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Reaction kinetics, gel character and strength of ambient temperature cured alkali activated slag–fly ash blends

X. Gao, Q.L. Yu *, H.J.H. Brouwers

Department of the Built Environment, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

HIGHLIGHTS

- Slag/fly ash ratio and activator modulus show synergetic effects on reaction.
- Activator modulus has a more significant influence on early age reaction.
- Gel structures remain stable regardless of activator modulus and slag/fly ash ratio.
- Slag content shows a dominating effect on compressive strength.

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ABSTRACT

Room temperature cured alkali activated slag/fly ash blends have shown their advantages in field applications. Given that alkali activated materials are extraordinarily sensitive to the composition of the starting materials, identifying their influences is essential for their application. This paper focuses on the effects of two compositional factors: activator modulus (SiO_2/Na_2O from 1.0 to 1.8) and slag/fly ash mass ratios (between 90/10 and 50/50) on reaction kinetics, gel characters and compressive strength. The results show that when lowering the activator modulus, the early age reaction is significantly accelerated with a higher reaction intensity, and increasing the slag content also leads to an increased reaction rate, especially at low activator modulus. Regardless of the two influential factors, the main reaction products are chain structured C-A-S-H gels with similar water contents and thermal properties, and no typical N-A-S-H type gels are formed in the system. Slight differences in terminal Si—O bonds and crystallization temperature are caused by the activator modulus and slag/fly ash mass ratios, respectively. The compressive strength results show that the optimum activator modulus changes with the slag/fly ash mass ratio, and higher slag/fly ash mass ratios prefer higher activator moduli in general, while either too high or too low activator modulus has detrimental effect on strength. Understanding the reaction, gel structure and strength changes are fundamental for determining key manufacturing parameters and tailoring the properties.

1. Introduction

Alkali activated material has attracted great attention in recent years due to its excellent performances such as mechanical properties [1–3], durability [4–7], thermal stability [8,9] and low environmental impacts [10]. It is usually produced by mixing alkaline activator solutions with solid raw materials. Alkali activated systems can be classified into two types: calcium and silica enriched (Ca + Si) system and aluminosilicates dominated (Si + Al) system [11]. The represented precursor of calcium enriched system is ground granulated blast furnace slag (GGBS), and the reaction product is a C-S-H (I) type gel with a lower Ca/Si ratio and a high Al incorporation [12]. While the typical starting materials of Si + Al system are class F fly ash or metakaolin, having N-A-S-H type gels with three-dimensional network as the major final product [13].

Recently, there is a growing interest of mixing two different alkali activation systems together to form a blended $Na_2O–CaO–Al_2O_3–SiO_2$ system as several improved properties can result, including modified setting times [14], improved workability [15], reduced shrinkage [16], enhanced mechanical properties and durability [17]. Later studies were focused on understanding the gel compatibility and phase composition in the blended system: generally, both coexistence and interactions take place between C-A-S-H and N-A-S-H type gels [11,18]. Two typical gels can form

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* Corresponding author. Tel.: +31 (0)40 247 2371; fax: +31 (0)40 243 8595.
E-mail address: q.yu@bwk.tue.nl (Q.L. Yu).

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simultaneously within one system [19]; the presence of calcium leads to the formation of C-A-S-H type gels and destroys the N-A-S-H gel structure to some degree by partially replacing sodium with calcium to form (N,C)-A-S-H gels [20–22], while the increased availability of aluminates strongly influences the C-S-H composition and structure [23]. In addition, a higher degree of cross-linking within the reaction products is achieved [24]. Those investigations in the microstructural understanding provide solid theoretical support for further researches on blended alkali activated system.

It has been known that in alkali activated Ca + Si or Si + Al system, the silicate from activator participates in the formation of hydrated C-A-S-H or N-A-S-H gels together with solid silicate sources, and there exists an optimal silicate content in terms of mechanical properties, either insufficient or excessive silicate supply may restrict the formation of an ideal gel structure and lead to a matrix with relatively low strength [25]. Also, the relations between the silicate content and mechanical properties were well established in the individual system [2,25,26]. However, in the case of alkali activated blended systems such as slag/fly ash, the raw material composition plays a more complex role: the silicate from the activator may involve in the formation of all type of typical hydrated gels such as C-A-S-H, N-A-S-H and (N,C)-A-S-H; the silicate from different raw materials may exhibit different de-polymerization rates and availability under different conditions such as curing temperature and alkaline concentration. Thus despite a consensus about the binding mechanisms has been reached in the previous studies, different conclusions were drawn in determining the optimal parameters in strength: some studies showed a decrease in compressive strength with the increase of fly ash content, such as Weiguo et al. [27]; Kumar et al. [28] and Garcia et al. [18]. While other studies indicated that there is an optimum ratio between slag and fly ash, for instance Chi and Huang reported the critical fly ash content is 50% [29], a 20% fly ash content by Yang et al. and a 65% fly ash content by Zhang et al. [30–31]. Differences in critical raw materials' relative content and activator parameters were also reported [15,32–35]. Different used activators and curing conditions make it difficult to make valid comparison between those studies. Therefore, in order to tailor the properties of alkali activated slag/fly ash blends for desired applications, it is necessary to carry out a systematic study considering the effects of raw materials, activators and curing conditions simultaneously.

On the other hand, alkali activated materials manufactured under ambient temperature exhibit several superiorities in field application, but there exists limited studies about the combined influence of activator and raw materials on the comprehensive properties of room temperature cured slag/fly ash mixtures. In this paper, a preliminary study for tailoring the properties of alkali activated slag/fly ash blends was carried out, and the influences of activator modulus and slag/fly ash ratios on reaction, gel characters and strength were addressed. Slag dominated mixes (at least 50% by mass) were chosen due to the superior mechanical properties under room temperature, different slag/fly ash ratios were used to give different starting $CaO–Al_2O_3–SiO_2$ compositions; different activator moduli were used to provide various levels of extra silica, and the constant total Na_2O content was applied to exclude its influence on total extra silicate content. The reaction kinetics and gel characters were investigated by isothermal calorimetry, Fourier transform infrared spectroscopy (FTIR) and thermogravimetry/differential scanning calorimetry (TG/DSC) analysis.

2. Experimental study

2.1. Materials

The solid materials used in this study were ground granulated blast furnace slag (GGBS, supplied by ENCI B.V., the Netherlands) and Class F fly ash according to ASTM C 618 (supplied by Vliegasunie B.V., the Netherlands) [36]. The median particle size (d50) is 27.16 μm for slag and 22.06 μm for fly ash. The chemical compositions of slag and fly ash were analyzed by X-ray fluorescence, and the result is shown in Table 1. The alkali activator used was a mixture of sodium hydroxide pellets (analytical level) and sodium silicate solution that is composed of 27.69% SiO_2, 8.39% Na_2O and 63.9% H_2O by mass. The desired activator moduli (Ms, SiO_2/Na_2O molar ratio) were achieved by adding different amounts of sodium hydroxide pellets into sodium silicate solution, the solution after mixing was cooled down to ambient temperature prior to use. Distilled water was added in order to reach the desired water/binder ratio.

2.2. Sample preparation

In the mix design stage, the equivalent sodium oxide (Na_2O) content was kept at 5.6% by mass of the binder in all samples, five levels of activator moduli (Ms from 1.8 to 1.0) were used (assigned as A to E) to provide different extra silicate contents from activator to the solid material. The fly ash/slag ratios of 90/10, 80/20, 70/30, 60/40 and 50/50 by mass were used (represented as 1 to 5). The water/binder ratio was kept constant as 0.35; the water consisted of the water added from distilled water and the water contained in the original sodium silicate solution. The chosen Na_2O content and water/binder ratio were preliminarily determined that would provide sufficient alkalinity without efflorescence and satisfying flow ability, respectively. The detailed information of mix proportions is listed in Table 2. Paste samples were prepared using a laboratory mixer, the solid materials were added into the mixer followed by activating solution, then the mixtures were mixed at a slow speed for 30 s, and stopped for 30 s before another 120 s at a medium speed. The fresh paste was poured into plastic molds of 40 × 40 × 160 mm^3 and vibrated for 1 min, then covered with a plastic film on the top surface for 24 h; finally all specimens were demolded and cured at 20 °C and relative humidity of 95% until the testing age.

2.3. Testing methods

The compressive strength tests were carried out according to BS EN 196-1 [37]. 40 × 40 × 40 mm^3 cubes were prepared and tested at the ages of 7 and 28 days respectively, and the strength value for each mix was obtained from the average of six specimens. The isothermal calorimetry analysis was conducted under a constant temperature of 20 °C for 72 h. Solid raw materials were firstly mixed with the activating solution for about 1 min, then the mixed paste was transferred into the ampoule and loaded into the calorimeter. Fourier Transform infrared spectroscopy (FTIR) measurement was performed in a Varian 3100 instrument with the wavenumbers ranging from 4000 to 600 cm^{-1} at a resolution of 1 cm^{-1}, and each sample was scanned for 50 times. Thermogravimetry and differential scanning calorimetry (TG/DSC) analysis was conducted in a STA 449-F1 instrument, grinded powder samples were firstly heated to 105 °C and held for 2 h, then up to 1000 °C, both at 5 °C/min with nitrogen as the carrier gas. Both FTIR and TG/DSC analysis to the samples were carried out at the age of 28 days.

Table 1
Major chemical compositions of the raw materials.

Oxides (%)	Fly ash	GGBS
SiO_2	54.6	35.5
Al_2O_3	24.36	13.6
CaO	4.44	38.6
MgO	1.43	10.2
Fe_2O_3	7.2	0.48
Na_2O	0.73	0.35
K_2O	1.75	0.48
SO_3	0.46	1.27
LOI	2.80	1.65

Table 2
Mix proportions of AA-slag/fly ash pastes.

	Slag/fly ash	Na (%)	Activator modulus					W/B
			A	B	C	D	E	
1	90/10	5.6	1.8	1.6	1.4	1.2	1.0	0.35
2	80/20	5.6	1.8	1.6	1.4	1.2	1.0	
3	70/30	5.6	1.8	1.6	1.4	1.2	1.0	
4	60/40	5.6	1.8	1.6	1.4	1.2	1.0	
5	50/50	5.6	1.8	1.6	1.4	1.2	1.0	