80
C(I)33FA(I)67W40	0.33	0.67	0.40	1.21

origin from France is used as partial cement replacement material in the fly ash–cement pastes.

Table 1 lists the chemical compositions of the portland cement and fly ash according to the EN 196-2 (2005) respectively prEN 196-2.2 (2005), together with the free CaO of the fly ash, determined in accordance with NBN EN 450-1 (2005). The theoretical mineralogical composition of the clinker, derived from the chemical analysis using the modified Bogue calculation, is also given in Table 1.

The portland cement ('C(I)') and fly ash ('FA(I)') were mixed together with water. The mass ratio of cement to binder (cement and fly ash or 'CM') varied from 100 over 65 and 50 to 33%. Table 2 summarizes the mix proportions of the four investigated binder pastes. The water ('W') to binder ratio was kept constant at 0.40.

Methods

Isothermal calorimetry

A chemical reaction such as the hydration of a fly ash cement paste can often be measured by the heat release during this reaction. Isothermal calorimetry has

been used by several researchers to quantify the hydraulic activity of portland cement and the pozzolanic activity of fly ash [2, 3, 8–10]. Calorimetry provides continuous measurements and is therefore a convenient method to study the early stage of hydration where the heat rate is relatively high. Pozzolanic reactions are known to take action at later stages involving low heat rate, which makes them difficult to follow by calorimetry [3].

First, 10 g of cement and fly ash were mixed together, after which water was added. The paste mixture was placed in the calorimeter to measure the heat release at a constant temperature of 20°C. Each test was performed in triplicate. Immediately after mixing a first peak appears. Because the mixing takes place outside the calorimeter, this peak has not been measured entirely. In practice, concrete is not cast immediately after water addition: the heat corresponding to the first peak remains in the concrete mixer and only contributes to a slightly higher initial temperature [8]. The heat generation during the first peak only amounts to a few percent of the total heat liberated. Therefore, the first peak can be left out of the further analysis [8]. The recorded heat evolved per time unit q was expressed per gram cement and per hour after calibration. The cumulative heat Q was the integral of the rate with time.

Thermogravimetry

Differential thermal analysis and thermogravimetry are ones of the best among various methods to measure the reduction of the calcium hydroxide content and assess the pozzolanic activity in hardening cementitious materials. Thermogravimetric experiments (TG) also allow determining the non-evaporable water or chemically bound water content. This is defined as the loss of mass between 105 and 1000°C minus the ignition loss of the original cement [11] and minus the loss due to carbonation. The chemically bound water obtained using TG is proportional to heat of hydration and can be used as a measure of hydration [3]. The non-evaporable water is an integrated part of the structure of the gel solid and can only be driven off at temperatures above 105°C. Unbound water in the cement paste is called free water or capillary water. Only capillary water is unimpededly accessible for the cement hydration. Powers' measurements showed that at complete hydration and without possible carbonation one gram of cement binds approximately 0.23 g of water chemically and 0.19 g of water is absorbed on the surface of the gel solids [11]. Complete and unimpeded hydration is therefore only possible at W/C ratios above 0.42 (=0.23+0.19). If a small sample of cement paste hydrates under water, the volume reduction due to

chemical shrinkage will be replaced by imbibed water from the surroundings. This water will, thereafter, be freely available for the cement hydration. At a W/C lower than 0.42 free access to water will increase the maximum degree of hydration. Separation of the non-evaporable water content into two components, one due to the dehydration of calcium hydroxide and the other due to the dehydration of other hydrates, can facilitate the study of pozzolanic and cementitious activity [12]. The losses due to the dehydration of calcium hydroxide and due to the decarbonation of calcium carbonate, were determined by a graphical technique, mentioned by [12]: during both losses corrections were made for the concurrent dehydration of other compounds.

The ages of testing were 3 and 18 h and 1, 2, 3, 7, 14, 28 and 56 days for all mixes and 4, 6 and 12 months for the C(I)100FA(I)0W40 and C(I)50FA(I)50W50 pastes and 8 months for the C(I)65FA(I)35W40 and C(I)33FA(I)67W40 pastes. For each binder mixture, cylinders with 74 mm height and 48 mm diameter were made. The cylinders were rotated at a speed of 5 rotations per minute for a period of six hours to prevent bleeding. Afterwards they were cured in a water bath at a temperature of $20 \pm 2^\circ\text{C}$. At the desired age of testing, the cylinders were ground into small pieces. The hydration of the pastes was stopped by soaking the samples in methanol in order to replace the capillary water with methanol during 1 week. To minimize the possible influence of methanol, the samples were dried afterwards in a desiccator over silica gel for another week prior to testing as indicated by [3] and as reported by Parrott [13] for alite paste. During the thermogravimetric experiments, all specimens were decomposed at a temperature range from 25 to 1100°C at a rate of $10^\circ\text{C min}^{-1}$. The tests were performed in a non-oxidized atmosphere (argon) to avoid superposition of peaks attributed to the combustion of coals in the fly ash and the calcium hydroxide decomposition.

Results and discussion

Thermogravimetry

The calcium hydroxide content plays a dominant role in the interaction between the hydration of cement and the pozzolanic reaction of fly ash. The evolution of calcium hydroxide, shown in Fig. 1, is expressed per gram cement, since all calcium hydroxide originates from the hydration of the cement clinker. To emphasise the changes at early age, the time axis is displayed logarithmically.

Figure 1 shows that up to 1 day the calcium hydroxide content of all samples is not significantly different for the different pastes. From 2 till 7 days (for

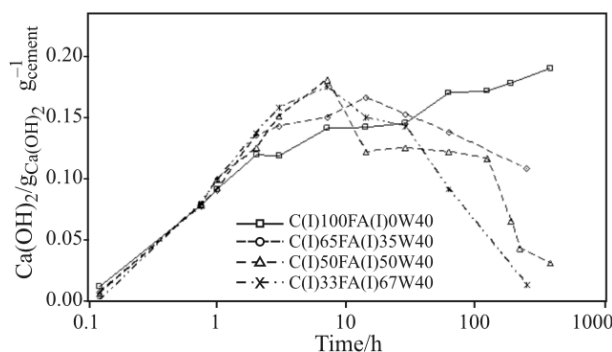


Fig. 1 Measured mass loss in TG due to the dehydration of calcium hydroxide

the 'C(I)65FA(I)35W40'-paste even up to 14 days) the pastes with fly ash exhibit a higher calcium hydroxide content than the portland cement paste (C(I)100FA(I)0W40). This corresponds with the theory, proposed by [1–3, 12], that fly ash serves as a thermodynamic favourable nucleus and therefore accelerates the cement hydration. After attaining a maximum calcium hydroxide content at 7 and 14 days, respectively, the Ca(OH)_2 -loss of the samples with 50 and 67% replacement (C(I)50FA(I)50W40 and C(I)33FA(I)67W40) respectively with 35% replacement (C(I)65FA(I)35W40) starts to decline due to the ongoing pozzolanic reaction. The time delay (7 to 14 days) before the pozzolanic reaction becomes noticeable, seems to be shorter for pastes with higher fly ash content. The values 7 to 14 days correspond with data from other investigators [2, 12]. The pozzolanic reaction may, however, start earlier with a smaller calcium hydroxide depletion than production. The reduced slope of C(I)33FA(I)67W40 between 3 and 7 days compared to the one between 2 and 3 days could suggest this theory. After one year of curing, the calcium hydroxide content of the mixes with 50 to 67% fly ash is diminished significantly compared the mixes with pure portland cement and with 35% fly ash.

Figure 2 gives the evolution of the chemically bound water w_b , corrected for the mass loss due to the decarbonation. Since cement is the main reagent up to 7 days, the mass loss is expressed in that time period per gram cement. The mass loss beyond 7 days, originates from the decomposition of the calcium hydroxide and hydrates as well by the cement hydration as by the pozzolanic reaction. It is therefore expressed per gram binder. Figure 2a shows that more water is chemically bound per gram cement up to seven days, when fly ash partially replaces the cement content. Between 18 hours and 3 days, the slope of the mass loss of the pastes with fly ash is much steeper than the one of the pure portland cement paste. From 3 to 7 days, the slope of the pastes with high volume fly ash content (50 to 67%) tends to reduce resulting in a less steeper slope than for the pure portland cement.

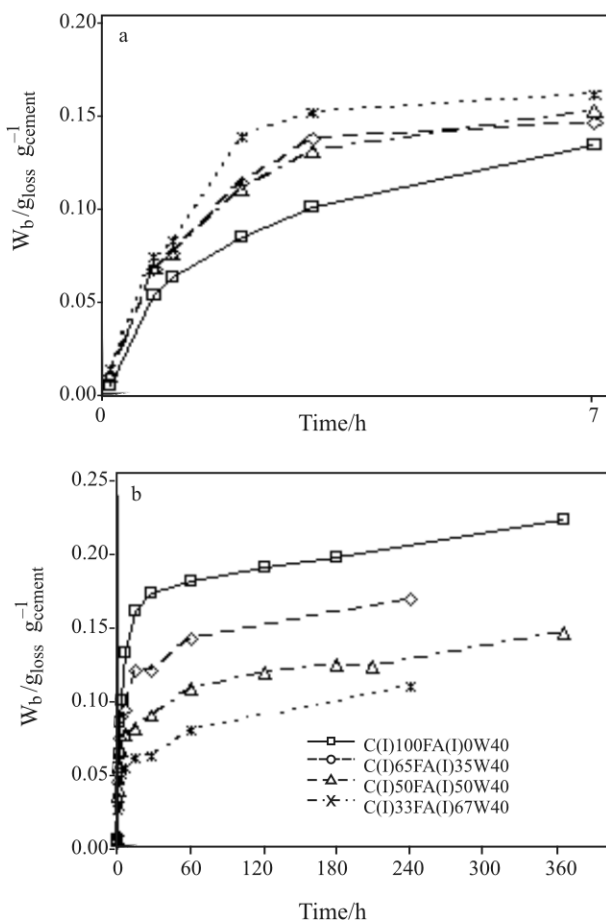


Fig. 2 Chemically bound water (105–1000°C) expressed a – per g cement during the first 7 days and b – per g binder

After 7 days, the chemically bound water increases equally for all pastes, but at all ages it is significantly with smaller per gram binder with increasing fly ash content. These observations are in agreement with the results, reported by Marsh [12]. From the thermogravimetric tests performed on cement pastes with 30 and 50% fly ash, he concluded that at early and intermediate ages the hydrates which form, have a higher water content/unit mass than that specified in the formula $C_3S_2H_3$. He also stated [12] that the initial hydrate formed from the reaction of fly ash with calcium hydroxide binds a substantial amount of water, over and above that contributed by the calcium hydroxide. As the reaction proceeds, the C–S–H can be represented by $C_3S_2H_3$. Besides these hydrates, he suspects a direct chemical reaction between the water and the ash [12]. The hydrate formed from this direct action, binds probably more water per unit mass than does the hydrate formed from the pozzolanic reaction.

The rate of the relative mass of chemically bound water shows more clearly the kinetics of the non-evaporable water content (Fig. 3). One should keep in mind that the measurements have been performed discontinuously and that the curve, shown for

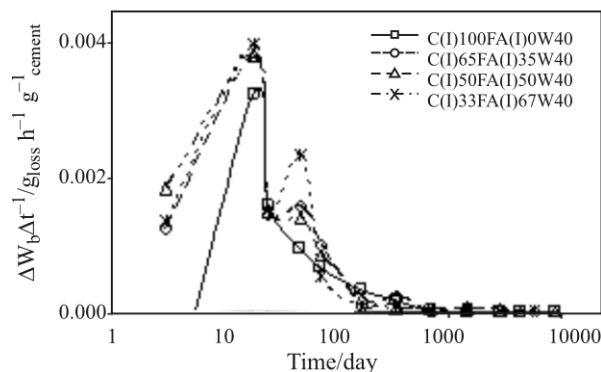


Fig. 3 Rate at which water is chemically bound water

each paste, is a smooth curve drawn through the measured data. Before three hours no data are available. For the pure portland cement paste a single peak can be distinguished, which occurs between 3 hours and 1 day. For the pastes with fly ash, also a second and even a third peak is shown, which appear between 1 and 3 days, respectively 7 days and 2 months. The latter time interval corresponds to the time interval at which the calcium hydroxide starts to decrease.

Influence of methanol exchange

As mentioned before, the capillary water has been replaced by methanol to stop the hydration. This technique, also used to characterize the microstructure of hydrated cement, assumes that the original microstructure of cement paste is less affected if drying takes place by removal of water with a solvent. Some researchers, however, suspect that interactions with the solvent can influence the degree of hydration and other physical characteristics of the hydrated cement system. Day [14] concluded that methanol reacts with calcium hydroxide to form a ‘carbonate-like’ material. Similar observations were made by Knapen *et al.* [15] and Beaudoin [16]. Also according to [16], the surface area of calcium hydroxide samples nearly tripled after 24 h immersion in methanol. Parrot [13] reported that no special features were detected by differential thermal analysis of cement pastes, treated with organic liquids and specifically methanol. By using thermogravimetric analysis, X-ray diffraction, infra-red spectroscopy and mercury intrusion porosimetry, Thomas [17] concluded that no alterations were obtained for solvent-treated $Ca(OH)_2$ -samples. In this section the influence of the methanol replacement on the results of the chemically bound water and the calcium hydroxide has been determined and compared with the standard deviation of the measurement technique.

Figure 4 shows the thermogravimetric mass losses, determined at the age of 1 year of the paste mixtures C(I)100FA(I)0W40 and C(I)50FA(I)50W40.

The bold line represents the mass loss of the sample without any pre-treatment ('direct measurement') and the thin line gives the mass loss of the samples after soaking in methanol for 1 week and drying in a desiccator over silica gel for another week ('methanol exchange'). Both curves are similar, except from two intervals: 20 to 140°C and from 600 to 900°C. The difference in mass loss in the temperature range 20–140°C can easily be explained by the capillary pore water which is still present in the sample of the direct measurement, but not in the sample after methanol exchange. Pane and Hanssen assume in their measurements that the free water can evaporate in the temperature range of 20–140°C [3]. If methanol reacts with the hydration products, the difference in the second temperature interval 600–900°C could be correlated to the decomposition of reaction products formed by the methanol and paste hydrates. This theory is in accordance with the findings of Knapen *et al.*, Beaudoin *et al.* and Day [14–16].

For the pure portland cement paste (C(I)100FA(I)0W40), the chemically bound water after the methanol exchange (0.223 g/g binder) is lower than obtained in the direct measurement (0.231 g/g binder), while the calcium hydroxide after methanol treatment (0.189 g/g cement) is even somewhat higher than when obtained in the direct measurement (0.179 g/g cement). For the sample paste with 50% replacement (C(I)50FA(I)50W40), the total amount of chemically bound water respectively the calcium hydroxide after the methanol treatment (0.147 g/g

binder respectively 0.031 g/g cement) are both lower compared to the amounts obtained in the direct measurement (0.153 g/g binder respectively 0.041 g/g cement). After methanol exchange, calcium hydroxide seems to decompose at somewhat higher temperatures compared to the direct measurement: the temperature range shifted from 415–455 to 439–474°C for the C(I)100FA(I)0W40 paste and from 406–434 to 436–456°C for the C(I)50FA(I)50W40 paste. At the age of 1 day and 1 year, the test after methanol exchange was repeated. The standard deviation on the chemically bound water, s_{wb} , respectively on the calcium hydroxide, s_{CH} , was 0.006 g/g binder and 0.01 g/g cement.

The difference in the amounts of chemically bound water is around 1.5 times the standard deviation s_{wb} for the pure portland cement paste and precisely 1 time the standard deviation for the paste with 50% fly ash. The difference in the amounts of calcium hydroxide is exactly 1 time the standard deviation s_{CH} for as well as the pure portland cement paste as for the paste with 50% fly ash.

Figure 5 shows the mass loss of unreacted, untreated fly ash and cement and of fly ash and cement submerged for one week in methanol and then dried for another week in a desiccator (thin line). The main difference between the curves of Fig. 5 appear in the temperature range of 600 to 950°C. This is also valid when comparing the samples of the 1 year old (fly ash →) cement pastes (Fig. 4). In this temperature range, the mass loss can be replaced by a tri-linear approximation (Fig. 5). The three lines represent three mass losses, called CO(1), CO(2) and CO(3) hereafter. If it is assumed that the temperature ranges during which the three losses occur, are normally distributed, then the 95% confidence interval are respectively [595, 676°C], [674, 728°C] and [726, 900°C].

The correlation between CO(1) and the fly ash content and between CO(1) and curing time is very low. At the age of 1 year CO(1) increases after methanol exchange for as well as the C(I)100FA(I)0W40 as for the C(I)50FA(I)50W40: 0.0080 respectively 0.0177 g/g binder compared to 0.0034 respectively 0.0100 g/g binder. CO(2) exhibit a weak dependency

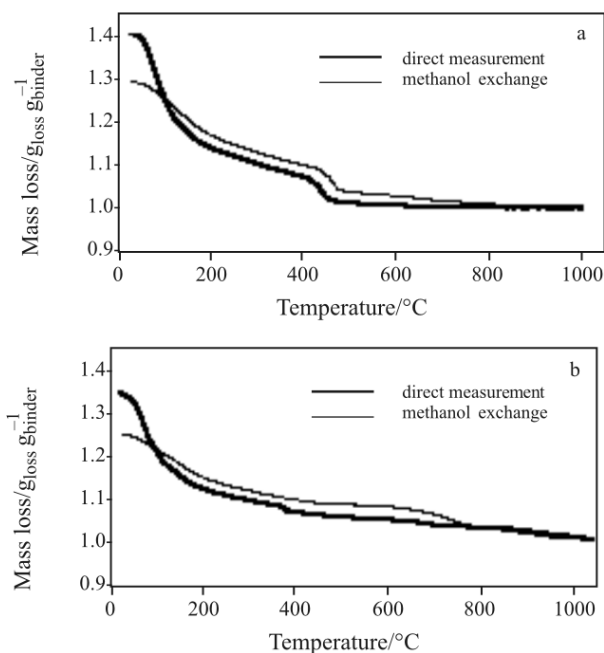


Fig. 4 Comparison of mass loss in TG between direct measurement and after methanol exchange at the age of 1 year for a – C(I)100FA(I)0W40 and b – C(I)50FA(I)50W40

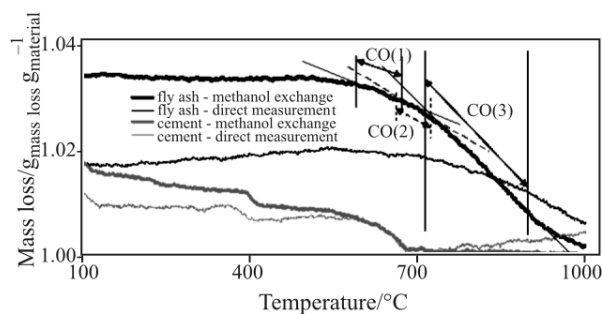


Fig. 5 Mass loss of fly ash (direct measurement and after methanol exchange)

with the fly ash content independently from the curing time of the paste. At the age of 1 year, the mass loss CO(2) of the pure portland cement paste C(I)100FA(I)0W40 has increased significantly after methanol treatment. A similar but much smaller increase can be observed for the paste C(I)50FA(I)W40 with 50% replacement by fly ash. The mass loss CO(2), averaged in time, amounts for the pastes C(I)100FA(I)0W40, C(I)35FA(I)65W40, C(I)50FA(I)50W40 and C(I)33FA(I)67W40 after methanol exchange respectively 0.0068, 0.00711, 0.0111, 0.0119 g/g binder with corresponding standard deviation (on the average) of 0.0004, 0.0004, 0.0005, 0.0004 g/g binder.

Figure 6 shows the mass losses CO(3) for all paste mixes after methanol treatment. Also the corresponding mass loss of the direct measurements of the pastes C(I)100FA(I)0W40 and C(I)50FA(I)50W40 at the age of 1 year is shown. The mass loss CO(3) increases with time and with increasing fly ash content. The mass loss at the age of 1 year is much higher after methanol exchange compared to the direct measurement for C(I)100FA(I)0W40, while it is only slightly higher for the C(I)50FA(I)50W40 paste. Mass losses during this interval are due to carbonation of the sample and not to the interaction with methanol.

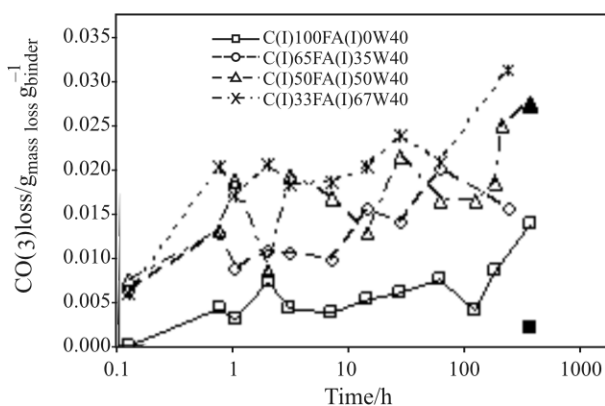


Fig. 6 Mass loss CO(3) in function of time

Isothermal calorimetry

Due to the assumption that the cement content is the main reagent in the first 7 days, the heat release of the paste mixtures, measured isothermally during this period, is expressed per unit mass of cement. Under this assumption all measured heat during this period is considered to be derived from the hydration of cement and all water is considered to be available for this reaction. The active effect of the fly ash in this case is limited to its promoting role in the hydration of cement clinker. Figure 7 shows the rate of heat development at 20°C as $J g^{-1}$ cement per h and the total heat as $J g^{-1}$ cement. In Fig. 7, the slope of the acceleration

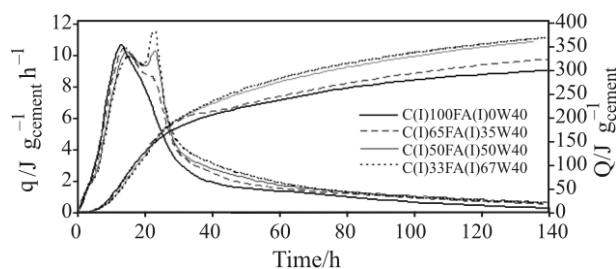


Fig. 7 Rate of heat development and cumulative heat at 20°C vs. time

and the second peak in the rate of heat development decrease with increasing fly ash content. This corresponds with data from [4]. Both phenomena are caused by a dilution effect. Before 18 h, the hydration of cement is decreased when fly ash is present in the paste mix. After 18 h of curing, a third hydration peak appears in all cement pastes. In the pure portland cement this peak is a very small peak, barely noticeable, but it increases with higher fly ash content and is correlated with the hydration of C_3A (the reaction of ettringite to monosulphate [5, 8]). The C_3A content of the cement used in this study is around 5.6%. The third hydration peak is especially noticeable in the binders with high volume fly ash, since fly ash will enhance and accelerate the ettringite formation by offering nucleation sites [2, 5].

After 1 day, the effect of the larger water availability for the hydration of the cement and the extra-nucleation sites offered by the fly ash for the hydration of C_3S and C_3A , leads to a higher cumulative heat. The total heat release increases with increasing fly ash content (and with increasing water to cement ratio). The time period (between 1 and 7 days) wherein this effect is noticed, is in accordance with the time period of the higher chemically bound water content, shown in Fig. 2.

By multiplying the ultimate hydration ratio of Mill (Eq. (1)), based on the water-to-cement ratio of each mixture, with the theoretical heat release according to Bogue [18], the heat release of the cement hydration of the C(I)100FA(I)0W40, of the C(I)65FA(I)35W40, of the C(I)50FA(I)50W40 and of the C(I)33FA(I)67W40 binders should be 310, 350, 371 and 397 $J g^{-1}$, respectively. The measured cumulative heat at 20°C of these binders amounts to 315, 343, 373 and 376 $J g^{-1}$ after 7 days. These values correspond with the calculated total heat releases of the different fly ash–cement pastes.

$$\alpha_{\text{Mill}} = \frac{1.031 \frac{W}{C}}{0.194 + \frac{W}{C}} \quad (1)$$

Relation between isothermal calorimetry and thermogravimetry

The heat release and the chemically bound water content have been used in the past to quantify the reaction degree of the pure portland cement pastes. When fly ash is present in the paste, the measured heat and chemically bound water could be from the cement hydration as well as from the pozzolanic reaction. To make an estimation of both reaction rates, several measuring techniques should be combined. Before doing so, the results from both techniques must be consistent with each other. Figure 8 plots the calcium hydroxide content and the chemically bound water content vs. the total heat release during the first seven days of curing.

The correlation between the total heat release and the chemically bound water content (Fig. 8a) changes with fly ash in the paste mixes. At 7 days the four curves tend to converge together. When, on the other hand, the calcium hydroxide content of the first seven days is plotted against the total heat release (Fig. 8b), an identical correlation is found for all pastes mixtures. The following two phenomena can explain these two observations: the first 7 days the hydration of several cement clinkers (C_3S and C_3A) is accelerated by the presence of fly ash and secondly more water will be initially involved in the hydration

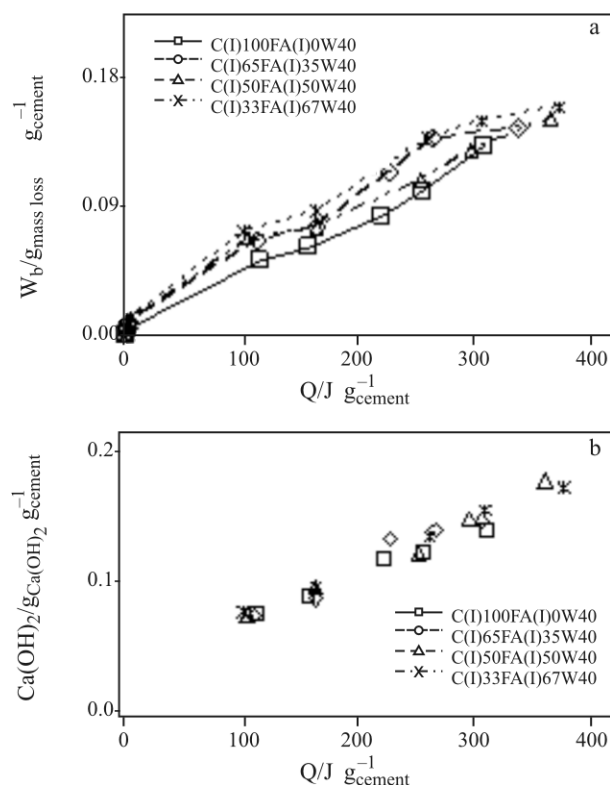


Fig. 8 Total bound a – water content and b – calcium hydroxide content vs. total heat release ($J g^{-1}$ cement) during first 7 days of curing

of cement, leading to more porous calcium silicate hydrates with a higher water content. Isothermal calorimetry can give a quantitative indication for the cement hydration (1st phenomenon), but it gives no idea on the water combined in the CSH hydrates (2nd phenomenon). After 7 days, it becomes too difficult to quantify with this technique the reaction ratio of the fly ash, since the pozzolanic reaction releases very little heat. Calculating a hydration or reaction degree from the chemically bound water content, determined with thermogravimetric experiments, is also difficult. Fly ash as cement replacement material leads not only to a higher W/C ratio and therefore to a higher hydration degree. The water content combined in the CSH phases varies also at young age, and later on it will depend on whether the CSH is a reaction product from the cement hydration or from the pozzolanic reaction of the fly ash. Thermogravimetric experiments do not allow determining the stoichiometry of the CSH phases.

Conclusions

From the thermal analysis and isothermal hydration tests, performed on binders with constant water content and different fly ash to cementitious material ratio, the following conclusions can be drawn:

- The depletion of calcium hydroxide during the pozzolanic reaction is noticeable from 7 to 14 days on. Before the age of 7 days, more water is chemically bound per gram cement, when fly ash partially replaces the cement content. Also the relation between the total heat release and the total amount of chemically bound water is changed in the presence of fly ash. The relation between the total heat release and the calcium hydroxide, on the other hand, does not change whether fly ash is present or not in the paste mix.
- Replacement of the free water by methanol to stop the hydration had little or no effect on the measured amount of calcium hydroxide and chemically bound water. But the methanol replacement technique influenced the measured amount of calcium carbonate and led to a broader temperature range wherein calcium carbonate decomposed. At the age of 1 year, the calcium hydroxide seemed to decompose at a slightly higher temperature interval when the pastes were soaked in methanol for one week.
- The isothermal rate of hydration of the pastes with fly ash clearly exhibits a third hydration peak. This could well be due to the conversion of ettringite, which has been enhanced by the presence of fly ash, to monosulphate. In the first 18 hours, the rate of heat release by the hydration of cement is dimin-

ished in the presence of fly ash. Afterwards the cement hydration is accelerated, indicated by the higher total heat release caused by a dilution effect and the active effect of the fly ash on the cement reaction. At seven days the total heat release per g cement corresponds to the theoretical heat release according to Bogue, corrected with the ultimate hydration degree of Mill, which takes the larger water-to-cement ratio of the fly ash-cement pastes into account.

The evolution of the calcium hydroxide content can give an indication for the pozzolanic reaction. To have an exact quantitative determination of the fly ash reaction, results from other techniques such as QXRD has to be taken into consideration.

Acknowledgments

The authors wish to acknowledge the FWO and BOF for financial support and appreciate the support of Prof. I. Van Driessche and Dr. E. Bruneel in performing the thermal analysis and in remarks on interpretation of the results.

References

- 1 A. Wang, C. Zhang and W. Sun, *Cem. Concr. Res.*, 34 (2004) 2057.
- 2 K. Takemoto K., 7th International Congress on the Chemistry of Cement, Paris 1980 (subtheme IV-2), p. 29.
- 3 I. Pane and W. Hansen, *Cem. Concr. Res.*, 35 (2005) 1155.
- 4 V. Rahhal, *J. Therm. Anal. Cal.*, 78 (2004) 191.
- 5 W. Nocun-Wczelik, *J. Therm. Anal. Cal.*, 65 (2001) 613.
- 6 A. M. Neville, *Properties of Concrete*. Fourth and final edition Ed. 1995, Essex: Longman Group Limited, 844.
- 7 A. L. A. Fraay and Y. M. Haan, *Cem. Concr. Res.*, 19 (1989) 235.
- 8 G. D. Schutter, *Cem. Concr. Res.*, 29 (1999) 143.
- 9 B. Pacewska and I. Wilinska, *J. Therm. Anal. Cal.*, 86 (2006) 179.
- 10 V. Rahhal, R. Talero and A. Delgado, *J. Therm. Anal. Cal.*, 87 (2007) 331.
- 11 T. C. Powers, *J. Amer. Concr. Institute*, 18 (1946) 249.
- 12 B. K. Marsh, *Cem. Concr. Res.*, 18 (1988) 301.
- 13 L. J. Parrott, *Cem. Concr. Res.*, 13 (1983) 18.
- 14 R. L. Day, *Cem. Concr. Res.*, 11 (1981) 341.
- 15 E. Knapen, K. Van Balen and D. Van Gemert, 2nd International RILEM Symposium on Advances in Concrete through Science and Engineering, Quebec 2006.
- 16 J. J. Beaudoin *et al.*, *Adv. Cem. Based Mater.*, 8 (1998) 56.
- 17 M. D. A. Thomas, *Adv. Cement Res.*, 2 (1989) 29.
- 18 Bogue, *The Chemistry of Portland Cement*, Reinhold Publishing Corporation, New York 1947, p. 572.

Received: September 5, 2007

Accepted: July 4, 2008

OnlineFirst: September 20, 2008

DOI: 10.1007/s10973-007-8787-z