Journal of Thermal Analysis and Calorimetry, Vol. 97 (2009) 1, 71–76

POZZOLANIC REACTIVITY OF THE SUPPLEMENTARY CEMENTITIOUS MATERIAL PITCHSTONE FINES BY THERMOGRAVIMETRIC ANALYSIS

K. Vessalas[1], *P. S. Thomas*[1*], *A. S. Ray*[1], *J.-P. Guerbois*[1], *P. Joyce*[2] *and J. Haggman*[2]

[1]Centre for Built Infrastructure Research, University of Technology, Sydney PO Box 123, Broadway SW 2007, Australia
[2]Perlco Pty Ltd., Suite 701, Level 7, 121 Walker Street, North Sydney NSW 2060, Australia

Thermogravimetric (TG) analysis was applied to the characterisation of the pozzolanic reaction in mortars containing the supplementary cementitious materials (SCMs) pitchstone fines (PF) and fly ash (FA) as partial replacements for Portland cement (PC). TG analysis was used to determine the proportion of calcium hydroxide (CH) present from the hydration of the PC based on the dehydroxylation of the CH present in the blended PC-SCM mortars. The consumption of CH indicated that both SCMs underwent the pozzolanic reaction and that PF was found to compare favourably in its pozzolanic reactivity of FA, the industry and globally accepted standard artificial pozzolan.

Keywords: *fly ash, pitchstone fines, Portland cement, pozzolanic reactivity, thermogravimetric analysis*

Introduction

Portland cement (PC) comprises of two calcium silicate components, tricalcium silicate (alite, C_3S) and dicalcium silicate (belite, C_2S), which are responsible for the formation of strength developing calcium–silicate–hydrate (C–S–H) phases on cement hydration. The hydration of alite is responsible for rapid early strength development up to 28-day age. Beyond this age, the slower hydration of belite is responsible for the continued formation of the C–S–H strengthening phases, which develop the long-term strength [1–3]. The hydration of both alite and belite results in an accompanying release of calcium hydroxide (CH) based on the reaction paths given by Eqs (1) and (2):

$$2C_3S+6H\rightarrow C\text{–}S\text{–}H \text{ (nominally } C_3S_2H_3)+3CH \quad (1)$$

$$2C_2S+4H\rightarrow C\text{–}S\text{–}H \text{ (nominally } C_3S_2H_3)+CH \quad (2)$$

where in cement notation, C represents calcium oxide (CaO), S represents silicon dioxide (SiO_2), H represents water (H_2O) and C–S–H represents the strengthening phases produced which are of variable stoichiometry and predominantly amorphous in character. The CH produced is a by-product of the hydration reaction and is often considered desirable, as it helps prevent the corrosion of reinforcing steel strengthening elements in concrete structures, by offering passive film protection. However, the CH may also be utilised to produce further C–S–H strengthening phases through the pozzolanic reaction with amorphous silica-rich materials.

Pozzolans, in the form of supplementary cementitious materials (SCMs) utilised in the partial replacement of PC, are important to the construction industry due to their fundamental role in enhancing fresh and hardened state properties of cement-based building materials [4]. Enhanced workability, reduced permeability, improved resistance to the alkali-silica reaction, increased ultimate strength development and reduced susceptibility to physical and chemical attack are some of the properties that are imparted by a number of pozzolanic aluminous-silica rich industrial by-products including fly ash, silica fume, ground-granulated blast furnace slag, clay-brick waste and perlite [5–11].

The degree of pozzolanic reactivity (pozzolanicity) can be measured as a function of the relative strength of the blended PC-SCM mortar using pozzolan-free PC mortar as the control. ASTM C 311-05 [12] defines a pozzolan, or SCM, as an additive in a blended PC-SCM mortar that can provide at least 75% of the compressive strength of the control PC (pozzolan-free) mortar after 7 and 28-day age. As pozzolanicity is the reactivity of the added pozzolanic silica-rich SCMs to the CH liberated by the hydration of the PC, a measure of the consumption of CH may provide an alternate route to the determination of pozzolanicity [1–3].

Thermogravimetric (TG) analysis may be applied to the determination of the amount of CH present in blended PC-SCM mortars by measurement of the

---

[*] Author for correspondence: paul.thomas@uts.edu.au

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

mass loss on decomposition of the CH present. As over long periods of ageing partial carbonation of the CH occurs, the proportion of carbonated CH (calcium carbonate ($CaCO_3$)) may also be incorporated into the calculation of the proportion of CH produced by the hydration reaction. The CH derived from hydration of the PC may, therefore, be determined from the mass loss recorded with increasing temperature for the dehydroxylation of CH, L_{dx}, between 420 and 500°C and decarbonation of $CaCO_3$, L_{dc}, between 500 and 680°C, less any $CaCO_3$ already present in the PC based on Eq. (3) [2].

$$\text{CH as (CH+CaCO}_3\text{)}=4.11\ (L_{dx})+1.68\ (L_{dc}) \quad (3)$$

Although this equation gives a measure of the absolute mass of CH in the sample, to determine the pozzolanicity of a SCM a relative measure of the amount of CH present is required. An alternative method of determining the proportion of CH liberated by the hydration process is to determine the proportion of CH in terms of its equivalent mass of calcium oxide (C):

$$\text{C as (CH+CaCO}_3\text{)}=3.11\ (L_{dx})+1.27\ (L_{dc}) \quad (4)$$

If the total amount of C in the specimen is known, then the proportion of C as CH can be determined as a percentage of the total C present. A further consideration for the determination of the pozzolanicity is the delayed reaction of the SCM with the CH and the limited potential for the SCM to react with $CaCO_3$ in an alkaline environment. The lack of reactivity of the SCM to the $CaCO_3$ present would suggest that a more appropriate method for determining the degree of consumption is based solely on the CH present and, hence, the CH dehydroxylation according to Eq. (5).

$$\text{C as CH}=3.11\ (L_{dx}) \quad (5)$$

In this study, the proportion of CH was determined as the mass of C present as (CH+$CaCO_3$) using Eq. (4) and the mass of C present as CH using Eq. (5). In each case the proportion of C present as CH was determined as a percentage of the total C present in the specimen (less any $CaCO_3$ present in the PC prior to mixing when using Eq. (4)). Using these methods the pozzolanicity of pitchstone fines (PF), a natural pozzolan, is investigated and compared to fly ash (FA), the industry accepted standard artificial pozzolan. Blended PC-SCM mortars containing 40% PF and 40% FA substitution levels aged for 7, 28 and 91 days are investigated with the proportion of CH present compared to the proportion measured in 100% PC mortars (the control) containing no pozzolan additions.

Experimental

In preparing the mortar mixes, the following raw materials were utilised:

- Shrinkage limited Portland cement (Blue Circle Southern Cement Pty Ltd.)
- Graded pitchstone fines (Perlco Pty Ltd.)
- Eraring fly ash (Blue Circle Southern Cement Pty Ltd.)
- Raymond Terrace single washed sand (Rocla Quarry Products Pty Ltd.)
- Glenium 51 superplasticiser (BASF Construction Chemicals Pty Ltd.)

The chemical compositions, determined by X-ray fluorescence (XRF) of the raw materials used in this study, are given in Table 1. Both the graded pitchstone fines (PF) (99.3% passing the 75-μm sieve and 72.3% passing the 45-μm sieve) and the fly ash (FA) (97.3% passing the 75-μm sieve and 88.0% passing the 45-μm sieve) conformed to the ASTM C 618-05 [13] 45-μm particle fineness requirement.

Table 1 Chemical analysis of raw materials by XRF

Chemical composition	PC/%	PF/%	FA/%	Sand/%
SiO_2	20.5	68.53	65.9	98.4
Al_2O_3	4.5	12.94	24.0	0.69
Fe_2O_3	4.5	1.04	2.87	0.11
CaO	64.9	0.9	1.59	0.02
MgO	1.2	0.02	0.42	0.02
Na_2O	0.0	4.51	0.49	0.03
K_2O	0.46	2.58	1.44	0.17
LOI		7.90	1.53	

Mix designs were adopted from ASTM C 311-05 [12] with high-range water-reducing admixture (HRWRA) superplasticiser added to the water in compliance with the requirements of ASTM C 1240-05 [14] prior to the commencement of mixing. Preparation of mixes were carried out in accordance with ASTM C 305-06 [15] guidelines, with the inclusion of an additional step requiring pozzolan additions to be mixed with water for 30 s at 140±5 revolutions/min prior to adding any PC to the water. The mortar mix design proportions, shown in Table 2, were batched with fixed cementitious material-to-sand and water-to-cementitious material (w/cm) ratios of 1:2.75 and 0.48, respectively, as any increase or decrease in the latter ratio has been reported to decrease or increase compressive strengths, respectively [15]. Based on this methodology, three mortar mixes were prepared; a 100% PC (control) and two blended

Table 2 Mix designs for the mortar specimens

Mixture	PC/g	PF/g	FA/g	Sand/g	Water/g	HRWRA/mL
100PC	500.0	0.0	0.0	1375.0	241.6	0.6
40PF	300.0	200.0	0.0	1375.0	240.6	2.2
40FA	300.0	0.0	200.0	1375.0	241.9	0.2

PC-SCMs with 40% PF and 40% FA replacement of the PC (Table 2). Mortar cubes (50 mm) were moulded in compliance with ASTM C 109 and C 109M-05 [17] using the hand-tamping compaction technique for consolidation of mortar. The moulded 50 mm cubes were aged initially for 24-h in a moist environment and then immersed into saturated limewater [18]. The moulded cubes were subjected to compressive strength testing at 7, 28 and 91 days age [19]. Fractured pieces were collected from the central core. The fractured pieces were first reduced in fineness with a hammer followed by hand pulverising in a porcelain mortar and pestle. The fines were then stored in airtight bags in a freezer at –10°C to arrest ongoing hydration prior to TG analysis.

TG analysis was carried out on 25±1 mg samples using a TA Instruments SDT 2960 analyser, at a heating rate of 10°C min^{-1} from room temperature to 1000°C in an air atmosphere at a flow rate of 15 mL min^{-1}.

Results and discussion

Figure 1 shows typical TG data for the thermal decomposition of a sample of aged mortar. The TG curve can be separated into three distinct regions. Below 420°C, water is lost either as molecular water or from the dehydration of C–S–H gels, formed either from the hydration of the PC or from the pozzolanic reaction between the SCMs (where present) and CH. In the region between 420 and 500°C, the dehydroxylation of calcium hydroxide (CH) occurs with a peak at circa 450°C in the differential TG (DTG) curve. In the region between 500 and 680°C, the decarbonation of calcium carbonate ($CaCO_3$) is observed with an asymmetric decomposition peak in the DTG curve at circa 630°C. Mass loss data in the dehydroxylation (L_{dx}) and decarbonation (L_{dc}) regions of Fig. 1, were used to calculate the percent CH present in each of the mortar mixes shown in Fig. 2.

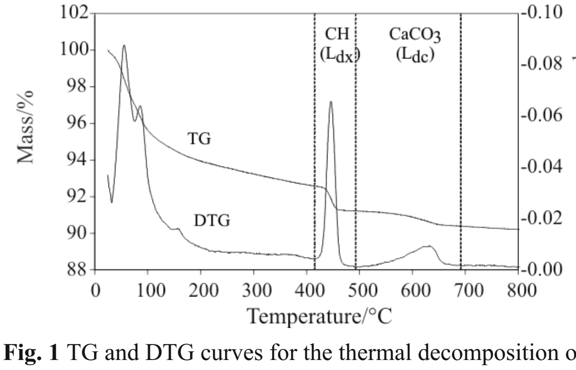

Fig. 1 TG and DTG curves for the thermal decomposition of a specimen taken from the centre of a 100% PC mortar cube aged for 28 days

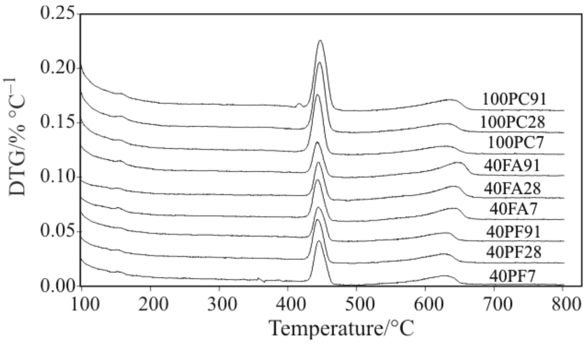

Fig. 2 DTG curves for the thermal decomposition of 100PC – 100% PC, 40FA – 40% FA and 40PF – 40% PF PC-SCM blended cements aged for 7, 28 and 91 days

Although Eq. (3) represents a simplified method of determining the % CH from the mass loss steps in the TG curve, the precision of the data strongly depends on the measured value of the total mass of cement, which contains a variable degree of molecular and C–S–H bound water. In this study, the proportion of CH present was determined as the mass of calcium oxide (C) present as CH using both Eqs (4) and (5). The mass loss was then calculated as a percentage of the total C present in the specimen (less any $CaCO_3$ present in the PC prior to mixing when using Eq. (4)). The total mass of C present in the blended PC-SCM mortar was determined from the proportion of C in the PC (64.9 mass%) and the amount of PC in the blended PC-SCM mortar (26.7 mass% for the control and 16.0% by mass in the SCM blended PC-SCM). C was also present in the SCMs (Table 1) and is included in the total mass of C present in the blended PC-SCM mortars. As the initial mass of each specimen was dependent on the proportion of water present, the total mass of C was calculated from the final mass recorded after heating to 1000°C. The mass loss data and the calculated percentages of C present as CH (Eq. (5)) and CH+$CaCO_3$ (Eq. (4)) are listed in Table 3.

It is apparent from Table 3 that there is significant difference in the amounts of CH present in the mortar

Table 3 Mass loss data for the determination of the % calcium hydroxide (CH) present in the hydrated mortar mixes. The CH is calculated using Eqs (4) and (5) as CaO (C) present as CH and is presented as a percentage of the total C present in the PC and blended PC-SCM mortars (based on the data in Table 1). L_{dx} and L_{dc} are the mass losses for the dehydroxylation step and the decarbonation step, respectively and ΔCH is the % change in CH present relative to the 100% PC mortar. The reported compressive strengths of cube specimens of these PC and blended PC-SCM mortars are also included [19]

Sample	Age/day	Strength/ MPa [19]	Final mass/ mg	Total C/ mg	L_{dx}/mg	L_{dc}/mg	C as CH (% of total C) (Eq. (5))	ΔCH/% (CH) (Eq. (5))	C as $CaCO_3$ (% of total C)	C as CH+$CaCO_3$ (% of total C) (Eq. (4))	ΔCH/% (CH+$CaCO_3$) (Eq. (4))
PC powder	–	–	23.93	15.531	0.0231	0.0785	0.46	–	0.64	–	–
100% PC mortar	7	24.9	22.83	3.951	0.2850	0.1848	22.5	0	5.3	27.8	0
	28	33.9	22.66	3.922	0.3490	0.2035	27.7	0	6.0	33.7	0
	91	38.0	22.31	3.861	0.3662	0.2366	29.5	0	7.2	36.7	0
40% PF+60% PC mortar	7	12.1	22.78	2.387	0.2265	0.1892	29.5	31.5	9.5	39.0	40.4
	28	20.4	22.19	2.326	0.2184	0.1876	29.2	5.5	9.6	38.8	15.4
	91	27.9	22.61	2.370	0.1814	0.1804	23.8	–19.3	9.1	32.9	–10.4
40% FA+60% PC mortar	7	13.5	22.97	2.424	0.1836	0.1927	23.6	5.0	9.5	33.1	19.1
	28	22.6	22.78	2.404	0.1509	0.1829	19.5	–29.5	9.0	28.5	–15.1
	91	31.6	22.84	2.410	0.1536	0.2272	19.8	–32.8	11.4	31.2	–15.0

cubes. The proportion of CH determined for the 100% PC samples was observed to increase with age, as would be expected, as the proportion of CH will increase as the hydration of the PC proceeds with increasing age [2]. Most of the CH is produced in the first seven days of hydration because of the rapid hydration of alite (C_3S). The hydration of alite is generally considered to be completed by 28 days. CH is continued to be produced up to 91 days (and beyond) but at a reduced rate due to the much slower rate of hydration of belite (C_2S).

The proportion of $CaCO_3$ for the 100% PC mortars after 7 days aging is observed to be significantly higher than that observed in the as-received PC powder (ca. 10 times). Carbonation of the hydrated PC must, therefore, occur at fairly early times and, possibly, mostly during preparation of the mortar cubes as, once the cubes had been removed from the moulds, the cubes were stored in saturated limewater, an environment that would be expected to inhibit further carbonation of the cubes. Inspection of the 100% PC mortar data, however, suggests that there is some increase in the proportion of $CaCO_3$ present with increasing aging suggesting that further carbonation may have occurred.

The carbonation of the CH is important in the PC as determination of the amount of CH produced by hydration is best represented as the CH present plus the carbonated CH as given by Eq. (4) (or Eq. (3)). Once carbonated, however, the carbonated CH ($CaCO_3$) will not likely to be involved in the pozzolanic reaction. Although there is some evidence of further carbonation with age, most of the carbonation appears to occur prior to the 7-day measurement. As the pozzolanic reaction is generally slow and occurs at longer times, any carbonated CH will not be available for the pozzolanic reaction. The degree of pozzolanicity is, therefore, best described by Eq. (5) which limits the reaction of the pozzolan to the available CH.

In the blended PC-SCM mortars, initially the proportion of CH is high, but decreases with increasing aging time. The relative proportion of CH (or ($CH+CaCO_3$)), in terms of the magnitude of ΔCH (or $\Delta(CH+CaCO_3)$) listed in Table 3, indicate that the proportion of CH is greater for both PC-SCM mortars at 7 days aging. The higher proportion of CH present in the PC-SCM blends may be explained by the water/PC ratio. For this series of mortar specimens, the water to cementitious material was kept constant (Table 2). As such, the substitution of 40% of the PC with an SCM resulted in an increase in the water/PC ratio. The increase in the water/PC ratio is likely to increase the degree of hydration of the PC due to the greater availability of water resulting in observed greater proportion of CH after 7 days.

Further aging of the PC-SCM mortars results in the consumption of CH. The ΔCH decreases with increasing aging with negative values being produced after 91 days aging for the PF mortars and after 28 and 91 days for the FA mortars. This trend suggests that the CH produced by hydration of the PC is being consumed by the SCMs added in the pozzolanic reaction resulting in strengthening C–S–H phases. This is confirmed by the strength data reported for these blends [19]. The replacement of 40% of the PC, not surprisingly, has a marked affect on strength with the strength of the PC-SCM mortars being approximately 50 of the 100% PC control. This difference narrows with aging time. After 91 days the compressive strengths of the PC-SCM mortars are approximately 75 of the 100% PC control. This increase in strength coupled with the consumption of CH indicates that the pozzolanic reaction is contributing to the strength of the PC-SCM blended mortar, even though it is delayed. It is apparent from the increase in strength and consumption of CH with increasing age that the PF is pozzolanic and is likely to be suitable as an SCM. The pozzolanic reactivity of the PF used in this study is, however, more retarded than the FA. This difference in reactivity is attributed, primarily, to the difference in particle size distributions of the two SCMs. Although both SCMs conform to the pozzolan particle fineness requirement [13], the PF is significantly coarser with only 72.3% passing the 45-μm sieve relative to 88.0% passing for the FA. It is likely that these observed differences in reactivity may be addressed by reducing the particle size of the PF.

Conclusions

The pozzolanicity of PC-SCM mortar has been investigated using thermogravimetric analysis. The proportion of CH measured in the PC-SCM mortars after short aging time (7 days) was found to be greater than that measured for the 100% PC control in the early stages of ageing. This relative increase in the proportion of CH was attributed to the increased water/PC ratio rather than an involvement of the SCM in the hydration process. The proportion of CH in the PC-SCM mortars, however, was observed to decrease with increased ageing, which when correlated to compressive strength development, indicated that both PF and FA underwent the pozzolanic reaction. The rate of pozzolanicity for the PF was observed to be less than that of the FA. This difference in rate was ascribed to the coarser particle size of PF and is expected to become comparable on particle size reduction of the PF.

Acknowledgements

The authors would like to thank the University of Technology, Sydney (UTS), for providing the necessary financial support for this research project, through its UTS Challenge Grants Scheme.

References

1 W. Roszczynialski, J. Therm. Anal. Cal., 70 (2002) 387.
2 J. I. Bhatty and K. J. Reid, Thermochim. Acta, 91 (1985) 95.
3 A. Moropoulou, A. Bakolas and E. Aggelakopoulou, Thermochim. Acta, 420 (2004) 135.
4 B. Uzal, L. Turanli and P. K. Mehta, ACI Mater. J., 104 (2007) 535.
5 S. K. Das and Yudhbir, Cem. Concr. Res., 36 (2006) 1827.
6 R. J. Detwiler and P. K. Mehta, ACI Mater. J., 86 (1989) 609.
7 C. Duran Atis and C. Bilim, Building Environ., 42 (2007) 3060.
8 A. L. A. Fraay, J. M. Bijen and Y. M. de Haan, Cem. Concr. Res., 19 (1989) 235.
9 M. O'Farrell, B. B. Sabir and S. Wild, Cem. Concr. Compos., 28 (2006) 790.
10 L. H. Yu, H. Ou and L. L. Lee, Cem. Concr. Res., 33 (2003) 73.
11 A. Ray, R. Sriravindrarajah, J. P. Guerbois, P. S. Thomas, S. Border, H. Ray, J. Haggman and P. Joyce, J. Therm. Anal. Cal., 88 (2007) 279.
12 ASTM C 311-05, Standard test methods for sampling and testing fly ash or natural pozzolans for use in Portland-cement concrete. 2005, ASTM Int.
13 ASTM C 618-05, Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, 2005, ASTM Int.
14 ASTM C 1240-05, Standard specification for silica fume used in cementitious mixtures. 2005, ASTM Int.
15 ASTM C 305-99, Standard practice for mechanical mixing of hydraulic cement pastes and mortars of plastic consistency. 1999, ASTM International.
16 K. Hover and T. Stokes, Concr. Int., 17 (1995) 52.
17 ASTM C 109/C 109M-05, Standard test method for compressive strength of hydraulic cement mortars (using 2-in. or [50-mm] cube specimens). 2005, ASTM Int.
18 ASTM C 511-05, Standard specification for mixing rooms, moist cabinets, moist rooms and water storage tanks used in the testing of hydraulic cements and concretes, 2005, ASTM Int.
19 K. Vessalas, A. S. Ray, P. S. Thomas, R. S. Ravindrarajah., P. Joyce, J. Haggman, P. A. Joyce and T. M. K. Vo, Cem. Concr. Res., in preparation.

ICTAC 2008

DOI: 10.1007/s10973-008-9708-5