Cement and Concrete Research 100 (2017) 129–139

Contents lists available at ScienceDirect

Cement and Concrete Research

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

Investigation on a green olivine nano-silica source based activator in alkali activated slag-fly ash blends: Reaction kinetics, gel structure and carbon footprint

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ARTICLE INFO

Keywords:
Olivine nano-silica
Alternative activator
Alkali activation
Slag-fly ash blends
CO_2 footprint
NMR

ABSTRACT

In this paper, a green olivine nano-silica is synthesized and applied as an alternative silicate source to prepare alkali activators, and a commercial waterglass based silica source is studied as a reference. The synthesis route and characterization of olivine nano-silica is presented. The effects of silicate origin and dosage on activator characteristics, reaction kinetics, gel structure and strength are investigated and the CO_2 footprint is evaluated. The results show that increasing the activator modulus significantly increases the high crosslink Q contents in the alkali solution, nano-silica based ones exhibit slightly higher percentages of Q3 sites. Nano-silica based mixes exhibit comparable properties regarding the reaction intensity, chemically bound water content and strength. Gel compositions of both nano-silica and waterglass based samples are characterized in detail by using solid ^{29}Si and ^{27}Al MAS NMR. Moreover, replacing commercial waterglass by this alternative silicate source reduces the CO_2 emission between 20.4% and 29.0%.

1. Introduction

The production of ordinary Portland cement (OPC) is accompanied with a number of environmental issues such as carbon emissions, consumption of natural clays and high energy costs. In order to reduce those negative impacts, great attention has been paid to applying alkali activated materials as alternatives to Portland cement. This type of material generally exhibits reduced energy costs and carbon emissions [1,2] together with excellent mechanical properties, durability and thermal resistance [3–6]. Two typical binding systems can be classified based on the chemical composition and the reaction mechanism of the starting materials: One is the Si + Ca system, having C-A-S-H type gel as the main reaction product [7]; another is the Si + Al system, having N-A-S-H type gel within a three-dimensional network as the major reaction product [8]. The typical precursors for these two systems are slag and metakaolin/class F fly ash, respectively [1,8].

Growing efforts have been spent on the blended alkaline system recently. Due to the fact that mixing calcium enriched aluminosilicates dominated precursors results in a series of modified properties including the setting times, workability, shrinkage, mechanical properties and durability [9–12]. Micro-scale analyses reveal that the reaction products are stable coexisting C-A-S-H and N-A-S-H type gels [13–15], indicating a desirable gel compatibility. Besides, the effects of key synthesizing factors such as activator type and dosage, raw materials' composition and curing conditions on reaction kinetics, gel characters, mechanical properties and durability issues have been also intensively investigated [16–20].

In terms of the alkali activators, it is widely accepted that a mixture of silicates and caustic alkalis ($M_2O{\cdot}nSiO_2 + MOH$, where M often refers to Na or K) results in the best mechanical properties and lowest porosity [3,21] compared with other types of activators, and the most commonly used cation is Na due to its relatively low cost and availability. This mixed activator benefits the reaction process by offering alkaline conditions in a moderate and continuous manner, meanwhile providing extra silicate sources that contribute to the formation of reaction products [22]. However, the sodium silicate based activator is the main contributor of energy consumption and carbon emission in alkali activated materials [23]. The production of sodium silicates includes the melting of sodium carbonate and quartz sand at high temperatures (usually around 1400 to 1500 °C), and this process results in a total carbon dioxide release of 403 to 540 kg/ton and an energy consumption between 420 and 1250 MJ/ton [24]. Moreover, the estimated cost of one ton of equivalent silica from commercial sodium silicate solution is currently > 2100 USD [25].

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http://dx.doi.org/10.1016/j.cemconres.2017.06.007
Received 14 March 2017; Received in revised form 11 May 2017; Accepted 29 June 2017

Therefore, in order to obtain a more sustainable alkali activated binder, it is of great interest to design new alkali activators with reduced environmental impacts and lower costs. Exploring alternative silicate in the activator has been proven to be an effective approach. Rodriguez et al. [26] used chemically modified nano-silica and MOH to activate class F fly ash; Zivica et al. [27] applied modified silica fume as alternative activator in alkali activated slag; Puertas et al. [21] developed a mixed activator by dissolving industrial glass waste in NaOH/Na_2CO_3 solution and used it in alkali activated slag; Bernal et al. [28] prepared silicate based activators by mixing silica fume or rice husk ash with NaOH to activate metakaolin/slag blends. These researches show that alternative silicate based activators could provide comparable mechanical properties and similar micro scale characters compared with commercial sodium silicate based resources. However, there are limited mechanism studies regarding the effect of alternative silicates as activator on the blended alkaline system.

On the other hand, the olivine nano-silica, produced by the dissolution of olivine, exhibits advantages with regard to carbon emission, energy consumption and total costs [29]. This type of amorphous nano-silica is produced under temperatures lower than 95 °C and can have a specific surface area between 100 and 400 m^2/g and primary particles as low as 10 nm [30]. Thus it indicates the potential as a sustainable silicate source in the preparation of alkali activators while providing desirable reactive silica. The objective of this study is to evaluate the olivine nano-silica as an alternative activator in alkali activated slag-fly ash blends. The effects of olivine nano-silica on activator characteristics, reaction kinetics, mechanical property and the structure of reaction products are analyzed. Micro-scale analyses are carried out by using an isothermal calorimeter, ^{29}Si and ^{27}Al MAS NMR spectroscopy and thermo-gravimetric/differential scanning calorimeter; and furthermore the total carbon emission of the related mixtures is computed.

2. Experiment

2.1. Materials

The solid precursors used in this study were ground granulated blast furnace slag (GGBS, provided by ENCI, the Netherlands) and a commercial Class F fly ash. Their major chemical compositions were analyzed by X-ray fluorescence, as shown in Table 1. The X-ray diffraction patterns of the used slag and fly ash are shown in Fig. 1, which were measured by using a Cu X-ray tube with a step size of 0.02° and a 2θ range from 15° to 55°. The slag shows a peak hump between 25 and 35° due to the amorphous components and no significant crystalline phases were observed; while the fly ash has an amorphous hump between 15 and 30° and contains crystalline phases such as quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), magnetite (Fe_3O_4) and hematite (Fe_2O_3). Concerning the alkaline activators, analytical level of sodium hydroxide pellets (99 wt %), a commercial sodium silicate solution (27.69% SiO_2, 8.39% Na_2O and 63.92% H_2O by mass) and laboratory prepared olivine nano-silica (19.04% SiO_2 and 80.96% H_2O by mass) were used; the olivine nano-silica was produced by dissolving olivine in acid at low temperatures, followed by a washing and filtering process, and the detailed synthesizing route and characterization is presented in Section 3.1. Reference activators with desired modulus were prepared by adding the appropriate amount of sodium hydroxide pellets into the sodium silicate solution. Distilled water was used in order to reach the desired water/binder ratios. Alkali activators with the same activator modulus were prepared by mixing sodium hydroxide pellets with olivine nano-silica and water to achieve the same chemical compositions as the references. The mixed activator solution was cooled down to room temperature prior to further use.

Table 1
Major chemical composition of GGBS and fly ash.

Oxides (wt%)	FA	GGBS
SiO_2	54.62	30.23
Al_2O_3	24.42	12.58
CaO	4.44	40.51
MgO	1.43	9.05
Fe_2O_3	7.21	0.60
Na_2O	0.73	–
K_2O	1.75	0.43
SO_3	0.46	3.47
LOI	2.80	1.94

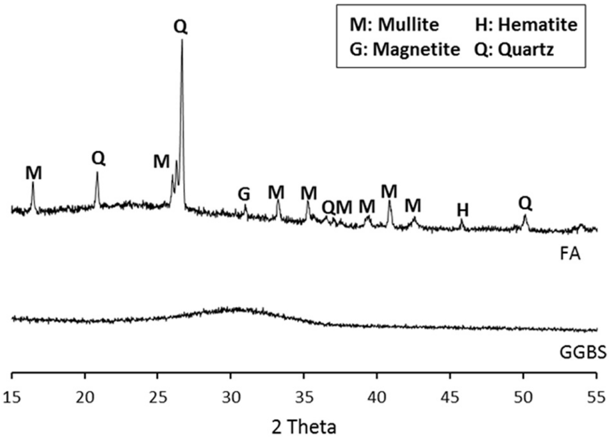

Fig. 1. XRD patterns of GGBS and fly ash.

2.2. Experimental program

The activators used in this study had an equivalent sodium oxide (Na_2O) content of 5% by mass of the solid precursors, and the water/binder ratio was kept constant as 0.4 in all mixtures. The water consisted of the added distilled water and the water contained in the activator solution. The chosen Na_2O content and water/binder ratio were taken from the previous studies that ensure sufficient alkalinity without efflorescence and satisfying flowability, respectively [31,32]. The slag/fly ash mass ratio was fixed at 70/30 and three levels of activator modulus (1.8, 1.4 and 1.0) were used. The detailed information of the mix proportions is listed in Table 2 (where WG and NS represent commercial waterglass and olivine nano-silica, respectively).

The reaction kinetics was studied by using an isothermal calorimeter (TAM Air, Thermometric) for the first 72 h under a constant temperature of 20 °C. The solid raw materials were firstly mixed with the activating solution externally and vibrated for about 1 min, then the paste was injected into the ampoule and loaded into the calorimeter.

The compressive strength tests were carried out according to EN 196-1 [33], and each obtained value is an average of three specimens. Samples were prepared using a laboratory mixer; firstly the solid raw materials were added, followed by the activating solution. The fresh samples were casted into plastic molds covered with a plastic film for the first 24 h, then demolded and cured at a temperature of 20 °C and a relative humidity of 95% until their testing age.

Table 2
Mix proportions of alkali activated slag-fly ash composites.

Activator			Solid raw materials		w/b
Type	Na_2O	Ms	Slag	Fly ash	
A:	5%	1.8	70	30	0.4
WG + NaOH					
B:		1.4			
NS + NaOH					
		1.0			