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Mohd. Nadeem Qureshi [α] & Somnath Ghosh [σ]

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Keywords : alkali activated blast furnace slag, K_2O content, compressive strength, XRD, microstructure.

I. Introduction

Ground granulated blast furnace slag 'GGBFS' is one of the 'greenest' of construction materials. It is a by-product from the blast-furnaces manufacturing iron. By comparison with Portland cement, manufacture of alkali activated blast furnace slag (AABFS) paste requires less than a fifth of energy and can save up to 80% of CO_2 emission caused by the cement industries. Each year, India produced up to eleven million tonnes of GGBFS which can be significantly utilized in manufacturing of construction material which is environment- friendly and will greatly reduce primary energy, saves bulk of quarrying as well as potential landfill. Blast furnace slag consists primarily of silicates, alumina-silicates and calcium-alumina-silicates and can be good raw material for making high materials which can be utilized in various civil engineering applications.

Blast furnace slag as a byproduct have a different composition depending on the raw materials and the industrial processes; hence, each slag differs in response to activation (Wang et al, 1994; Bakhrev et al, 1999). The optimum slag composition for blast furnace operation falls in CaO-MgO- Al_2O_3-SiO_2 system (Osbom et al, 1954). Many researchers have confirmed that water-glass is a very effective activator (Glukhovsky et al, 1978; Shi et al, 1989a; Shi et al, 1989 b). Many results confirmed that the effect, that an activator has on strength development may be different for slag of different origins. The results on activation of Australian slag by a combination of NaOH and Na_2CO_3 were published elsewhere.(Collins and Sanjayan,1998).

Alkali activated blast furnace slag paste behaves differently than OPC. There is insufficient knowledge about the relationship between alkali activated slag properties and synthesizing parameters of alkali activation. The present study was conducted to study the effects of alkali contents (% K_2O+ % Na_2O) on compressive strength on alkali activated blast furnace slag paste. The mineralogical and microstructure changes were studied using XRD and scanning electron microscopy.

II. Experimental Investigation

a) Materials

i. Slag

Ground granulated blast furnace slag used in this investigation obtained from the Tata Metalliks Ltd. Kharagpur, India. The chemical composition is given in Table 1. Its density was 2900 kg/m^3. Slag was ground to the particle size 100% passing 45 micron sieve. The moisture content was less than 1%. Based on the chemical composition, blast furnace slag is classified as an acidic with the basicity coefficient Kb = (CaO + MgO+Fe_2O_3)/(SiO_2+Al_2O_3) = 0.82 and the hydration modulus = (CaO + MgO + Al_2O_3)/SiO_2 =1.84. It consists of 85% glass and having some crystalline components such as akermanite, gehlenite, quartz etc.

ii. Alkaline Activator

The alkaline activator liquid was the combination of sodium silicate and potassium hydroxide pellets. Laboratory grade potassium hydroxide was supplied by Merck India Ltd. (84% purity with K_2O =83.93% and 16.07% water) and sodium silicate solution (Na_2O=8%, SiO_2=26.5% and 65.50% water) with silicate modulus ~3.3 and bulk density of 1410 kg/m^3 was supplied by Loba Chemie Ltd. India, were used to adjust the desired composition of AABFS.

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Table 1 : Chemical composition of blast furnace slag by XRF

Chemical composition	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	S	MnO	LOI*
Mass (%)	32.5	33.5	18.5	8.00	0.40	0.5	0.55	0.7

* Loss on ignition

b) Test methods and preparation of test specimens

i. *Compressive strength and split tensile strength*

The alkali activated GGBFS paste specimens (50mm x 50mm x 50mm) were tested for compressive strength using 20 ton capacity digital compressive testing machine with a loading rate of 20 MPa/min. The compressive strength tests were conducted at the age of 3, 7 and 28 days. Three specimens of each series at each age were crushed in a digital compression testing machine in accordance with ASTM C-109-02 and the average strength of three specimens is reported as the compressive strength. The split tensile strength at the age of 28 days was tested in accordance to ASTM C-496, using 50 mm diameter by 100 mm long cylinders.

ii. *Workability*

The workability was assessed using mini flow table test as per ASTM C 1437-07 with a modification; the table was raised and dropped 15 times in about 15 seconds. The mini flow table apparatus was used as per ASTM C 230/C 230M. The workability of the mix was determined by measuring the diameter of paste flow on a flow table in two perpendicular directions after 15 drops in 15 seconds and the average value is considered as a flow diameter. The percentage increase in flow diameter with respect to the initial diameter of mould is considered as flow value.

iii. *XRD and SEM/EDAX*

To perform the XRD analysis, paste sample was carefully removed from the core of the sample to be tested. Each sample was finely ground (passing 45 microns) and then analysed using XRD. The mineralogical phases present in the specimens were monitored by means of X-ray diffraction (XRD) using a Rigaku Miniflex XRD machine with Cu-Kα radiation in steps of 0.5^0 (2theta) at a rate of 1^0 (2 theta) per minute, sweep from 10^0 to 90^0 (2 theta), according to the diffraction powder method. The results were compared with the International Centre for Diffraction Data (ICDD) database.

Scanning Electron Microscopy (SEM) was used to record micrographs while energy dispersive x-ray spectroscopy (EDAX) was used for semi - quantitative analysis. A JEOL JSM 6360 equipped with an Inca Oxford EDX analyzer was used for obtaining SEM micrographs and EDAX spectra of raw slag and alkali activated blast furnace slag specimens.

iv. *Preparation of alkali activated paste*

The alkali activated blast furnace slag (AABFS) paste was prepared by varying % K_2O ratio from 4 to 10 % by keeping constant percentage of SiO_2 = 8 %. The compositional change in AABFS mix was obtained by adjusting the quantity of potassium hydroxide (KOH), sodium silicate solution and water. The activator solution was prepared at least one day prior to casting of test specimens. The water / slag ratio was kept constant equal to 0.32. The chemical composition of AABFS mix and corresponding compressive strength of specimens are presented in Table 2.

For making AABFS paste specimens, the blast furnace slag and activating solution in desired proportion was first mixed together for five minutes in a Hobart Mixer to get homogeneous paste. The fresh paste mix had a sticky nature with good workability. The fresh mix was then transferred into 50 mm ×50 mm ×50 mm steel moulds and vibrated for two minutes on vibrating table to remove any entrapped air. The specimens were left at room temperature for 24 hours, then demoulded and kept in water in fully immersed condition at room temperature until testing was done. The tests were conducted at the age of 3, 7 and 28 days.

Table 2 : Detail of mix composition of alkali activated blast furnace slag paste

Mix ID	Mix Composition							
	% K_2O	%Na_2O	%SiO_2	SiO_2/(K_2O+Na_2O)	w/b	w/s	H_2O/K_2O	Slag/ alkaline activator
AABFS4-8	4	2.41	8	1.24	0.297	0.32	8.5	2.79
AABFS6-8	6	2.41	8	0.95	0.283	0.32	5.5	2.58
AABFS8-8	8	2.41	8	0.76	0.279	0.32	4.13	2.41
AABFS10-8	10	2.41	8	0.64	0.274	0.32	3.3	2.25

- % of mass added with respect to the total mass of slag
- Binder = mass of (Slag + K_2O+Na_2O+ SiO_2)

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III. Results and Discussion

a) Workability

Fig.1 presents the effect of alkali content on the workability of blast furnace slag paste. The alkali content (% K_2O) was varied from 4% to 10% by weight of slag while keeping silica content and water to slag ratio of the mix constant at 8% and 0.32 respectively. The minimum and maximum flow (%) of 41 % and 74.5% was observed for alkali content of 4% and 10% respectively. It can be noticed that, % flow increased linearly with increase in % K_2O. The percentage increase in flow was observed to be 14%, 24% and 33.5% with an increase in alkali content from 6% to 10% respectively. The alkali activated blast furnace slag paste mix AABFS4-8 was very stiff while AABFS10-8 showed high workability. Increasing the alkali content decreases viscosity of mix resulting in an increase in flow. As the % K_2O values increased (greater KOH concentration), the amounts of water (w/b and H_2O/K_2O) necessary to ensure the pastes to reach normal consistency decreases, hence causing greater slag grain particles solubilization, which enabled greater formation of C-S-H gel, which is responsible for greater workability of fresh paste samples and for mechanical strength when the material is hardened.

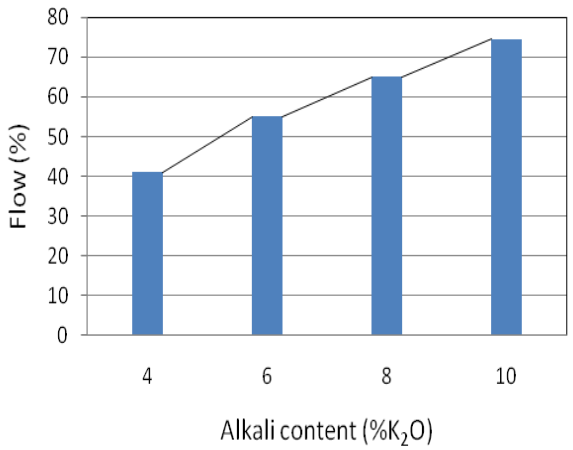

Figure 1 : Effect of alkali content (% K_2O) on flow (%) of AABFS paste

b) Direct compressive strength

Table 2 presents synthesis parameters and the compressive strength of AABFS paste specimens produced at alkali content (% K_2O) varied from 4% to 10%. Water to slag ratio and silica content was kept constant to 0.32 and 8 % respectively. Fig.2 shows the compressive strength of paste specimen at the age of 3, 7 and 28 days. As shown in Fig.2, compressive strength increases with increase in alkali content from 4% K_2O to 8 % K_2O and reaches maximum 51.44 MPa for alkali content of 8% . This increase in compressive strength may be due to increase in cations from potassium hydroxide which provide charge balance and anions in sodium silicate reacts with Ca^{2+} dissolving from the surface of the slag grains and forms the primary C-S-H (Shi and Li, 1989). Further increase in alkali content reduces the compressive strength of 45.82 MPa for alkali content (% K_2O) of 10%. Due to further increase in alkali content, all the slag particles might not be completely utilized for the production of C-H-S gel and degree of reaction of the system might reduce. The minimum compressive strength of 42.80 MPa the age of 28 days was observed in 4% K_2O. Fig. 3 presents strength development of AABFS paste with an age. The percentage increase in 28 days compressive strength over 7 days compressive strength after water curing was 40.23, 27.6%, 26.69% and 26.57% for alkali content of 4%, 6%, 8% and 10% respectively. The high early strength of 30.7 MPa and 24.45 MPa at 3 days curing time was observed in the specimens having 8% and 10 % K_2O content, indicating higher percentage of potassium hydroxide increases the early strength of AABFS paste. This may be due to the strong alkaline environment, higher OH^- concentration to overcome the – O –Si – O- Al – O- chain decomposition activation energy, making the phase of calcium rich to hydrate rapidly, thus showing a rapid increase of strength of slag. Many studies have confirmed that the modulus of the water glass has a significant effect on the properties of alkali activated slag cements. 10.92% reduction in 28 days compressive strength was observed to increase in alkali content from 8% to 10%, probably due to excess K^+ ions in the framework, the slag grains might not

C-S-H gel and the degree of reaction of the system might remain moderate. In the present study, the optimum silicate modulus SiO_2 /(K_2O+Na_2O) ratio of this type of slag is around 0.8 (Fig.4). The optimum silicate modulus phenomenon to the formation of "primary C-S-H" and /or polymerization of silicate anions in the water glass, which promotes the hydration of slag and the formation of less porous structure (Shi et al, 1989). The alkali metal cations in the original materials or added alkali metal hydroxides are considered important due to their catalytic role.

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Table 3 : Workability, Compressive strength and Split tensile strength of AABFS paste

Mix ID	Workability (Flow %)	Compressive Strength (MPa)			Split tensile strength (MPa)
		3 days	7 days	28 days	28 days
AABFS4-8	41	18.38	30.52	42.8	4.52
AABFS6-8	55	26.60	37.6	48	5.1
AABFS8-8	65	30.7	40.6	51.44	5.81
AABFS10-8	74.5	24.45	36.2	45.82	4.76

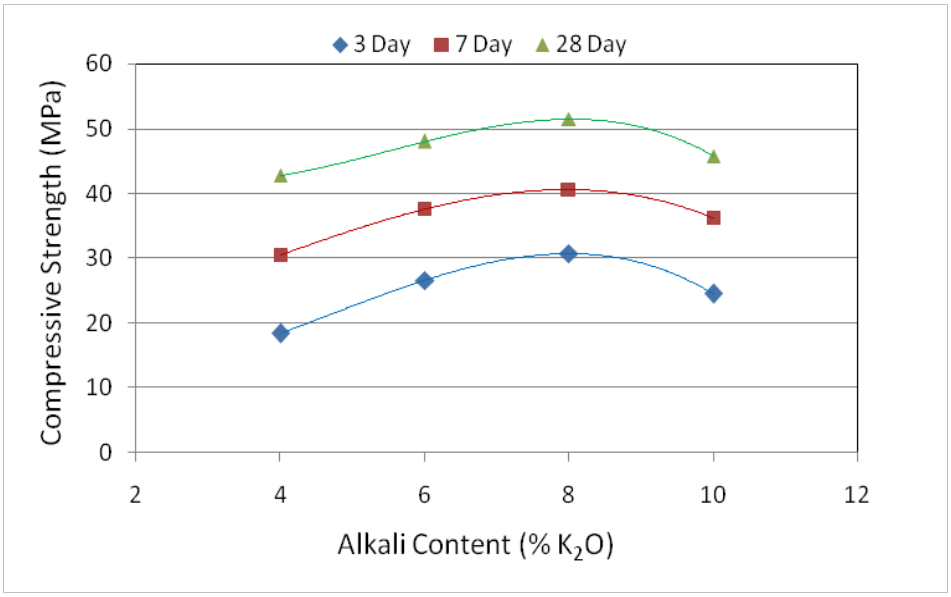

Figure 2 : Compressive strength development with an age of various alkali content

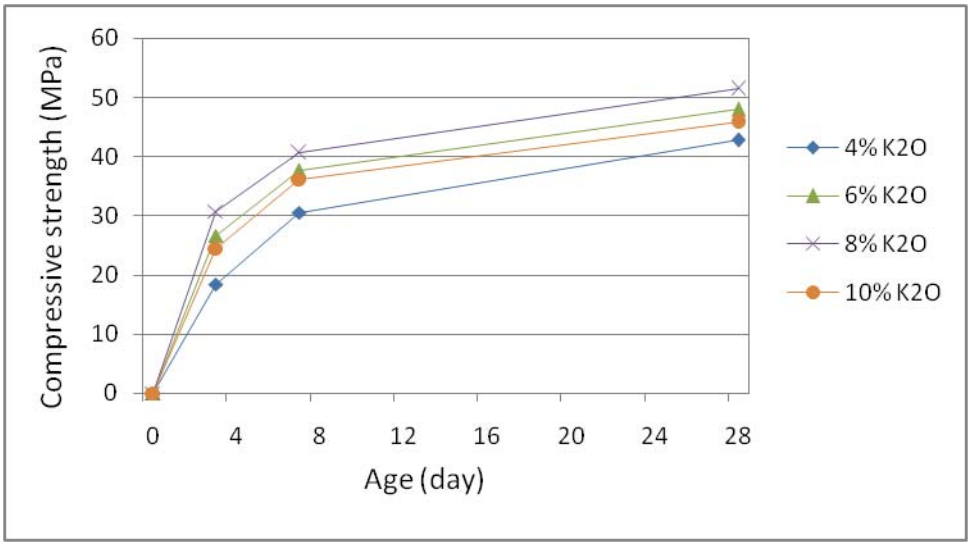

Figure 3 : Compressive strength development of alkali activated blast furnace slag paste with an age (8% SiO_2)

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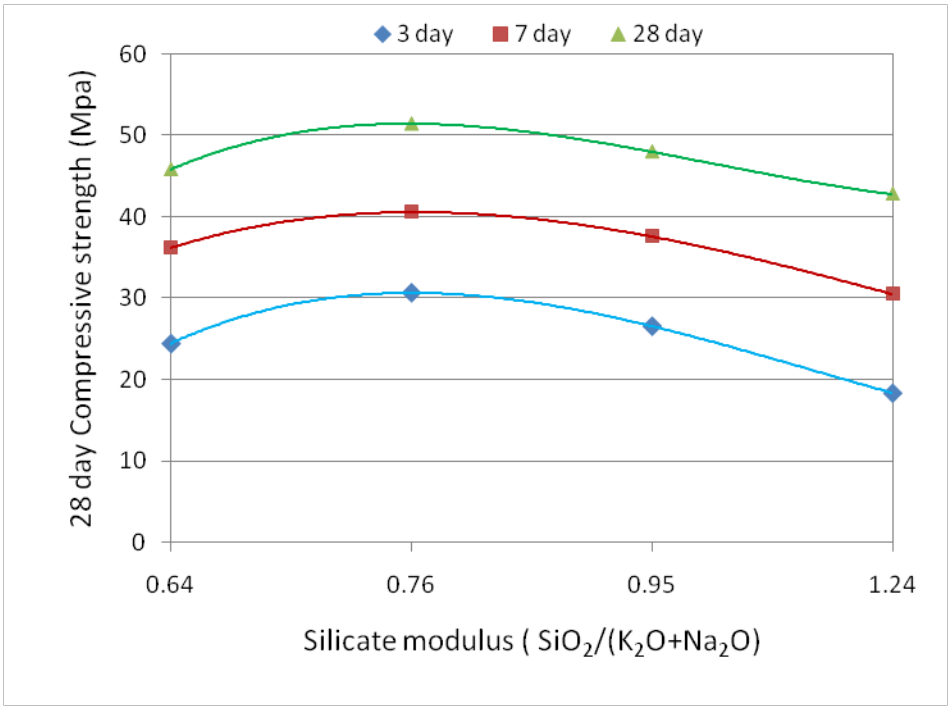

Figure 4 : Effect of silicate modulus - $SiO_2/(K_2O + Na_2O)$ on 28-day compressive strength of AABFS paste

c) Effect of alkali content on split tensile strength of AABFS paste

Fig. 5 shows the relationship between alkali content and split tensile strength. AABFS paste specimens produced with alkali content (% K_2O) varied from 4 % to 10%. Water to slag ratio and silicate content was kept constant to 0.32 and 8% respectively. In Fig. 5, it was observed that split tensile strength increases with increase in alkali content until 8% K_2O content, thereafter there is a decrease in split tensile strength for 10% K_2O content. The maximum and minimum split tensile strength of 5.81 MPa and 4.52 MPa was observed in 8% and 4% K_2O content.

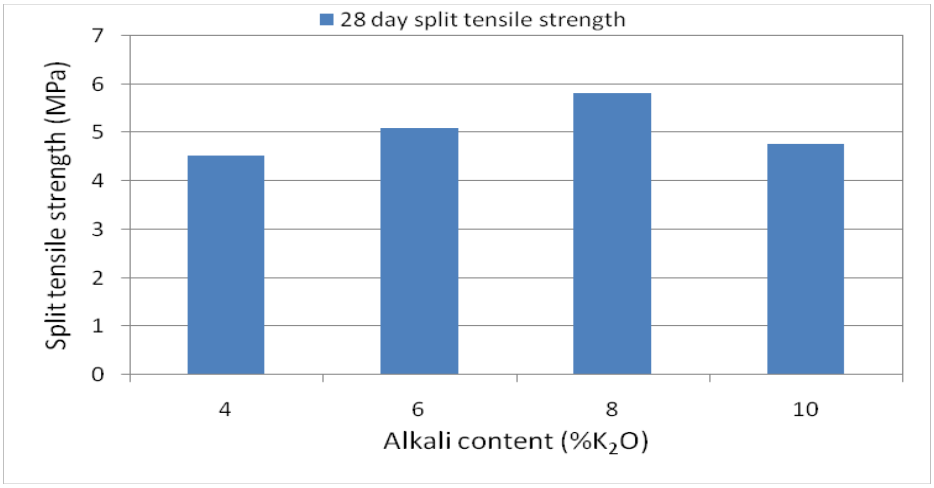

Figure 5 : 28 day split tensile strength of the AABFS paste with various alkali contents

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d) Mineralogical Investigation by XRD

The alkali activated specimens that produced the best results for compressive strength is considered for XRD analysis. Fig.6 shows an X-ray diffraction pattern of untreated blast furnace slag and alkali activated blast furnace slag with various alkali contents (% K_2O). GGBFS was predominantly amorphous with small amount of crystalline phases such as akermanite, gehlenite and quartz. Comparing the XRD spectra of the original raw slag with those of hardened alkali activated slag paste specimen, the AABFS paste specimen is mainly amorphous in view of the large diffuse diffraction peak at about 20 - 40 (2θmax Cu K) . In addition, several sharp characteristic peaks are also seen from Fig.6. The alkaline cations act as a destruction catalyst, based on the wave character of activated slag cement, during the destruction of the glassy slag structure and formation of hydrates [Krivenko, 1992]. The XRD patterns of alkali activated specimens show the formation of amorphous C-S-H gel that has resulted in a decrease in porosity and higher compressive strength. X-ray diffraction studies of alkali activated slag paste proved that calcium silicate hydrates (C-S-H) are the main phase having noticeable amorphous character.

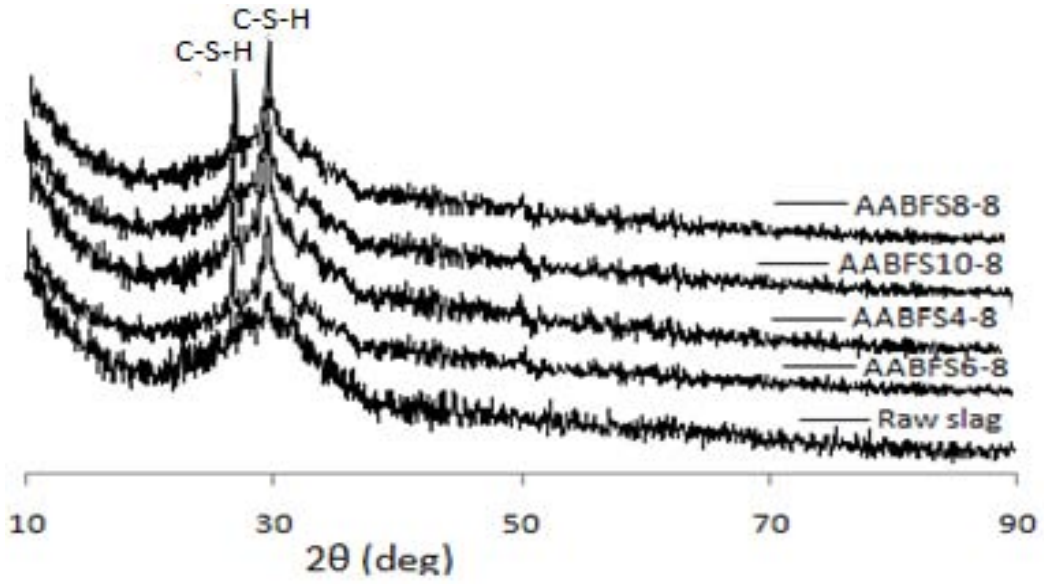

Figure 6 : XRD patterns of alkali activated blast furnace slag paste at curing time of 28 days

e) Microstructure study by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDAX)

Samples for Microstructure of AABFS hardened specimen was investigated using scanning electron microscopy, which is reflected in Fig.7. Alkali activated specimens with the highest compressive strength of all systems which were studied at the age of 28 days were considered for SEM and EDAX. The micrographs were taken with the objective of analyzing their micro structural evolution. Table 4 shows elemental analysis of raw slag and alkali activated blast furnace slag paste determined by EDAX. The Ca/Si, Ca/Si and Si/Al ratio of raw slag was 1.08, 1.63 and 1.5 respectively. Fig. 7 shows the SEM micrograph and the EDAX of the alkali activated GGBFS paste with K_2O content of 4% and 6 %, at curing time of 28 days. The matrix of AABFS4-8 which was not fairly uniform. Some of the slag grains were not dissolved in alkaline solution. As seen from EDAX, the increase in Ca/Al (2.26) and Si/Al (2.38) ratio occurs with incorporation of the activators. The matrix of AABFS6-8 was having some fine pores on the surface of the specimens with some partially dissolved slag grains as observed in Fig. 7. This indicated that, not all the slag grains form C-S-H gel, the decrease in Ca/Si (0.79), Ca/Si (1.73) and Si/Al (2.18) was observed.

Fig. 8 show SEM micrographs and EDAX results of alkali activated GGBS with K_2O content of 8% and 10%. It can be seen that the paste obtained by activation using a lower percentage of K_2O content shows more unreacted slag grains as compared to the paste obtained form activation using a higher percentage of K_2O, resulting increase in C-S-H gel formation which in turns increase in compressive strength. Thus the matrix of AABFS8-8 was little different from other type of specimens as the microstructure was very dense with fewer unreacted

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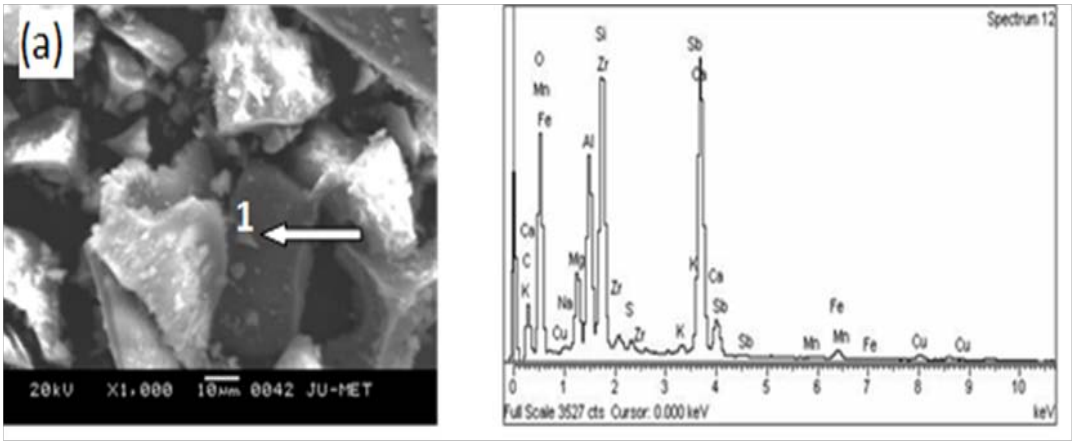
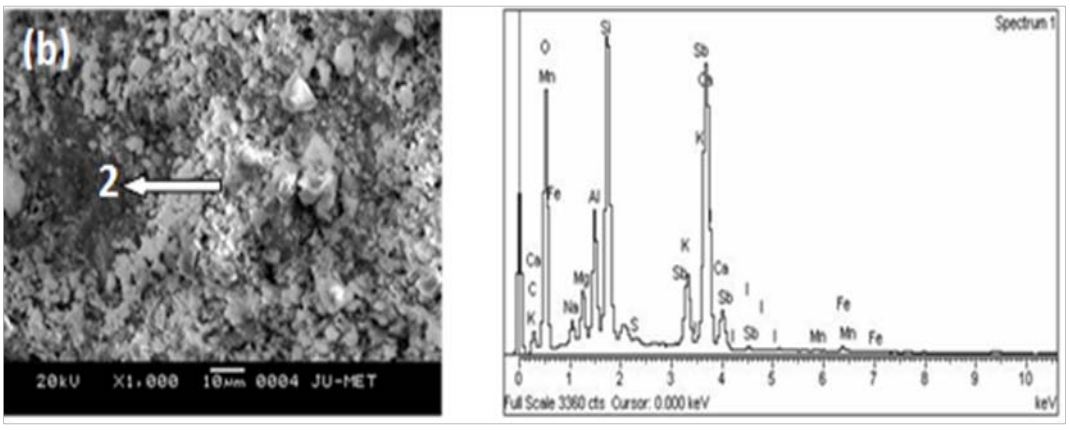
slag grains and less micro cracks and porosity, hence responsible for higher strength. Spot analysis at the arrow pointer of EDAX spectrum indicates that there was an increase in atomic % of Ca/Si (0.97), Ca/Al (2.3) and Si/Al (2.36) ratio with 8 % of K_2O. Silicates anions of alkaline solutions increases, the Ca/Si ratio in the main C-S-H decreases and the contents of of Q3 units increases resulting in an increase in compressive strength.(Jimenez and Puertas, 2003). The matrix of AABFS10-8 was very dense with fewer unreacted slag grains. But some micro cracks were found on the border of C-S-H and unreacted silica which reduces the strength compared to AABFS8 8 specimens.

The major hydration product found in all alkali activated GGBS specimens was amorphous to poorly crystalline C-S-H (I) gel with Ca/ Si ratio ranging from 0.79 – 1.01

Table 4 : Semi- quantitative elemental analysis of raw slag and alkali activated blast furnace slag by EDAX; points of analysis are shown in Fig. 7 and 8

Spot	Element atomic ratio (%)								Ratio		
	Na	Mg	Al	Si	S	K	Ca	Fe	Ca/Si	Ca/Al	Si/Al
Arrow-1	0.19	2.3	4.16	6.26	0.21	0.15	6.79	0.38	1.08	1.63	1.50
Arrow-2	1.45	2.14	4.0	9.55	0.15	1.88	9.04	0.22	0.94	2.26	2.38
Arrow-3	1.07	2.28	4.09	8.92	0.3	1.75	7.11	0.15	0.79	1.73	2.18
Arrow-4	1.29	3.24	5	11.82	0.45	2.89	11.52	0.3	0.97	2.3	2.36
Arrow-5	0.92	2.03	3.76	8.61	0.31	2.26	8.70	0.26	1.01	2.31	2.28





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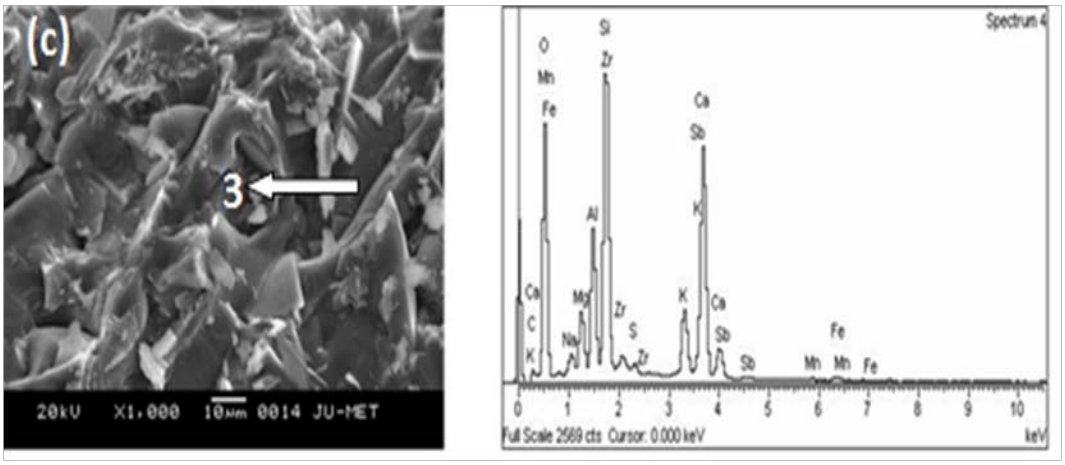

Figure 7 : SEM-EDX characterization of raw slag and alkali activated blast furnace slag paste with 4 % K_2O (AABFS4-8) and 6% K_2O (AABFS6-8) at a curing time of 28 days

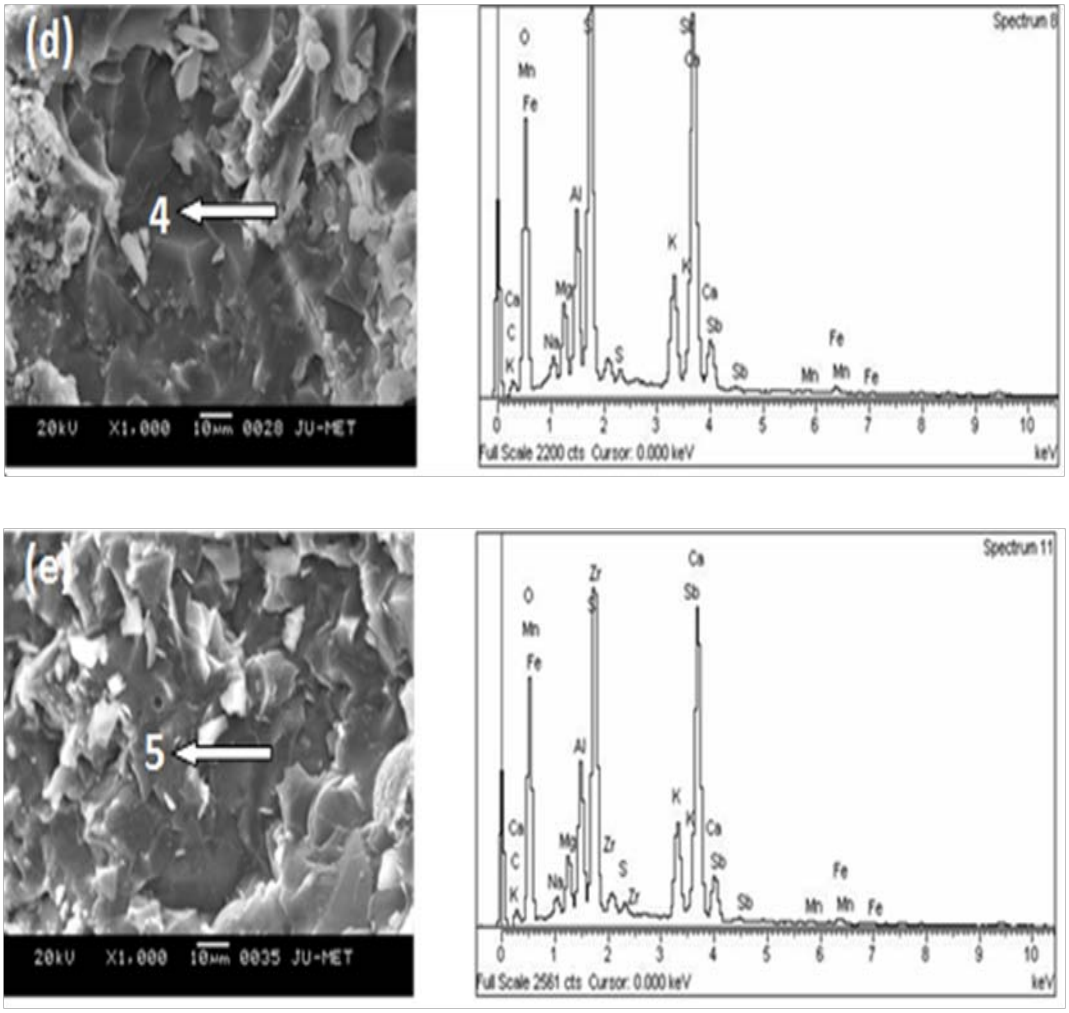

Figure 8 : SEM-EDAX characterization of alkali activated blast furnace slag paste. (d) 8 % K_2O (AABFS8-8) and (e) 10% K_2O (AABFS10-8) at a curing time of 28 days

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IV. Conclusions

The effect of alkali content (% K_2O) on the direct compressive strength of AABFS paste specimens has been investigated. Based on experimental study, the following conclusions are drawn.

1. The K_2O dosage had a significant influence on the strength of AABFS paste. The K_2O is needed to maintain the alkalinity of the mixes, the condition needed to assist the dissolution of slag and the adsorption of ions in solution on the surface of slag.
2. The rate of increase in compressive strength with an age also depends upon the percentage of alkali content. Maximum compressive strength and split tensile strength was found to be 51.44 MPa and 5.81 MPa for 8 % K_2O by keeping % SiO_2 equal to 8%.
3. The major hydration product found in all alkali activated GGBS specimens was amorphous to poorly crystalline C-S-H (I) gel with a Ca / Si ratio of 0.79 – 1.01.
4. As the percentage of alkali content increases from 4 % to 8 %, it in turn increases the C-S-H gel and thus increases denseness of the matrix and refines the pore structure, as observed in an SEM study.
5. The optimum silicate modulus SiO_2 / (K_2O+Na_2O) of AAGBFS paste was found to be around 0.8 (Fig.4).
6. The compressive strength of the paste can be controlled by judiciously choosing the K_2O percentage and silicate modulus.

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