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Investigating the role of reactive silica in the hydration mechanisms of high-calcium fly ash/cement systems

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Abstract

High-calcium fly ashes (ASTM Class C) are being widely used as a replacement of cement in normal and high strength concrete. In Greece such fly ashes represent the majority of the industrial by-products that possess pozzolanic properties. Even thought the contribution of factors, such as fineness and water/binder ratio, on the performance of fly ash/cement (FC) systems has been a common research topic, little work has been done on examining whether and to what extent reactive silica of fly ashes affects the mechanisms occurring during their hydration.

The work presented herein describes a laboratory scale study on the influence of active silica of two high-lime fly ashes on their behavior during hydration. Volumes up to 30% of Greek high-calcium fly ashes, diversified both on their reactive silica content and silicon/calcium oxides ratio, were used to prepare mixes with Portland cement. The new blends were examined in terms of compressive strength, remaining calcium hydroxide, generation of hydration products and microstructural development. It was found that soluble silica of fly ashes holds a predominant role especially after the first month of the hardening process. At this stage, silica is increasingly dissolved in the matrix forming additional cementitious compounds with binding properties, principally a second generation C–S–H. The rate however, that fly ashes react in FC systems seems to be independent of their active silica content, indicating that additional factors such as glass content and fineness should be taken into account for predicting the contribution of fly ashes in the final performance of pozzolanic cementitious systems.

Keywords: High-lime fly ash; Active silica; Glass; Hydration kinetics; Performance prediction

1. Introduction

High-lime fly ashes are the main industrial by-product generated in Greek thermal power plants, representing the 80% of the total fly ash production. Despite the fact that natural gas has already been introduced in the Greek energy sector, the rate at which fly ashes will be derived, at least during the forthcoming years, is expected to steadily increase. This posts not only an additional environmental concern but primarily a necessity for their greater utilization in different market sectors. At the moment the utilization rate of this material in the construction sector is still impoverished (about 10%), since it is being handled with a lot of skepticism [1]. The major reason for this timidity is its rather peculiar chemical composition, which apart from being very diversified, is also characterized by high free lime and sulphur contents, factors that threaten the concrete's durability [2]. On the other hand, the self-cementitious properties of those ashes diminish their dependency from calcium hydroxide liberated from hydrated Portland cement and result in improved early strengths compared to low-lime fly ashes [3].

In the literature there is consensus that the use of fly ash not only achieves energy and material saving [4,5], but also imparts improved quality to the final product in terms of strength and durability [6,7]. Even thought the beneficial role of fly ash in cementitious systems has been fairly well established, the potential of this by-product has not been explored fully yet. Current research is emphasizing on the role of parameters that affect the behavior of fly ashes during the hardening process. Factors such as fineness [8,9], water to cementitious materials ratio [10], curing temperature [11] and

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alkalinity of the pore solution [12,13] have been thoroughly examined in an attempt to explain the reactivity of this material and relate its pozzolanic potential with the evolution of the hydration procedure. However, the majority of the published work is concerned with ashes bearing low to moderate calcium contents, overlooking a wide range of different fly ashes, those with high calcium content.

During the 80s, several workers highlighted the distinct behavior of Class C fly ashes during hydration. Marsh and Day [14] for example, compared the hydration of a Class C fly ash to a low lime fly ash, indicating that the combined CH [2] per unit weight of fly ash was substantially higher for the high lime one. Diamond [15] tested two high calcium fly ashes, the one with a surplus of crystalline free lime and the other with lime mainly incorporated in the glass phase of the ash. He concluded that the reaction is mainly located in the depolymerized fly ash glass. Later, Tishmack et al. [16] examined the potential influence of such ashes on ettringite formation. He deduced that the addition of high-lime fly ashes in cementitious systems favors the monosulfate phases rather than ettringite. Other authors [17,18] showed that the rate of heat development in blended cement incorporating different fly ashes increases with calcium content of fly ash. Finally, a very handy approach concerning Greek high-calcium fly ashes was attempted by Papadakis [19] who proposed a simplified scheme describing the reactions occurring when those ashes are added in hydrating Portland cement and applied mathematical expressions for the resulting products.

Notwithstanding the fact that hydration of fly ash/cement (FC) systems has been one of the subjects that attracted a lot of attention from numerous researchers, the challenge of associating its mechanisms with some of the characteristics inherent in the pozzolan remains of paramount importance. The present study aims at enlightening the hydration kinetics and microstructure development of cementitious systems that incorporate high-lime ashes by stressing out the role of one of their inborn parameters, reactive silica. Reactive silica is the main active constituent located in the glass phase of the fly ash [20] and the fraction of the total silica participating in the pozzolanic reactions [21]. In previous publications, the authors have pointed out the effect of active silica in the strength development of FC systems [22], while Antiohos et al. [23] proposed optimum lignite burning conditions for obtaining ashes rich in reactive silica. Lately, Papadakis et al. [24] after examining several supplementary cementing materials described a model for predicting the activity index and efficiency factor of a blended system by measuring the active silica that it contains.

The results presented herein are part of an ongoing research program that intends to correlate the active silica of high-lime fly ashes with the hydration kinetics of the corresponding fly ash/cement systems. The final target of this effort is to elucidate the mechanisms dominating during the hardening of the aforementioned systems, but also to designate if and to what extent active silica affects this procedure.

2. Strategy

2.1. Materials for experimentation

A rapid hardening Portland cement (CEM I 52.5R according to European Standard EN 197-1) and two high-calcium fly ashes (from Ptolemais region) were used in this study. For reaching the goals set during the investigation, the ashes were selected so as to diversify on their active silica content and silicon/calcium oxides ratio. In particular, the fly ash designated here as T_f is rich in active silica while the second fly ash (designated as T_d) possesses less active silica but more calcium oxide. The ashes were also selected on the basis of their similar free lime contents so as to highlight the role of active silica during hydration and especially on the depletion of calcium hydroxide occurring in the corresponding FC pastes. Finally, in an attempt to incapacitate the physical effect of fly ashes on their pozzolanic activity, they were both ground prior to use in a lab ball mill, so as to obtain ashes of similar fineness. Generally, Greek high-lime ashes are relatively fine materials as received, so a few minutes grinding was sufficient for accomplishing the target set. The particle size distribution of the ground ashes is shown in Fig. 1. The chemical compo-

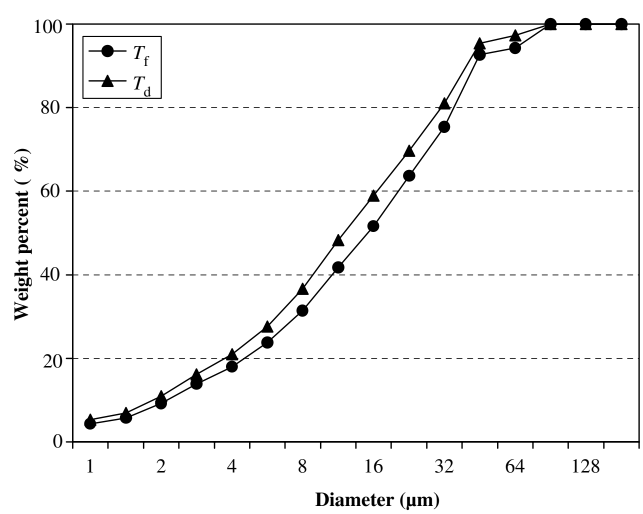

Fig. 1. Particle size distribution of ground fly ashes.

[2] Cement notation chemistry is used throughout this paper, where: H: H_2O, C: CaO, S: SiO_2, A: Al_2O_3, F: Fe_2O_3, $\overline{S}$: SO_3, CH: $Ca(OH)_2$.