Assessing the porosity and shrinkage of alkali activated slag-fly ash composites designed applying a packing model

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HIGHLIGHTS

- A particle packing model is used to design alkali activated slag-fly ash composites.
- The relation between porosity and ingredients of alkali activated binder is studied.
- Activator modulus of 1.4 presents the optimum strength in all cases.
- Lowering activator modulus and slag content is efficient to reduce drying shrinkage.

ARTICLE INFO

ABSTRACT

This paper addresses the fresh behaviors, gel structure, strength, porosity and drying shrinkage of alkali activated slag-fly ash composites designed by applying the modified Andreasen & Andersen model. The results show a large variation of slump flows and setting times when using different slag/fly ash ratios and activator moduli. The microstructure analyses by FTIR and TG show the gel structure remains stable after 1 d of curing, and mixes with higher slag contents and lower activator moduli show slightly higher bound water content. The main reaction product is a chain structured C-A-S-H type gel regardless of slag/fly ash ratio and activator modulus, but a slightly higher main absorption band is shown in samples with high fly ash contents. A 28-d compressive strength of about 90 N/mm^2 is achieved and a higher content of slag leads to a higher strength and lower porosity in general. An optimum activator modulus of 1.4 in terms of strength is shown, while an increase of activator modulus between 1.0 and 1.8 benefits the pore structure refinement. Both slag content and activator modulus strongly affect the drying shrinkage, and using a high amount of fly ash and low activator modulus can effectively reduce the drying shrinkage.

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1. Introduction

Alkali activated materials (AAM) have been extensively studied in recent years due to their lower environmental impacts [1,2] compared to ordinary Portland cement (OPC) and superior performances such as mechanical properties [3], durability [4], thermal resistance [5] and acid resistance [6]. This type of material is usually produced by mixing alkaline activator solutions with solid precursors. The most commonly used activators are sodium hydroxide, carbonate, silicate or a mixture of those; while the solid raw materials are usually amorphous Ca, Si and Al contained powders such as slag, fly ash, metakaolin, silica fume, red mud and natural pozzolans. Based on the chemical composition of the raw materials, alkali activated materials can be classified into two types: calcium and silica enriched (Ca + Si) system and aluminosilicates dominated (Si + Al) systems [7]. The typical precursor of calcium enriched system is ground granulated blast furnace slag, having a tobermorite-like C-A-S-H gel with a low Ca/Si ratio and a high Al content as major reaction product [8]. The represented materials of Si + Al systems are class F fly ash or metakaolin, having three-dimensional N-A-S-H type gels as the major products [9]. Both systems exhibit distinct behaviors due to their differences in reaction mechanism and gel characteristics.

Recently, growing interests have been paid to blended alkali systems (Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$ systems) that are prepared by mixing high calcium contained raw materials with low calcium aluminosilicates, since the blended binder system exhibits modified properties regarding setting times, workability, shrinkage, mechanical properties and durability compared to the individual ones [10–13]. The structure of the reaction products in the blended system is mainly depending on the activator type and dosage, raw

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materials composition and curing conditions. Micro-scale investigations identified that the reaction products are generally stably coexisting C-(A)-S-H and N-A-S-H type gels with high amounts of cross-linking [14–16,69]; also the large amount of available calcium and aluminate affect the original structure of N-A-S-H and C-(A)-S-H gels, respectively [17–19]. The recent achievements in understanding the blended alkali systems provide solid theoretical support for the further researches; also those modified properties demonstrate a promising future for the application of alkali activated materials.

On the other hand, it is commonly accepted that an optimal packing of granular ingredients is the key for achieving excellent mechanical strength and durable structures [20–22], and several mix design methods have been proposed in cement based system such as the Linear Packing Density Model, Solid Suspension Model and Compressive Packing Model [23–25]. Among those design methodologies, the modified Andreasen & Andersen particle packing model, which is based on the integral particle size distribution approach of continuously graded mixes [26], shows conveniences by considering fine particles into the design process. While presently, when designing the recipes of alkali activated blended mortars and concretes, key manufacturing parameters from the aspects of activator and raw material are the main concerns, while to the authors' knowledge limited attention has been paid to the packing of the granular ingredients. It is possible that by giving additional consideration to the particle packing in the mix design stage, the binders in alkali activated system will be used in a more efficient manner, while certain fresh and hardened properties may also improve as a result.

Another important issue of alkali activated materials is the shrinkage, since it is well linked to the cracking tendency and consequently the durability related properties. The previous investigations revealed that the alkali activated high calcium system usually exhibits a higher degree of drying shrinkage than the cement based system [27,28], while the alkali low calcium systems can show a lower value than OPC [29]. It was also concluded the activator type and content, the physicochemical properties of the raw material and curing conditions are the key factors that affect the shrinkage behaviors [30,31]. However, there still exists very limited study about the relationships between key synthesizing factors and the shrinkage in alkali activated blended systems. In overall, the objective of this study is to design the room temperature cured alkali activated slag-fly ash blended mortars by applying the modified Andreasen & Andersen particle packing model; while the effects of key synthesizing factors on shrinkage and porosity are investigated. In addition, the fresh behaviors, gel structure development and compressive strength are also addressed and their relations with shrinkage and porosity are discussed.

## 2. Experiment

2.1. Materials

The solid precursors used in this study were ground granulated blast furnace slag (GGBS, provided by ENCI B.V., the Netherlands) and a commercial Class F fly ash. Their major chemical compositions were analyzed by X-ray fluorescence and are shown in Table 1. Besides, limestone powder was used as filler while a micro sand (0–1 mm, provided by Graniet-Import Benelux B.V., the Netherlands) and a normal sand (0–2 mm) were used as fine aggregates. The specific densities of solid materials are presented in Table 2 while the detailed particle size distributions of all solid materials are given in Fig. 1. Concerning the alkaline activators, a mixture of sodium hydroxide (pellets, analytical level of 99 wt.%) and commercial sodium silicate solution (27.69% SiO_2, 8.39% Na_2O and 63.92% H_2O by mass) was used, due to the advantages in providing additional silicate and continuous alkali conditions of this activator. The desired activator modulus (Ms, SiO_2/Na_2O molar ratio) was achieved by adding the appropriate amount of sodium hydroxide into the sodium silicate solution. Distilled water was added in order to reach the desired water/binder ratio. The mixed activator solution was cooled down to room temperature for 24 h before further use.

Table 1
Major chemical composition of slag and fly ash.

Oxides (wt.%)	FA	GGBS
SiO_2	54.62	34.44
Al_2O_3	24.42	13.31
CaO	4.44	37.42
MgO	1.43	9.89
Fe_2O_3	7.21	0.47
Na_2O	0.73	0.34
K_2O	1.75	0.47
SO_3	0.46	1.23
LOI	2.80	1.65

Table 2
Specific densities of the solid materials.

Solid materials	Specific density (kg/m³)
Slag	2930
Fly ash	2300
Limestone powder	2710
Micro sand	2720
Normal sand	2640
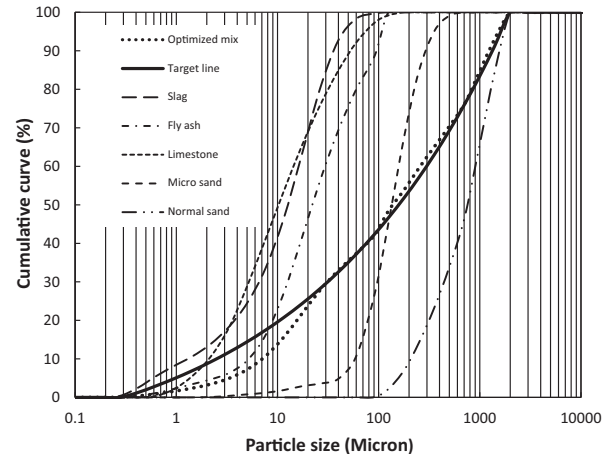
Fig. 1. Particle size distributions of the raw materials, the target curve and the resulting integral grading line of a sample mix.

2.2. Mix design methodology

The mixes of alkali activated slag-fly ash mortars were designed using the modified Andreasen and Andersen (A&A) model in order to maximize the packing of the granular solid materials:

$$P(D) = \frac{D^q - D^q_{min}}{D^q_{max} - D^q_{min}} \qquad (1)$$

where P(D) is a fraction of the total solids materials that are smaller than the particle size D (μm), D_{max} is the maximum particle size (μm), D_{min} is the minimum particle size (μm) and q is the distribution modulus. The distribution modulus (q) in the modified A&A model is used to determine the proportion between the fine and coarse particles in the mixture. Higher values of q would lead to a coarse mixture; while lower values will result in mixes with enriched fine particles and result in an increased water demand. Brouwers [32,33] suggested that a theoretically q value range of 0–0.28 would result in an optimal packing. Hunger [21], Yu [65], Ng [67] and Borges [68] recommended a q value in the range of 0.20–0.25 for the design of cement, geopolymers and gypsum as the binder. In order to achieve an ideal workability, the value of q is fixed at 0.23 for all mixtures in this study.

The proportions of each individual material in the mix are adjusted until an optimum fit between the composed mix grading curve and the target curve is reached, using an optimization algorithm based on the least squares method (LSM), namely the deviation between the target curve and the composed mix expressed by the residual sum of squares (RSS) at defined particle sizes is minimal [22,36]. Therefore, the optimized mixture will possess a compact matrix due to the optimal packing. This mix design method has been successfully adopted to design concretes with different types [34,35,65]. An example of the detailed mix designs