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# Effects of sulfate on cement mortar with hybrid pozzolan substitution

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## ABSTRACT

Sulfate is one of the most important chemical risks which affect the durability of concrete and reinforced concrete structures. Therefore, this study investigates the effects of sulfate on blended cement mortars. In this paper, cement mortar specimens were prepared with the substitution of CEM I 42.5 R cement with Fly ash + Bottom ash + Blast-furnace Slag at the ratios of 5%, 10%, 15%, and 20% along with a control specimen without additives. These prepared cement mortar specimens were then cured for 2, 7, 28, 90, 180, and 360 days either in potable water or 10% sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) solution. Cement paste specimens were subjected to the initial setting, final setting, and volumetric expansion tests in accordance with the TS EN 196-3 standard. Cured for 2, 7, 28, 90, 180, and 360 days, cement mortars were subjected to compressive strength tests as per the TS EN 196-1 standard while length change tests were conducted as per the ASTM C 1012 standard.

It was found that the compressive strength of cement mortars blended with 5% Fly ash + Bottom ash + Blast-furnace Slag cured in sodium sulfate for 360 days was approximately 2% higher than that of the cement mortar without additives. The length change of specimens obtained from cured in sodium sulfate solution shows best results in higher additive ratio. These all length changes ratio are greater than 0.087% ratio which is maximum length change expansion in potable water. This study suggests that 15% and 20% additive ratios are effective in reducing unfavorable effects of sulfate.

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## 1. Introduction

The use of fine-grain mineral additives may have an impact on a number of properties of fresh and cured concrete depending on the amount and properties of the materials used. One or more goals can be reached with the use of mineral additives in fresh concrete such as improving the workability, reducing bleeding or segregation, decreasing hydration temperature, reducing alkali-silica reaction, improving water tightness, improving strength, improving resistance to sulfate, producing cost-effective concrete, etc. [1,2]. Usage of blast furnace slag and fly ash enhances the mechanical qualities of the concrete [3–5]. It has been observed that compressive strength decreases when the quantity of fly ash is increased and the quantity of cement is decreased [6,7].

Recently, durability of concrete and its resistance to aggressive environments have been receiving interest. Sulfate is the origin of various significant problems in concrete operations. Magnesium sulfate and sodium sulfate are among the most devastating min-

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eral salts (alkalis) which are dissolved and available in the ground and underground waters commonly in contact with concrete. Bonding with the calcium aluminates hydrated in the cement, sulfates form expanding crystals. Increasing in time, such an expansion is reported by many authors to lead to cracks in concrete and crumbling [8–13].

Several studies were conducted with the purpose to explore the effects of using mineral additives. Sulfate resistance of pozzolans was reported it was found that concrete produced with pozzolans performs well [14–18]. Monteiro et al., in their study on the effects of sulfate on concrete, suggested that there are critical thresholds for concrete's resistance to sulfate attack and reported that concrete did not suffer any damage over the 40 years of sulfate impact when the amount of C<sub>3</sub>A was lower than 8% and the water/cement ratio was lower than 0.45. Authors also found that the use of 25% and 45% fly ash as a substitute for cement decreased the level of expansion [19]. In their study on the properties of fly ash, Garg et al. suggested that fly ashes have different impacts depending on the composition of the coal used, the burning type, burning temperature, ash collection method used, and oxidation conditions [20]. In their research on the effects of the fineness of the fly ash used, Monzo et al. noted that the fineness of fly ash has a significant effect on pozzolanic reactions, that fly ash can be sieved or

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ground in order to increase its fineness, and that large and small particles can be separated using air. Authors also suggested that pozzolanic reaction starts at the surface of the fly ash grain and that increased fineness of fly ash increases the pozzolanic reaction. They have also noted that fineness of the fly ash is important in improving the surface properties of the interface between aggregate and cement paste [21]. Having studied the long-term effects of fly ash, Chalee et al. explored the effects of the use of fly ash on concrete under high humidity, temperature and sea conditions at the end of 7 years. It was observed that increased substitution ratio with fly ash reduced chloride permeability and pitting corrosion. No rust formation was observed at the end of 7 years on the fittings embedded 5 cm into the concrete of 25-50% fly ash substitution and 0.6 water/binder ratio. Authors reported better results obtained from 0.45 water/binder ratio [22]. Zhuqing et al. reported that the use of fly ash in concrete affects the pore structure of concrete which is suggested as one of the most important factors in the durability of concrete [23]. Kurama et al., in their investigation aimed at defining and assessing the usability of bottom ash in concrete, substituted Portland cement up to 25% with bottom ash and bottom ash was subjected to grinding, separation and electrostatic separation in order to reduce the amount of unburned carbon. The results of the study showed that substitution of Portland cement up to 10% with bottom ash improves the mechanical properties of concrete and, therefore, this material is suitable to be used in concrete [24]. Jaturapitakkul et al., in their research on the use of bottom ash, have reduced the size and porosity of bottom ash after grinding and used the material obtained for their tests. The experimental study showed that ground bottom ash can be used as pozzolanic material [25]. Lopez et al. investigated the effects of blastfurnace slag in cement mortars and found that slag with finer grains acts favorably in the face of sulfate effect which in turn offered the minimum expansion ratio [26]. Having explored the effects of blast-furnace slag on the durability of concrete, Lukowski et al. reported better durability performance obtained from cement mortars modified with blast-furnace slag when compared to the control specimens [27]. Sadok et al. investigated the effects of blast-furnace slag use and reported that use of slag reduces porosity and water absorption. Moreover, authors reported lower chloride diffusion for 50% blast-furnace slag substitution [28].

The use of mineral additives as concrete components finds itself an important role in today's engineering activities with respect to their impact on the environment and cost-effective concrete manufacturing. The use of such additives reduces carbon dioxide ( $CO_2$ ) emissions and energy consumption which in turn reduces the adverse impact of cement production on nature while decreasing concrete costs. Nevertheless, studies must focus on improving the durability of concrete and explore waste materials which can be used as mineral additives. The purpose of this study is to study the effect of sulfate on cement mortar with hybrid pozzolan substitution.

## 2. Materials and methods

## 2.1. Materials

#### 2.1.1. Cement

Portland cement type CEM I 42.5 R which complies with TS 197-1 was used in this study. Physical and chemical properties of the cement used are shown in Table 2.1 [29].

## 2.1.2. CEN reference sand

Sand used in this study was CEN reference sand mentioned in the TS 196-1 standard [30].

#### Table 2.1

Chemical and physical properties of CEM I 42.5 R cement.

| Chemical composition (%)                            | CEM I 42.5 R |
|---|--------------|
| CaO   | 67.46        |
| SiO <sub>2</sub>                                    | 13.48        |
| Al <sub>2</sub> O <sub>3</sub>                      | 3.69         |
| Fe <sub>2</sub> O <sub>3</sub>                      | 7.78         |
| MgO   | 1.29         |
| Na <sub>2</sub> O                                   | 0.36         |
| K <sub>2</sub> O                                    | 0.98         |
| SO <sub>3</sub>                                     | 4.82         |
| Physical properties                                 |              |
| Specific weight (g/cm3)                             | 3.18         |
| Specific surface area (Blaine) (cm <sup>2</sup> /g) | 3352         |
| Loss on Ignition (%)                                | 1.98         |
| Specific surface area (Blaine) (cm <sup>2</sup> /g) | 3352         |

#### 2.1.3. Bottom ash, blast-furnace slag and fly ash

Bottom ash used in this study was calcined at 900 °C in order to minimize the carbon content of the ash. The fineness of the bottom ash used was ensured using a ring grinder. Table 2.2 shows the chemical analysis results and Blaine fineness of the bottom ash and blast-furnace slag.

#### 2.1.4. Water

Two types of curing liquids were used in this study. First was potable water (PW) and the second was  $100 \text{ g/l} \text{ Na}_2\text{SO}_4$  solution (SS) prepared as per the ASTM C 1012 standard [31].

#### 2.2. Method

#### 2.2.1. Mixture proportions

The proportions of all the mixture components are given in shown in Table 2.3. Three materials applied in equal proportions.

Mortar specimens were prepared as per the ASTM C 1012 standard for length change measurements and as per the TS EN 196-1 standard for compression tests [30,31].

## 2.2.2. Setting time and volumetric expansion

FA + BA + BFS was substituted for cement at the ratios of 0%, 5%, 10%, 15%, 20%. Setting time and volumetric expansion calculations of cement pastes with different additive ratios were performed in accordance with TS-EN 196-3 Standard [32], while flexural and compressive strength tests were performed in accordance with TS-EN 196-1 Standard for 7th, 28th, 90th, 180th, and 360th day [30].

#### 2.2.3. Compressive strength test

Compressive strength test was performed as per the provisions of TS EN 196-1 standard [30]. Prepared in the size of  $40 \times 40 \times 1$  60 mm six prismatic specimens were then exposed to potable

## Table 2.2

Chemical composition of bottom ash, blast-furnace slag and fly ash.

| Chemical Composition (%)                               | Bottom<br>Ash | Blast-Furnace<br>Slag | Fly<br>Ash |
|--|---------------|-----------------------|------------|
| SiO <sub>2</sub>                                       | 37.45         | 37.17                 | 45.37      |
| Al <sub>2</sub> O <sub>3</sub>                         | 9.03          | 9.67                  | 11.16      |
| Fe <sub>2</sub> O <sub>3</sub>                         | 8.02          | 0.99                  | 7.40       |
| CaO  | 18.08         | 39.63                 | 14.15      |
| MgO  | 5.79          | 5.40                  | 4.69       |
| Na <sub>2</sub> O                                      | 1.67          | 0.28                  | 2.07       |
| P <sub>2</sub> O <sub>5</sub>                          | 11.75         | 3.64                  | 8.28       |
| K <sub>2</sub> O                                       | 1.88          | 1.25                  | 4.19       |
| SO <sub>3</sub>  | 6.29          | 1.89                  | 2.64       |
| Specific surface area (Blaine)<br>(cm <sup>2</sup> /g) | 4350          | 3750                  | 2200       |
| Loss on ignition                                       | 2.82          | 1.07                  | 1.48       |

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