Construction and Building Materials xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Quantitative assessment of parameters that affect strength development in alkali activated fly ash binders

Ali Kazemian [a,*], Asghar Gholizadeh Vayghan [b], Farshad Rajabipour [b]

[a] The Sonny Astani Department of Civil and Environmental Engineering, Viterbi School of Engineering, University of Southern California, Los Angeles, CA, USA
[b] Department of Civil and Environmental Engineering, Pennsylvania State University, University Park, PA, USA

HIGHLIGHTS

- Activator composition can be described using only two essential parameters: modulus (n) and alkalinity (pH).
- Concurrent increase in n and pH is desirable for achieving high strength binders.
- There is an optimum liquid to solid ratio to achieve highest compressive strength.
- Extended steam curing can profoundly impact strength development of binders.
- Statistical study proves the significance of the selected combination of parameters in estimating the compressive strength.

ARTICLE INFO

Article history:
Received 28 June 2014
Received in revised form 16 April 2015
Accepted 2 May 2015
Available online xxxx

Keywords:
Fly ash
Geopolymer
Activator composition
Compressive strength
Curing method

ABSTRACT

The influence of activator composition (pH, modulus), activator to fly ash ratio, $(L/S)_{vol}$, and curing on strength development of alkali activated fly ash (AAFA) mortars is investigated. A statistical analysis is performed to evaluate the significance of these parameters and to develop a preliminary regression model for predicting the 1-day strength. The results show that to achieve high strengths, activators with very high pH ($\geqslant$15.0) or high pH and moderate modulus (pH $\geqslant$ 14.75, $n \geqslant 0.75$) are needed. Such activators have high viscosity and lead to low workability. AAFA strength does not monotonically increase with reducing $(L/S)_{vol}$, but is maximum at intermediate $(L/S)_{vol}$.

1. Introduction

A geopolymer is an alternative non-Portland cement binder for concrete, which is synthesized by mixing of a reactive aluminosilicate powder (solid) with a highly alkaline activating solution (liquid). The aluminosilicate powder could be a material of geological origin (such as calcined clays or metakaolin), or an industrial byproduct, such as coal fly ash (FA) [1,2]. Geopolymers are a subset of a broader category of alkali activated binders, which also includes materials formed by activation of metallurgical slags [3]. The major motivation for development of these new binders is to improve concrete sustainability by replacing Portland cement, which is the concrete's major ingredient with the highest embodied energy (approximately 5.7 MJ/kg of cement) and carbon footprint (0.87–0.97 kg/kg of cement) [4,5]. In comparison with Portland cement, alkali activated binders have a fraction of the energy use and CO_2 footprint; although the use of alkaline activators introduces some environmental costs such as increased risk of eco-toxicity [6,7]. In addition to environmental benefits, alkali activated binders could be advantageous due to their strong durability against fire, water and chloride penetration, and chemical/acid attack [8,9].

The focus of the present study is class F fly ash geopolymers; also known as alkali-activated fly ash (AAFA) binders. Pulverized coal fly ash is an industrial byproduct of coal fueled power plants. Due to its large availability and low cost, fly ash is commonly considered the most appropriate precursor for geopolymer concretes [1]. Unlike Portland cement which readily reacts with water, a strong alkaline solution (also known as "activator") is needed to dissolve fly ash amorphous phases and initiate formation of the aluminosilicate binder. The activator solution is often a mixture of alkali silicate (e.g., $Na_2O{\cdot}nSiO_2{\cdot}mH_2O$ also known as water glass), alkali hydroxide (e.g., NaOH), and water [1].

* Corresponding author. Tel.: +1 562 964 2066.
E-mail address: ak_civil85@hotmail.com (A. Kazemian).

http://dx.doi.org/10.1016/j.conbuildmat.2015.05.078
0950-0618/

To allow market acceptance of alkali-activated fly ash (AAFA) concretes as a viable alternative to Portland cement concrete, user friendly and practical guidelines must be developed to allow engineers and material suppliers to design and proportion AAFA concrete mixtures to achieve target performance (e.g., compressive strength). Towards this goal, the first step is to identify and quantify the most important parameters that determine the performance of AAFA mixtures. In this paper, we focus on the compressive strength. Unlike Portland cement concrete, whose compressive strength is primarily related to the water to cementitious materials ratio (w/cm), a long and confusing list of parameters can be found in the literature, affecting the strength development in AAFA concrete [10–13]. Examples include different parameters that describe activator chemistry (e.g., Na_2O/SiO_2, H_2O/Na_2O, SiO_2/Al_2O_3, Al_2O_3/Na_2O, molarity of NaOH, NaOH to sodium silicate mass or volume ratios, etc.), fly ash mineralogy, water to solids ratio, and curing conditions. This diversity of reported influential parameters is confusing, even intimidating, for practitioners and makes it difficult to even compare the results from different research studies on AAFA concretes.

2. Research objectives

The goal of this study is to identify and quantitatively evaluate a short list of critical parameters that govern strength development in AAFA concrete. To start, one can argue that these critical parameters fall within the following categories:

(1) Fly ash properties.
(2) Activator composition.
(3) Activator (liquid) to fly ash (solid) ratio.
(4) Curing method and duration.

There have been recent attempts [14,15] to evaluate the effect of fly ash composition and properties (e.g., bulk composition, mineralogy, and particle size) on compressive strength of AAFA. However, there has not been a systematic effort to explicitly assess the effect of items (2)–(4) on the strength development. The present article serves this research need.

Although a variety of parameters have been used in the literature to describe activator composition, fundamentally two parameters, the activator's pH and modulus (n = the molar ratio $[SiO_2]/[Na_2O]$) are suggested by theory to have the largest impact. These are the same factors that vendors of sodium silicate solutions use to characterize their products. The pH (or alkalinity) is the factor that dictates the rate of fly ash dissolution into pore water [16–18], while the modulus quantifies the concentration of active SiO_2 species in pore water that can readily precipitate as solid geopolymer binder upon reaction with Al and Ca species dissolved from fly ash. The activator modulus has been shown to have a large impact on the microstructure and strength development of alkali activated binders [19,20]. Also, the activator's water content (mass% of water in activator solution) can impact the rheology and strength development, as shown in this paper. However, given that water content is inter-related with pH and modulus, two out of these three parameters would be sufficient to describe the impact of activator composition on compressive strength of AAFA binders.

The activator (liquid) to fly ash (solid) ratio is another parameter that deserves attention. In Portland cement concrete, a mass based w/cm is used to quantify the initial porosity of the material, which inherently impacts the strength development over time. Smaller w/cm corresponds with smaller porosity and higher strength. In AAFA binders, however, the density of activator can be drastically different from one mixture to another, depending on the activator composition. As such, only a volumetric liquid/solid ratio $(L/S)_{vol}$ would be appropriate to quantify and take into account the initial porosity. While a smaller $(L/S)_{vol}$ translates into smaller porosity, it also means that less activator is available to catalyze the dissolution and reaction of fly ash. As such, the effect of $(L/S)_{vol}$ in strength development of AAFA binders is not as straightforward as that of w/cm in Portland cement binders, and requires further research.

Finally, there is disagreement on the need for moist curing of fly ash geopolymer. While water is needed to allow dissolution of fly ash, it has been suggested that water is released back into the pores due to condensation of dissolved species to form geopolymer binder (or gel) [1,2]. Many past studies [10,14,21,22,24,29] have interpreted this to mean that preserving moisture (i.e., moist curing) is not needed for AAFA to develop strength and suggested only a dry curing (not even steam curing) at elevated temperatures starting from the time of casting. This assumption needs further evaluation.

To address these knowledge gaps, in this study, an experimental program was designed and executed to determine how activator composition (pH and modulus), $(L/S)_{vol}$, and different curing methods affect strength development of AAFA mortars. Also, a statistical study, using multiple linear regression (MLR) method, is carried out to assess the effects of activator composition and $(L/S)_{vol}$ on the 1-day compressive strength of AAFA mortar.

3. Experimental program

3.1. Material properties

In this study, ASTM C618-12a class F fly ash was used to produce AAFA mortars. The fly ash was obtained from Hatfields Ferry power plant, in Masontown, Pennsylvania, United States. Based on the results of the quantitative XRD, the fly ash consisted of approximately 70% amorphous materials, and mineral phases including quartz, mullite, and hematite. The chemical composition of the ash and the particle size distribution parameters are presented in Table 1. The specific gravity of fly ash was measured using He pycnometry as 2.45. The alkali activator was a mixture of sodium silicate ($Na_2O{\cdot}nSiO_2{\cdot}mH_2O$), sodium hydroxide (NaOH), and distilled water. The precursor sodium silicate had a modulus n = 3.32, pH = 11.3, and specific gravity = 1.39 at 20 °C. It contained 28.6% SiO_2, 8.9% Na_2O, and 62.5% water by mass. Analytical grade NaOH pellets were dissolved in distilled water to prepare 4, 8, and 12 M solutions. The NaOH solution was allowed to cool down to the room temperature prior to use in the mixtures. Natural river sand, conforming to ASTM C33M-11a, was used in all mortar mixtures. The sand had an oven dry specific gravity of 2.70, and absorption capacity of 0.5%.

3.2. Mixture proportions

To evaluate the effect of activator composition on strength development, initially eight AAFA mortars G1–G8 were prepared using activators of different compositions (Tables 2 and 3). The activators were designed to yield pH in the range 14.0–14.95 and modulus n = 0.22–2.52. These mortar mixtures all had a $(L/S)_{vol}$ = 0.81 and sand volume fraction of 49%. Additionally, four mortars were

Table 1
Chemical composition and some physical parameters of fly ash.

Oxide	Mass%
SiO_2	47.0
Al_2O_3	22.1
Fe_2O_3	20.0
CaO	2.27
MgO	0.80
K_2O	2.03
Na_2O	0.49
SO_3	0.80
P_2O_5	0.26
TiO_2	1.03
LOI	1.58
Particle size distribution parameters (μm)	
d10	1.18
d50	7.96
d90	31.99

Please cite this article in press as: Kazemian A et al. Quantitative assessment of parameters that affect strength development in alkali activated fly ash binders. Constr Build Mater (2015), http://dx.doi.org/10.1016/j.conbuildmat.2015.05.078