# Shrinkage and strength development of alkali-activated fly ash-slag binary cements

Maryam Hojati *, Aleksandra Radlińska

*Department of Civil and Environmental Engineering, The Pennsylvania State University, 3127 Research Drive, State College, PA 16801, United States*

## HIGHLIGHTS

- Shrinkage characteristics of different alkali-activated fly ash-slag binders were evaluated.
- Utilization of higher-pH sodium silicate activator mitigated autogenous and drying shrinkage.
- Strength development and setting time properties of different binary binders were measured.
- Addition of larger amount of slag to binary binder led to a quicker set, higher strength and stiffness.
- Activating by higher-pH sodium silicate solution resulted in a slower setting, higher strength and stiffer matrix.

## ARTICLE INFO

## ABSTRACT

This paper evaluates the effect of fly ash and slag proportions and the type of activating solution on shrinkage and strength development of alkali-activated binary fly ash-slag mixtures (mortar and paste), cured at room temperature. Three different volumetric ratios of slag/fly ash were considered: 10%, 15%, and 20%. Two activators with different pH and modulus, n = $(SiO_2/Na_2O)_{mol}$ were utilized. The liquid to solid volume ratio of all binders was maintained at 0.75. The results showed that while the addition of slag significantly shortens the time of setting (up to 178 min), and increases the compressive strength (up to 93%) and bulk modulus (up to 43%), it also results in higher autogenous shrinkage, but smaller mass loss during drying. Measured drying shrinkage of mixtures with various slag contents was similar, likely due to counteracting effects of binder stiffness and degree of saturation. Fly ash-slag binders activated at higher pH exhibited larger chemical shrinkage, but lower autogenous (up to 21%) and drying shrinkage (up to 47%) magnitude.

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## 1. Introduction

Environmental concerns related to the production of ordinary Portland cement (OPC) [1,2] have encouraged the researchers to explore alternative cementitious materials. Among the available alternatives, alkali-activated cements (AACs) have received much attention, as they can provide a 100% substitute for OPC, with notably lower greenhouse gas emissions [3,4]. AACs are produced by dissolution-precipitation reactions of a solid precursor (e.g., [calcium] aluminosilicate materials such as fly ash and/or blast furnace slag (BFS)) in contact with an alkaline activator (e.g., an aqueous solution of alkali hydroxide and/or silicate) [5]. With a proper formulation and curing conditions, AACs can potentially offer similar or superior material properties in comparison to OPC binders [6].

However, there are some drawbacks related to AAC, including diminishing sources of fly ash and slag and concerns related to safe handling of chemical activator. According to the dermal irritation data [7], a sodium silicate solution with high modulus (n = $(SiO_2/Na_2O)_{mol}$) but low concentration could lessen the concerns regarding the safe handling. On the other hand, as the fresh OPC is a caustic substance, it also has the risk of developing skin problems for workers [8,9].

Based on the composition and calcium content of the solid precursor, three types of AACs can be defined: high-calcium, low calcium and intermediate calcium alkali-activated binders. According to previous studies [10], high calcium AACs are binders with Ca/(Si + Al) ratio of about 1, which is commonly a result of an alkali activation of BFS. The main reaction product in this group is a calcium-aluminosilicate-hydrate, or C-A-S-H type gel with a disordered tobermorite-like structure [10–13]. The second, low calcium group is produced by alkali activation of aluminosilicate materials with

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* Corresponding author.
 *E-mail address:* hojati.maryam@gmail.com (M. Hojati).

low calcium contents (e.g., metakaolin or class F fly ash). The major reaction product in these binders is a structurally disordered three-dimensional sodium aluminosilicate-hydrate (referred to as N–A–S–H or geopolymer) with the zeolite-like structure [10,14–16]. These binders often require heat or steam curing (e.g., at 60 °C) to facilitate the dissolution of fly ash or metakaolin [17,18]. It was demonstrated that the presence of alkali-metal and alkali-earth cations as a network modifier could influence the reactivity of glassy phase in aluminosilicate source materials [10]. As such, the calcium content in the initial precursor or in any form of additives has an indispensable role in the properties of N–A–S–H gels. The intermediate calcium AACs could be formed by activation of class C fly ash (which has higher calcium content compared to class F) or blends of high-calcium compounds such as BFS with class F-fly ash or metakaolin. The reaction products in this group is highly dependent on the calcium content, but it is believed to be an inter-mix of C-A-S-H and N-A-S-H, referred as N-C-A-S-H, at the early age [19,20].

The microstructural evolution of alkali-activated fly ash-slag (AAFS) was investigated extensively over the past few years [19–25]. The studies looked into how different parameters, such as fly ash to slag ratio, type of employed fly ash (which could influence the chemical composition, reactivity and the morphology of fly ash), temperature and the properties of activating solution (including pH and activator modulus) influence the final product of binary AAFS binders [21–26]. Ismail et al. [23] found that the hydration product of AAFS is a blend of N-C-A-S-H gel incorporated into the N-A-S-H gel formed by fly ash activation [23]. Lee et al. [24] reported that the hybrid product of blended system (i.e. N-C-A-S-H) has a close chemical composition as C-A-S-H type gel, but with different silicate structures. Ye and Radlińska [27] studied the interaction mechanisms and the phase assemblage of AAFS. Their results indicated that the microstructure of AAFS is largely influenced by fly ash to slag ratio and activator type, and that greater quantity of slag or sodium silicate both result in denser microstructure. Type of fly ash could also be an effective feature on the properties of binary system; however, Messina et al [26] showed that even the mechanical properties of alkali activated weathered fly ash could be improved by the addition of BFS. As mentioned before, low calcium AACs often require heat curing to achieve appropriate strength development [17,18,28]. It has been reported that alkali-activated class F fly ash (AAFA) binders can reach over 60 MPa compressive strength after curing at elevated temperature (65 to 80 °C) for 24 h [29,30]. However, heat curing process makes AAFA more appropriate for the precast industry, where it is feasible to provide an elevated temperature curing [31,32]. Heat curing also requires additional energy and results in added cost. Alternatively, blending a small dose of calcium (e.g., 10% of BFS or OPC) to AAFA could result in binders that develop desirable mechanical properties even when cured at ambient temperature [33]. Mechanical properties of binary binders cured at room temperature (compared to similar AAFA systems), are improved when C-S-H and N-A-S-H gels are incorporated into the final product [10,19,34]. Past research [35] indicated that mechanical strength of these hybrid systems could reach over 100 MPa after 28 days curing at room temperature. Lee and Lee [31] studied the effect of activating solution and slag addition on the setting characteristics of AAFS and found that increasing slag content, sodium silicate and sodium hydroxide concentrations could shorten the setting time of AAFS pastes. Besides strength development, durability of AACs also plays an important role in their performance in infrastructure components. For example, shrinkage and the resulting cracking can affect the service-life of any concrete binder. Researchers have found that alkali-activated slag (AAS) exhibits significantly higher drying shrinkage than OPC [36–38]. At the same time, drying shrinkage of AAFA pastes cured at high temperatures was shown to be lower

than or similar to OPC pastes [39,40]. The shrinkage performance of calcium-added AAFA remains poorly understood; with only few studies reporting shrinkage of AAFS cured at room temperature [41–43]. For AAFS, the drying shrinkage has been found to be generally larger than that of OPC. It was reported that the drying shrinkage of the hybrid binders increased with higher aqueous silica contents in the activator [41–43]. There is a disagreement on the effect of slag versus fly ash proportions on shrinkage of the hybrid binders. While some studies [41,42] reported that drying shrinkage increased with higher slag contents, another study [43] showed that higher slag content led to a lower drying shrinkage. Lee et al. [41] showed that higher slag and soluble silica contents led to larger chemical, autogenous, and drying shrinkage. They also highlighted the need for further research to characterize the shrinkage of these hybrid binders.

The objective of this paper is to experimentally investigate the shrinkage (chemical, autogenous, and drying), setting, and mechanical properties development in AAFS binders, where a small amount of slag (10%, 15% and 20% by volume) is added to fly ash, to improve the setting and mechanical properties of binders cured at room temperatures. In addition, the effect of activator composition on shrinkage is studied.

## 2. Experimental procedures

### 2.1. Materials

The paste and mortar samples in this study were prepared by alkali activation of a blend of class F fly ash [44], meeting requirements of ASTM C 618-15 [45] (obtained from First Energy, Hatfield's Ferry power plant, Masontown, Pennsylvania, USA) and grade 120 ground granulated blast furnace slag [36], meeting ASTM C989M-14 [46] requirements (provided by Lehigh Hanson Slag Cement). The composition and physical properties of the raw materials are shown in Table 1. Semi-quantitative X-ray diffraction (XRD) showed that fly ash consisted mainly of amorphous phases (>70% mass) and minerals, including quartz, hematite, and mullite. The slag mostly included an amorphous phase with trace amounts of crystalline gypsum ($CaSO_4$) and alite ($Ca_3SiO_5$) [21]. The sand used in the mortar preparation was a manufactured siliceous sand meeting ASTM C33M-13 requirements with the bulk dry specific gravity of 2.70 and absorption of 0.46%. Table 2 displays more information about particle size distribution of fly ash, slag and sand.

### 2.2. Mixture Design and specimen preparation

Six different AAFS binder mixtures were designed and tested in this work. All pastes and mortars were mixed following ASTM C 305-13 [47], where a blend of fly ash and slag powders was added into an aqueous activator. The cementitious (powder) materials with three different volumetric slag-to-fly ash ratios (S/FA = 10%, 15% or 20%) were mixed using two activators with different modulus (n = $(SiO_2/Na_2O)_{mol}$ = 1.13 or 1.44) and pH values (14.44 or 14.04), as shown in Table 3. The liquid (activating solution) to solid binder (fly ash + slag) volumetric ratio of all mixtures was 0.75.

Alkali activators were prepared following the method outlined in [19] by mixing a commercially available aqueous sodium silicate with either *2 M* or *6 M* sodium hydroxide (NaOH) solution. The commercial aqueous sodium silicate consisted of 18.0% mass $Na_2O$, 28.8% $SiO_2$ and 53.2% $H_2O$. It had specific gravity of 1.6 g/cm³ at 20 °C, and pH = 13.70. The mass ratio of sodium silicate to sodium hydroxide solutions for all mixtures was maintained at 2.0. The middle number in the Mix ID in Table 3 represents the volume percentage of slag, and the *6M* or *2M* reflects the molarity of the NaOH solution.

### 2.3. Test methods

Table 4 provides a summary of the tests performed in this study. A brief explanation of all experimental techniques utilized in this work has been presented in this section.

#### 2.3.1. Fresh properties

The setting time of AAFS binders was measured using Vicat needle, based on a modified ASTM C191-13 [48] procedure proposed by Hardjito [29]. In the modified procedure, the prepared paste was cast in two layers into the standard mold and each layer was tamped with a rod 25 times. The specimen was placed in a moist room (100% RH, 23 ± 0.5 °C) during the test. After the initial 30-minute period, the penetration depth of the Vicat needle was recorded in 15-minute time intervals, until the initial and final setting times were obtained.