Construction and Building Materials 181 (2018) 487–494

Contents lists available at ScienceDirect

Construction and Building Materials

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

Geopolymerization behavior of ferrochrome slag and fly ash blends

S.K. Nath

CSIR-National Metallurgical Laboratory, Jamshedpur 831 007, India

HIGHLIGHTS

- Geopolymerization behavior fly ash and ferrochrome slag has been studied.
- Low reactivity of fly ash at ambient condition can be overcome by addition of FCS.
- FCS addition results better compressive strength and well bridged microstructures.
- Geopolymer gel and C,M-A-S-H gel coexist in blended samples and improves strength.

ARTICLE INFO

Article history:
Received 25 January 2018
Received in revised form 7 May 2018
Accepted 8 June 2018

Keywords:
Ferrochrome slag
Fly ash
Geopolymer
Reactivity
Microstructure
Compressive strength

ABSTRACT

This study highlights on the development of blended geopolymer cement by utilization of two industrial wastes namely ferrochrome slag (FCS) and fly ash. Geopolymer cement with 100 wt% FCS is considered as control batch. Then FCS is gradually replaced by introducing fly ash. The result obtained by isothermal conduction calorimetry shows that higher heat of reaction with intensified peak in slag rich specimens. The appearance of Si—O—Si/Al bond vibration at lower frequency in slag dominated reaction indicates the structural alteration and formation of new calcium and magnesium rich gel. The main reaction product in blended geopolymer samples is identified as N-A-S-H and C,M-A-S-H (where, N = Na_2O, A = Al_2O_3, C = CaO, M = MgO, S = SiO_2, H = H_2O) based heterogeneous hydrated gel with varying Si/Al, and Na/Ca ratios. Higher compressive strength is attained in slag based reference sample due to its higher degree of reaction, formation of more gel phases and development of compact microstructure.

1. Introduction

The term "geopolymer" is coined by Joseph Davidovits to describe an alumino-silicate binder materials consisting of tetrahedral aluminate and silicate units formed by the alkali activation of alumino-silicate bearing source materials such as calcined clay, fly ash [1]. Geopolymer production is more environmental friendly and the resultant products are more durable than Portland cement binder [2–4]. Fundamentally any alumino-silicate powder material can be used for geopolymer synthesis. Therefore, a large number of naturally occurring and synthetic solids are being tried for geopolymer production [5–9]. Additionally, it has the potential to valorize the industrial waste materials and to immobilize the heavy and toxic elements inside the structure [6–9]. Thus, there is a paradigm shift in the research trend for geopolymer synthesis from naturally occurring and pure material to waste and by-products [6,7].

Ferrochrome slag (FCS), a byproduct is produced during the production of ferrochrome alloy steel in submerged electrical arc furnace. Around 1.1–1.6 ton slag is generated in per ton of ferrochrome production depending on feed materials [10]. Globally, ferrochrome production is estimated about 8.9 million tons in the year 2011 [10,11]. Using this data, the annual generation of FCS is calculated around 12.5 million tons which is also increasing by 2.8–3.0 wt% in every year. A small percentage of produced slag is being used for road construction and rest part is simply discarded. Accumulation of such material in huge quantity requires large surface areas which is rather un-favourable in economic aspects. Additionally, dumping of such waste on the open land causes severe environmental problems such as leaching by water and pollution of nearby water sources, chemical degradation, environmental pollution and lack of aesthetics. Due to stringent environmental regulatory and sometimes local community pressures, simple storage of such slag may no longer be considered a sustainable practice. Therefore, it is necessary to examine this waste material in appropriate ways of utilization. Thus research significance for bulk utilization of such type of material is increasing rapidly. Very limited research data is available on FCS used as road construction, cement additive and aggregate form in construction work [12,13].

E-mail address: snath@nmlindia.org

https://doi.org/10.1016/j.conbuildmat.2018.06.070
0950-0618/

Fly ash is the by-product powder material of thermal power plants generated during combustion of coal. Huge amounts of fly ash are generated day to day to meet up the requirement of high energy throughout the world. Only a part of this are utilized and rest is simply dumped. Unplanned dumping of such huge amounts of fly ash are causing an environmental pollution and creating big concern for the future. In the last two decades, many countries have initiated to utilize fly ash as additive to cement and concrete in building materials. Recently fly ash has become a material of interest for the synthesis of geopolymer due to its alumino-silicate composition, free flowing nature, low water demand and high workability [7,8,14–16]. During geopolymerization, fly ash particles interact with alkali solution and leads to the formation of structurally disordered, highly cross-linked alkaline alumino-silicate-hydrate (N-A-S-H) gels [16]. Finally, these gels solidify, bind the un-reacted particles, harden and develop strength. However, the low reactivity of fly ash and consequent slow setting and strength development has been a limiting factor. Two different approaches have been followed to overcome the low reactivity of fly ash at ambient condition- (a) by addition of high reactive material such as granulated blast furnace slag (GBFS), granulated corex slag (GCS), granulated lead smelter slag (GLSS), granulated silico-manganese slag (GSS) etc. [17–19] and (b) by mechanical activation of fly ash [20]. Mechanical activation is an energy intensive process. Therefore, blending with high reactive powder is more favorable. Mainly CaO bearing high reactive materials are mixed to improve the reactivity. It is recognized that CaO participates into activation process and produces C-S-H/C-A-S-H gel along with geopolymer gel which results adequate strength development [17–19]. It is also expected that the reactivity of the blends to be improve due to incorporation of significant amount of glassy phases which are more vulnerable to react than stable crystalline phases.

Air cooling is the normal industrial practice for liquid FCS solidification. In this process solid slag is generated in lumpy form with negligible glass content [21]. It normally contains lower amount of reactive CaO compare to other reported slags used for blending [22,23]. Thus its applications are limited as inert coarse aggregate in concrete structures [23,24]. The utilization potential of ferrochrome slag into geopolymer system has been studied only by Karakoc et al. [22]. These authors reported that this slag is suitable for geopolymer binder at ambient temperature curing. Though, it is not clear whether they have used air cooled or water quenched granulated slag. This slag as a blended component with fly ash in geopolymer system is yet to be explored. The purpose of above blending can be justified with the geopolymerization behavior and availability of both materials. Fly ash is easily available at everywhere and its generation volume is much higher (100 times higher only in India) than FCS. Therefore by blending, total volume of the resource material for geopolymer synthesis is augmented. In addition, this research work has the great potential to overcome the low reactivity of fly ash and to utilize more fly ash with FCS into geopolymer binder at ambient conditions.

2. Materials and methods

Ferrochrome slag (FCS) used for this study was collected from an Alloy Steel Plant, Durgapur, India. Slag was received in lump form with wide variation of size. The lumpy slag was crushed in jaw crusher then milled into ball mill for 2 h for obtaining median particle size, $D_{50} \leq 25$ μm. Class F fly ash was obtained from Tata Power Co Ltd., Jamshedpur, India. The chemical analysis of slag powder and fly ash was carried out by using Inductive coupled plasma optical emission spectrometer (ICP-OES) (Make: Varian Inc.) and further verified in X-ray florescence (XRF, Make: Bruker, US). Loss on ignition (LOI) was measured by calculating the weight loss upon heating. Pycnometer bottle was used to determine specific gravity of slag powder and fly ash, following Archimedes principles. Particle size distribution (PSD) of powder raw materials was measured in Laser particle size analyzer (Make: Malvern, UK). The mineralogy of raw materials and geopolymer samples were analysed by using D8 Discover X-ray diffractometer (XRD, Make: 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. Table 1 shows the oxide content and physical characteristics of the raw materials.

Table 2 shows the mix proportion used for this study. The sample with 100 wt% FCS is considered as control batch. Then gradually fly ash percentage was increased to replace FCS. Sample nomenclature has two parts, alphabetic presents initial of the slag and numerical represents their respective percentage. Alkali solution of 6 M was prepared by dissolving analytical grade sodium hydroxide flakes (purity ~97%, Merck, Germany) into required amount distilled water and used for ICC study. Powder blend was mixed manually with alkaline solution in the ratio of 2:1, into calorimeter bottle. Then the bottles in sealed condition were loaded into calorimeter channels. The time elapsed was around 2–3 min between mixing and loading into calorimeter. Isothermal conduction calorimeter (ICC, Make: TA instrument) was used to monitor the geopolymerization by measuring the heat of reaction with time, at ambient (~27 °C) temperature.

Microstructural analysis of the reaction products was carried out with Fourier transforms infrared spectroscopy (FTIR), X-ray diffraction (XRD), and Scanning electron microscope with Energy dispersive X-ray spectroscopy (SEM-EDX). For FTIR, pellet samples were prepared by mixing with KBr powder. FTIR (Make: Thermo Electron Corporation) in transmittance mode was used to measure the absorption spectra of the bonds in the range of 400–4000 cm^{-1}. Field emission gun-scanning electron microscope (FEG-SEM, Make: FEI, Netherlands) fitted with energy dispersive X-ray spectrometer (EDX) operated at 15.0 KV was used for morphological analysis of reacted samples, after gold or silver coating on fractured surface.

Cube (50 × 50 × 50 mm) specimens were made for compressive strength testing. 6 M NaOH and sodium silicate (SS) solution in 1:1 vol ratio was taken as activator solution. The SS solution contained around 7.5 to 8.5 wt% Na_2O, 25 to 28 wt% SiO_2 and rest amount of water with a modulus ratio (Ms = n(SiO2)/n(R2O)) of about 3.45. Sodium silicate solution was used to get sufficient strength at the initial stage. The same reason has been reported in published literatures [17,25]. The powder mix was mixed with alkali solution (around 26 wt%) in a mechanical mixer to make a homogenous and consistent paste, then casted in cube shaped moulds made with alkali resistant steel. The casted samples were de-moulded after hardening and kept in plastic cover at 27 ± 2 °C temperature for curing and testing at different age. AIMIL equipment (ACTM) was used for compression test after 7, 14 and 28 days curing.

3. Results and discussion

3.1. Raw materials characterizations

Silica and alumina is present abundantly in both raw materials. The ratio of SiO_2/Al_2O_3 is 1.06 and 1.79 in FCS and fly ash respectively. The studied slag also contains CaO and MgO as major oxide component and iron oxide and chromia as minor. The other minor oxide content of fly ash is iron oxide and CaO. Particle size distribution (PSD) of ground FCS and fly ash is shown in Fig. 1. Compare to fly ash, FCS is coarser with larger median particle size, though the maximum size is similar. Both crystalline peaks and glassy hump are detected in XRD analysis of both raw materials, as shown in Fig. 2(a, b). The broad diffused hump is present at 20–30° 2θ range corresponding to glassy or amorphous phase in fly ash. Similarly, FCS is characterized with the presence of a broad diffuse halo in between 15 and 40° 2θ. The major crystalline phases in fly ash are identified as quartz (JCPDS 85-0796) and mullite (JCPDS

Table 1
Chemical analysis and physical properties of raw materials.

Chemical Analysis		
Constituents (Wt.%)	FCS	Fly ash
SiO_2	27.70	51.20
Al_2O_3	26.05	28.60
CaO	12.55	2.15
MgO	25.30	0.75
Cr_2O_3	4.15	NF
FeO + Fe_2O_3	2.20	8.10
LOI	0.70	2.70
Physical properties		
Specific gravity	3.01	2.3
Median particle size (μm)	18.36	9.67