

Investigation of blended cement hydration by isothermal calorimetry and thermal analysis

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Abstract

Hydration of portland cement pastes containing three types of mineral additive; fly ash, ground-granulated slag, and silica fume was investigated using differential thermal analysis, thermogravimetric analysis (DTA/TGA) and isothermal calorimetry. It was shown that the chemically bound water obtained using DTA/TGA was proportional to heat of hydration and could be used as a measure of hydration. The weight loss due to $\text{Ca}(\text{OH})_2$ decomposition of hydration products by DTA/TGA could be used to quantify the pozzolan reaction. A new method based on the composition of a hydrating cement was proposed and used to determine the degree of hydration of blended cements and the degree of pozzolan reaction. The results obtained suggested that the reactions of blended cements were slower than portland cement, and that silica fume reacted earlier than fly ash and slag.

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1. Introduction

Today, blended cements are widely used in pavement and bridge deck constructions. Optimal as well as efficient uses of blended cements can offer economic benefits in such large-scale projects. To ensure the lifetime of structures like concrete pavement and concrete bridge, performance of blended cements must be investigated. One of the key behaviors that strongly ties to the performance of blended cements is hydration. For this reason, studies on blended cement hydration have been conducted intensively in the past few years. Some of these investigations have been done in systems containing blast furnace slag [1], silica fume [2], and fly ash [3–5], which are among the mineral additives used more frequently in constructions.

Hydration, representing mass conversion of different phases in the cement paste, ties closely to the microstructure

of concrete, which in turn relates to important physical properties such as strength, elastic moduli, toughness, diffusivity and permeability. However, unlike the hydration process in ordinary portland cement, the hydration process in blended cements is considerably more complex. It involves reactions of mineral additives or pozzolanic materials in addition to the hydration of portland cement.

Since almost all chemical reactions are followed by heat generation, hydration of complex systems like blended cements can be quantified from heat of hydration. In the past, isothermal calorimetry has been frequently used to detect the reactivity of different pozzolans. Zhang et al. [6], Langan et al. [3], and De Schutter [7] have investigated reactivities of fly ash, blast furnace slag and silica fume using isothermal calorimeter. Although the heat development from the calorimeter is able to capture different pozzolanic activity heat is a measure of the combined portland cement–water reaction and pozzolanic reaction in blended cement paste. In order to optimize the use of blended cements, one must understand and be able to quantify the pozzolanic reaction. Calorimetry method

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however can provide continuous measurements and is a convenient method to study the early phase of hydration where the heat rate is relatively high. Pozzolanic reactions are known to take action at later stages involving low heat rate [3,6,7], which makes them difficult to follow by calorimetry.

Differential thermal analysis (DTA) combined with thermogravimetric analysis (TGA) is more suitable for studying hydration at later stages. This technique has been applied to cement–fly ash systems [4,5,8] and cement–blast furnace slag systems [9]. Hydration of pozzolanic materials such as silica fume, metakaoline, fly ash or slag with $\text{Ca}(\text{OH})_2$ have also been studied in Refs. [10–14], that reported how $\text{Ca}(\text{OH})_2$ could activate reactions of various types of pozzolan and mineral blended in ordinary cement. In Ref. [10], some methods to measure the degree of pozzolan reaction have been described but these are not as simple as DTA/TGA. In Refs. [11–13], the investigations were focused more on determining the reactivity of different pozzolans. Meanwhile, in Ref. [14], the reactivity and reaction products of rice husk in lime solution were investigated. Unfortunately, the studies above rarely proposed the method(s) that can be used to obtain the degree of hydration of blended cements or the degree of pozzolan reaction.

This study focuses on the quantitative analysis of blended cement hydration using two experimental techniques: isothermal calorimetry and thermal analysis. The objectives are to determine the degree of hydration of blended cements, and the degree of reaction of the pozzolans. Marsh and Day [4] and Marsh et al. [5] suggested a method of measuring the pozzolanic reaction due to fly ash. The analysis herein is also based on the method suggested above but we support it with isothermal calorimeter measurements and a model to quantify the ultimate amount of chemically bound water using a three-parameter hydration model.

2. Experiments

2.1. Materials

A type I ordinary portland cement (OPC type I) was used in all mixes. Two water to binder ratios (w/b) of 0.35 and 0.45 were chosen. These values are quite common in practice. Concrete with w/b=0.35 is often used for bridge decks, while w/b=0.45 is widely used for concrete pavement slabs especially in Michigan, USA. In addition, to reduce chloride permeability and improve durability the concrete often contains mineral additives. In this study, three mineral additives were used: a class F fly ash (FA), ground-granulated blast furnace slag (GGB), and silica fume (SF). Their fractions relative to the weight of binder were kept the same. The blended cement mixes contained 25% FA, 25% GGB, and 10% SF cement replacement by weight. These

proportions can be considered moderate and common in practice for users of FA and GGB. The use of 10% SF is high but typical for achieving higher strength concrete. Each mix is labeled according to its w/b and is listed in Table 1. The compositions of type I cement and the mineral additives are given in Table 2.

2.2. Thermal analysis (DTA/TGA)

DTA locates the ranges corresponding to thermal decompositions of different phases in paste, while TGA simultaneously measures the weight loss due to the decompositions. To study the effect of temperature on hydration (kinetics), the measurements were conducted for paste specimens cured at three isothermal conditions: 9, 23, and 34 °C. The ages of testing were 0.25, 0.5, 1, 2, 3, 7, 14, 28, and 180–210 days.

The cement paste was cast in the form of slab specimens approximately 100 mm in thickness. After mixing, the slab specimens were cured at the designated temperature and were turned upside down every 30 min for a period of 6 h to prevent bleeding. Prior to testing, these slab specimens were cured in lime-saturated water until the designated age of testing. Small pieces were first obtained by crushing the slab. The pieces were then ground using mortar and pestle until particles measuring about 0.5 mm in diameter were obtained. To stop hydration, exchange water, and prevent carbonation, the samples were soaked in methanol and stored for 1 week. The methanol was replaced at least three times during the storage period. As indicated by Day [15], the use of methanol may influence the measurement of $\text{Ca}(\text{OH})_2$ content. Our data for the specimens treated and untreated with methanol however, showed very little differences in $\text{Ca}(\text{OH})_2$ content as long as the specimens were dried in a desiccator for about a week prior to testing. A related result, confirming the minor effect of methanol, was also reported by Parrott [16] for an alite paste. It is worth mentioning that the sample was also prepared for the sorption measurement whose analysis is a subject of our forthcoming paper. Because of this, each sample underwent methanol treatment which is thought to preserve a more stable paste microstructure [17].

All specimens were decomposed at a temperature range between 21 and 1100 °C at the rate of 10 °C/min. Two

Table 1
Mix design information

Mix no.	% OPC I	% Additives	w/b
45-1	100	0	0.45
45-2	75	25 (FA)	0.45
45-3	75	25 (GGBF)	0.45
45-4	90	10 (SF)	0.45
35-1	100	0	0.35
35-2	75	25 (FA)	0.35
35-3	75	25 (GGBF)	0.35
35-4	90	10 (SF)	0.35

Table 2
Compositions of type I cement and mineral additives

Compound (%)	OPC I	Fly ash	GGBF	SF
SiO ₂	20.4	57.4	37.5	94.5
Al ₂ O ₃	5	18.2	7.8	0.3
Fe ₂ O ₃	2.5	5.3	0.4	0.9
CaO	62.4	8.3	38	0.5
MgO	3.4	3.7	10.7	0.9
SO ₃	2.8	0.9	3.2	–
Na ₂ O	0.3	1.14	0.3	–
K ₂ O	0.7	1	0.5	–
TiO ₂	–	1.2	0.4	–
P ₂ O ₅	–	0.36	–	–
Mn ₂ O ₃	–	–	0.6	–
SrO	–	0.7	0.1	–
ZnO	–	0.1	–	–
Lost ign. (%)	–	0.2	0.6	1.9

	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Blaine (cm ² /g)
OPC I	53.7	18	9.1	7.6	4290

important quantities were obtained from DTA/TGA. First, the chemically bound water, defined as the mass loss due to decomposition between the boiling temperature and 1100 °C (w_b), which can also be understood as the amount of water needed for cement to react. In our test system, distilled water alone (the same as used in the mixes) started to boil at 100 °C and turned completely into gas at around 140 °C. We expect that the free (physically bound) water in the pore and surface of the paste sample also behaves similarly. So w_b was calculated within a temperature range of 140–1100 °C. This is slightly different from the common practice which uses 105 °C instead of 140 °C as a starting temperature. However, if the sample is dried properly then one should not worry about the error induced by the difference in the starting temperature. Indeed, all of our DTA/TGA curves indicated that the error is negligible. Our initial test on unhydrated cement indicated some mass loss within a temperature range of 600–780 °C associated to the decomposition of calcium carbonate. This mass loss, about 1% of the initial weight, is illustrated in Fig. 1 as CO_{loss} . Since the paste sample consists of unhydrated cement, a correction on the calculation of w_b had to be made. Such a correction was done by subtracting the mass loss within a temperature range of 600–780 °C from w_b . Such a mass loss is labeled CO_{loss} in Fig. 1.

The second important quantity is the mass loss corresponding to the decomposition of $Ca(OH)_2$ (labeled as CH_{loss} in Fig. 1) which occurs between 440 and 520 °C. Variations of w_b and CH_{loss} with time were reported after being normalized by the ignited weight of the sample. The weight loss needs to be corrected since, as also observed by Marsh and Day [4], it includes the weight loss associated with chemically bound water. Such a correction has been applied to some representative data points and it was found that in most cases the corrected CH_{loss} changed by as much as 5% less than the uncorrected CH_{loss} . Since this brought only insignificant changes to the overall analysis, the

correction was disregarded. In addition, a study by Midgley [18] also reported that CH_{loss} measured from DTA or TGA without correction appeared to be accurate and reliable to represent the true amount of $Ca(OH)_2$.

2.3. Isothermal calorimetry

The isothermal heat was measured on pastes specimens hydrated at 15, 23, and 34 °C. The lowest allowable temperature for the measurement was 15 °C. Thus, only data from 23 and 34 °C hydration can be compared with the hydration data obtained using DTA/TGA. The test duration was about 3 weeks. Beyond this period, the measurement is not sensitive enough to capture the low heat generation rate.

Cement paste was cast at room temperature. The mixing water was cooled or heated prior to mixing, while the cement and mineral additives were kept at room temperature. This was done in order to produce mixes whose temperatures were close to the measurement temperatures (15, 23, and 34 °C). Since the mass of the sample was relatively small, mixing was performed manually by stirring the cement, additive, and water with a wooden stick. The data measured was the rate of heat, which after being normalized by the solid weight and calibrated, was expressed in J/h/g. The value was then reported as the

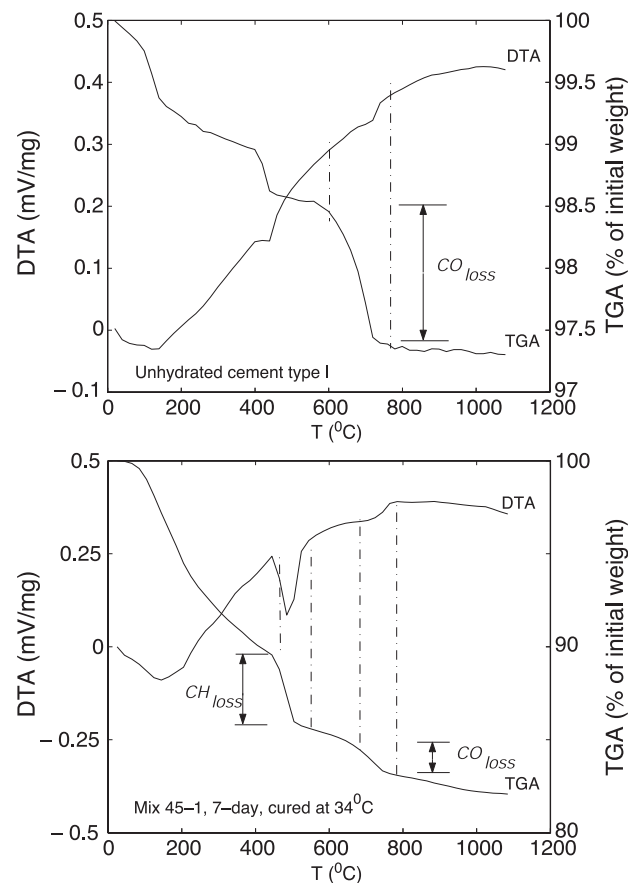


Fig. 1. DTA/TGA data and the measured hydration quantities.

cumulative heat, which was the integral of the rate with time.

3. Results and discussion

3.1. Heat of hydration

Plots of isothermal heat of hydration (Q) of all mixes at 23 and 34 °C are given in Figs. 2 and 3. Each figure has two sets of curves corresponding to mixes having two different water–binder ratios (w/b), 0.45 for the first set and 0.35 for the second set. At first glance, it is clear that systems with w/b=0.35 produce heat lower than the ones with w/b=0.45. This is to be expected since the space available for the growth of hydration products is smaller for the lower w/b systems. Thus, hydration is slightly retarded in systems with low w/b. The same trend was also found for the mix hydrated at 15 °C. The other unique feature is that higher hydration temperature produce higher heat initially. However, this is not necessarily true for the ultimate heat of hydration. Many studies [19–21] have reported that at

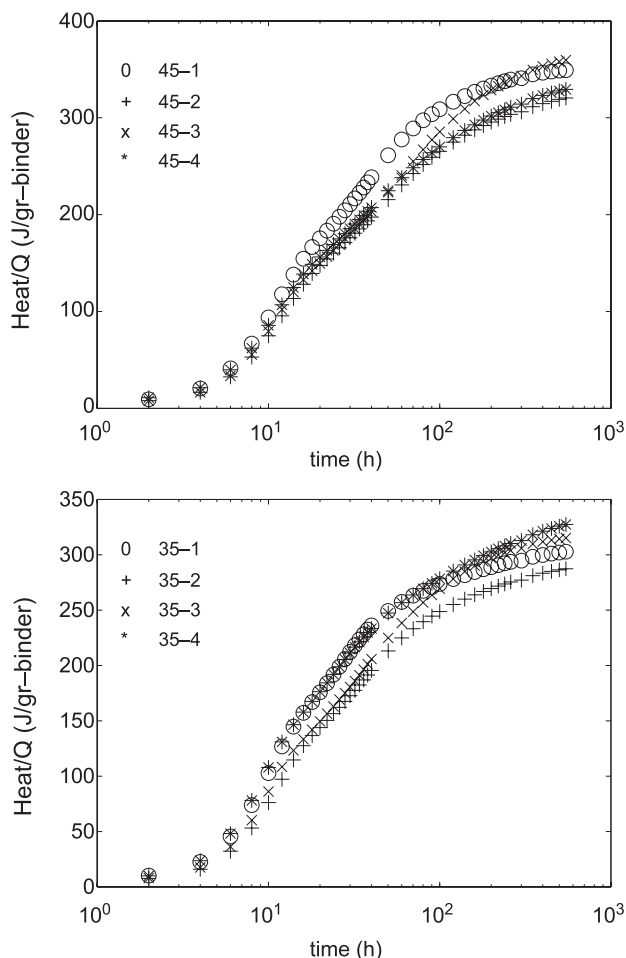


Fig. 2. Isothermal heat of hydration at 23 °C.

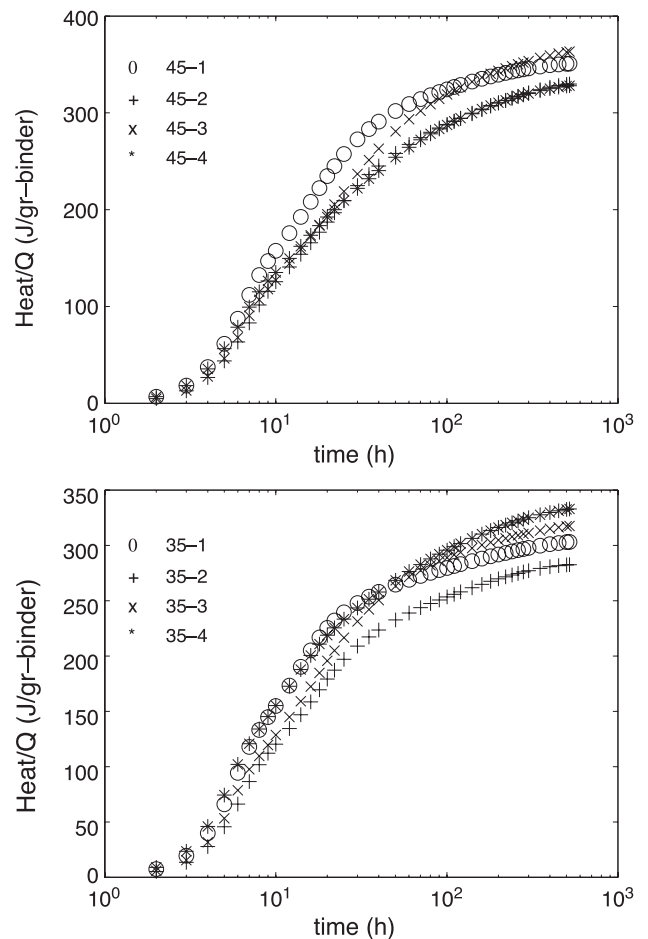


Fig. 3. Isothermal heat of hydration at 34 °C.

higher temperatures the degree of hydration initially develops faster but the ultimate values are lower.

The pozzolanic reactions can be seen by observing differences in heat of hydration between ordinary portland cement (OPC) systems (mixes 45-1 and 35-1) and blended cement systems. A slightly different trend in heat of hydration was found between the lower w/b systems and the higher w/b systems attributed to the effect of mineral additives. The overall trend is still the same. For the pastes containing fly ash, the heat development appears to be lower than the pastes made of OPC for the entire measurement period. This is not what is observed in pastes made with ground-granulated blast furnace slag (GGB). Although, GGB pastes do not generate higher heat initially, they seem to generate heat higher than the OPC pastes later on. Such a difference may be attributed to the slag reaction. The silica fume (SF) pastes exhibit this behavior even earlier than the GGB pastes, although this is not the case for the pastes with higher w/b. Such a behavior is due to the pozzolanic reaction as well.

It is important to remember that higher heat of hydration does not necessarily mean higher degree of hydration. The degree of hydration of different mixes must be calculated by normalizing the heat with its ultimate value. Results

presented here suggest that mixes containing GGB or SF reach higher ultimate heat of hydration than the mixes containing OPC alone. However, heat measurement alone may not be sufficient to accurately determine the ultimate value, especially if it is measured only up to 21 days. The data from DTA/TGA can be used to determine the ultimate quantity, since they were obtained up to 180–210 days.

3.2. DTA/TGA

The two most important quantities needed to quantify degree of hydration are the amount of chemically bound water (w_b) and the weight loss corresponding to the decomposition of calcium hydroxide (CH_{loss}). The degree of hydration of ordinary portland cement (OPC) pastes are obtained by normalizing w_b to its maximum value, $w_{b,\infty}$. For type I OPC pastes, the maximum value of w_b ranges from 0.23 to 0.25 g bound water per g ignited sample [22,23]. According to the analysis by Copeland et al. [22], the value of 0.23 is typical for type I portland cement.

In Figs. 4 and 5, variations of $w_b/0.23$ for different mixes 45-1 and 45-2 are plotted with time. Data for the other mixes were not plotted since they exhibit a trend quite similar to that shown in Figs. 4 and 5. As mentioned in the beginning, the pastes hydrated isothermally at 9, 23, and 34 °C. Two of these curing temperatures are similar to the temperatures where heat of hydration were measured. This allows direct comparisons between heat of hydration (Q) and w_b . However, the use of the amount of chemically bound water as a measure of hydration in blended cement systems is yet to be justified. Results presented herein are used only to distinguish the differences in hydration process of blended systems in terms of normalized chemically bound water ($w_b/0.23$).

From Figs. 4 and 5, it is seen that $w_b/0.23$ for blended systems is, for some curing time, less than that for OPC. In

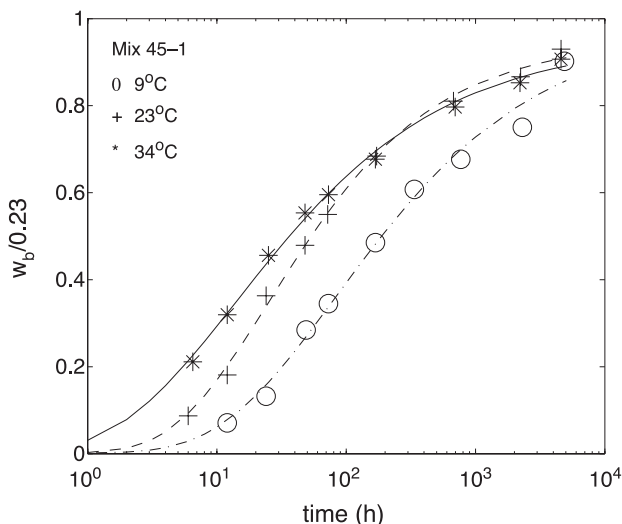


Fig. 4. Chemically bound water of mix 45-1.

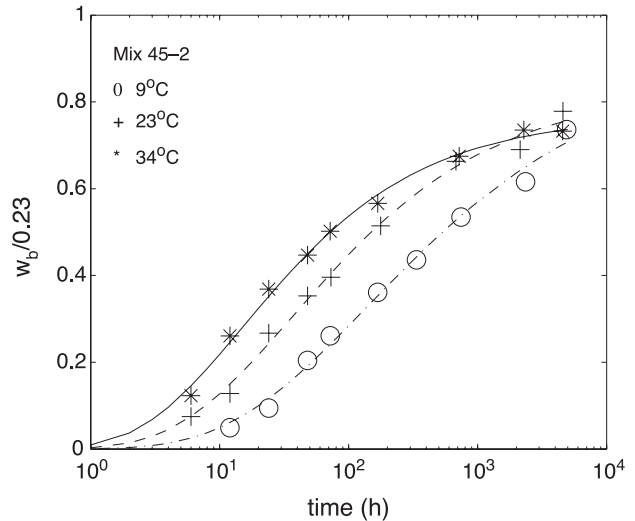


Fig. 5. Chemically bound water of mix 45-2.

the early hydration period, this difference in amount of chemically bound water is very close to 25% for FA pastes and GGB pastes, and close to 10% in SF pastes. This finding is associated to the fact that in the beginning only the OPC portion of the total binder (OPC and pozzolan) hydrates with water. In other words, the difference is proportional to the OPC fraction in each blended system, i.e. OPC is 25% less in FA and GGB pastes, and 10% less in SF pastes.

The plots of isothermal heat of hydration as a function of combined water are shown in Fig. 6. The data points in each plot correspond to measurements at two temperatures, 23 and 34 °C, and at two water–binder ratios (w/b). For each system, a unique relation exists between Q and w_b . The only factor that differentiates each mix is the type of binder. Indeed, in each figure, all data points seems to merge into a single curve.

A slightly nonlinear relation can be deduced from each figure showing Q – w_b plots. In fact, it is not important as long as Q and w_b relate to each other uniquely and both are monotonically increasing, as hydration products always increase with time and therefore so do Q and w_b . Hence, just like Q , w_b also measures the degree of hydration of blended cement pastes. The remaining question now is how to quantify the degree of pozzolan reaction.

3.3. Effect of temperature

The hydration data was fitted by a three-parameter equation (TPE) similar to the one used by Hansen and Pedersen [24] for describing the strength development in concrete. This equation is written as:

$$\alpha = \alpha_{\infty} \exp \left[- \left(\frac{\tau}{t} \right)^a \right] \quad (1)$$

where α can be used to describe degree of hydration, heat of hydration or chemically bound water and α_{∞} represents the corresponding apparent ultimate value. The other two

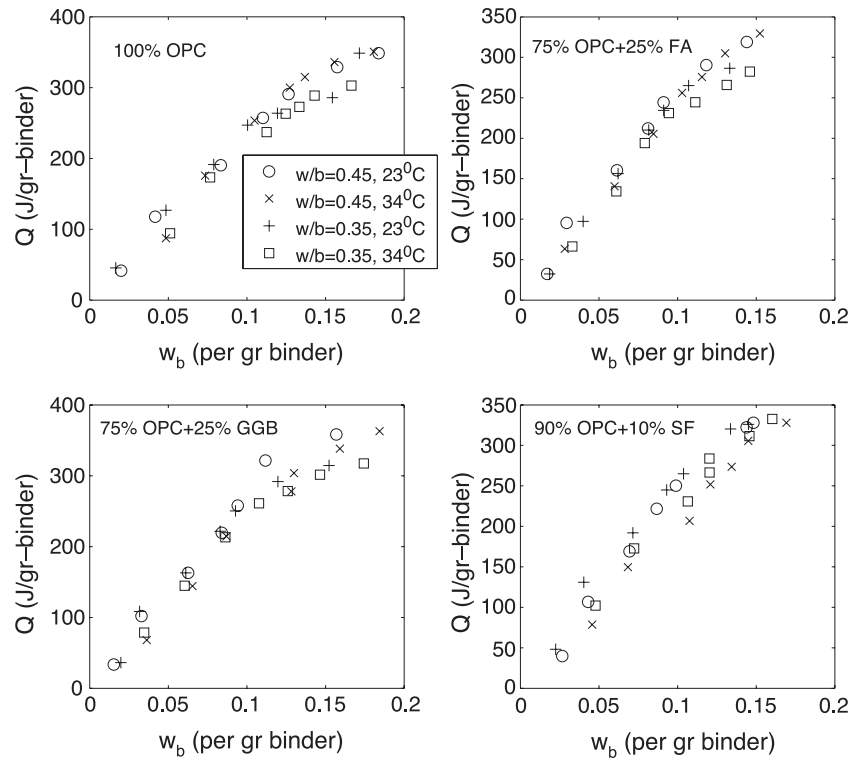


Fig. 6. Relations between heat of hydration and chemically bound water.

parameters, τ and a , control the intercept and the curvature of the plot in the logarithmic scale. Although mathematically simple, TPE has been very useful and successfully applied to characterize non-isothermal hydration [25]. All three parameters in TPE, α_∞ , τ , and a can be used to describe the effect of temperature. Fits of experimental hydration data are shown as lines in Figs. 4 and 5. As has been discussed, the rate of hydration is generally higher when hydration takes place at higher temperature, as quantified by either $w_b/0.23$ versus time or Q versus time.

As has been confirmed in many studies [19–21], $w_b/0.23$ in OPC is seen to reach higher ultimate values at lower temperature. This has been shown in Tables 3 and 4 where the parameters of TPE for the normalized bound water are listed. The systems with blended cements also exhibit the same behavior. This is not surprising since the blended systems are still dominated by OPC. This further implies that w_b can represent the overall hydration of blended systems. However, we still need to confirm this by comparing w_b with heat of hydration. In addition, $w_{b,\infty}$ needs to be determined for the blended systems in order

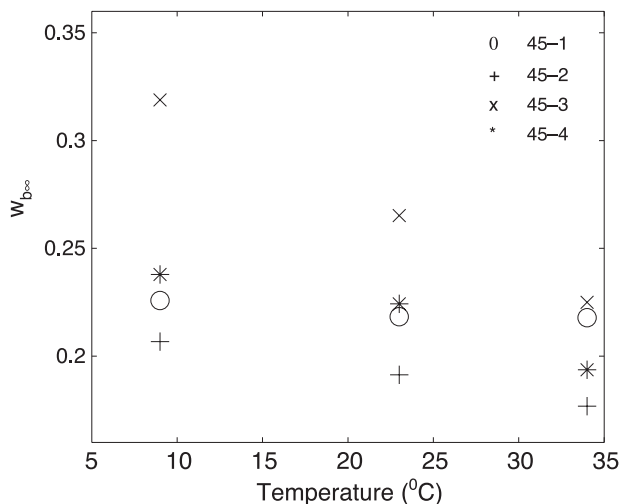
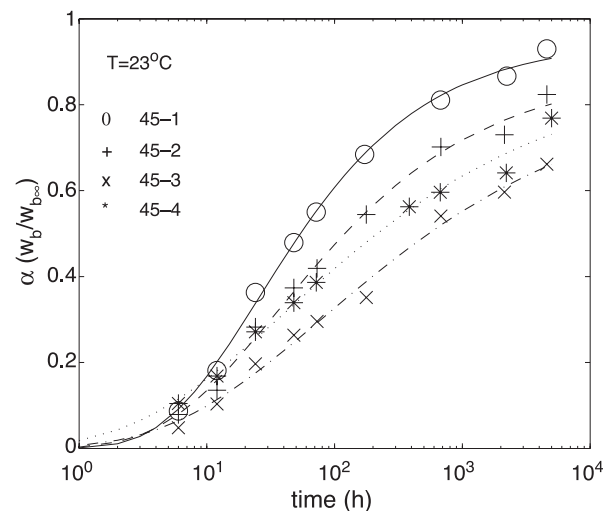
Fig. 7. Relations between $w_{b,\infty}$ and temperature, $w/b=0.45$.

Fig. 8. Degree of hydration of blended cement pastes.

Table 3
TPE parameters for bound water data, w/b=0.45

T (°C)	$w_{b,\infty}/0.23$	τ	a
<i>Mix 45-1</i>			
9	0.982	84.043	0.484
23	0.949	25.399	0.5895
34	0.947	14.152	0.4704
<i>Mix 45-2</i>			
9	0.899	142.14	0.402
23	0.832	36.914	0.482
34	0.769	15.271	0.545
<i>Mix 45-3</i>			
9	1.387	459.99	0.2607
23	1.153	82.955	0.3575
34	0.978	19.267	0.4946
<i>Mix 45-4</i>			
9	1.034	126.05	0.3576
23	0.975	43.172	0.3592
34	0.842	11.483	0.5304

for the degree of hydration (α) to be calculated, i.e. $\alpha = w/w_{b,\infty}$.

4. Degree of hydration of blended systems and pozzolans

4.1. Procedure for determining the degree of hydration

In general, the degree of hydration is defined as Q/Q_∞ or $w_b/w_{b,\infty}$ which requires Q_∞ or $w_{b,\infty}$ to be determined. In this study, the heat data were not measured long enough (up to 21 days) to allow for accurate determination of Q_∞ . The chemically bound water was however, measured on mature paste specimens (up to more than 200 days old) and hence, the predicted values of $w_{b,\infty}$ based on TPE could be used.

Table 4
TPE parameters for bound water data, w/b=0.35

T (°C)	$w_{b,\infty}/0.23$	τ	a
<i>Mix 35-1</i>			
9	0.860	68.08	0.523
23	0.877	23.439	0.593
34	0.845	9.328	0.5102
<i>Mix 35-2</i>			
9	0.892	135.16	0.388
23	0.848	40.062	0.3806
34	0.756	15.038	0.497
<i>Mix 35-3</i>			
9	1.112	220.84	0.2866
23	0.976	51.405	0.4147
34	0.983	23.205	0.4381
<i>Mix 35-4</i>			
9	0.929	94.778	0.354
23	0.840	28.092	0.434
34	0.796	9.7606	0.5115

Table 5
Values of maximum ultimate bound water and ultimate heat (per g binder)

Mix	$w_{b,\infty}$	$Q_{0,\infty}$ (J/g)	Q_∞ (J/g)
100% OPC	0.228	388.44	438.74
75% OPC+25% FA	0.217	356.84	453.40
75% OPC+25% GGB	0.318	455.19	582.96
90% OPC+10% SF	0.256	388.03	513.85

$w_{b,\infty}$ used must be obtained for mixes having w/b=0.45 because in these mixes, hydration was allowed to reach the higher values, while for mixes having w/b=0.35 hydration is limited by the capillary space.

From Tables 3 and 4, it can be seen that the ultimate bound water increases as temperature decreases. The plot of the ultimate chemically bound water ($w_{b,\infty}$) versus temperature is given in Fig. 7. A linear relation can be seen in this figure. The maximum value of $w_{b,\infty}$ can be found by extrapolation at the lowest possible hydration temperature, which in this study was chosen to be 0.5 °C. The degree of hydration of each paste mix is therefore,

$$\alpha(t) = \frac{w_b(t)}{w_{b,\infty}(T \approx 0.5^\circ\text{C})} \quad (2)$$

The calculated maximum values of $w_{b,\infty}$ is listed in Table 5.

Plots of α with time are shown in Fig. 8. Surprisingly, the lowest degree of hydration (around 66% at more than 200 days) is exhibited by GGB paste. Meanwhile, the degree of hydration of FA paste and SF paste are relatively high (around 80% after more than 200 days). Another interesting finding is that for OPC, $w_{b,\infty}$ is very close to 0.23 g/g ignited solid, just as suggested in literature [22]. This supports the validity of the procedure used. The same idea can also be applied to heat of hydration. However, the maximum values of heat of hydration determined using the above procedure correspond to the short-term heat measurement ($Q_{0,\infty}$). The plots of $Q(t)/Q_{0,\infty}(T \approx 0.5^\circ\text{C})$ are shown in Fig. 9. It is clear that $Q(t)/Q_{0,\infty}$ exhibits a trend similar to $w_b(t)/w_{b,\infty}$. This finding

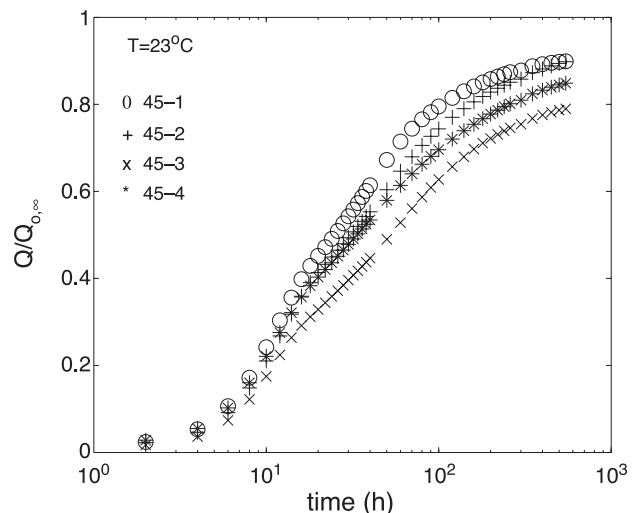
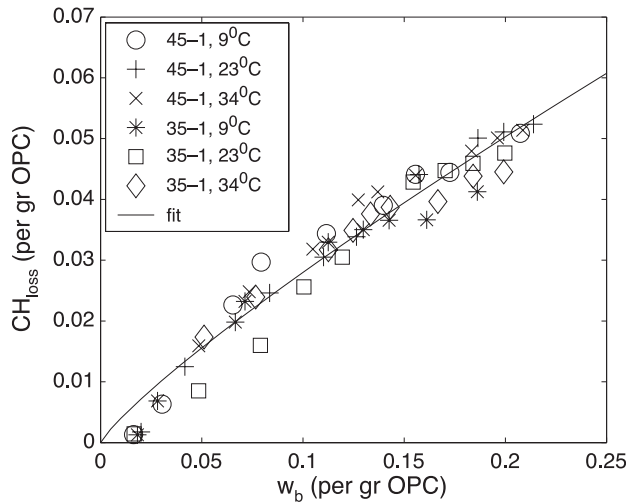


Fig. 9. Q/Q_∞ of blended cement pastes from short-term heat measurement.

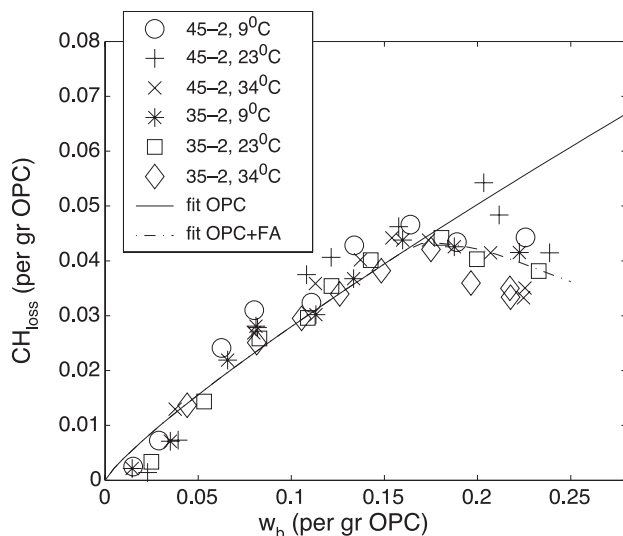
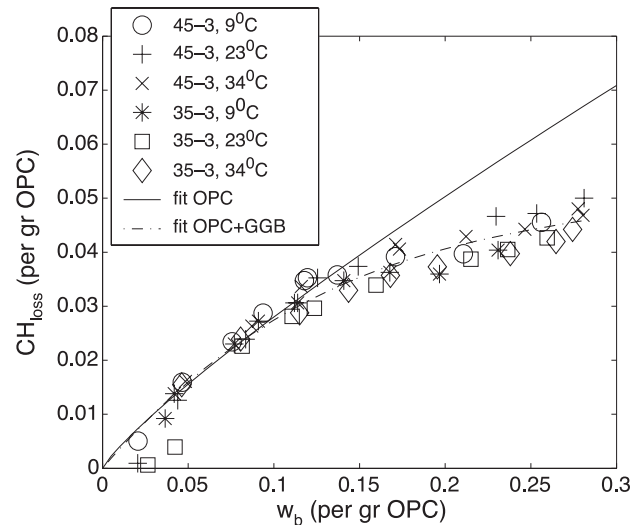
Fig. 10. Relation between CH_{loss} and w_b for OPC.

suggests that w_b represents the overall degree of hydration and supports the validity of the above procedure.

A more accurate prediction of the maximum ultimate heat (Q_{∞}) can be done with the help of the relations between Q and w_b shown in Fig. 6. By fitting such relations, values of Q_{∞} corresponding to maximum $w_{b,\infty}$ can be found. The values of both $Q_{0,\infty}$ and Q_{∞} obtained using the above method are listed in Table 5. Notice that Q_{∞} in Table 5 represents the characteristic heat of hydration per unit weight of binder. Values slightly below 500 J/g have been reported in literature [26,27] for OPC type I, which are consistent with the present finding.

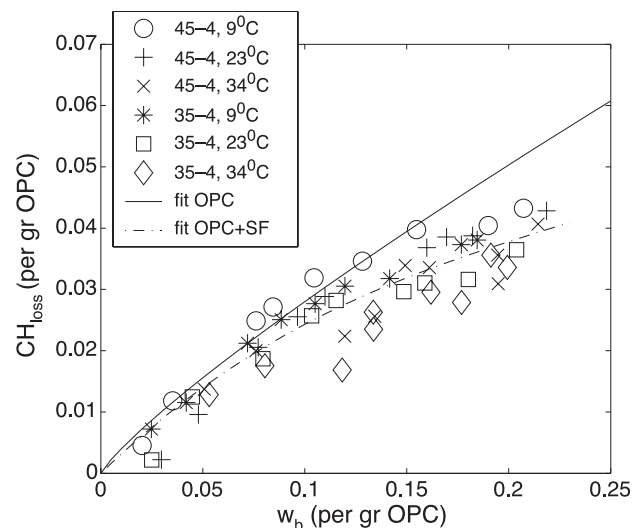
4.2. The degree of hydration of fly ash, slag, and silica fume from DTA/TGA

Pozzolans can react with hydration products (calcium silicate hydrate and calcium hydroxide) of OPC and water. Calcium hydroxide (CH) is known to react with FA and SF,

Fig. 11. Relation between CH_{loss} and w_b for 75% OPC+25% FA.Fig. 12. Relation between CH_{loss} and w_b for 75% OPC+25% GGB.

and GGB and water [10,28]. This becomes more evident as the amount of CH is plotted against curing time. For OPC pastes, CH increases as the age increases indicating a proportional relation with the degree of hydration or w_b . In pastes containing FA, GGB, and SF, CH initially increases then drops as it is consumed more and more by pozzolans. How specifically FA, GGB, and SF react with water and CH is not the subject of this investigation. However, from the experimental data it is evident that CH produced by blended cement hydration (containing FA, GGB, and SF) is less than CH produced by OPC hydration [12,28]. Based on this argument, the variation of the amount of CH with time can be used as a measure of pozzolan reaction. In this work, only the weight loss associated with the decomposition of CH (CH_{loss}) can be accurately measured. However, as shown by Midgley [18] this weight loss is very close to the amount of water in CH and therefore, is proportional to the amount of CH.

Variations of CH_{loss} with w_b are shown in Figs. 10–13. All data points were generated from measurements at three

Fig. 13. Relation between CH_{loss} and w_b for 90% OPC+10% SF.

temperatures and for two w/b. In correlating CH_{loss} to w_b , it was assumed that CH was produced only by OPC, not by OPC and pozzolan. Therefore, CH_{loss} and w_b were normalized by the weight of OPC in each mix, which was estimated from the proportion between OPC and pozzolan, e.g. 75% OPC+25% FA. This means that $(\%OPC) \times w_b / g-OPC = w_b / g-binder$. CH_{loss} versus w_b in each system seems to follow one unique trendline. For OPC pastes, CH_{loss} changes almost linearly with w_b . This comes with no surprise since the hydration products, which are proportional to w_b , include CH. However, for pastes containing pozzolans the amount of CH is less, especially in FA pastes. Such a trend has been experimentally confirmed [26].

In order to estimate the degree of hydration of pozzolans, a reference $CH_{loss}-w_b$ plot is needed. Clearly, this would be the plot for OPC. The difference in $CH_{loss}-w_b$ plot obtained for each blended cement system relative to $CH_{loss}-w_b$ plot for OPC is assumed to define the reduction of CH due to pozzolanic reactions. This difference normalized by its ultimate value is defined as the degree of pozzolan reaction (α_p). To calculate such a difference, the data points need to be curve-fitted. The result of fitting the data is illustrated in Figs. 10–13. In these figures, the $CH_{loss}-w_b$ plot for OPC is indicated by the solid line. The degree of pozzolan reaction is calculated from:

$$\alpha_p = \frac{CH_{loss}^{OPC}(w_b) - CH_{loss}(w_b)}{CH_{loss}^{OPC}(w_{b,\infty}) - CH_{loss}(w_{b,\infty})} \quad (3)$$

$$\alpha_p(t) = \frac{\Delta CH_{loss}(w_b(t))}{\Delta CH_{loss}(w_{b,\infty})} \quad (4)$$

Then from the inversion of Eq. (1), the time can be expressed in terms of w_b :

$$t = \tau \left[\ln \left(\frac{w_{b,\infty}}{w_b} \right) \right]^{-1/\alpha} \quad (5)$$

so $\alpha_p(t)$ can be found. The degree of pozzolan reaction determined by the above calculation is shown in Fig. 14. As seen, SF starts reacting earlier than FA or GGB, while GGB appears to react earlier than FA. These findings confirm the observation on heat of hydration (Figs. 2 and 3), that the pozzolan reactions in pastes containing SF and GGB occur early. Fig. 14 also provides the information on how reactive different types of mineral additive are.

5. Conclusions

Experimental results on hydration kinetics of blended cements obtained using DTA/TGA and isothermal calorimetry are presented in this paper. A procedure based on the composition of hydrating cement has been proposed and then used to determine the degree of hydration of blended

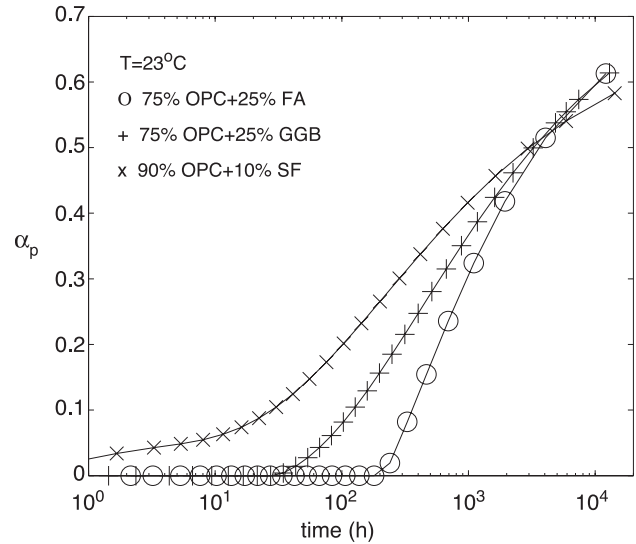


Fig. 14. Degree of pozzolan reaction.

systems and the degree of pozzolan reaction. Based on the presented findings, effects of temperature and water–binder ratio on hydration are found very important and can be well captured by isothermal calorimetry and DTA/TGA. In particular, the temperature effect has been quantified using a three-parameter hydration equation (TPE). This study warns that maximum ultimate bound water and heat of hydration are temperature dependent. Using parameters generated by TPE, the values of maximum ultimate bound water and heat of hydration are extrapolated. Such quantities are very important since they are needed for calculating the degree of hydration from $\alpha = w_b / w_{b,\infty}$ and $\alpha = Q / Q_\infty$.

For the blended systems considered here, the overall degree of hydration can be quantified using chemically bound water obtained using DTA/TGA together with TPE. The result indicates that the overall hydration is retarded by the presence of pozzolans, particularly in the paste containing ground-granulated slag. In addition to determining the overall degree of hydration, a method based on measurements of decomposition of $Ca(OH)_2$ together with TPE can be used to quantify pozzolanic reactions. The result suggests that ground-granulated slag (GGB) and fly ash (FA) in cement paste react more slowly compared to silica fume (SF).

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