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Improved processing of blended slag cement through mechanical activation

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Use of granulated blast furnace slag has become increasingly popular in the manufacture of blended cement, generally referred to as Portland Slag Cement (PSC). Replacement of clinker by slag not only offers energy savings and cost reductions compared to the Ordinary Portland Cement (OPC), but also other advantages such as low heat of hydration, high sulfate and acid resistance, better workability, and good ultimate strength. Typically in India, 40–50% ground granulated blast furnace slag (GBFS) is used in PSC. The use of slag in blended cements is restricted by the low hydraulic activity of slag, i.e., slow hydration reaction and, consequently, slow development of compressive strength as compared to OPC [1].

The scope of application of treatment in milling devices may be roughly divided into three main areas—coarse grinding, fine grinding, and mechanical activation [2]. Attempts have been made to overcome the problem of slow strength development in PSC through fine grinding and mechanical activation [2] of the blended cement constituents, namely the clinker and the slag [1, 3]. In controlled particle size distribution (CPSD) cements, relatively low hydraulic activity of GBFS is compensated by increased reactivity of clinker due to increased fineness [4, 5]. It is also reported that for the same incremental increase in fineness, slag fineness gives better compressive strength than clinker [6]. In spite of these differing views on slag and clinker fineness, there is a general consensus that the strength properties largely depend on fine grinding of blended cement constituents [7].

Fine grinding and mechanical activation are generally believed to be associated with large energy consumption and this has resulted in the search for an energy efficient device. Sekulic *et al.* [8] studied mechanical activation of OPC in different types of mills such as a laboratory ball mill, a vibro mill with balls, and a vibro mill with rings. Attrition mills, sometimes referred to as stirred ball mills, are highly effective devices for rapid grinding of solid materials down to the sub-micrometer range and mechanical activation [9, 10]. In this paper, results of our studies on the effect of milling blended cement constituents in an attrition mill are reported. The focus is on strength and microstructure development, when blended cement constituents are mechanically activated. Replacement of clinker with up to 95% slag has been explored, and the results obtained are compared with industrial cement prepared from the same raw material.

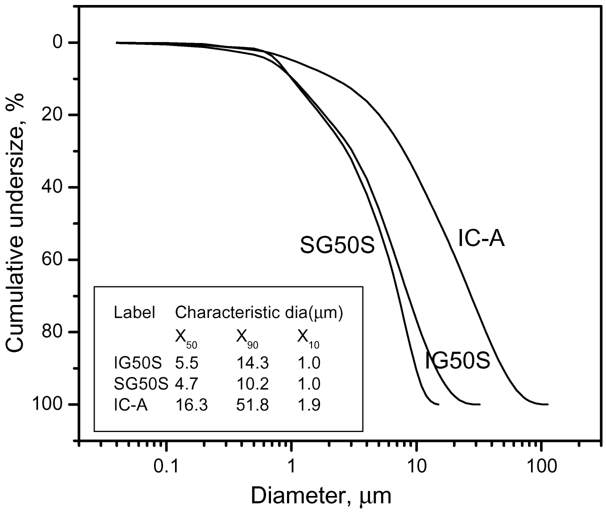

Figure 1 Particle size distribution of IC-A, IG-50S, and SG-50S cement samples. Characteristic particle diameters of cement samples are also included.

PSCs are finely ground mixtures of cement clinker, GBFS, and gypsum. The PSC constituents and industrial cement samples used in the investigation were obtained from an Indian plant located in the state of Chattisgarh. Quantitative X-ray powder diffraction pattern

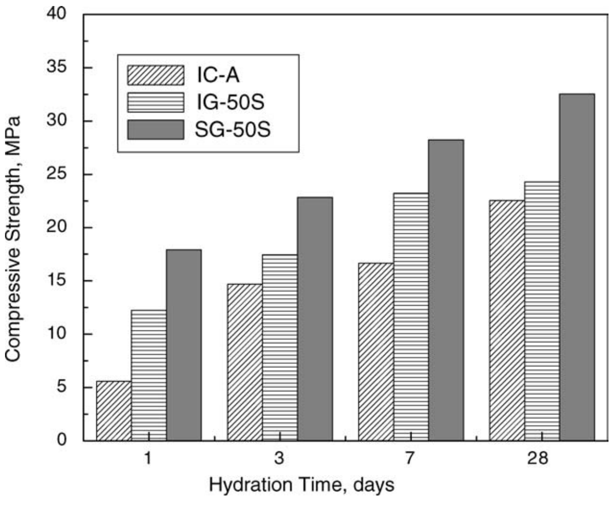

Figure 2 Variation in compressive strength IC-A, IG-50S, and SG-50S cement samples after 1-, 3-, 7-, and 28-day hydration.

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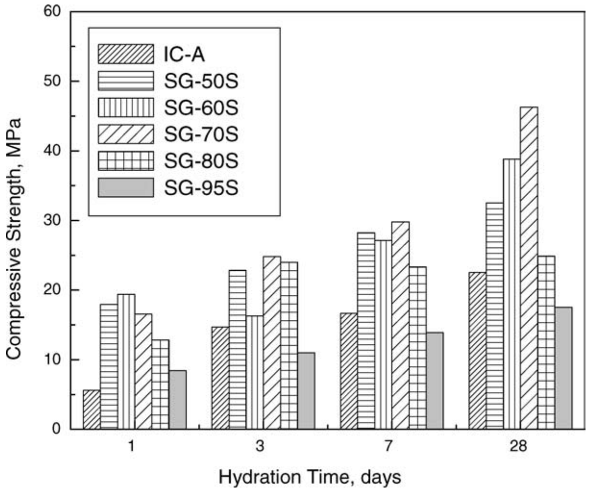

Figure 3 Variation in compressive strength of separate grounded cement in relation to slag content after 1-, 3-, 7-, and 28-day hydration.

analysis by SIROQUANT^{TM} phase analysis software based on the Rietveld method (developed by CSIRO, Australia), indicated the following mineralogical composition of the clinker (in weight percent): C_3S, 60.6%; C_2S, 21.9%; C_3A, 11.1%; and C_4AF, 6.4% (C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3).

The chemical and physical properties of the slag used for these studies are summarized in Table I.

A batch-type Attrition Mill (PE 075, Netzsch, Germany) was used for milling of raw materials. Both inter-grinding and separate grinding techniques were applied to produce the blended cement samples. For inter-grinding, slag and clinker in the 1:1 ratio were wet milled together in isopropyl alcohol. In a separate grinding stage, slag and clinker were milled in separate batches and after drying mixed together in different proportions. 5% chemical gypsum was added in all the cases. Milling was carried out for 10 min at 1000 rpm using 2 mm steel balls as the grinding media. The particle size distribution of the milled samples was determined using a laser diffraction particle size analyzer (Model: CILAS-1180). The particle size distributions of inter-ground cement (IG-50S) and separate ground cement (SG-50S) samples, along with the industrial cement (IC-A), are given in Fig. 1. The median sizes (X_{50}) of IG-50S and SG-50S were 5.5 and 4.7 μm, respectively, much smaller than the industrial cement that was characterized by an X_{50} value of 16.3 μm.

TABLE I Chemical, physical, and mineralogical characteristics of the slag

Constituent (wt%)/parameter	BF slag (SL)
Chemical composition	
SiO_2	33.1
Al_2O_3	21.6
Fe_2O_3	0.87
CaO	33.0
MgO	8.85
MnO	–
S (sulphide)	–
[(CaO + MgO + Al_2O_3)/SiO_2]	1.9
Physical properties	
Phases present	Glass and Gehlenite C_2AS (35-0755)
% Glass content	93.9
Specific gravity	2.88 g/cm^3
Feed size	X_{50} = 94.5 μm
Morphology	Angular particles

The compressive strength of the cement mortars was determined after 1 day, 3 days, 7 days, and 28 days as per Indian standard [IS:4031 (Part 6)]. Fig. 2 shows the development of compressive strength with time in the cements prepared with attrition milling (IG-50S and

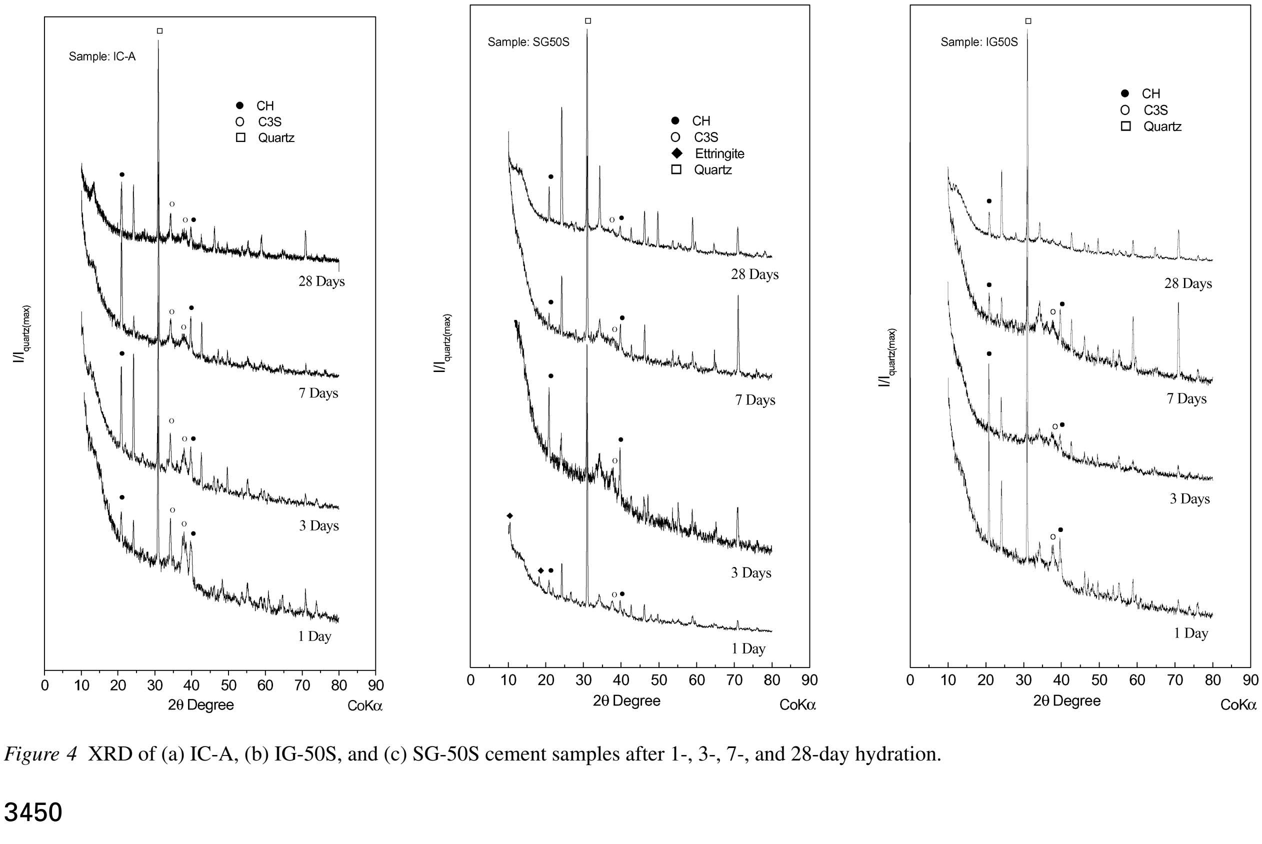

Figure 4 XRD of (a) IC-A, (b) IG-50S, and (c) SG-50S cement samples after 1-, 3-, 7-, and 28-day hydration.

SG-50S) and the industrial cement (IC-A). Much higher 1-day strengths were observed for IG-50S and SG-50S as compared to IC-A. In both the cement samples, the strength obtained after 1-day hydration was about 50% of the 28-day strength. In contrast, the 1-day strength for IC-A was only 25% of the 28-day strength. IG-50S and SG-50S showed higher strength than IC-A up to 28 days. Also, the strength development was better in SG-50S than in IG-50S. There was no significant increase in the strength of IG-50S beyond 7 days. However, compressive strength increased continuously with hydration time for SG-50S.

To find the maximum amount of slag that can be incorporated in cement without decrease in strength below the value for commercial cement (IC-A), separate ground blended cements were prepared with increasing amounts of slag. The samples containing 50, 60, 70, 80, and 95% slag were coded as SG-50S, SG-60S, SG-70S, SG-80S, and SG-95S, respectively (the numerals in the sample code indicate the percent of slag replacing clinker). Fig. 3 shows the variation of compressive strength with hydration time for the samples containing different amounts of slag, and the commercial cement sample IC-A. The 1-day strength was higher than the commercial sample (IC-A) in all the cement samples prepared in the laboratory. The 3- and 7-day strength was higher than that of IC-A for all the laboratory produced cement samples containing up to 80% slag. It is interesting to note that the 28-day strength increased with an increase in slag content up to 70% slag and then decreased. The 28-day strength of SG-70S was ∼2 times higher than that of the commercial cement. The 28-day strength for SG-80S was higher than that for IC-A. However, the sample containing 95% slag showed a slightly lower strength than IC-A. The above results indicate that slag can safely replace clinker up to 80% without any deterioration in properties.

In order to find a possible explanation for the development of compressive strength, the hydrated cement samples were characterized using XRD and SEM. Fig. 4a, b, and c show typical XRD patterns of cement samples IC-A, SG-50S, and IG-50S after 1-, 3-, 7-, and 28-day hydration. The analysis of XRD patterns indicated the presence of the following phases: Quartz [85-1086], Ettringite [41-1451], Alite (C_3S) [86-0402], Belite (C_2S) [86-0298], Gehlenite (C_2AS) [79-2421], and Portlandite (CH) [72-0156]. The C-S-H gel phase, responsible for the strength development and formed due to the hydration of clinker phases (C_3S and C_2S) and slag, is not easily characterized by XRD due to its amorphous nature. Hence, the variations in the characteristic peaks of C_3S at ∼2.77 Å and CH at 4.92 Å were examined in detail to monitor the progress of hydration. C_3S is consumed during the hydration reaction. The intensity of the characteristic peak of C_3S can be used as a measure of the progress of the hydration reaction. Hydration of C_3S and C_2S results in the formation of CH [11]. CH formed during the hydration reaction of clinker may be consumed in the hydration of slag [12]. Thus, the intensity of the characteristic peak of CH, especially for the samples hydrated up to 28 days, can be used as a measure of the reactivity of the slag; higher peak intensity signifying less consumption of CH and in turn, lower reactivity of the slag. Based on XRD results, it was found that C_3S was consumed faster or had greater reactivity in the separate ground sample (SG-50S) followed by the inter-ground sample (IG-50S) and industrial cement (IC-A). Consumption of CH begins much earlier in the attrition-milled samples (SG-50S and IG-50S) than in the commercial sample. Also, it was found that after 28 days of hydration, a greater amount of CH phase was present in the commercial sample IC-A than in the SG-50S and IG-50S.

Typical SEM micrographs of IC-A, IG-50S, and SG-50S after 1-day hydration are given in Fig. 5a, b, and c, respectively. As shown in Fig. 5a, large unreacted

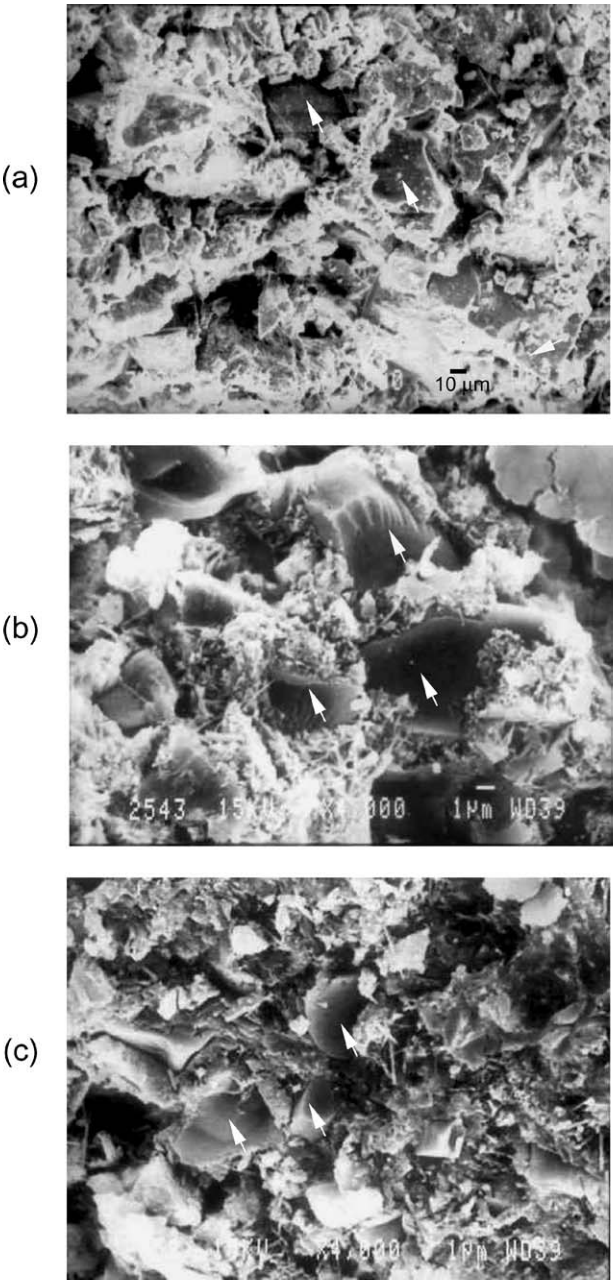

Figure 5 SEM micrographs of (a) IC-A, (b) SG-50S, and (c) IG-50S after 1-day hydration (the unreacted slag particles are marked with an arrow).

slag particles embedded in the hydrating clinker matrix were observed in the microstructure of IC-A (the magnification of the micrograph in Fig. 5a is 10 times lower than in Fig. 5b and c). The amount of unreacted slag observed was much less in the attrition milled samples after 1-day hydration. Further, it was observed that IG-50S had unreacted slag particles of greater size than SG-50S (Fig. 5b and c). The hydration of slag milled for different lengths of time has indicated that the amount and nature of gel formed during hydration strongly depends on the particle size of the slag [13]. Slag with smaller particle size hydrates faster. Based on the size of slag particles, as revealed during SEM examination, the following order of reactivity of slag is suggested: SG-50S > IG-50S > IC-A. These results are in agreement with the observations inferred from XRD results. The strength development (Fig. 2) follows the same sequence as observed for the reactivity of cement constituents.

The results discussed above indicate that fine grinding and mechanical activation in an attrition mill can be used to alter the reactivity of blended cement constituents, in particular slag. As a result greater amount of slag can be incorporated in the blended slag cement. Separate grinding of the constituents appears to be more effective as compared to inter-grinding.

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