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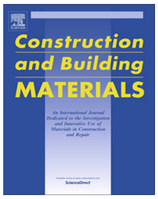

Evaluating the hydration of high volume fly ash mixtures using chemically inert fillers

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HIGHLIGHTS

- Isothermal calorimetry measurements are used to evaluate fly ash hydration.
- The approach presented decouples the physical and chemical effects of fly ash.
- Inert fillers are used to replace the fly ash fraction.

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ABSTRACT

Fly ash is frequently used as a replacement for cement in concrete. However, questions remain regarding the influence that fly ash has on the hydration of cement. This paper examines physical aspects (e.g., surface nucleation, cement particle spacing) and chemical aspects (e.g., pozzolanic and hydraulic reactions) of the fly ash and cement in mixtures containing high volumes of fly ash. In addition to using fly ash, a chemically inert filler was used consisting of a blend of fine silica sands with approximately the same particle size distribution as that of the fly ash. The paper compares reactivity results from 1) cement, 2) cement-fly ash and 3) cement-inert filler systems. Isothermal calorimetry measurements are used to quantitatively evaluate the role played by the fly ash in hydration of high volume fly ash mixtures. The results provide a decoupling of the physical and chemical effects of high volume fly ash on cement hydration.

1. Introduction

Fly ash is a by-product of coal combustion that has been broadly used by the concrete industry as a supplementary cementitious material (SCM) [1–9]. It can be used to replace cement, which decreases the clinker factor and embodied CO_2 [10–12] and generally improves workability and durability [13]. High Volume Fly Ash (HVFA) mixtures are typically designed with more than 50% (by mass) of the cement replaced with fly ash. However, fly ash is less reactive than cement, which can sometimes cause retardation and extended setting time issues, especially when employed at higher volumes [14–16]. The degree of reactivity for the fly ash depends on the type of fly ash used (e.g., a Class C fly ash has typically more hydraulic properties than a Class F fly ash) [17]. With both classes of fly ash, lower strengths are typically observed in HVFA concrete at early ages [18]. Typically, it is possible to counteract this strength loss by reducing the water-to-cementitious ratio [19], using accelerating additions, replacing a portion of the fly ash with a fine limestone powder, or switching to a more reactive Type III cement [20–24].

The reactivity of fly ash and its effect on cement hydration has been a focus of study throughout the 20th and into the 21st century [19–23]. It now becomes more relevant to understand due to the current tendency of using larger amounts of fly ash to replace cement in concrete. However, the reaction kinetics of fly ash-cement systems are complicated by the fact that the reactions of the cement and fly ash may interact and, more importantly, by the difficulty in measuring the degree of reaction of these two components independently [25]. Recently, several studies have focused on developing faster and more reliable techniques for physical and chemical characterization of fly ash that can be related to fly ash reactivity [26–32].

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According to ASTM C595, a pozzolan is defined as "a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form compounds possessing cementitious properties (pozzolanic activity)." Fly ash is one of the materials that falls into this category. The pozzolanic reaction typically starts at later ages, since fly ash needs $Ca(OH)_2$ formed during cement hydration for the reaction. Depending on the fly ash characteristics and the alkalinity of the pore solution, its reaction with $Ca(OH)_2$ will occur earlier or later [33,34]. It is often thought that the pozzolanic effect is more dominant than any other effects (e.g., filler effects) [35–37], especially at later ages.

It is generally accepted that, under most circumstances, concrete containing fly ash is more durable than conventional ordinary Portland cement (OPC) concrete, due mainly to the pore refinement produced by the pozzolanic reaction that converts the calcium hydroxide ($Ca(OH)_2$) formed during cement hydration to additional calcium silicate hydrate gel (C-S-H), resulting in a reduction in the permeability/diffusivity of the matrix [34,38]. The pozzolanic reaction can also cause a size reduction and densification of the interfacial transition zone (ITZ) region between the aggregates and the cement matrix, often considered to be a weak interface due to the higher porosity as compared to the bulk matrix. The reaction between fly ash and the ($Ca(OH)_2$) in this ITZ region reduces its local porosity.

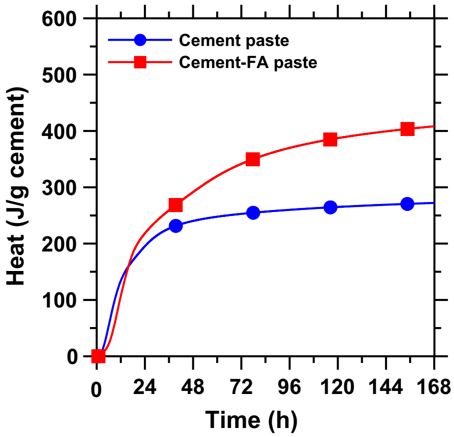

Fig. 1. Examples of measured heat release in cement and cement-fly ash blended pastes. Uncertainty for these values will be presented later in the text (Fig. 5 discussion).

A common technique to determine the reactivity of cementitious materials is by using an isothermal calorimeter. The hydration reaction is exothermic; therefore, measuring the heat release of these materials indicates how much of the material has reacted. When comparing the heat release between plain cement and fly ash-cement systems, it can be mistakenly interpreted that the difference in heat release between these two systems is solely due to the fly ash reactivity. Typical cumulative heat release curves for cement and cement-fly ash pastes are shown in Fig. 1 where the heat release per g of cement of a 100% OPC and a 40% (by volume) fly ash – 60% OPC system are plotted as a function of time. In the conventional practice of normalizing the heat release per g of cement (as in Fig. 1), the fly ash is considered to act as an inert material; therefore, the difference in heat observed is purely due to the presence of fly ash, which can have physical and/or chemical effects on the cement hydration, instead of just providing additional chemical reactions (hydraulic and pozzolanic) that increase the heat release. Inert fillers with similar particle size distributions (PSD) to the pozzolanic materials under study have been used in the past in an attempt to decouple the chemical and physical effects of SCMs, based on compressive strength measurements [39].

The present investigation explores the idea that the chemical reactivity of the fly ash is not the only aspect to consider when fly ash is mixed with cement. Fly ash can also act like a filler [19], especially at very early ages, prior to its chemical reaction. In addition, retardation of the initial hydration reactions of cement (and consequently, of initial setting time) due to dilution and interaction with some fly ash components is commonly observed [21,40]. These effects have been examined in detail in systems containing fillers other than fly ash [41–43].

As mentioned above, the reactivity of the fly ash, particularly Class F fly ash, depends on the alkalinity of the pore solution and the availability of $Ca(OH)_2$, both of which build up over a few days. Therefore, the amount of reaction of fly ash in the first day or so is often negligible and changes in hydration kinetics may be dominated by the physical filler effect. Three combined physical effects may occur; 1) cement dilution as an increase in the water-cement mass ratio (w/c) produces a larger separation distance between cement particles, 2) deflocculation (that is, a decrease in the flocculation level of cement particles, as the fly ash particles break up some of the flocculated cement 3-D network structure, also improving the paste rheology [44]), thus promoting a better cement hydration since more cement surfaces per unit volume of cement are exposed, and 3) provision of new nucleation sites via the fly ash surfaces that may promote the formation of additional hydration products. A graphical representation of these concepts is shown in Fig. 2. This was done by adapting a hard core-soft shell

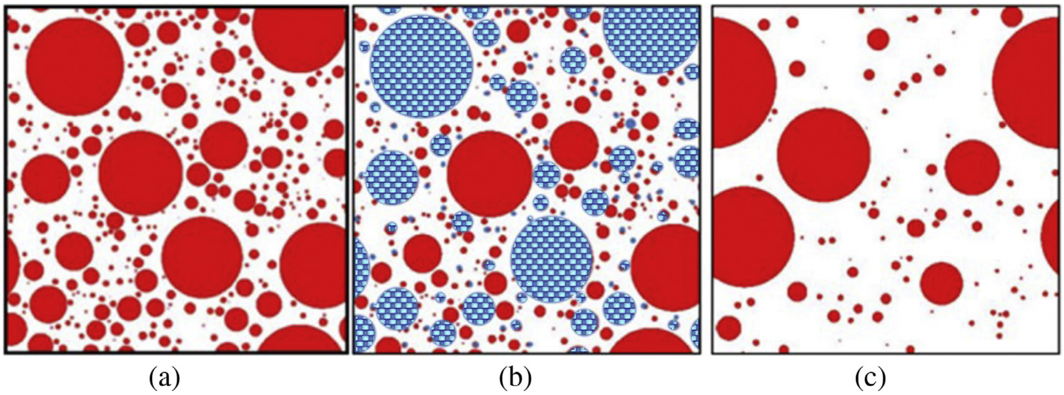
(a) (b) (c)

Fig. 2. (a) w/c = 0.30 plain system, (b) 60% fly ash (or inert filler) system, and (c) w/c = 0.67 plain system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)