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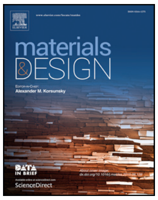

Mechanical and microstructural characterization of alkali sulfate activated high volume fly ash binders

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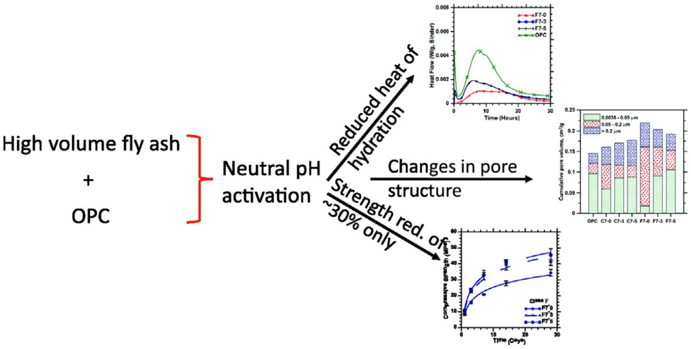
HIGHLIGHTS

- 70% reduction in clinker factor results in only a 30% reduction in strength.
- Neutral pH activation, avoids the drawbacks of caustic activators.
- Pore structure refinement through neutral pH activation.
- Hybrid reaction products quantified through spectroscopic techniques.
- Volumetric expansion lower than conventional binders.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents a detailed characterization of cementitious blends containing high volumes of fly ash, activated using pH-neutral alkali sulfates. It is shown that this methodology, while resulting in a clinker factor reduction of 70%, provides requisite early-age strengths while compromising the 28-day strengths by only 30–40% as compared to plain OPC mixtures. The early age heat release for blends containing Class F fly ash is reduced by about 50% as compared to the straight OPC mixture. The overall pore volume increases with sulfate addition for the Class C fly ash based binder while it decreases when Class F fly ash is used, indicating the beneficial effect of the sulfate activation process in conjunction with a low calcium fly ash. The differences in reaction product constitution are brought out using thermal analysis and FTIR spectroscopy. ^{29}Si NMR spectroscopy coupled with Gaussian spectral deconvolution on Class F fly ash-OPC blends provides valuable information on the changes in $Q^n(mAl)$ structures with addition of sodium sulfate, indicating the changes in the reaction products. From a durability perspective, Class F fly ash-based binders are found to be less susceptible to external or internal forms of sulfate attack as compared to plain OPC or the corresponding unactivated mixtures.

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1. Introduction

Development of methodologies to reduce the consumption of ordinary Portland cement (OPC) in concrete construction has been an area of active research. The use of high volumes of fly ash or slag as OPC replacement in conventional concretes, and the activation of these materials using alkaline agents has been explored in detail. The latter approach has resulted in the development of a distinct class of binder materials that are OPC-free. The synthesis of these binders that typically employ a combination of caustic activators and elevated temperature curing, their fundamentally different chemistry, and properties have been extensively reported [1–6]. However, these approaches are not without significant drawbacks that impede their adoption by the industry. For instance, the use of high volumes of fly ash in OPC-based concretes result in delayed setting and reduced early-age mechanical properties. On the other hand, alkaline activation of fly ash requires the use of highly alkaline activators including alkali silicates and/or hydroxides [7–10], thereby posing issues with storage and handling. Such issues limit the sustainability-related benefits offered by these systems. Studies have attempted to alleviate some of the concerns associated with alkali activated systems through the use of powder activators, and some success has been obtained [11–13].

The use of neutral salts such as sulfates and carbonates of sodium and potassium as activators of fly ash in high volume fly ash-based concretes is a potential option for sustainable concretes [1,14–19]. Rather than relying on caustic alkalis to create a binder with fly ash as the sole source material, this approach adopts a combination of high volumes of fly ash along with OPC and the neutral salt. This study investigates the influence of sodium sulfate addition to high volume fly ash-OPC blends from the viewpoints of reaction kinetics, reaction product formation and chemistry, and the resultant properties. Emphasis is given to the understanding of the influence of calcium in these systems by using both Class F and C fly ashes as starting materials. The use of gypsum (calcium sulfate) as an activating agent was also considered, but the lack of alkalinity provided to the system resulted in less effective activation, especially for Class F fly ash binders. Thus, activation by sodium sulfate is only reported.

2. Experimental program

2.1. Materials and mixture proportioning

The source materials used in this study are one Class F and C fly ash (FFA and CFA respectively), each conforming to ASTM C 618 [20], and OPC conforming to ASTM C 150. The chemical compositions of the source materials are shown in Table 1.

Fig. 1(a) shows the particle size distributions (PSD) of the OPC and Class C and F fly ashes used in this study, determined using laser diffraction. It is seen that class C fly ash is the finest of the three powders and has the smallest median particle size (d_{50}) followed by OPC and class F fly ash. Fig. 1(b) shows the x-ray diffraction (XRD) spectra of the source materials. Class F fly ash consists of a halo in the 2θ range of 20° to 30°, while Class C fly ash has a more pronounced halo in the 25° to 35° range, indicating increased amorphous content in the material.

The mass replacement level of OPC by fly ash was 70% (corresponding to replacement levels of ~75% by volume). The activating agent used was reagent grade sodium sulfate powder. The activator was proportioned by mass of the binder, at 3% or 5%. A water-to-powder ratio (w/p) in the range of 0.35 to 0.45 (mass-based) demonstrated sufficient workability for both the OPC-fly ash (Class C and F) binder systems, and hence a value of 0.40 is used in this study. For the compressive strength tests, mortars were prepared with a sand volume fraction of 50%. The mortars were stored in the molds at 23 ± 1 °C for 24 h after which they were removed and stored in a moist chamber (23 ± 1 °C, >98% RH) until the respective testing durations. The paste specimens for characterization studies were stored in sealed conditions until the age of testing.

Table 1
Chemical composition and physical properties of OPC, Class C and F fly ash.

Phase (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	LOI	S.G
OPC	21.0	3.8	3.5	63.7	1.8	3.0	0.1	2.0	3.15
Class C FA	35.5	19.6	5.9	23.0	4.0	2.8	–	0.8	2.54
Class F FA	59.3	22.9	4.6	5.31	–	0.4	1.4	0.6	2.34

2.2. Test methods

Isothermal calorimetry experiments were carried out for 72 h at a temperature of 25 °C in accordance with ASTM C 1679. The activator powder was added to the binder mixture. Water was then added to the binder (OPC + fly ash) and the mixture was placed in the calorimeter chamber. The time elapsed between mixing of the paste and placing it in the calorimeter was not >2 min. The compressive strengths of the mortars were determined in accordance with ASTM C 109. The strengths of the three replicate 50 mm cube specimens were determined at ages of 1, 3, 7, 14 and 28 days of moist curing. Vicat test was performed in accordance with ASTM C 191 to determine the influence of the activator on the initial and final setting times of the paste.

The pore structure of both OPC and the Class C and F fly ash-sulfate activated pastes were evaluated using mercury intrusion porosimetry (MIP). This test was performed by initially degassing the sample under vacuum and filling with mercury under low-pressure of 345 kPa, followed by high pressure (up to 414 MPa) intrusion of mercury. The surface tension and contact angle used for the analysis were 0.485 N/m and 130° respectively. The pores in the material are assumed to be cylindrical in shape in order to apply the Washburn equation for size determination.

Thermo-gravimetric analysis (TGA) was performed using a Perkin Elmer simultaneous thermal analyzer (STA 6000). TGA was performed on samples at ages of 1, 3, 14 and 28 days. The thermal analysis procedure used was as follows: the sample was heated to 50 °C and then held for 1 min, and then heated to 995 °C at a rate of 15 °C/min. The amount of CH (in %) in the samples were determined from the mass loss (%) by multiplying it by the ratio of molecular weights of CH to that of water.

X-Ray diffraction was carried out using a Siemens D-5000 diffractometer in a θ-θ configuration using Cu-Kα radiation ($\lambda = 1.54$ Å). The samples were scanned on a rotating stage between 10° and 60° (2θ) in a continuous mode with a step scan of 0.02° and step rate of 0.5/second. High-Score Xpert Analysis software was used for phase identification.

Multiple spectroscopic techniques were applied in order to characterize and quantify the reaction product phases formed in these systems. Fourier Transform Infrared (FTIR) Spectroscopy was performed on the powdered samples after 1, 3, 14 and 28 days of hydration. A Mattson Genesis FTIR spectroscope configured with an Attenuated Total Reflectance (ATR) attachment was used to obtain the spectra in the wavenumber range of 700 cm^{-1} to 4000 cm^{-1}. ^{29}Si Magic Angle Spinning (MAS) NMR spectroscopy was carried out on selected Class F fly ash-OPC blend pastes after 28 days of hydration using a Varian Solids NMR spectrometer. The resonance frequency used for ^{29}Si NMR spectroscopy was 59.7 MHz with a spinning rate of 10 kHz. The spectra were obtained after irradiating the samples with a π/2 pulse. Deconvolution of the NMR data was performed using a Gaussian line shape function in the −60 to −120 ppm range. The ^{29}Si resonances were analyzed using the standard Q^n(mAl) Classification, where n denotes the number of bridging oxygens per SiO_4 tetrahedron, and m denotes the number of neighboring AlO_4 tetrahedra. Class C fly ash blends were not investigated using NMR spectroscopy because of the signal interference due to an increased iron content.