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STUDY ON CEMENTITIOUS PROPERTIES OF STEEL SLAG BY PARTIAL REPLACEMENT OF CEMENT

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ABSTRACT

Steel slag is the byproduct of the basic oxygen furnace and its disposal is cited as the biggest problem. Steel slag of Bokaro steel plant is characterized using X-ray diffraction analysis, X-ray fluorescence, electron microscope. The composition of the steel slag has the great influence on its cementitious properties. Mortar blocks are prepared with the replacement of cement by 5, 10, 15 and 20 % of steel slag. Cementitious properties of steel slag are checked by normal consistency, initial and final setting time, soundness, compressive strength. Silica modulus suggests that steel slag has significantly less amount of calcium silicate in its composition. The study reveals that fine steel slag can be utilized for cement replacement up to 10% does not show any adverse effect of the early as well as latter strength. Beyond 10% cement replacement would affect the compressive strength achieved after 90 days of curing. The study would help policymakers to adopt steel slag as a resource for partial replacement of cement.

Keywords: cement, steel slag, replacement, compressive strength.

I. INTRODUCTION

Steel slag is a solid waste generated from basic oxygen furnace and is a mixture of metal oxides and silicon dioxide and may contain metal sulfides along with metal in the elemental form. Steel slag output is approximately 20% by mass of the crude steel output [1]. Increase in production capacity of steel production also increases the production of the steel slag. Global slag production was 250 Mt from the 1.6 billion tons of steel production in 2014 [2]. Asia alone contributes to 60% of steel slag production. On an average US and developed countries uses 70 to 80 % of the steel slag, Australia utilizes 60 to 70 %, whereas India utilizes less than 20 % of its slag generated [3]. Steel slag composition may vary from place to place and process conditions of the furnace. Steel slag is having several utilities like use as rail ballast material, as an antiskid aggregate in bitumen mix and also in the process of adsorption, which help in removal of toxicants like Cu and Cr(iii) [4]–[7].

Researchers look for the sustainable technologies which are economical [8]. Steel slag is known to have cementitious properties due to presence of β -C₂S, C₃S, C₄AF and C₂F. Its utilization would result in the solid waste minimization as well as saving the natural resources. Cementitious properties increases with its basicity [9]. Due to presence of free lime the use steel slag is limited. Properly aged steel slag would not show expansion [10]. Steel slag has better cementitious properties than the fly ash [11]. Use of alkali activators like Na₂SiO₃ increases the cementitious property of the steel slag [9]. Studies indicate super-fine steel slag to have higher compressive strength for first 100 days and lowers the strength after 100 days as compared to the ordinary steel slag [12]. Studies indicate that steel slag can be converted to amorphous material by rapid quenching which has the enhancing effect on the hydration properties of the steel slag [13]. The concrete with steel slag shows lower early strength, higher late strength, get permeability, drying shrinkage and carbonation resistance as compared to pure cement concrete. Activity of the cementitious minerals in steel slag is much lower than that in Portland cement [14]. It is related to the crystalline state, the cementitious phases of steel slag crystallize much better than that of Portland cement clinker owe to the low cooling rate of steel slag. Addition of limestone powder to certain extent improve compressive and flexural strength of cement mortar [15]. Steel slag when used in of 30 % substitution of the cement, the compressive strength is better than ASTM C150 standard. Also steel slag has no heavy metal dissolution problem [11], [16].

Rise in curing temperature up to 50°C is also found helping in higher hydration and early compressive strength in comparison with the limestone powder mix [17]. Additionally when 3% of CaCO₃ and 2% of CaSO₄.2H₂O was added to the binding material where 30% of the cement is replaced by steel slag, 3 days compressive strength

increased by 59.9% and 28 days compressive strength increased by 17.8%. It is found that CaCO_3 accelerates the hydration of C3S [18]. Superfine steel slag ($D_{50} = 2.52 \mu\text{m}$) is found having better cementitious properties as compared with the ordinary steel slag. Too much superfine steel slag is found to decrease strength of cement mortar [19]. Use of course steel slag with superplasticizers such as Glenium 51 showed good long term compressive strength of mortar [20]. It is observed that with increase in fineness of the steel slag, the water requirement of normal consistency and the setting time increased [21].

Attempts are also made to make cement free steel slag cementitious material with the use of compound agent like blast furnace slag, gypsum and silicates. The investigation shows that compressive strength of the mortar can reach 70 MPa [22]. Maximum up to 20% of Steel slag powder can be mixed with ground granulated blast furnace slag in cement-based materials. Flexural and compressive strengths of mortars was found higher [23]. A mortar sample containing 37.5 wt% carbonated BOF slag ($<0.5 \text{ mm}$) is found to be providing better replacement to the natural aggregate [24]. Compressive strength increased with increase in replacement of fine aggregate [25]. Steel slag with 5 % gypsum shows more hydration products and lower hydration exothermic rate as compared with only steel slag paste [26]. A blend of basic oxygen furnace steel slag with EAF slag and coal bottom ash when mixed in a ratio of 85:12.75:2.25 provides improved cementitious properties with low free lime content [27]. Based on a review of current literatures, it is obvious that blended cement has a low early-age strength and long initial setting time by replacing part of cement with steel slag. In order to improve the activity of steel slag, methods of mechanical activation, mineral modification and alkalinity activation are used. In the present study steel slag is used for replacement of the cement.

II. MATERIALS AND METHODS

Steelmaking slag is collected from Bokaro steel plant. The steel slag is characterized by sieve analysis, X-ray diffraction analysis, X-ray fluorescence, electron microscope. Sand of grade 1, 2 and 3 is used in the present study. Vicat apparatus is used for measuring normal consistency and setting time. Mortar blocks of the size of 70.6 mm X 70.6 mm X 70.6 mm (HEICO Ltd) is used to make blocks. Compressive strength is measured with automatic compressive testing machine (AMIL Ltd).

Steel slag is screened for different particle sizes, and fine sand of below 90 microns is used for these studies. Cementitious properties of steel slag are checked by normal consistency, initial and final setting time, soundness, compressive strength. The parameter like activity modulus, lime saturation factor, silica modulus, hydraulic activity and alumina modulus are also monitored. Soundness is checked by le-chateliers apparatus, mortar blocks of the size of 70.6 mm X 70.6 mm X 70.6 mm (HEICO ltd) are made and the compressive strength is measured with automatic compressive testing machine (AMIL Ltd), normal consistency and change in the setting time were recorded using vicat apparatus. Finer steel slag of the size below 90 micron is used for these studies. The slag was taken in to a small tank and was kept submerged for one hour for the completion of the adsorption process. It is suggested in most of the studies that adsorption is a spontaneous process. Three grades of sand i.e. grade I, grade II and grade III are taken in equal ratio in making of mortar blocks as per IS 650: 1991. Grade I is having an aggregate of size less than 2 mm and greater than 1mm, grade II is having an aggregate of size less than 1 mm and greater than 0.5 mm and grade III is having an aggregate of size less than 0.5 mm and greater than 0.09 mm. Cement to sand ratio is kept as 1:3. The mortar blocks with the replacement of cement by 5, 10, 15 and 20 % of the steel slag were prepared and their compressive strength with increasing the load at the rate of 2.9 KN/S. XRD of steel slag, cement and mix of cement and slag is studied and discussed.

III. RESULTS AND ANALYSIS

Characterization of materials

Fine steel slag and cement used in the study is shown in Figure 3. The steel slag is a whitish dusty and the size of the grain varies from 0.75 microns to 4 mm in diameter. Sieve analysis is done and it shows that the steel slag are a well graded. Figure 2 shows the surface morphology of steel slag particle shows sharp edges, partly dense, and partly porous. The BET surface area, pore diameter and the pore volume measured for the sample is $11.608 \text{ m}^2/\text{g}$,

4.06 nm and 0.010 cc/g respectively. Figure 1 shows the BET isotherm plots for the increase in volume of gas adsorbed onto the surface of the steel slag as pressure increases. According to the IUPAC, the material can be classified as mesoporous material. This is also confirmed by the studies done elsewhere [28]. Figure 3 shows the similarity in the texture of steel slag and the cement. Table 2 provides the X-ray fluorescence of the steel slag and cement from which Activity Modulus, Hydraulic activity, Alumina Modulus, Silica Modulus, Lime Saturation factor and C_3S are calculated using equations as given in Table 3.

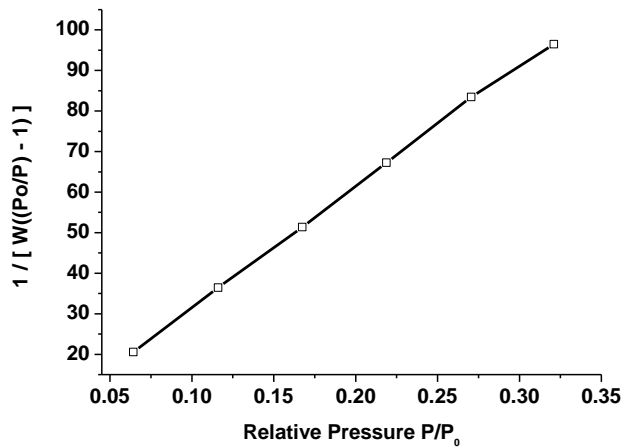


Figure 1: BET of Steel Slag

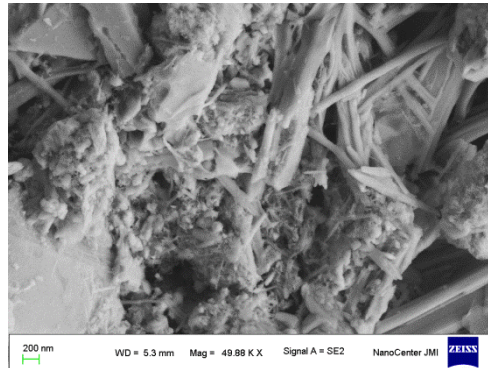


Figure 2: SEM of Steel Slag



Figure 3: Samples of Slag and Cement

Figure 4 shows the XRD pattern of the cement, slag (Oslag) and the sample containing Cement and slag (slag50) in a ratio of 1:1. The samples were hydrated with the water content as per the requirement for the measurement of normal consistency. The samples were crushed after 24 hours. The sample of cement has Ca(OH)_2 at 27 and 29.2 $^\circ$, C_3S & CaCO_3 theta, C_2S , C_3S and C_4AF 30 to 35 theta, FeO and Fe_3O_4 35.5 to 36. Oslag was not having well developed phases. However, slag50 has got very developed phases in the range of 27 to 36 theta. Portlandite Ca(OH)_2 is the most abundant phase in the steel slag which is due to high percentage of CaO in the slag [29]. C_3S phase is found to be a weak in the Oslag but the cement was having C_3S phase well developed. C_3S content is found improved in slag50. Increase in quartz (60.8°) is also found in Slag50. It can also be seen that, Ca(OH)_2 phase has reduced significantly and had reacted with the cement. C_3S , C_2S is the primary strength contributing phase and has increase in Slag50. Ca(OH)_2 is produced by hydration of calcium silicate phase. Main hydration products were C-S-H, Ca(OH)_2 , and ettringite, C_3S and C_2S . FeO (41.725° , 35.927° , and 60.482°) in the slag is transformed into FeO(OH) in the strong alkali phase of hydrated cement phase.

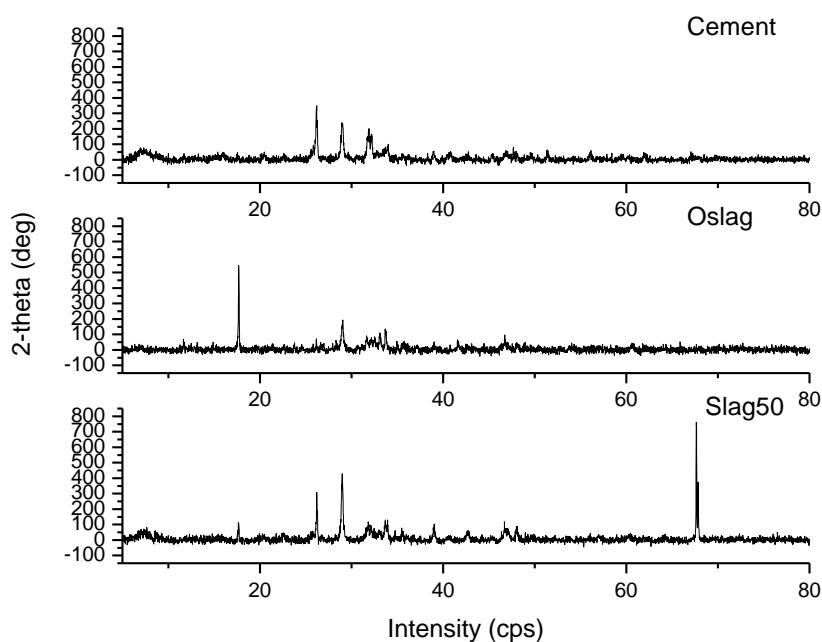


Figure 4: XRD of slag, cement under different compositions

Mortar blocks were prepared by replacing the cement by the steel slag up to 20 %, while the composition of the sand remained the same. Table 1 show that, the water requirement of the mix was not significantly reduced. Initial and final setting time of the cement remained unaffected till the cement replacement up to 10%. The final setting time increased drastically when the cement replacement was done up to 20%. Soundness checked by the le-chateliers experiments shows the increase in expansion of the sample when the mix contains the cement replacement 15 and 20 %.

Table 1: Composition of mortar and its properties

Replacement of Steel slag	20 %	15 %	10 %	5 %	0 %
Cement (gm)	160	170	180	190	200
Slag (gm)	40	30	20	10	0
Sand of Grade 1, 2 and 3 in equal proportion (gm)	600	600	600	600	600
Water requirement (%)	36.21	36.63	36.90	37.7	38.34
Initial Setting Time (min)	100	50	45	45	30
Final Setting Time (min)	620	320	220	180	180
Soundness (mm)	11	10	8	8	8

Table 2: Properties of Slag and Cement

Sample	Steel Slag	Cement
CaO (%)	46.21	60.84
Fe ₂ O ₃ (%)	14.89	3.2
SiO ₂ (%)	9.52	20.31
MgO (%)	2.51	3.17
Al ₂ O ₃ (%)	1.94	5.24
SO ₃ (%)	0.25	1.12
Activity Modulus	5.32	3.41
Hydraulic activity	50.37	47.05
Alumina Modulus	0.13	1.64
Silica Modulus	0.57	2.41
Lime Saturation factor	1.22	0.93
C ₃ S	80.73	50.35

Table 3: Equations used for cementious properties

$$Z = (CaO + MgO + Al_2O_3) / SiO_2 [30] \quad (1)$$

$$i = 20 + CaO + Al_2O_3 + 0.5 MgO - 2SiO_2 [30] \quad (2)$$

$$AM = Al_2O_3 / Fe_2O_3 \quad (3)$$

$$SM = SiO_2 / (Al_2O_3 + Fe_2O_3) \quad (4)$$

$$LSF = CaO / (2.8 SiO_2 + 1.2 Al_2O_3 + 0.6 Fe_2O_3) \quad (5)$$

$$C_3S = 4.071 CaO - 7.6 SiO_2 + 6.718 Al_2O_3 + 1.43 Fe_2O_3 + 2.852 SO_3 \quad (6)$$

Lime saturation factor (LSF) is the ratio of alite to balite in the clinker. In cement sample LSF is less than 1 show that no free lime is present in the cement sample. However, the steel slag sample has free lime in it. XRD also confirms the presence of free lime. However, this free lime reacts with the water to form Ca(OH)₂ [29]. Silica Modulus (SM) provides the information of presence of calcium silicates in the given sample. SM suggests that steel slag has significantly less amount of calcium silicate in its composition. Alumina Modulus (AM) as shown that the slag is low on aluminate and ferrite phases. Activity Modulus for Slag as well as cement is found to be good ($Z > 1.6$). Hydraulic activity (excellent $i > 16$) [30].

The compressive strength of the mortar replacing cement by 0, 5, 10, 15 and 20% of steel slag are compared for a period of 7 days, 28 days and 90 days. The samples of the mortar replacing cement by 0, 5, 10, 15 and 20% of steel slag are coded as C100, CSBA5, CSBA10, CSBA15, CSBA20 respectively. The results are given in Figure 5. The latter compressive strength of the slag in CSBA20 and CSBA15 was not satisfactory. The CSBA5 and CSBA10 gained early as well as later strength conforming to Indian Standards IS:8112 for OPC and IS:456 for PSC[31]. Thus, it can be said that, fine steel slag can be the option for the cement replacement up to 10%. Other studies confirm that performance of the mortar increase with the addition of steel slag [18], [19], [21], [32].

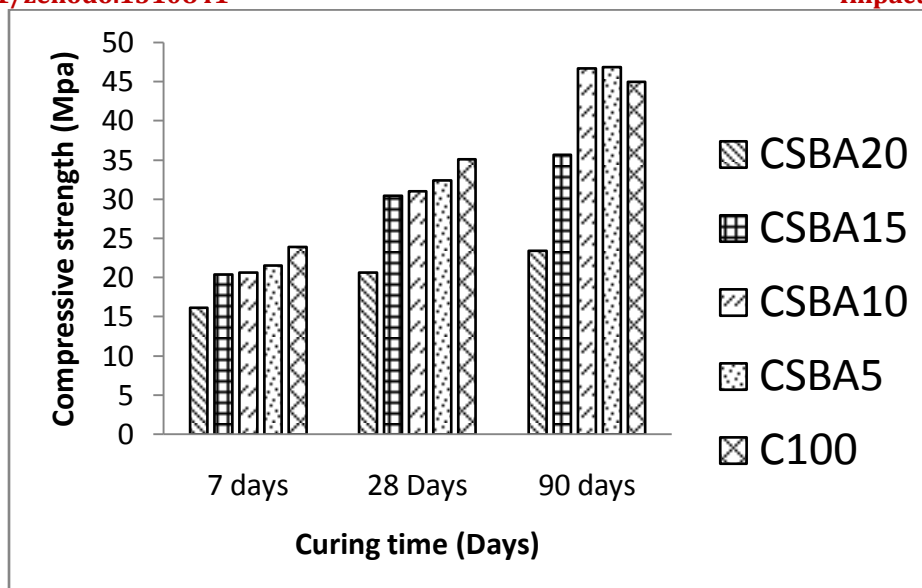


Figure 5: Compressive strength of steel slag

IV. CONCLUSION

The study reviews the recent development in the cementitious properties of the steel slag. The studies are done on the finer steel slag. The slag and the cement look similar when visually compared. The XRD of the cement shows well developed C_3S , C_2S whereas those phases are not found developed in the steel slag. The free lime content is found more in steel slag which brings soundness in the mortar mix having cement replacement 15 and 20%. It is also found that cement replacement more than 10 % decrease the latter compressive strength of the mortar. Thus, it can be concluded that the finer steel slag having the said composition can be used as cement replacement option up to 10%. The study revalidates that steel slag can be used as cement replacement and thus saving natural resources utilised for the cement manufacturing.

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