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Reducing setting time of blended cement paste containing high-SO_3 fly ash (HSFA) using chemical/physical accelerators and by fly ash pre-washing

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ABSTRACT

Reducing the carbon footprint of the cement industry has become one of the main concerns of researchers in the field. This study explores different strategies to reduce the setting retardation effect of high-SO_3 fly ash (HSFA) on cement paste. The SO_3 phase was found to correspond to hannebachite ($CaSO_3 \cdot 0.5H_2O$). Chemical (calcium chloride), physical (fine limestone powder), and pre-washing strategies were investigated as means to reduce or eliminate the retardation. Each of these strategies showed some potential to decrease the retardation effect. A combination of fine limestone powder and HSFA pre-washing showed almost the same accelerating power as the calcium chloride, offering a good alternative when chloride incorporation is restricted. The retardation effect can be associated with a combined extension of the induction period and a depression of the initial silicate reactions of the clinker phases. A methodology to assess the hannebachite content based on a thermogravimetric analysis (TGA) technique is proposed, allowing a good alternative control approach for field conditions or for where X-ray (XRD or XRF) equipment is not readily available.

1. Introduction

Environmental concerns, such as energy consumption and CO_2 emission reductions, have taken special relevance in the construction industry during the last decades [1]. The use of supplementary cementitious materials (SCMs) as a means to reduce the cement content in concrete mixtures [2–4] and enhance the durability of the material and increase the service life of concrete structures [5] has become a topic of increasing interest among researchers.

Fly ash (FA), a by-product of coal combustion in thermal power plants, has been successfully used as an SCM for partial cement replacement [6–13]. The effects and contributions of FA on rheology and setting [9,14], phase assemblage [15,16], strength development [8,14,17], and durability [18–20] have been widely studied.

Some FAs may exhibit a strong retardation effect on the initial setting of cement paste, compromising their feasibility as a cement replacement material, although the interaction mechanism producing the retardation has not been described in detail. Fine limestone powder has been successfully used to accelerate the rate of reaction of cement clinker and partially offset the retardation effect [21], and its efficiency has been also studied in blended FA-limestone systems [15,16,22].

Environmental concerns about coal power plants' flue gas emissions have led to the widespread adoption of desulfurization units, high efficiency burners, and particulate material precipitators [23,24]. While these technologies have indeed exhibited a positive impact on the emissions level and their composition, they can also affect the composition of the FA generated, as some of the residues extracted from the flue gas may be precipitated along with the FA.

This project describes a systematic assessment of the feasibility of using FA that contains sulfur compounds that are combined with the solid phase during precipitation. Stage one is focused on the characterization of the sulfur-rich compounds and their interaction with cement phases at early (from mixing up to 7 d) and later ages. Among the effects at early ages, setting time retardation is a critical

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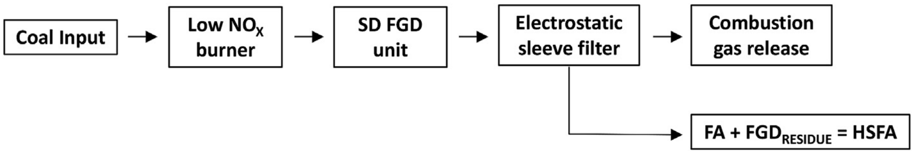

Fig. 1. Schematic diagram of the coal burning unit of the power plants from which the FA considered in this study was collected.

issue that needs to be addressed for a successful use of these FAs. The current study explores several alternatives to offset the observed retardation of initial setting time in cement paste mixtures incorporating these sulfur-rich FAs.

2. High-SO_3 fly ash (HSFA): semi-dry flue gas desulfurization (FGD) process

The pollutants that can be released as a result of combustion in a coal power plant are particulate matter, sulfur dioxide (SO_2), nitrogen oxides (NO_X), carbon monoxide (CO), carbon dioxide (CO_2), unburned hydrocarbons, dioxins, and furans [25]. Several technologies have been developed to reduce the amount of pollutants in the exhaust gas and therefore, comply with the increasingly stricter regulations concerning the environmental impact of these industries.

Regarding the twin power units from which the FA samples were collected for this study, two technological devices were installed to reduce pollutants in the exhaust gas (Fig. 1). First, the use of a low-NO_X coal burner leads to a reduced amount of this pollutant in the gas fraction, with the remaining compounds retained in the solid particles of the combustion flux. Following the combustion stage, a semi-dry flue gas desulfurization (SD-FGD) unit, consisting of a solution of calcium hydroxide ($Ca(OH)_2$), is injected as atomized fine droplets into the flux. Calcium hydroxide combines with the SO_2 in the flue gas, leading to the formation of calcium sulfite ($CaSO_3$) and water. In some plants, a forced oxidizing stage is included after the FGD to transform this calcium sulfite into gypsum ($CaSO_4 \cdot 2H_2O$), which has commercial value. Furthermore, a first sleeve filter is usually placed between the burner and the FGD unit to collect the FA before intermixing with the FGD by-products, especially when this FA is viewed as a valuable by-product itself. However, none of these stages are implemented in the power units considered in this study, consistent with commercial practice at many existing power plants. Because of the joint collection of FA and the by-products of the FGD unit, the obtained FA exhibits high levels of SO_3-rich compounds when it is collected from the power plant.

For the purpose of this study, high-SO_3 fly ash (HSFA) is defined as any FA material with a measured SO_3 content above the maximum of 5.0% prescribed by ASTM C618 [26]. The aim of the inclusion of this restriction in the standard was to limit the amount of gypsum in FA, which can lead to sulfate-related deleterious reactions in concrete [27,28]. However, for a dry or semi-dry FGD process, previous related studies have shown that the formed by-product solid sulfur-rich phase is mainly composed of calcium sulfite ($CaSO_3$) [23,29–31]. Thus, the stability (reactivity) of this compound and difference in its chemical behavior relative to its oxidized form (gypsum), needs to be understood to assess the feasibility of the utilization of HSFA in cement-based materials.

3. Materials and methods

Two different fly ash samples (named FA-1 and FA-2) were selected for this study. Both ashes were obtained from a power plant with the desulfurization process described in the previous section. Because of this FGD scheme, high amounts of sulfur-rich compounds are found in the ashes. The chemical and physical nature of these materials are addressed in the forthcoming sections.

Table 1
Chemical composition of OPC and HSFA samples (mass %) and phase composition of OPC.

	OPC	FA-1	FA-2	LS
SiO_2	21.59	37.42	34.57	–
Al_2O_3	3.82	23.79	21.15	–
Fe_2O_3	3.05	3.34	3.01	–
CaO	64.34	18.12	21.05	–
Na_2O	0.54	1.02	0.95	–
K_2O	0.46	0.44	0.51	–
MnO	0.06	0.08	0.07	–
TiO_2	0.33	1.02	0.87	–
MgO	1.84	1.58	0.99	–
P_2O_5	0.19	0.37	0.34	–
SO_3	2.87	8.78	10.39	–
LOI	1.60	3.47	4.62	–
SiO_2+ Al_2O_3+ Fe_2O_3	28.46	64.55	58.73	–
C_3S	68.51	–	–	–
C_2S	11.72	–	–	–
C_3A	6.58	–	–	–
C_4AF	9.83	–	–	–
Sp. gravity (g/cm^3)	3.122	2.117	2.274	2.750
SSA (m^2/g)	1.27	4.12	4.77	1.53

Type I ordinary Portland cement (OPC) was used for the entire experimental program. Chemical compositions of the OPC and HSFA samples were determined by X-ray fluorescence (XRF), and the results are shown in Table 1, along with the phase composition of the OPC as determined by quantitative X-ray diffraction (QXRD). Limestone (LS) powder (calcite) was obtained from a local supplier. The calcium carbonate ($CaCO_3$) content was determined by thermogravimetric analysis, measuring 98%. The specific gravity of the materials was determined using nitrogen pycnometry. The specific surface area (SSA) of the powder materials was determined by gas adsorption using the Brunauer-Emmett-Teller (BET) method, with a Micromeritics TriStar II[1] analyzer. Nitrogen (N_2) was used as the analysis gas.

For the XRF analysis, the fusion beads sample preparation method was used, using lithium tetraborate ($Li_2B_4O_7$) as the fluxing agent. By this method, the compounds in the ashes are oxidized and therefore, no distinction between different oxidation states can be obtained. This implies that the elemental quantification is obtained as an overall value of abundance in the sample, independent of the oxidation state of the actual compounds present. Both HSFA correspond to Class C FA according to the ASTM C618 classification scheme [26]. In addition, the same standard establishes a 5.0% limit for SO_3 content, which is well surpassed for both FA studied (thus corresponding to HSFA based on the definition presented before).

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[1] Certain commercial products are identified in this paper to specify the materials used and the procedures employed. In no case does such identification imply endorsement or recommendation by NIST, EPFL or Universidad del Desarrollo, nor does it indicate that the products are necessarily the best available for the purpose.