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Controlling workability in alkali-activated Class C fly ash

Watanyoo Rakngan [a], Trevor Williamson [a], Raissa D. Ferron [a], Gaurav Sant [b], Maria C.G. Juenger [a,*]

[a] Department of Civil, Architectural, and Environmental Engineering, The University of Texas at Austin, 301 E. Dean Keeton St. C1748, Austin, TX 78712, USA
[b] Department of Civil and Environmental Engineering, University of California, Los Angeles, CA 90095, USA

HIGHLIGHTS

- Alkali-activated Class C fly ashes have high strength but poor workability.
- Retarders, silica modulus, and mixing intensity can change workability.
- Workability modification can reduce strength, particularly when retarders are used.

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ABSTRACT

Alkali-activation of Class C fly ashes can produce Portland cement-free binders that take advantage of sodium aluminosilicate hydrate (N-A-S-H) and aluminum-substituted calcium silicate hydrate (C-A-S-H) phases for strength development. However, alkali-activated Class C fly ashes suffer from poor workability and rapid setting; traditional water-reducing admixtures are not effective. In this study, different methods to modify the workability of alkali-activated Class C fly ash mixtures were investigated. Retarders decreased the mixture stiffness and delayed setting, but strength development suffered. Increasing mixing intensity slightly improved workability without significantly impacting strength. Controlling silica modulus significantly improved workability, but the impact on strength was inconsistent.

1. Introduction

Alkali-activated materials (AAM) are a class of binders for concrete that contain no Portland cement, but instead consist of aluminosilicate powders mixed with alkaline solutions. They can be categorized based on the composition of the system. When the source materials contain primarily silicon and aluminum (e.g. metakaolin, some Class F fly ash, and some natural pozzolans), the primary reaction product in the hardened material is a sodium aluminosilicate hydrate phase (N-A-S-H). N-A-S-H phases are sometimes called “geopolymers,” a term that is sometimes used to refer to the AAM as a whole. When the source materials contain calcium along with silicon and aluminum (e.g. blast furnace slag, some Class F fly ash, and Class C fly ash), the reaction products contain a mixture of phases, including N-A-S-H phases, aluminum-substituted calcium silicate hydrates (C-A-S-H), and some crystalline phases [1].

Most research studies on alkali-activated fly ash are based on low calcium, Class F fly ash [1]. Class C fly ashes, which generally contain more than 20% CaO, have been shown to produce a stronger concrete than Class F fly ashes when alkali activated [2] and a denser microstructure with smaller pores [1]. However, alkali-activated Class C fly ash often exhibits rapid stiffening and setting [2,3], which can inhibit workability. Further, several studies have demonstrated variability in the strength development of alkali-activated Class C fly ash systems with changing fly ash and activating solution compositions [4–6].

Alkali-activated Class C fly ashes can be promising binders for concrete if their workability problems can be overcome. In Portland cement systems, chemical admixtures (e.g. water reducers) are frequently used to combat problems with workability. However, using water reducers and superplasticizers for AAM is complicated because: (i) most are not stable in highly alkaline solutions (pH > 13) [7], (ii) they have been shown in some cases to have no direct effect on material consistency (e.g. mortar flow) [8,9], (iii) they can negatively impact strength development [10], and/or (iv) they have variable results depending on the activator

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* Corresponding author.
E-mail address: mjuenger@mail.utexas.edu (M.C.G. Juenger).

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solution composition [11,12]. This necessitates further investigation of chemical admixtures or other methods of workability modification for AAM.

Retarding admixtures can also be used in concrete to modify workability. Collins and Sanjayan [13] examined the effects of an admixture containing sodium gluconate on alkali-activated blast furnace slags. Workability was improved, but one-day compressive strength was reduced when this known retarder was used, particularly as dosage increased. Rattanasak et al. [14] examined the effects of selected chemical admixtures on the setting time and compressive strength of alkali-activated high-calcium fly ash. The changes in the initial and final setting times were negligible when $CaSO_4$ was added to the pastes. Addition of Na_2SO_4 at dosages of 1 wt% and 2 wt% considerably delayed the initial setting time, but the final setting time was unaffected. Addition of sucrose at dosages of 1 wt% and 2 wt% did not affect the initial setting time, whereas the final setting time was significantly delayed. Addition of 1 wt% addition of $CaCl_2$, $CaSO_4$, Na_2SO_4 and sucrose increased the compressive strength of the mortars by 9–25%. However, 2 wt% addition of $NaSO_4$ resulted in smaller increases in strength (3–6%) or even a strength reduction compared to the 1 wt% addition. Antoni et al. [15] examined the use of borax as retarding admixture for alkali-activated high calcium fly ash. Borax additions of 1–7 wt% of fly ash extended the setting time of pastes compared to the control mixture without borax. The compressive strength also slightly increased with the addition of 1 wt%–5 wt% borax, while the compressive strength slightly reduced with the addition of 7 wt% borax.

Addition of silica to the activating solution has also been shown to improve the workability of alkali-activated binders. For example, increasing the sodium silicate to alkaline solution ratio from 0 to 0.4 improved the flow and the compressive strength of alkali-activated slag pastes [16].

In the work presented here, a variety of chemical admixtures and mixing methods were used to quantify the effects of these variables on the workability and compressive strength of alkali-activated Class C fly ash. Six admixtures were chosen based on results reported in prior literature and included: sodium gluconate, a commercial cement hydration stabilizer, borax, a commercial naphthalene sulfonate-based admixture, sodium sulfate, and fumed silica. The mixing process plays a key role in workability. Increasing the intensity of mixing can result in increasing the initial workability state of a cementitious mixture (e.g. a reduced yield stress, reduced viscosity, or increased slump/slump flow) [17,18]. In alkali-activated fly ash, increasing the mixing time has been correlated with increases in setting times [19]. However, a reduction in the initial workability state (e.g. slump), as well as a workability loss, have also been reported with increases in mixing intensity in cementitious materials [20–22]. Thus, the influence of the mixing process on the workability and strength of the AAM was also examined. Alkali-activated pastes were examined using mini-slump and compressive strength testing using three different Class C fly ashes to examine the effect of material variability on properties.

2. Materials and methods

2.1. Materials

Three sources of ASTM C618 [23] Class C fly ash from the three different power plants in the United States, referred to as P, B, and R, were used. The oxide compositions of the fly ashes, provided by the supplier, are shown in Table 1. In spite of coming from different sources, the fly ashes have quite similar compositions, with calcium oxide contents ranging from 24 to 29% and silica to alumina ratios of 1.87–1.89. Similarly, the fly ashes had similar particle size distributions with median sizes of 11–13 μm.

Table 1
Composition and Properties of Class C fly ashes.

Oxide or Property	P	B	R
Al_2O_3 (%)	17.44	17.51	19.59
SiO_2 (%)	32.55	35.79	37.00
CaO (%)	28.95	26.89	23.88
Fe_2O_3 (%)	5.48	5.99	6.32
K_2O (%)	0.46	0.56	0.54
MgO (%)	6.45	6.25	4.76
Na_2O (%)	1.86	1.96	1.73
SO_3 (%)	2.98	1.99	2.01
TiO_2 (%)	1.32	1.15	1.42
P_2O_5 (%)	0.89	0.81	1.20
d_{50} (μm)	11.68	11.34	13.48

A 4 M sodium hydroxide solution was used as the activating solution in this study. This concentration was chosen because it has been shown to provide adequate strength in geopolymer mortars [24]. It should be noted that higher concentrations can result in higher strengths [24,25]. The solution was prepared by diluting reagent-grade 50 wt% NaOH solution (ACROS Organics) with ultrapure water (Nanopure). NaOH solutions were allowed to equilibrate at room temperature for at least 24 h before use. When employed, most admixtures were dissolved in the activating solution immediately prior to mixing of the pastes. Reagent-grade chemicals used as admixtures included: sodium gluconate (Sigma-Aldrich), sodium tetraborate decahydrate (borax) (Sigma-Aldrich), and anhydrous sodium sulfate (Fisher). Two commercial admixtures were also tested: Sikament N (Sika) and Recover (Grace). Sikament N is a high range water reducing admixture that contains sodium naphthalene sulfonate as the main ingredient. It meets the requirements of ASTM C494 [26] as a Type A and F admixture. For general concrete applications, dosage rates of 390–1000 mL/100 kg of cementitious materials are recommended by Sika. Recover is a hydration stabilizer and complies with ASTM C494 [26] as a Type D retarder. It is an aqueous solution of hydroxycarboxylic acid salts and compound carbohydrates and has sodium gluconate, sucrose, and water as the main ingredients. For traditional applications, dosage rates of 130–390 mL/100 kg of cement are used. Pretesting of proper dosage rates is recommended by the manufacturer.

Aerosil 200 fumed silica (Evonik) was also used as an admixture. The silica was allowed to dissolve in the activating solution longer than the previously mentioned admixtures in order to allow for more complete dissolution. The fumed silica was dissolved in the 4 M NaOH solution to achieve a silica modulus (SiO_2/Na_2O molar ratio) of 1 (120 g SiO_2 in 1 L of solution) after the initial 24 h equilibration period, and the resulting sodium silicate solution was allowed to equilibrate for another 24 h.

2.2. Methods

Most alkali-activated fly ash pastes were prepared using a planetary mixer (Hobart N50). A mass ratio of NaOH solution to fly ash (solution-to-powder ratio) of 0.45 was used for all specimens. When using the planetary mixer, the mixing procedures followed the mixing procedures for pastes as described in ASTM C 305 [27]. For the planetary mixing, the first speed revolved the paddle at a rate of 140 ± 5 rpm, with a planetary motion of approximately 62 rpm. The second speed revolved the paddle at a rate of 285 ± 10 rpm, with a planetary motion of approximately 125 rpm.

For some pastes, an overhead mixer (SCILOGEX OS40-S) was used to determine the effect of mixing method on properties. The mixing procedures for the overhead mixer were as follows: