



Activation energies of high-volume fly ash ternary blends: Hydration and setting



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ARTICLE INFO

Article history:

Received 9 November 2013
Received in revised form 30 May 2014
Accepted 20 June 2014
Available online 17 July 2014

Keywords:

Apparent activation energy
Calcium carbonate powder
High-volume fly ash
Hydration
Isothermal calorimetry
Setting

ABSTRACT

Because ready-mixed concrete is placed under a wide variety of environmental conditions, the influence of temperature on the hydration reactions and the accompanying setting process is of critical importance. While contractors are generally quite comfortable with the temperature sensitivity of conventional ordinary Portland cement (OPC) concretes, more sustainable mixtures containing high volumes of fly ash (HVFA), for example, often present problems with delayed setting times and increased temperature sensitivity. Based on isothermal calorimetry and Vicat needle penetration measurements, this study demonstrates that the high temperature sensitivity of such HVFA mixtures can be effectively moderated by the replacement of a portion of the fly ash with a fine calcium carbonate powder. In addition to accelerating and amplifying hydration and reducing setting times at a given temperature, the presence of the fine CaCO_3 powder also lowers the apparent activation energy for setting for temperatures below 25 °C. The reactivity of the CaCO_3 in these mixtures is quantified using thermogravimetric analysis. Comparison of results for CaCO_3 powders of nominal sizes of 1 μm and 17 μm , replacing 10% by volume of the cement in an OPC mixture, indicates that the former is highly superior in accelerating/amplifying hydration and reducing setting times.

Published by Elsevier Ltd.

1. Introduction

While high volume fly ash (HVFA) concretes have been investigated for many years [1], recent interest in sustainability has created renewed interest in these mixtures. The generally acceptable performance of these mixtures at later ages from both a strength and durability viewpoint is often offset by their reduced constructability, as exemplified by delayed setting times, low early-age strengths, and increased sensitivity to temperature (curing) [2,3]. Recent studies have focused on the ability of calcium carbonate (CaCO_3) powder additions to mitigate the first two of these deficiencies in HVFA concrete mixtures [4–10], with finer (1 μm particle size) CaCO_3 being particularly efficient in this regard [7–10]. The fine CaCO_3 particles provide a greatly increased surface area for the precipitation and growth of hydration products [8] and also participate to a small extent in reactions with the cement phases to produce more voluminous [6] and potentially stiffer [11] carboaluminate hydration products. While a few studies have included temperature as a variable [12,13], the former even including an analysis of activation energies for initial and final setting,

neither of them used a CaCO_3 powder that is as fine as that employed in the present study. In the study of Ezziane et al. [12], for example, the replacement of cement with 5–25% CaCO_3 on a mass basis resulted in increased setting times under all investigated curing conditions (20 °C, 40 °C, and 60 °C).

Activation energy analysis has been often applied to both hydration and setting processes in cement-based materials [12,14–17], and is, of course, the basis for the well-known and standardized maturity method for predicting insitu concrete strength development [18,19]. The basic premise in an Arrhenius-based approach is that the rate parameter, k , for the process of interest (hydration, setting, or strength development) is a function of temperature that can be described as:

$$k = Ae^{\left(-\frac{E_A}{RT}\right)} \quad (1)$$

where A is a kinetics constant, E_A is the apparent activation energy (typically reported in units of kJ/mol), R is the universal gas constant [8.314 J/(mol K)], and T is absolute temperature in K. This equation can be conveniently applied to transform temporally varying results measured at one temperature to a second temperature, a so-called time–temperature transformation. The equivalent time, t_e , at a reference temperature, T_r , can be determined as:

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$$t_e = e \left[-\frac{E_A}{R} \left(\frac{1}{T_i} - \frac{1}{T_r} \right) \right]_t \quad (2)$$

where T_i and t are the measurement temperature and time, respectively. For example, curing a concrete specimen for 12 h at 40 °C would be equivalent to curing for 26 h at 25 °C, for a system with an apparent activation energy of 40 kJ/mol.

In a similar manner, results obtained at two different temperatures can be analyzed to estimate the apparent activation energy for the process. For two sets of experimental conditions, Eq. (2) can be rearranged to solve for the apparent activation energy as:

$$E_A = \frac{-\ln \left(\frac{t_1}{t_2} \right) R}{\left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \quad (3)$$

Eq. (3) can be applied numerically to specific events, such as the measured initial setting times at two different temperatures in this study, or can be applied graphically to continuous data, such as isothermal calorimetry curves in this study, to assess the value of the apparent activation energy that provides the best overlap of the multiple (transformed) data sets. For example, initial setting times of 2.39 h and 3.93 h measured at 25 °C (298.15 K) and 15 °C (288.15 K), respectively, would correspond to an activation energy of 35.5 kJ/mol according to Eq. (3). The term apparent activation energy is employed to indicate that cement hydration consists of a complex set of reactions, each with its own individual activation energy. Thus, only an apparent value is obtained when analyzing such a system in a simple composite manner. This study investigates the apparent activation energies for hydration and initial setting in a variety of HVFA ternary blends for temperatures of 15 °C, 25 °C, and 40 °C.

2. Materials and experimental procedures

Materials employed in this study were equivalent to those utilized in a recent study on sustainable concretes employing high volumes of fly ash and fine (1 μm) CaCO₃ powder [9,10]. A new batch of the Type I/II cement used in the previous study was obtained from a local supplier. According to its mill test certificate report, the cement has a Blaine fineness of 372 m²/kg and an estimated Bogue phase composition of 58.5% C₃S, 11.2% C₂S, 6.4% C₃A, and 9.6% C₄AF on a mass basis, after adjusting for the 3.7% CaCO₃ content of the ground cement powder. The measured oxide compositions and densities of the cement and the two fly ashes used in this study are provided in Table 1. The measured particle size distributions (PSD, laser diffraction with isopropanol as the solvent) of all powder materials are provided in Fig. 1. Both a Class C and a Class F fly ash were examined, with their respective CaO percentages of 24.6% and 0.7% by mass providing a reasonable representation of the expected extremes in these values for the fly ashes commonly available in the US. The Class C fly ash is

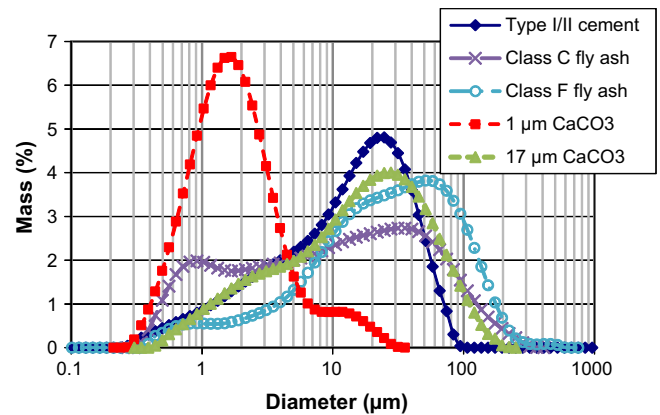


Fig. 1. Measured differential particle size distributions for the various powders employed in the present study. Results shown are the average of six individual measurements and error bars (one standard deviation) would fall within the size of the symbols on the plot.

hydraulic and retards cement hydration considerably [7–10]. CaCO₃ powder of two different particle sizes (nominally 1 μm and 17 μm) was used to replace a portion of the cement or fly ash in some mixtures. It has a reported density of 2710 kg/m³ and a reported MgCO₃ content of 1% by mass. The finer material has a measured (BET) surface area of 9.93 m²/g, while the coarser material has a value of 0.83 m²/g [8]. No chemical admixtures were employed in the present study of pastes.

To provide the fairest comparison of results, all paste mixtures were prepared utilizing volumetric proportioning, maintaining a constant volume fraction of water and powders (cement, fly ash, and CaCO₃) [7–10,20], based on a control cement-only paste with a water-to-cement ratio by mass (w/c) of 0.35. Most previous studies, including those in [12,13], have performed mass-based replacements and maintained a constant water-to-solids ratio on a mass basis, thereby confounding the change in water volume fraction (initial porosity) due to the differing densities of cement, fly ash, and CaCO₃ powder with the change in binder chemical composition. Mixtures were prepared where 10% of the cement was replaced by an equal volume of CaCO₃ powder or where either 40% or 60% of the cement by volume was replaced with fly ash–CaCO₃ blends. Mixture designations are summarized in Table 2; for example, C45L15 indicates a paste mixture where 60% of the cement by volume has been replaced, 45% by Class C fly ash and 15% by fine CaCO₃ powder. The performance of the fine and coarse CaCO₃ powders was only contrasted in the Portland cement–CaCO₃ binary blends, as an equivalent contrast in HVFA ternary blends had been conducted previously [8].

All powders for a given mixture were pre-blended for 30 min in a shaker-mixer that employs rotation, translation, and inversion to

Table 1

Oxide composition percent by mass, loss on ignition, and density of the cement and the Class C and Class F fly ashes.

Property	Type I/II cement	Class C fly ash	Class F fly ash
SiO ₂ (%)	19.4	38.4	59.7
Al ₂ O ₃ (%)	4.5	18.7	30.2
Fe ₂ O ₃ (%)	3.2	5.1	2.8
CaO (%)	62.3	24.6	0.7
MgO (%)	3.4	5.1	0.8
SO ₃ (%)	2.9	1.4	0.02
Na ₂ O (%)	0.52 eq.	1.7	0.2
K ₂ O (%)	See Na ₂ O	0.6	2.4
Loss on ignition (%)	2.7	0.3	0.8
Density	3150 ± 10 kg/m ³	2630 kg/m ³	2160 kg/m ³

Table 2

Powder mixture proportions (volume) and designations.

Designation	% Cement	% F ash	% C ash	% Fine CaCO ₃	% Coarse CaCO ₃
Control	100				
L10	90			10	
L10coarse	90				10
F40	60	40			
F30L10	60	30		10	
C40	60		40		
C30L10	60		30	10	
F60	40	60			
F45L15	40	45		15	
C60	40		60		
C45L15	40		45	15	

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