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Evaluation of the suitability of ground granulated silico-manganese slag in Portland slag cement

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HIGHLIGHTS

- The suitability of GSS as a blended cement component is explored.
- Hydration behavior and binder properties of the slag cement pastes are examined.
- Low initial reactivity of GSS due to lower C/S and pozzolanic characteristics.
- A sharp increase in compressive strength in GSS is observed after 7 days of curing.
- Portlandite, C-S-H, and C-A-H are detected as major hydration phases.

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ABSTRACT

Granulated silico-manganese slag (GSS), a by-product of ferro-alloy production, has been used to replace granulated blast furnace slag (GBFS) in Portland slag cement (PSC). Calorimetric studies have shown changes in the hydraulic behavior in the cement containing GSS. These changes are early peak acceleration corresponding to the hydration, decrease in the rate and heat of hydration, formation of a new calorimetric peak and continuation of hydration for a longer period than the cement containing GBFS. X-ray diffraction (XRD) analysis of the hydrated cement revealed the typical hydration phases such as portlandite, C-S-H and C-A-H ($C{=}CaO$, $S{=}SiO_2$, $A{=}Al_2O_3$, $H{=}H_2O$).[1] The GSS bearing cement is also contained with manganese rich hydrated phases. The peak occurrence in the Fourier transform infrared spectroscopy (FTIR) at 1472, 1419 and 870 cm^{-1} corresponding to carbonate bond is associated with the existence of Ca^{2+} for a longer duration allowing it to react with atmospheric carbon-dioxide. The partial replacement of GBFS by GSS has shown marginally lower compressive strength at early ages which has achieved almost similar strength after 28 days curing.

1. Introduction

For more than a century, the successful performance of granulated blast furnace slag (GBFS) in Portland slag cement (PSC) has established it as a resource material [1,2] and now it is a priced commodity in many countries. This has driven the cement industry to look for cheaper alternatives with properties comparable to GBFS. GSS is one such alternative that can potentially be used as blending material in slag cements. It is a by-product generated during production of silico-manganese alloy by carbothermic reduction in submerged arc furnace. The chemical composition of SiMn slag resembles with blast furnace slag with presence of CaO, SiO_2, Al_2O_3 and MnO as major constituent. To understand its similarity, the authors have plotted the position of SiMn slag in $CaO\text{-}SiO_2\text{-}Al_2O_3$ ternary diagram along with blast furnace slag in Fig. 1. From this diagram, it is obvious that SiMn slag is richer in SiO_2 and has less CaO than GBFS. The one major difference is presence of MnO in ~5–10 wt%. GBFS is more basic ($C/S = \sim 1\text{–}1.22$) than SiMn slag ($C/S = 0.6\text{–}0.75$). When this ratio exceeds 1, it is considered as good reactive. The reactivity and performance of slag depends on its chemical and mineralogical composition and glass content. The hydration of slag increases with Ca/Si and Al_2O_3 content. According to Whittaker et al. [3], alumina rich slag shows faster reaction and more heat evolution. They showed that an increase in Al_2O_3 content from 7 to 12 wt% resulted in the formation of AFm phases, reduced the C-S-H volume, and exhibited high compressive strength. In the present studies, the difference in Al_2O_3 content between both slags is small but the Ca/Si ratio in GBFS is higher. Due to the chemical similarity, the use of these

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[1] Throughout the text cement nomenclatures are used such as $C{=}CaO$, $A{=}Al_2O_3$, $S{=}SiO_2$, $H{=}H_2O$ etc.

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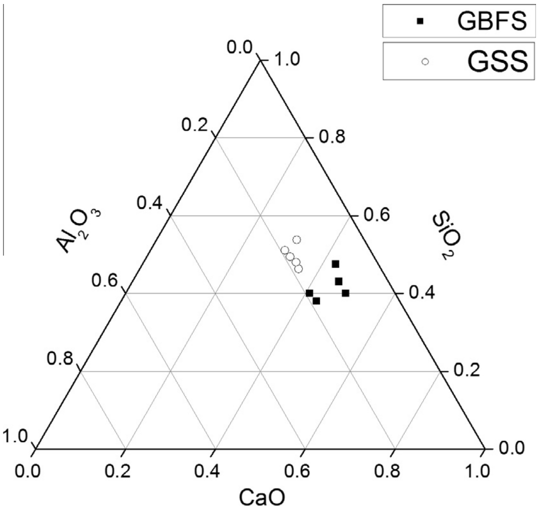

Fig. 1. Ternary diagram of CaO-SiO$_2$-Al$_2$O$_3$ showing position of blast furnace slag and SiMn slag.

slags as blended cement component and its impact on chemical stability, engineering properties and technical viability has been studied [4–9]. However, its reactivity, which is lower than GBFS, is an area of concern. The reactivity of SiMn slag is associated with its structure. Due to the Industrial practice of air quenching of molten slag, it forms the slag lumps, which are partly glassy and partly crystalline. The glassy phase participates in active reaction whereas the crystalline remains un-reactive. Recently, use of mechanical activation for altering the reactivity of SiMn slag and subsequently its use in Portland slag cement [9], and alkali activated cement [10] has been reported.

Another potential method of improving reactivity is increasing glass content by granulation of slag. The benefits of granulation have been discussed [4], where ferro-manganese slag has been used as blended cement component after granulation. In the present work, the reactivity of SiMn slag has been altered by granulating it using water quenching. Because of water quenching, the molten slag has been solidified rapidly and disintegrated into small fragments of 1–2 mm size. These fragments were mostly glassy, and attributed with higher reactivity than the lump slag obtained by air quenching method.

The objective of the present work was to evaluate the suitability of GSS as blended cement component. Portland slag cement with 40 wt% GBFS has been used as reference sample. GBFS has been replaced by GSS gradually and its effect on hydraulic behavior was studied using an isothermal conduction calorimeter (ICC). Fourier transform infrared spectroscopy (FTIR) has been used for structural analysis of cement samples. A differential thermo gravimetric analysis (DTG) was used to see the decomposition pattern of the hydrated phases upon heating. Hydrated phases were detected by X-ray diffractometry (XRD). Microstructural analysis of the reaction product was carried out using a scanning electron microscope with elemental analyzer (SEM-EDX). The physical properties such as compressive strength and setting time were measured as per Indian standard [11]. An attempt has been made to correlate the reaction with structure and properties development.

2. Materials and methods

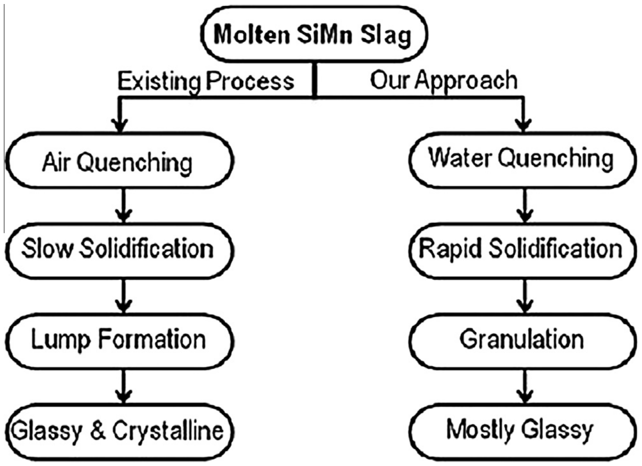

Fig. 2. Flow sheet showing granulation of SiMn slag.

The approach adopted for SiMn slag granulation and its result is shown diagrammatically in Fig. 2. During the water quenching, jet spray of cold water was given to molten slag. As a result, the water was entrapped in molten slag, the water becomes superheated and converted to superheated steam and expanded rapidly. This resulted in fragmentation and sudden cooling of slag. Due to rapid cooling, there was insufficient time available for crystallization and the slag cooled into glassy phase. In air quenching, the surface of molten slag which is in contact with air cools rapidly whereas the inner side of slag cools down slowly forming crystalline phases. Glass is thermodynamically metastable and more reactive than crystalline one of similar composition. Due to glassy nature and smaller fragments, granulated slag is easier to grind than the air quenched one and require less energy in grinding.

GSS was received from Jindal Steel and Power, Raigarh, Chhattisgarh, India and GBFS was obtained from Tata Steel Ltd, Jamshedpur, India. Both raw slags were milled separately in a ball mill for 2 h in order to obtain powder with a grain size lesser than 45 μm. The clinker used for this study was collected from Grasim Industries, Chhattisgarh, India. The lump was then pulverized and ball milled for 2 h to obtain a grain size of lesser than 45 μm. The chemical analysis of slags and clinker was carried out using combination of equipments such as inductive coupled plasma optical emission spectrometer (ICP-OES) (Vista MPX, Varian), X-ray florescence (XRF, SRS 3400, Make: Bruker, US) and conventional wet chemical method. The specific gravity of raw materials was measured in a pycnometer bottle using Archimedes principle. The particle size distribution (PSD) of both slags was measured using a laser particle size analyzer (MASTERSIZER, Malvern, UK). The mineralogical phases of the raw slags and cement samples were identified by D8 Discover XRD (Bruker, US) using 2θ angle range of 10–70° with a scan rate of 0.2 s per step and a step size of 0.02°. The CuKα radiation (=1.5418 Å) was generated at 40 kV and 40 mA.

Five different batches (SC40, SC30, SC20, SC10 and SC00) were designed for this study. Each batch comprised of 60 wt% cement clinker and 40 wt% slag powder. The batch nomenclature was done according to initials of slag cement (SC) and percentage of GBFS in the respective batches. For example the reference batch SC40 denotes the cement contains 40 wt% GBFS. In following batches, 10 wt% GBFS was replaced by GSS. Usually gypsum is added in commercial cement as retarder to slow the setting process otherwise it gives the flash setting. As the GSS containing cement has shown slower early strength development and delayed setting time, gypsum was not added in the batches.

The hydration reaction of different batches was studied in an 8 channel ICC (TAM Air, Thermometric AB, Sweden) at 27 °C temperature. The rationale of selecting 27 °C temperature is based on the Indian cement standard IS: 4031, 1988 [11], which define ambient temperature as 27 ± 2 °C. For sample preparation, 5 g of dry cement powder was mixed with 3 ml water. Mixing was done outside in