AN INVESTIGATION ON ENHANCING BLAST FURNACE SLAG CONTENT IN PORTLAND SLAG CEMENT THROUGH ALKALI ACTIVATION

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ABSTRACT

The present paper highlights the experiments carried out at laboratory scale before plant scale production in identifying: (a) suitable activator/s either in combination or single (b) to arrive at optimum dosage of the activator/s at enhanced slag addition (c) to get suitable particle size distribution to achieve desired strength development in the product (d) to choose appropriate blend ratio of slag from two different sources keeping in mind the cost economics, feasibility to get required strength development etc. The present investigation has helped in enhancing the slag content from 35 % to 51 % with significant improvement in quality parameters like compressive strengths at initial ages (i.e. 1 and 3 days) without hampering the later strengths. The paper also deals with durability studies carried out on concrete prepared with this cement system and with Portland cement for comparison . The results reveal the better durability potential of this cement system over Portland cement concrete. The above investigation substantially improves the conditions for utilizing blast furnace slag in appreciable quantities during cement production and helps in reducing the manufacturing cost and carbon dioxide emissions. The paper also reviews the background and prior art of the investigation.

1. INTRODUCTION

Extensive research works have been done and well documented world wide on alkali activation of slag cement as it is drawing more attention because of their performance and utilization of byproducts in its manufacture.(1) Compared to Portland cements, alkali activated slag cement has some advantageous properties including rapid development of high strength, good durability and high resistance to chemical attack.(2,3,4,5)

It is generally agreed that the performance and microstructure of alkali activated slag cements are determined by chemical and mineralogical compositions of slag, the dosage and nature of activator(s) used(1) Unless a chemical activator is present further hydration is inhibited. Portland cement, gypsum and many alkalis have been used as activators and it has been observed that the rate of hydration is faster at high alkali concentrations.(2)

The present investigation is aimed to achieve:

- To enhance the percentage addition of slag through alkali activation
- To improve compressive strengths of slag cements at initial ages particularly at 1 and 3 days and without hampering of later strengths at 28 day.
- To ascertain the durability characteristics of concretes made out of cement under investigation vis-à-vis ordinary Portland cement.

2. MATERIALS AND METHODS

2.1 Granulated blast furnace slag

It is a non-metallic co-product produced in the production of iron. Iron ore, iron scrap and fluxes (limestone and dolomite) are charged into blast furnace along with coke or fuel. The coke is combusted and produced carbon monoxide, which reduces the iron ore to a molten iron product. It consists primarily of silicates, alumino silicates, and calcium-alumino-silicates. If the molten slag is cooled and solidified by rapid water quenching to a glassy state, little or no crystallization occurs.

The chemical composition of slag can vary over a wide range depending on the nature of the ore, the composition of limestone flux, the coke consumption and kind of iron being made. These variations affected the relative content of four major constituents, lime, silica, alumina and magnesia. Table 1 gives chemical composition of slags from different countries.(7)

Table 1 – Chemical Composition of blast furnace Slags (%)

Source	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	MnO	S
UK	40	35	16	6	0.8	0.6	1.7
Canada	40	37	8	10	1.2	0.7	2.0
France	43	35	12	8	2.0	0.5	0.9
Germany	42	35	12	7	0.3	0.8	1.6
Japan	43	34	16	5	0.5	0.6	0.9
Russia	39	34	14	9	1.3	1.1	1.1
South Africa	34	33	16	14	1.7	0.5	1.0
USA	41	34	10	11	0.8	0.5	1.3

The following characteristics are considered in judging the suitability of blast furnace slag in India as per in IS: 12089(12).

a. The percentage oxide shall satisfy the following:

$$\frac{CaO + MgO + Al_2O_3}{SiO_2} \geq 1.0$$

b. Manganese oxide – 5.5% (max)
c. Magnesium Oxide – 17.0% (max)
d. Sulfide Sulfur – 2.0% (max)
e. Glass Content – 85.0% (min)

Table 2 – Chemical and Physical Characteristics of blast furnace slags in the present investigation.

Parameter	Slag 1	Slag 2
Chemical (%)		
SiO_2	33.9 – 36.0	32.1 – 37.0
Al_2O_3	16.0 – 19.0	16.0 – 20.0
Fe_2O_3	1.1 – 2.2	0.5 – 1.5
CaO	32.0 – 35.0	32.0 – 35.0
MgO	8.0 – 9.4	7.9 – 10.0
Sulfide Sulfur	0.5 – 1.5	0.8 – 1.6
MnO	0.4 – 0.6	0.2 – 0.5
TiO_2	0.3 – 0.5	-
Na_2O	0.4 – 0.65	0.3 – 0.5
K_2O	0.4 – 0.7	0.4 – 0.6
Chlorides	Traces	Traces
Physical		
Glass Content (%)	85.0 – 96.0	85.0 – 97.0
Density (kg/lit)	1.0 – 1.5	0.8 – 1.2
Moisture (%)	0 – 2.0	2.0 – 10.0
Granulometry (%)	+ 3.35 mm = 40 – 43% + 1.18 mm = 85 – 92% - 1.18 mm = 8 – 11%	1 – 3% 16 – 18% 80 – 85%

2.2 Portland Cement Clinker

The second ingredient in cement composition in accordance with this invention is cement clinker. Clinker, consisting mostly of calcium silicates, obtained by heating to incipient fusion a predetermined and homogeneous mixture of materials principally containing lime (CaO) and silica (SiO_2) with smaller proportion of alumina (Al_2O_3) and iron oxide (Fe_2O_3). The range of chemical composition of Portland clinker is shown in the table 3 and table 4:

Table 3 – General range of chemical and phase of composition of clinker

Parameter	**%**
SiO_2	19 – 25
Al_2O_3	2 – 8
Fe_2O_3	3 – 6
CaO	60 – 65
MgO	1 – 6
Alkalis (as Na_2O equivalent)	0.2 – 1.5
LSF(Ratio)	0.66 - 1.02
C_3S	20 – 60
C_2S	20 – 30
C_3A	0 – 16
C_4AF	1 – 16
Free Lime	0 – 3

Table 4 – Chemical and Phase composition of clinker in the present investigation

Parameter	**%**
SiO_2	21.67 - 22.03
Al_2O_3	5.14 - 5.54
Fe_2O_3	4.36 - 4.96
CaO	65.0 - 65.69
MgO	0.82 - 1.36
Na_2O	0.1 - 0.3
K_2O	0.3 - 0.4
Alkalis as Na_2O	0.22 – 0.38
LSF(Ratio)	0.91 - 0.93
C_3S	46.6 - 51.0
C_2S	24.0 - 27.0
C_3A	5.0 - 7.2
C_4AF	13.3 - 15.2
Free Lime	1.1 - 2.0

2.3 Alkali activator

The characteristics of the same are given in Table 5:

Table 5 – Characteristics of alkali activator used in the present investigation.

Parameters	Characteristics
Colour	White
Flow ability	Good, free flowing
Moisture (%)	< 0.5%
pH	6.5 – 10.0
Purity (%)	> 99.0
Chloride content (%)	< 0.2

3. EXPERIMENTAL

Various feasibility trials with different activators, single and combinations at different doses, at different fineness of slag, at different slag content have been carried out to identify the suitable activator for incorporating 50 % plus slag without hampering the quality of the product. By these investigations it is deciphered that alkali activator with given composition of slags and clinker will give the desired results.

In order to optimize, (i) the dosage of alkali activator, (ii) percentage incorporation of both Slag 1 and Slag 2 (ratio) (iii) fineness of resultant product, many trials have been conducted using alkali activator (Chemical grade) in the laboratory.

3.1 Methodology

The physical and chemical characteristics of resultant Portland Slag Cement have been evaluated as per the procedure given in Indian Standard specification IS: 4031(13) and IS: 4032(14). Many trials have been conducted with different activators at different doses.

Subsequently, some more trials were conducted by using commercial grade alkali activator and the results are shown in table 6.

Table 6 Lab Ball Mill Trial with 51% Slag Cement Ground With alkali activator.

Feed Composition & Test Carried Out	Sample (A)	Sample (B)
Clinker (%)	X	X
Slag 1 (%)	Y	Y
Slag 2 (%)	Z	Z
Gypsum (%)	P	Nil
Alkali Activator (%)	Nil	b
Residue (90mic)%	2.35	2.50
Blaine's (m^2/kg)	326.00	325.00
N. C (%)	27.00	27.00
Compressive Strength (Mpa)		
1 Day	8.50	12.3
3 Days	20.20	23.2
7 Days	30.30	32.70
28 Days	51.20	53.5

Finally, confirmatory trials have been carried out to establish the repeatability before initiating the production of Portland Slag Cement on large scale at plant. Table 7 shows the results of confirmatory trials.

Table 7 Lab Ball Mill Trial With alkali activator – Confirmatory Trial

Feed Composition & Test Carried Out	Sample (C)	Sample (D)
Clinker (%)	X	X
Slag 1	Y	Y
Slag 2	Z	Z
Gypsum (%)	Nil	Nil
Alkali activator (%)	b	b
90mic Residue %	2.70	2.60
Blaine's (m^2/kg)	330	324.00
Compressive Strength (Mpa)		
1 Day	12.5	12.10
3 Day	24.6	23.50
7 Day	33.0	32.70
28 Day	54.2	54.5

3.2. Plant scale trial

Plant scale trial has been carried out with optimum combination of raw materials derived from laboratory trials and the results are as follows:

Table 8 Quality of the Cement

Parameters	35% slag Cement	51% slag Cement	% of Improvements
Residue% (90 mic)	1.6	1.40	
Blaines (m^2/kg)	329	338	
Compressive Strength (Mpa)			
1 day	10.3	13.6	32.0
3 days	25.7	27.1	5.5
7 days	36.9	38.4	4.1
28 days	54.7	54.1	

4. BACKGROUND OF INVESTIGATION INCLUDING PRIOR ART

In the present investigation the role of alkali activators performing the dual function of activating the slag at initial ages (i.e. 1 day), as well as activating the dormant sulfur phases in the clinker, is innovatively tapped. Though there are many activators like NaOH, Na_2SO_4, water glass (Na_2SiO_3), Na_2CO_3, KOH, K_2SO_4 for alkaline activation of slag, not all would perform the aforementioned dual objectives.(7) Hence, the key for success lies in selection, assessment of particular activator, and its compatibility with the given slag and clinker composition.

The initial stage of investigation was mainly concentrated in selecting the right kind of activator / activators compatible with the given slag and clinker compositions. After this stage is over, the next phase of investigation carried out to fix the proper dose of activator, proper proportioning of slags from two different sources in view of achieving the desired quality in the cement and economy. The laboratory trials carried out have been reconfirmed by repeated trials before taking trials in plant scale.

In present study, clinker, slags and activator have been interground in a cement ball mill to predetermined fineness and evaluated its performance in the laboratory. During the investigation one of the important ingredients in cement manufacture i.e. gypsum has been eliminated totally, primarily due to the use of sulfur containing phases from clinker in lieu of gypsum.

Alkaline activation of slag

The principle of alkaline activation of slag has been known since 1940's.(6) Although many attempts have been made to explain the hydration process of alkali activated slag cement, the roles of activators are still not well documented(1).

C-S-H with low C/S ratio is the major hydration product of alkali slag cement although the minor hydration products may vary with the nature of slag and activator used. Solubility curves of C-S-H and N-C-S-H in corporate into C-S-H in 3 different mechanisms: (a) neutralization of acidic Si – OH groups by Na^+ or K^+, (2) ion exchange of Na/K for Ca (3) Cleavage of Si – O – Si bonds by Na^+ or K^+ with attachment of Na^+ or K^+ to Si. Depending on the C/S ratio of C-S-H one or another mechanism may dominate, however the 3 mechanisms co-exist(1,7,8,9,10)

The incorporation of alkali into C-S-H increases as C/S ratio of the C-S-H decreases. The main restriction for the incorporation of alkali into the structure of C-S-H is probably the condition of electro neutrality. The incorporation of alkalis affects the solubility curve of C-S-H. However, alkalis in C-S-H can be leached out easily. The lumping out of alkalis from C-S-H moves its solubility curve towards its original curves.(11)

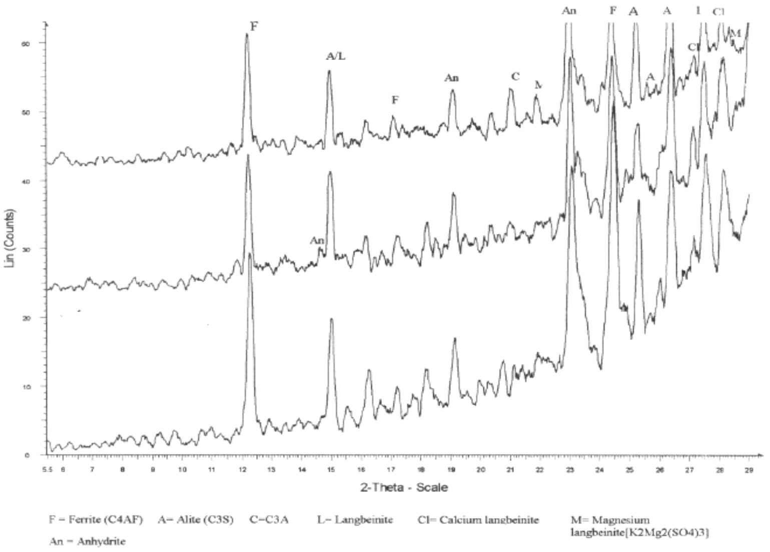
The presence of alkalis keeps a high pH value in the solution, which is important to initiate and to continue the hydration of the slag(7). However, alkalis are not really involved in the hydration process and hydration products. Alkalis can be simply regarded as catalysts rather than reactants. However, anion or anion groups of activators have a great effect on the hydration, structure formation and properties of hardened alkali activated slag cements.

‘S’ containing phases in clinker

Sulfur is incorporated into the clinker during the pyro processing operations. Sulfur could enter the system through the limestone or fuel (pet coke/coal). The distribution of sulfur in the clinker mineral phases was determined by examining the clinkers using X-ray fluorescence, X-ray diffraction and selective extraction techniques.

The alkali content in most plants is low, which indicates that the sulfur available in the system may not be fully matched by alkalis to form alkali sulfates. Hence, there exists a possibility of the formation of other sulfur bearing compounds or incorporation of sulfur in the clinker mineral phases.

The XRD pattern analysis as shown in the figure indicates that the major sulfate containing phase is the anhydrite ($CaSO_4$) and calcium langbeinite ($Ca_2K_2(SO4)_3$). This may be attributed to the low concentration of alkali in the kiln feed.



Typically, 50% of the sulfates are incorporated in the silicate phases, while the rest remain in the interstitial phase as anhydrite and needle-shaped crystals of calcium langbeinite.

Activation of ‘S’ containing phases in clinker

Sulfate is added to cement to control aluminate hydration and to enhance tricalcium silicate hydration, promoting improved strength development. The amount, form and fineness of sulfate dictate its solubility and, therefore, its effect on aluminate hydration. This interaction between the sulfate and clinker phases is important as it influences concrete workability, strength, setting time, drying/shrinkage and expansion and, hence, durability.

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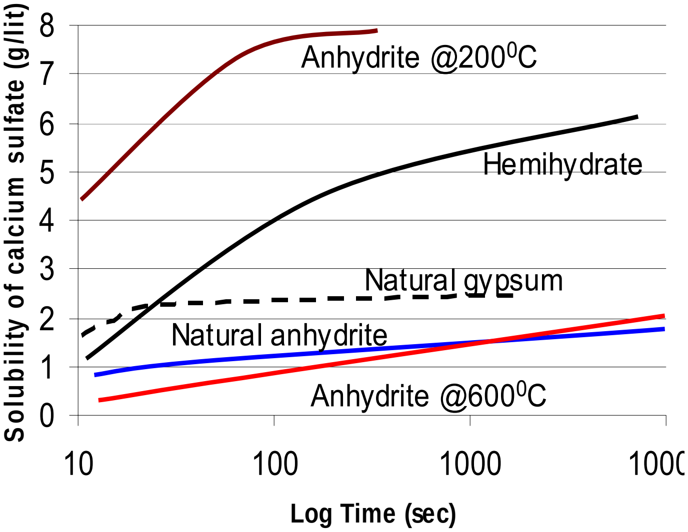
During the process of grinding cement clinker, the friction inside the grinding mill generates heat. When it reaches to certain temperature, the gypsum added in the grinding mill in the manufacture of Portland slag cement, may undergo partial or complete dehydration to form gypsum hemihydrate ($CaSO_4 . \frac{1}{2}H_2O$) or anhydrite ($CaSO_4$) respectively or both.



The above figure depicts the solubility of the different $CaSO_4$ phases.

Gypsum hemihydrate, upon addition of water dissolves rapidly and precipitates to form gypsum dihydrate. If the composition of hemi hydrate is very high, it may undergo rapid hydration to produce false set, otherwise known as premature stiffening in hydrated cement. Sometimes false set occurs in the product after being aerated or in storage. Also, low hemihydrates content would lead to inadequate control of aluminates hydration. The hydration of aluminates phases would lead to voluminous hexagonal aluminates hydrates form instead of combining with sulfate to form ettringite.

Anhydrite that is formed within the grinding mill (at temperatures of about 100 - 110°C) is also highly soluble, as it develops from the hemihydrate phase, and has the same crystal structure.

However, anhydrite, which is formed in the cement kiln (at temperatures higher than 600°C), is much harder than gypsum and has the slowest dissolution rate of the three sulfate forms, in part due to its large size resulting from its hardness. It undergoes hydration very slowly with a very low reactivity. As such, it is not of much practical utility. However, when certain activators are added to the hydrating anhydrite, the hydration and subsequent reactions could be enhanced considerably.

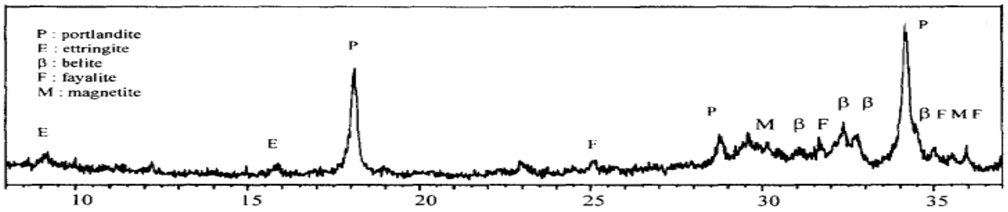
The dormant anhydrite within the clinker phases could be activated using such activators to have an appropriate amount of sulfate ions available, which would control the aluminates hydration, leading to paste of proper plasticity, normal setting and hardening properties.

A mechanism of conversion of anhydrite into gypsum in the presence of activators is suggested. The hydration of anhydrite involves a dissolution-nucleation-growth process. Typically, the dissolution takes place through the formation of transient double salts.

The most suitable activators would be those which fulfill the dual function of the activation of slags as well as the activation of anhydrite simultaneously. This would ensure that the slag is available for the cementitious as well as subsequent pozzolanic reactions; while the aluminates hydration is also retarded using the sulfates already existing within the clinker.

Many trials have been conducted with different activators, viz., Na_2CO_3, KOH, NaOH, and K_2SO_4 at different doses. The trials with these activators indicated that the activators exhibiting the best properties due to the slag activation and the retardation of aluminates hydration was K_2SO_4.

XRD pattern analysis as shown in the following figure indicates that the ettringite phase is formed even in the absence of addition of gypsum in the mill. This may be attributed to the reaction of sulfur-containing phases (such as insoluble anhydrite) in the clinker.



The optimum dosage of the best activator was determined based on the best performance of the cement in terms of its early age strength as well as its 28-day strength.

5. DURABILITY STUDIES

Two grades of concretes are prepared from normal Portland cement and the cement under investigation in identical conditions and results are shown below:

Table 9 Durability characteristics of Portland cement and Portland slag cement

Specimens	Slump (mm)	Compressive Strength at 28 days, N/mm2	Permeability 1 X 10^{-12} m/s	Weight loss % at 30 days immersion	Resistivity ohm / cm	Chloride permeability, coulombs
OPC - 30	12	28	2.25	17.0	42000	1700
PSC - 30	41	32	1.7	9.2	52000	475
OPC - 45	18	46	1.89	21.1	45900	1560
PSC - 45	13	48.2	1.2	13.6	55158	340

Note: Mix Proportions

- 1:2.20:2.83:0.54 (M30)
- 1:2.26:1.95:0.37 (M45)

Cement Content

- 350 kg/m3 (M30)
- 515 kg/m3 (M45)

The above data reveal that both the grades and varieties of concrete are showing more or less same characteristics but there are some identifiable advantages in the concrete of slag cement over Portland cement concrete. This can be seen in the property like, chloride diffusivity. Normal Portland cement concretes show low to moderate values (1800-4000 coulombs) and the concrete of slag cement show below 1000 coulombs indicating low chloride diffusivity. Similarly, the value of weight loss % of slag cement concrete was much lower than the normal Portland cement concrete.

6. CONCLUSIONS

Based on the above studies, the following conclusions are drawn:

- The alkali activation method is quite effective in enhancing the slag percentage from 35 % to 51 % with very remarkable improvement in compressive strength at 1 and 3 days without hampering the later strength.

- The compatibility of alkali activator/s with given clinker and slag composition is very significant in achieving desired properties in slag cement.

- The increase in slag content (in slag cement) has helped in reducing the cost of manufacture of slag cement which resulted in good savings.

- The durability studies conducted on concretes of slag cement show better durability potential vis-à-vis Portland cement concrete.

- The optimization of particle size distribution /fineness is very crucial in achieving higher compressive strength at all ages.

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