



Reaction kinetics, microstructure and strength behavior of alkali activated silico-manganese (SiMn) slag – Fly ash blends



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HIGHLIGHTS

- Industrial waste materials have been used for alkali activated cement development.
- SiMn slag and fly ash blended to overcome limitations for alkaline cement production.
- Co-existence of geopolymer gel with C-(A)-S-H gel improves the binder properties.
- Slag addition altered the reactivity and developed compact microstructures.
- Fly ash addition slowed down the reaction rate and formed uniform, compact matrix.

ARTICLE INFO

Article history:

Received 14 October 2016

Received in revised form 21 February 2017

Accepted 21 April 2017

Available online 29 April 2017

Keywords:

Fly ash

SiMn slag

Alkali activated cement

Reaction kinetics

Gel morphology

Strength

ABSTRACT

Two industrial waste namely air cooled silico-manganese (SiMn) slag and fly ash has been used synergistically to develop alkali activated cement at ambient temperature. Isothermal conduction calorimetric studies (ICC) revealed that addition of SiMn slag resulted in an increase in reactivity. A new hump in ICC after 1.4 h of reaction is appeared in blends rich with SiMn slag, which is due to the formation of primary C-(A)-S-H gel. The shift in band corresponding to Si-O-Si/Al at $\sim 1000\text{ cm}^{-1}$ towards lower frequency in Fourier transform infrared spectrum with slag inclusion suggest the structural reorganizations and formation of a new calcium rich gel. The main reaction product is detected as (N)-A-S-H and C-(A)-S-H (where, N = Na_2O , A = Al_2O_3 , C = CaO, S = SiO_2 , H = H_2O) based heterogeneous hydrated gel with varying Si/Al, and Na/Ca ratios. Both Si/Al ratio (obtained in EDX analysis) of gel phases and compressive strength increases with slag introduction. The improvement of mechanical strength with increasing slag is associated with more reactive CaO content of the slag, and co-existence of C-A-S-H and N-(C)-A-S-H type gel in the reacted matrix.

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1. Introduction

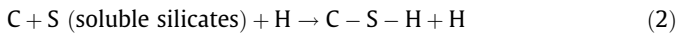
Alkali activated cement is a special class of binder, generated by hydration of solid pozzolanic or cementitious powder material in presence of alkali at ambient or near ambient temperatures. This type of binder known as 'alkaline cement' was tested around 50 years ago [1–3]. Later in 1972, Davidovits introduced the term 'geopolymer', to classify an alumino-silicate three dimensional network structure formed by alkali activation of alumina and silica bearing source material such as metakaolin, fly ash [4]. This binder has been considered as sustainable alternative of ordinary Portland cement (OPC), as it reduces green house gas emission and requires lower energy during production [3–5]. However, this binder has

little impact on environment, which has been discussed in several published literatures [5–8]. The main responsible factor for the above issue is counted by the CO_2 emission during the synthesis of alkali activator such as Na_2O , Na_2SiO_3 etc. According to those research data, the total impact in terms of CO_2 release is much lesser, around 50 to 80%, in alkali activated cement than OPC production [8]. Moreover, it exhibits mechanical properties similar to the OPC binder, and shows excellent product durability [8–12]. However, controversy exists on durability issues of alkali activated binder, and a comprehensive report on this can be viewed from a review article published by Torgal et al. [8]. The same has not been discussed here as the topic is out of focus of this paper. Several waste or by-product materials have been used to synthesize alkali activated cement. Notable among them are fly ash, volcanic ash, granulated blast furnace slag (GBFS), granulated corex slag (GCS), cast iron slag, zinc slag, lead slag, ferro-chrome slag, mine tailing, municipal solid waste incinerator ash, granite dust etc. [10–24].

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Alkali activation is a complex process and heterogeneous nature of waste materials makes it more complicated. During alkali activation the Al-Si frameworks of the reactive glass portion of source materials break and the oxide component dissolute into alkali solution and finally alumino-silicate based hydrated phases are formed [25,26]. If reactive calcium oxide is present, it undergoes hydration, and becomes faster in presence of alkali [27]. The dissolution rate of CaO is higher than Al₂O₃ and SiO₂ in alkali solution [28,29], and actively participates in the reaction (2) with soluble silicates present in the system, and forms calcium silicate hydrate (C-S-H).



The alumina from glass particle of the raw material soluble into alkali solution and forms aluminate [Al(OH)₄] species. This species are interacted with silicate species and formed alumino-silicate oligomers. Finally a cross linked tetrahedral co-ordinated alumino-silicate network structure is formed by further polymerization [30]. The influence of calcium on geopolymerization behavior of alumino-silicate such as metakaolin, fly ash, volcanic ash by addition of calcium compounds which include lime, CaCO₃, GBFS etc. has been studied extensively [17,18,27,28,31–37]. A hydrated calcium-silicate (C-S-H) gel with C/S ratio lower than C-S-H gel of OPC hydration with little Al incorporation; is formed additionally from calcium bearing compound and coexist with a 'geopolymeric gel', (N)-A-S-H, which is formed by alkali activation of alumino-silicate source [27,28,31–36]. The coexistence of aforementioned two gels would be beneficial in terms of physical and mechanical properties and microstructural developments of such alkaline cement binder [17,18,32–36]. Thus, calcium bearing components are added often to overcome slow setting and hardening of fly ash geopolymer binder at room temperature [17,18,34–37]. Many successful attempts in this direction have been made with using waste and by-products such as GBFS, GCS etc. [17,18,34,35]. Till date no such literature is available on fly ash and SiMn slag blended alkali activated cement developed at ambient temperature.

Silico manganese (SiMn) slag is a by-product of silico-manganese alloy production in submerged electric arc furnace. About 1.2 to 1.4 ton slag is generated in per ton of SiMn alloy production. Worldwide SiMn slag generation is estimated around 14.8 million metric tons per annum and in India about 2.5 million metric tons generated, as per 2012 data provided by International Manganese Institute [38]. The majority of the produced slag is simply dumped as it has no such value added use except land filling. As a result, huge accumulation of such slag over the year causes environmental burden and pollution. SiMn slag contains SiO₂, Al₂O₃, CaO and MnO. Attempt has been made to utilize SiMn slag in Portland slag cement (PSC) [29,39–41] and alkali activated cement [42] using granulated one. The granulated slag consists with high glassy phases, forms during quenching, gives latent hydraulic and pozzolanic characteristics and makes it suitable for the above said applications. Air cooled SiMn slag, used in this study, contains more crystalline phases and less reactive than granulated one. In laboratory experiment we faced difficulties in alkali activation of only air cooled SiMn slag. When it comes in contact with alkali solution, produces hydrogen bubbles due to presence of Si metal in it. Due to fast setting and hardening, the bubbles are trapped inside giving rise to un-uniformly distributed porous body with bulging top surface (Fig. 1). This has been restricted its use as a feedstock for alkali activated binder. Fly ash is an alumino-silicate powder generated as a byproduct from a coal fired thermal power plant. Among waste and byproducts, it is most widely studied geopolymer precursor due to huge production in worldwide, easy availability, free flowing nature and finer size fraction [10,11,17,18,35–37]. It is reported that geopolymer produced from



Fig. 1. SiMn slag based alkali activated hardened sample.

fly ash exhibit good mechanical strength with improved durability [10,11]. But its low reactivity at ambient temperature led to slow setting of the fresh paste and poor strength development of the hardened samples, limits its use as ambient curing geopolymer cement [18,43].

In the present work, the limitation of both raw materials fly ash and SiMn slag for geopolymer synthesis is addressed by blending them. The lower reactivity of fly ash is compensated by adding higher reactive SiMn slag. The porous behavior of SiMn slag based alkali activated cement is overcome by the addition of fly ash, which control the rate of reaction. Subsequently bubbles have got sufficient time to escape due to delay in setting. Also, the un-reacted particles filled the pores leading to compact texture. Various combinations of fly ash and SiMn slag have been tried in order to get the optimum mechanical properties and desired structure. The reaction kinetics was studied by using Isothermal conduction calorimetry (ICC). An attempt has been made to establish a correlation between reaction kinetics with the structure and consequently mechanical properties of the developed cement.

2. Materials and methods

Class F fly ash was used for this study and collected from an integrated power plant, Tata Power Co Ltd., Jamshedpur, India. Air cooled SiMn slag was received from an Alloy Steel Plant, Shyam Ferro Alloys Ltd., Durgapur, India. SiMn slag was received in lump form, which was crushed in jaw crusher then milled into ball mill for 2 h for obtaining powder of <30 μm size. The chemical analysis of raw fly ash and milled slag was carried out by using a combination of analytical techniques such as Inductive coupled plasma optical emission spectrometer (ICP-OES) (Vista MPX, Varian), atomic absorption spectroscopy (AAS) (iCE 3000 series, Thermo Scientific), and conventional wet chemical method. For every particular component a single specific method was used. X-ray fluorescence (XRF, SRS 3400, Make: Bruker, US) was used to cross check the major oxide content. Loss on ignition (LOI) was estimated by measuring the mass loss after heating. Specific gravity of fly ash and slag powder was measured in pycnometer bottle following Archimedes principles. Laser particle size analyzer (MASTERSIZER, Malvern, UK) was used to measure the particle size distribution (PSD) of fly ash and slag powder. The powder was added in an aqueous suspension of distilled water, and a laser beam passed through the dispersed particulate sample. PSD were calculated by measuring the angular variation in intensity of the scattered light. The crystalline phases of raw materials and alkali activated samples were identified by using D8 Discover X-ray diffractometer (XRD) (Bruker, US) in 10 to 70° 2θ range, a scan speed of 0.2 s/step with step size of 0.02°. The CuKα radiation (=1.5418 Å) was generated at 40 kV and 40 mA. Chemical analysis and physical properties of the raw materials are shown in Table 1.

The details of batch composition for this study are shown in Table 2. The sample with 100 wt% fly ash is considered as reference batch. Sample nomenclature was done according to initial of the component and given number represents their respective percentage in that particular batch. Steps followed for calorimetry sample preparation; (i) preparation of 6 M alkali solution by dissolving analytical grade NaOH flakes (purity ~97%, Merck, Germany) into required amount distilled water, (ii) manual mixing of powder mixture with alkaline solution in the ratio of 2:1, into calorimeter bottle, and (iii) loading of the bottles in sealed condition into calorimeter channels. Isothermal conduction calorimeter (ICC) (TAM AIR, Thermometric AB, Jarafalla, Sweden), was used to monitor the reaction kinetics by measuring the heat evolution with reaction time at ~27 °C temperature. The rationale of selecting 27 °C is based on the Indian cement standard IS: 4031, 1988, which define ambient temperature as 27 ± 2 °C.

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