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# External sulfate attack on alkali-activated fly ash-blast furnace slag composite

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## HIGHLIGHTS

- External sulfate attack on alkali-activated binder (AAB) and CEM II was tested.
- Strength Loss and Strength Gain Index are used to evaluate resistance of binders.
- Both AAB based on fly ash-blast furnace slag and CEM II showed high resistance.
- Leaching of Si and decrease of Si/Al atomic ratio of AAB matrix was identified.
- Correlation between AAB microstructural and strength changes was established.

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## ABSTRACT

Reliable durability testing of alkali-activated binders, which might serve as a basis for the prediction of long-term field performance, is one of the main challenges towards broader commercial applications of AAB. This study investigated the influence of 5% $Na_2SO_4$ solution on mechanical and microstructural properties of alkali-activated binder based on fly ash and blast furnace slag (FA-BFS) composite. The influence of $Na_2SO_4$ solution was investigated during the period of 180 days and estimated by comparison with the reference samples simultaneously cured in a humid chamber and with the benchmark material CEM II. Strength, leaching (ICP-OES), pH, XRD, ATR-FTIR, and SEM/EDS analyses were performed. The Strength Loss Index was higher than 1 throughout the whole period of testing indicating strength increase during the exposure to sulfate attack rather than the loss of strength. Slower compressive strength development of the samples exposed to the sulfate solution in comparison with the reference samples was also observed. The exposure of alkali-activated binder to the sulfate solution led to a decrease in the Si/Al atomic ratio of binder matrix due to the leaching of Si, causing slower compressive strength development at the same time.

The accelerated testing method used confirmed high resistance both of alkali-activated binder based on fly ash-blast furnace slag and CEM II to external sulfate attack and at the same time confirmed its ability to discriminate the resistance of different type of binders to sulfate aggressive environment.



## 1. Introduction

Alkali-activated binders as an environmentally-friendly alternative to traditional Portland cement-based binders represent extremely rapidly advancing scientific-research area [1–4]. In recent years synthesis of alkali-activated fly ash-blast furnace slag (FA-BFS) composite has become highly attractive since such composites are showing some particularly attractive engineering properties. Besides involving the use of different wastes, joint activation of FA and BFS can compensate some of the disadvantages of alkali-activated sole materials, such as low strength [5–8], improper setting time [9,10] and high drying shrinkage [11–13].

The resistance of the material to the impact of aggressive environments (or its durability) is of utmost importance for commercial application. For concrete based on Portland cement sulfate containing solutions are amongst the most aggressive corrosive agents. The adverse effects of sulfate ions present in soils, natural or waste waters often cause deterioration of structure stability of concrete, followed by strength loss, expansion, spalling, cracking and finally disintegration of concrete elements [14–16].

CEN/TR 15697 report [17], prepared by Technical Committee CEN/TC 51 "Cement and building limes", provided a state of the

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art review of the international research literature dealing with testing/assessing performance of cements and related binders during external sulfate attack, whereby the development of a prescriptive EN for sulfate resisting cements has been complicated by national differences in the types of cement that are recognized to have sulfate resisting properties. Linear expansion, flexural and compressive strength, change in mass, appearance, and dynamic modulus are recognized as the main performance indicators for cement sulfate resistance testing, whereby strength testing is the most reliable method and pass/fail criteria should be based on the relative strength of specimens stored in the sulfate solution and in limewater [17]. On the other hand, RILEM state of the art report TC 211-PAE (Performance of Cement-Based Materials in Aggressive Aqueous Environments) [18] proposes different measures for improving the testing procedures for sulfate resistance. However, the proposed measures are highly descriptive and no particular method for sulfate resistance testing was recommended. Furthermore, RILEM Technical Committee 251-SRT (Sulfate resistance testing) [19] was created in 2013 with primary aim to provide recommendations regarding appropriate test methodologies and protocols for the analysis of sulfate resistance. As a starting point it was emphasized that sulfate-related phenomena are complex (they couple physics, chemistry and mechanics) and existing testing procedures related to external sulfate attack are not appropriate (poor ability to discriminate cements, insufficient accuracy, etc.). The need to develop other than expansion approach was also recognized. Finally, RILEM state of the art report TC 224-AAM (Alkali activated materials) [20] suggested that in general, the sulfate resistance testing methods to be used should be close to those applied for Portland cement systems, as this will help to create acceptance for the durability properties of alkali activated materials.

Recent review of the durability of fly ash/slag-based AAMs confirmed that the lack of appropriate protocols, specifications, and standards for a uniform durability testing method induced some divergences and even contradictions of some published results, making any eventual comparison between them more difficult [21]. Despite different testing protocols are being used, previous investigations have shown that binders based on alkali-activated FA or BFS generally exhibit similar or even better resistance to the influence of sulfate solutions with respect to the Portland cement [22–27]. On the other hand there are only a few studies regarding the influence of $Na_2SO_4$ solution on the structure and properties of alkali-activated FA-BFS composites, whereby paste microstructural changes [28], mortar [29], and concrete properties [30,31] were tested. Given the complexity of the reaction products of alkali-activated FA-BFS composites, as well as a large number of influential parameters (such as properties of industrial wastes used, different testing protocols - the synthesis and curing conditions applied, no clear pass/fail criteria, etc.), it is obvious that the existing data are rather limited. Therefore, the relationship between the structure and mechanical properties of these materials when exposed to sulfates still needs to be elucidated.

In this paper the external sulfate attack on alkali-activated fly ash-blast furnace slag composite was analyzed by using the accelerated (short-term) testing procedure. In order to generate reliable AAM durability testing results in the laboratory, which can be used for the prediction of long-term field performance, it is essential to link the microstructural changes and phase evolution to the strength testing. Therefore, the assessment of external sulfate attack is based on the strength loss and microstructural changes of alkali-activated FA-BFS composite. This testing procedure already confirmed its ability to discriminate the resistance of different type of binders to sulfate aggressive environment, such as alkali-activated BFS and Portland-slag cement [27].

Since there are no accepted pass/fail criteria for the short-term experiments, commercially available Portland-composite cement blended with FA and BFS (CEM II) was used as a benchmark material and tested under the same experimental conditions. This type of Portland cement is more appropriate as a benchmark material since ordinary Portland cement (CEM I) is well-known as highly susceptible to the external sulfate attack [32].

## 2. Materials and methods

### *2.1. Materials*

In this study, the following materials were used:

1. Fly ash (FA) from thermal power plant "Morava" – Svilajnac, Serbia.
2. Blast furnace slag (BFS) from "Zelezara Smederevo" d.o.o. – Smederevo, Serbia.
3. CEM II/B-M 42.5N – Portland-composite cement blended with FA and BFS from cement plant "Holcim Srbija", d.o.o. – Novi Popovac, Serbia.

Chemical composition of the initial materials (FA, BFS, and CEM II) is given in Table 1. Based on the chemical composition and according to the ASTM C618 standard [33], FA sample tested within this study can be classified as Class F.

Sodium silicate solution was used as an alkaline activator ("Galenika-Magmas il" d.o.o., Serbia; 26.50% $SiO_2$, 13.60% $Na_2O$). Sodium silicate modulus ($SiO_2/Na_2O$ mass ratio) was modified by adding solid NaOH (VWR, Germany, p.a. 99%).

Sulfate solution was prepared using $Na_2SO_4$ of 99% purity (Superlab, Serbia).

### *2.2. Synthesis of alkali-activated binder*

#### *2.2.1. Preparation of mortar and paste samples*

The sulfate resistance of AAMs is not only related to the sulfate concentration and type of cations present in the solution, but also depends on the binder gel composition [34]. Based on the results of our previous investigation [13] the optimal FA-BFS mixture and synthesis conditions for obtaining optimal gel composition were chosen. Therefore, FA-BFS composite was prepared by mixing equal mass of FA (50%) and BFS (50%) and then the composite was alkali-activated with sodium silicate solution of modulus 1.5. The concentration of the activator was 10% $Na_2O$ with respect to the FA-BFS composite total mass.

Mortars of alkali-activated FA-BFS composite were prepared by adding the activator solution of specified concentration to water and then mixing the solution with the composite and standard sand [35]. FA-BFS: sand ratio was 1: 3. Optimum amount of water for mortar samples, required to obtain similar workability as the benchmark material (CEM II), was determined by the flow table test (the mortar flow was 125 ± 5 mm). Water/binder (w/b) ratio was 0.39 (water in w/b ratio was calculated as water from sodium silicate solution + water added for appropriate consistency; binder in w/b ratio represents the sum of the FA-BFS composite and solid part of the activator). Mortars were homogenized in automatic mixer for 3 min and cast into three mortar prisms (40 mm × 40 mm × 160 mm) on vibrating table. Mortar of Portland-composite cement (CEM II) was prepared in accordance with the Serbian standard SRPS EN 196–1 (2008) [35], which is in compliance with the Europian EN 196–1 standard. The mix proportion of alkali-activated FA-BFS and CEM II mortars is given in Table 2.

Pastes of alkali-activated FA-BFS composite were prepared by mixing the FA-BFS composite with the alkali activator solution (in the same proportion as in the preparation of mortars) and water. W/b ratio of alkali-activated FA-BFS paste was 0.34. Dimensions of paste samples were 25 mm × 25 mm × 30 mm. For XRD and ATR-FTIR analyses, paste samples were crushed and milled in isopropyl alcohol for 60 min in order to stop further alkali activation reaction. After the milling, the samples were filtered, rinsed with acetone, dried in the laboratory oven at 50 °C

**Table 1**
Chemical composition of initial materials (% m/m).

| Initial mater. | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | S | $Na_2O$ | $K_2O$ | LOI at 1000 °C | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| FA | 55.23 | 21.43 | 7.42 | 7.94 | 2.61 | 0.81 | – | – | – | 1.66 | 97.10 |
| BFS | 37.50 | 7.27 | 0.73 | 38.48 | 10.86 | 0.39 | 1.51 | 0.54 | 0.26 | 2.13 | 99.97 |
| CEM II | 21.33 | 5.49 | 2.62 | 58.67 | 3.01 | 2.27 | – | 0.45 | 0.60 | 4.41 | 98.85 |