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Communication

Investigation of hydraulic activity of ground granulated blast furnace slag in concrete

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Abstract

Ground granulated blast furnace slag (GGBFS), a by-product of the steel manufacturing industry, being used as an effective partial cement replacement material, has already been proven to improve several performance characteristics of concrete. The reactivity of GGBFS has been found to depend on the properties of slag, which vary with the source of slag, type of raw material used, method and the rate of cooling. The present work aims at bringing out a novel relationship between the Hydraulic Index (HI) of slag at 7 and 28 days (HI7 and HI28) and the influencing properties of slag, namely, glass content, fineness and chemical composition by employing multiple regression analysis on 37 slag samples from various sources. HI7 and HI28, thus obtained, have been mapped onto a Slag Activity Index (SAI) plot, giving an indication of the ranges of strength of slag.

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1. Introduction

Blast furnace slag is a by-product obtained in the manufacture of pig iron in the blast furnace and is formed by the combination of earthy constituents of iron ore with limestone flux. When the molten slag is swiftly quenched with water in a pond, or cooled with powerful water jets, it forms into a fine, granular, almost fully noncrystalline, glassy form known as granulated slag, having latent hydraulic properties. Such granulated slag, when finely ground and combined with Portland cement (PC), has been found to exhibit excellent cementitious properties [1]. The reactivity of ground granulated blast furnace slag (GGBFS) is considered to be an important parameter to assess the effectiveness of GGBFS in concrete composites.

slag, various hydraulicity formulas have been proposed [2] as summarized in Table 1. However, it has been observed that these formulas do not adequately predict the strength

In order to predict the hydraulic activity of a blast furnace

performance expected from a slag, since the hydration reactions taking place are far more complex than indicated by these formulas [3]. From earlier research work, it has been accepted that the reactivity of slag is influenced by the slag properties such as glass content, chemical composition, mineralogical composition, fineness and the type of activation provided. Hence, the present work aims at obtaining the Hydraulic Index (HI) at 7 and 28 days (HI7 and HI28) by considering these crucial parameters influencing slag characteristics.

2. Physical and chemical characteristics of GGBFS

2.1. Physical characteristics

The specific gravity of the slag is approximately 2.90 with its bulk density varying in the range of 1200-1300 kg/ m³. The color of GGBFS is normally whitish (off-white).

2.1.1. Fineness

As with all cementing materials, the reactivity of slag is determined by its surface area. In general, increased fineness

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Table 1 Formulas proposed for assessment of hydraulicity of GGBFS

Serial number	Formula	Requirement for good performance	Preference
1	CaO/SiO ₂	1.3-1.4	1
2	(CaO + MgO)/SiO ₂	>1.4	1
3	(CaO + MgO)/	1.0 - 1.3	1
4	(SiO ₂ + Al ₂ O ₃) (CaO + 0.56 Al ₂ O ₃ + 1.4 MgO)/ SiO ₂	≥ 1.65	2
5	$(CaO + MgO + Al_2O_3)/SiO_2$	≥ 1.0	3

results in better strength development, but in practice, fineness is limited by economic and performance considerations and factors such as setting times and shrinkage. In the United Kingdom, GGBFS is marketed at a surface area of 375–425 m²/kg Blaine's, whereas some slags in the United States have a surface area in the range of 450–550 m²/kg; Canadian slags are about 450 m²/kg, while in India it is found to vary from 350 to 450 m²/kg Blaine's.

The fineness of GGBFS is a very important parameter, which is dependent on energy-saving and economic considerations, influences the reactivity of GGBFS in concrete, early strength development of concrete and water requirement. Swamy [4] reported that an increase in fineness of two to three times that of normal PC can preserve the benefits of material fineness on a variety of engineering properties such as bleeding, time of setting, heat evolution, high strength and excellent durability. Thus, for better performance, the fineness of GGBFS must be greater than that of cement.

2.1.2. Glass content

The glass content of slag is considered to be the most significant variable and certainly the most critical to hydraulicity. Several factors influence the degree of vitrification achieved during quenching, but the most important variable influencing the nature of slag is the temperature at which the furnace is tapped. The rate of quenching, which influences the glass content, is thus the predominant factor affecting the strengths of slag cements. Increasing crystalline contents reduce hydraulicity, but there is no well-defined or single relationship between strength and glass content, although some research has shown linear glass content-strength relationship [5]. Although a glassy structure is essential to reactivity, research has shown that there is no exact correlation of glass content to hydraulicity, and therefore, there is no guarantee that a high glass content will produce a highly reactive slag. Research data show that slag samples with as little as 30-65% glass contents are still suitable, but no specific minimum required glass content appears to emerge from these tests. Because of these uncertainties, most international standards judge slag activity by direct strength performance tests rather than include minimum glass content criteria [6]; although it has been heuristically reported that generally, the glass content of the slag should be in excess of 90% to show satisfactory properties.

2.2. Chemical characteristics

The chemical composition of the slag plays a key role upon which the HI has a bearing. From a chemical standpoint, slags can be classified into two types according to their basicity index. Several basicity indices have been defined by different authors, the simplest one being the CaO/SiO₂ ratio given by Nkinamubanzi [7] as given in Table 1. Metallurgists classify slag as either basic or acidic: the more basic the slag, the greater its hydraulic activity in the presence of alkaline activators [8]. At constant basicity the strength increases with the Al₂O₃ content, and a deficiency in CaO can be compensated by a larger amount of alumina (MgO). The influence of MgO as a replacement for CaO seems to depend both on the basicity and the MgO content of the slag. Variations in the MgO content up to about 8-10% may have little effect on strength development, but high contents have an adverse effect [8].

Further, Frearson [9] has mentioned that the presence of merwinite crystallites within the glass structure would improve the reactivity of slag. Moreover, it was observed that hydraulic activity increases with increasing CaO, Al₂O₃ and MgO and decreases with increasing SiO2 content. According to European Standard ENV 197-1:1992 and British Standards, the ratio of the mass of CaO plus MgO to the mass of SiO₂ must exceed 1.0. This ratio assures high alkalinity, without which the slag would be hydraulically inactive [10]. Lea [8] obtained similar trends on the CaO content and reported that the hydraulic value increases with the CaO/SiO₂ ratio up to a limiting point (not defined precisely), but CaO content beyond the limiting point makes granulation difficult and results in lower glass content as reported by Frearson [9]. In a later study, Frearson and Higgins [11] reported that the Al₂O₃ content of the slag influences the sulfate resistance of slag concrete and noted that an MgO level of about 13% is required for a satisfactory performance against the sulfate attack. The percentage of soluble sulfate (expressed as SO₃) is stipulated to be no greater than 4% and the percentage of total sulfur to be no

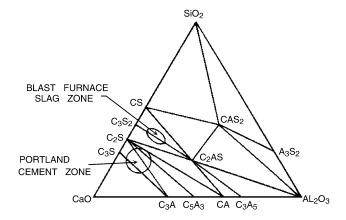


Fig. 1. Ternary diagram indicating composition of PC and GGBFS in the $\text{CaO-SiO}_2-\text{Al}_2\text{O}_3$.

greater than 2.5% for reasonable durability requirements. Moreover, according to Ganesh Babu and Sree Rama Kumar [12], the reactive glass content and fineness of GGBFS alone influence the cementitious/pozzolanic efficiency, or its reactivity in concrete composites, significantly within the limit of the above parameters.

3. Hydraulic reactivity of slag

Research carried out so far reveals that the hydration product that is formed when GGBFS is mixed with PC and water is essentially the same as the principal product formed when PC hydrates, i.e., calcium silicate hydrate (CSH) [2]. As seen in the ternary diagram in Fig. 1, PC and GGBFS lie in the same general field, although PC is essentially in the C_3S field, whereas GGBFS is found essentially in the C_2S field of the diagram. This is why GGBFS hydrates are generally found to be more gel-like than the products of hydration of PC, and so add denseness to the cement paste.

The hydration mechanism of GGBFS is different from that of cement. When GGBFS is mixed with water, initial hydration is much slower than PC mixed with water. Hydration of GGBFS in the presence of PC depends upon the breakdown and dissolution of the glassy slag structure by hydroxyl ions released during the hydration of PC and also the alkali content in cement. The hydration of GGBFS consumes calcium hydroxide and uses it for additional CSH formation. Research by Regourd [13], Vanden Bosch [14] and Roy and Idorn [15] have suggested that, in general, hydration of GGBFS, in combination with PC, at normal stage is a two-stage reaction. Initially and during the early hydration, the predominant reaction is with alkali hydroxide, but subsequent reaction is predominantly with calcium hydroxide.

The complexity of the influencing factors suggest that direct performance evaluations of workability, strength characteristics and durability are the most satisfactory measures of the effectiveness of GGBFS use. The ASTM C989 Slag Activity Index (SAI) is therefore recommended as a basic criterion for evaluating the relative cementitious potential of GGBFS.

4. Slag Activity Index

ASTM C989 defines SAI as the percentage ratio of the average compressive strength of slag cement (50–50%) mortar cubes to the average compressive strength of reference cement mortar cubes at a designated age, expressed as: SAI=Slag Activity Index, percent=(SP/ $P \times 100$) where, SP=average compressive strength of slag-reference cement mortar cubes [psi]; P=average compressive strength of reference cement mortar cubes [psi].

Based on this, slag was classified into three grades—Grade 80, Grade 100 and Grade 120 depending upon the

Table 2 SAI standards for various grades as prescribed in ASTM C989

Age and grade	SAI, minimum percent		
	Average of last five consecutive samples	Any individual sample	
7-day index			
Grade 80	_	_	
Grade 100	75	70	
Grade 120	95	90	
28-day index			
Grade 80	75	70	
Grade 100	95	90	
Grade 120	115	110	

relative compressive strength. Classification is in accordance with Table 2 (ASTM C989).

5. Hydraulic Index

To assess more critically towards high volume replacement of cement by slag and compare the same with other pozzolanic material, a new parameter, namely, Hydraulic Index (HI) could be introduced.

Keil [16] has defined the HI of the slag based on 70/30 as HI 70/30= $((a-c)/(b-c)) \times 100$ where: a=the strength of 70% slag/30% PC at time t; b=the strength of 100% PC at time t; c=the strength of 70% ground quartz/30% PC at time t.

This index gives a range of values from 0 to 100 or even greater, leading to a better range than that obtained in the ASTM SAI test, since the HI relates to the reactivity of the supplementary cementing material alone. The use of 70% slag content, higher than normally used, helps to distinguish the poor quality of slags from the good ones.

6. Novel relationships between HI7, HI28 and slag properties

Authors of this paper have studied a few more slag samples obtained from various sources in India. After determining the physical and chemical properties of these slag samples, it was observed that the oxide contents of each slag vary widely. Hence, the effect of each of these parameters on hydraulic index at 7 and 28 days (HI7 and HI28) need to be studied. Therefore, an effort is made to obtain such correlation among HI7, HI28 and the significant slag characteristics, namely, SiO₂, CaO, MgO, Al₂O₃, glass content and Blaine's fineness.

Hooton and Emery [17] have reported mortar cube strength data for 37 slag samples collected from various sources like America, Canada, Australia, France, Britain, etc. For this purpose, 50-mm mortar cubes were cast using ASTM Type I PC, commercially ground quartz and separately ground slag with relative densities in the range of 2.89

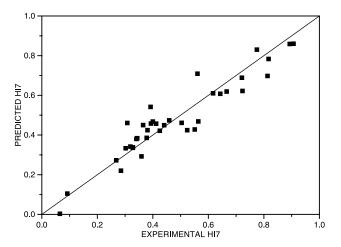


Fig. 2. Scatter of HI7 values (normalized).

and 2.97. A w/c ratio of 0.485 used for PC was reduced to 0.439 for mortars incorporating slag. For finely ground slag (\sim 498 m²/kg Blaine), a w/c ratio was further reduced to 0.419. Mortar cubes were moist cured at 23 °C and 100% relative humidity (RH) and then tested in compression at 7 and 28 days. The HIs were calculated from these strength results of slag cubes in comparison to those of PC and quartz cubes as per Keil's [16] approach.

Multiple regression analysis was then employed on this data to compute HI7 and HI28. The combination of different slag parameters affecting the HI has been tested. The first equation was developed using SiO_2 and glass content of slag. Further, two of the compositional moduli, namely, (C/S) and ((C+M+A)/S), often cited in the literature, have been incorporated along with the glass content to form Eqs. (2) and (3), respectively. Ultimately, the influence of all the significant physical and chemical characteristics of slag (SiO₂, CaO, MgO, Al₂O₃, glass content and Blaine's fineness) have been simultaneously taken into account to obtain HI7, giving rise to Eq. (4).

$$HI7 = 325.627 - 9.144(SiO_2) + 0.735(glass)$$

$$R = .888 \tag{1}$$

$$HI7 = -231.026 + 0.72(glass) + 205.738(C/S)$$

$$R = .914 \tag{2}$$

HI7 = -241.472 + 0.638(glass) + 149.729

$$\times ((C+M+A)/S)$$

$$R = .925 \tag{3}$$

$$\begin{split} HI7 &= -46.991 + 4.589(CaO) - 5.733(SiO_2) \\ &+ 4.582(Al_2O_3) + 2.93(MgO) + 0.633(glass) \\ &+ 3.5(Blaine) \end{split}$$

$$R = .941 \tag{4}$$

where Blaine represents Blaine's fineness in units of 500 m^2/kg .

The standard deviations for Eqs. (1), (2), (3) and (4) are 9.77, 8.64, 8.07 and 7.68, respectively.

From the values of the coefficient of correlation for each of these equations, the best correlation for HI7 has been found to be Eq. (4) with R=.941. A scatter (normalized between 0 and 1) of predicted HI7 values against their experimental counterparts, as obtained by authors and reported by Hooton and Emery [17], is depicted in Fig. 2.

Similarly, the relations for HI28 have been obtained as:

(5)

$$HI28 = -143.496 + 1.025(glass) + 132.21(C/S)$$

 $R = .801$

HI28 = -155.817 + 0.976(glass)

$$+99.603((C+M+A)/S)$$

$$R = .813$$
 (6)

$$\begin{split} HI28 &= -36.908 + 3.112(CaO) - 3.909(SiO_2) \\ &+ 2.989(Al_2O_3) + 2.425(MgO) + 0.966(glass) \\ &+ 12.5(Blaine) \end{split}$$

$$R = .815 \tag{7}$$

where again, Blaine represents Blaine's fineness in units of 500 m²/kg.

The standard deviations for Eqs. (5), (6) and (7) are 15.36, 14.95 and 15.84, respectively. The relationship of HI28 with glass content and SiO₂ gives an R value even less than .8 and hence, is not considered here.

Eq. (7) with R=.815, best predicts HI28. Fig. 3 shows a graph of a scatter of normalized values of HI28 from Eq. (7) vis-à-vis their corresponding experimental values.

It is then obvious from the exhaustive HI7 and HI28 relationships (Eqs. (4) and (7) above), that physical and

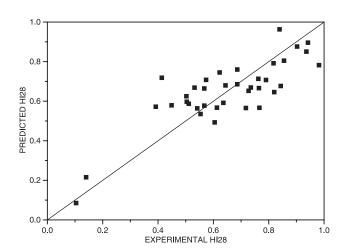


Fig. 3. Scatter of HI28 values (normalized).

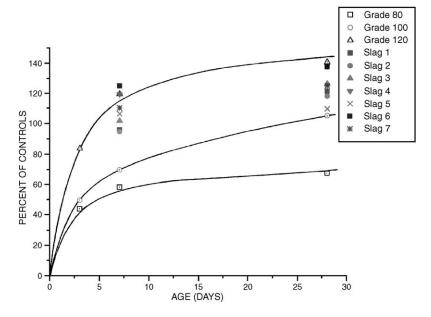


Fig. 4. Graph of SAI grades and HI7, HI28 values.

chemical properties, i.e., glass content, fineness and all major oxides such as CaO, SiO₂, Al₂O₃ and MgO of slag, in fact, do significantly influence the HI of slag both at 7 and 28 days. Further, the glass content and fineness have a remarkable effect on HI7 and HI28, as is evident from the significant values of their corresponding coefficients in these relationships.

It is now instructive to study the connection between HIs as obtained from Keil's [16] approach and SAI values as defined by ASTM C989. Fig. 4 portrays the curves for Grades 80,100 and 120 as per SAI. The values of HI7 and HI28 computed from the equations developed herein have been mapped on this plot. It has been observed that HI7 values in the range from 95 to 120 lie between the Grade 100 and Grade 120 curves, whereas HI7 of 125.22 (>120) lie above the Grade 120 curve. This means that at 7 days, SAI Grade 100 and Grade 120 numerically correspond to the HI (percent of controls) values of 100 and 120, respectively, as obtained from the HI7 equation developed in this work, leading to a direct correlation between SAI at 7 days and HI7. However, at 28 days, all the HI28 values lie within the Grade 100 and Grade 120 curves. Thus, Eqs. (4) and (7) could be gainfully employed for computing HI7 and HI28, given the significant physical and chemical characteristics of slag.

7. Conclusions

- The HIs are strongly correlated with the most significant physical and chemical properties of slag, namely, SiO₂, CaO, MgO, Al₂O₃, glass content and Blaine's fineness at both 7 and 28 days.
- 2. HI defined on 70/30 basis can be related with SAI having 50/50 basis, which in turn indicates the strength performance of slag.

- Using the equations developed in this work, the reactivity of slag can be determined knowing the physical and chemical properties of slag, even in the absence of mortar compressive strengths.
- 4. A wide range of variations in the slag characteristics can be accounted for in these equations, which not only predict the HI but also the strength performance of slag at 7 and 28 days.
- HI7 has been found to numerically correspond to the SAI Grade 100 and Grade 120 slag.

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