HBRC Journal (2012) 8, 177–184

Housing and Building National Research Center

HBRC Journal

http://ees.elsevier.com/hbrcj

Green binding material using alkali activated blast furnace slag with silica fume

Mohamad Sayed, Sayeda R. Zeedan *

Housing and Building National Research Centre (HBNRC), 87 El-Tahreer St., Dokki, Giza, P.O. Box 1770, Cairo, Egypt

Received 1 December 2011; accepted 3 April 2012

KEYWORDS

Slag;
Silica;
Alkali activation;
Compressive strength;
Microstructure

Abstract Recently million tons of cement is produced in Egypt accompanied with million tons of CO_2 emission which causes annually negative impact on the environment. Granulated blast furnace slag and silica fume are produced as by-product from iron and chemical industries with limited recycling facility. This paper represents an experimental study aimed to safe ferrosilicon alloy of slag and silica fume to produce cementless binding material using both of Sodium Hydroxide and water glass liquid (Sodium Silicate) as alkaline activator. Experimental program was designed to study silica/slag ratio, percentage of alkali activator, water/binding ratio, incorporation of superplasticizer, and curing condition on the properties of the produced binding material. Compressive strength and mineralogical analysis were conducted on the polymeric binding material to asses the effectiveness of the main variables. The tests were divided into two stages; in the first stage compressive strength was conducted for all mixes while X-ray, microscopic scan (SEM), and infrared analysis (IR) were carried out for the most pronounced promising mixes. The results showed that ratio of 25% of silica/slag is the most effective ratio and 5% of each of Sodium Hydroxide and Sodium Silicate was the optimum percentage of the alkaline activator. Additionally the use of superplasticizer is essential as it positively reduces the mixing water and maintains the binding material with acceptable workability.

1. Introduction

The last few years have shown extensive construction of cement factories in Egypt. The cement industry is considered as non friendly environmental industry due to the continuous emission of Co_2 and quarrying of raw materials (limestone and clay) accompanying the fabrication process. Many researchers from the world are working on this serious issue created by cement and one of the solutions is the introduction of polymeric cement by the development of inorganic alumina-silicate polymer. A binder can be obtained by the reaction of industrial by-products such as fly ash, silica fume, and blast furnace slag

---

* Corresponding author.
E-mail addresses: Mssa50@hotmail.com (M. Sayed), Zeedansun@yahoo.com (S.R. Zeedan).

Peer review under responsibility of Housing and Building National Research Center.

Production and hosting by Elsevier

1687-4048 © 2013 Housing and Building National Research Center. Production and hosting by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.hbrcj.2012.10.003

with the alkaline liquid. Depending on the nature of the raw materials to be activated by the alkaline liquid as activator, different reaction products are developed which have different microstructures. In the activation of slag, the main reaction product is a hydrated calcium silicate, like CSH gel, while in the activation of fly ash, the reaction product obtained is an inorganic polymer of amorphous nature formed by hydrated aluminosilicate chains.

Iron industry produces granulated blast furnace slag as by-product and it is consists mainly of calcium-magnesium aluminosilicate glass. Slag is currently used in the cement industry to produce “Slag Cement” and due to the limited usage of this type of cement in the construction industry; slag is highly accumulated in steel iron factories. Additionally silica fume is produced as a by-product from ferrosilicon alloy production and although it is used in the production of high strength concrete, the usage of this type of concrete is still limited accordingly; silica fume is facing the same recycling challenge. It is worth to mention that, most of the researcher’s efforts were focused on the use of fly ash as a basic material of the cementless binding material [1–7] and other researches were directed towards the alkali activation of blast furnace slag [8–12]. In Egypt, fly ash is not available due to the rare of thermal power station which depends on the pulverized coal and it is currently imported for research work and some industrial applications. Slag situation in Egypt is completely in contradiction with fly ash, it is currently accumulated in the iron and steel companies without real recycling applications.

This paper represents experimental trials to activate blast furnace slag as to produce cementless binding material. Blast furnace slag and silica fume were activated by the use of alkali solution. Compressive strength and mineralogical studies were carried out to determine the effect of the main variables. The tests were divided into two stages, in the first stage compressive strength was carried out for all mixes while the second stage focused on the hydrated products. X-ray, microscopic scan (SEM), and infrared analysis (IR) were carried out for the most pronounced and promising mixes obtained from the first testing stage.

2. Experimental work

The experimental program was designed to study four parameters which affect the strength of alkali activated slag. Curing condition, replacement ratio of silica, water/bending ratio, and finely the effect of superplasticizer were the main parameters studied through experimental program. The experimental work consists of nine mixes divided into three groups. The first group (A) was designed to study the effect of replacement ration of granulated blast furnace slag by silica fume. Silica fume was added by partial replacement of slag by 25% increment. The alkali activator was kept constant in group (A) equal to 3% for both of Sodium Hydroxide (NaOH) and Sodium Silicate (Na_2SiO_2-Water glass). The aim of the second group (B) was to study the effect of concentration of alkali activator. The concentration of the activator was increased from 3% to 4% and then to 5% and finally to 6% for both of NaOH and Na_2SiO_2. The purpose of the third group (C) was to study the effect of the utilization of high water reducer admixture (superplasticizer met the requirements for ASTM C-494 Type (F)). Two mixtures from group (B) (namely B2 and B3) were chosen for that purpose. Fig. 1 shows the main variables studied through the experimental program and Table 1 shows the description of the mixtures.

2.1. Materials

The chemical composition of the blast furnace slag and silica fume is shown in Table 2. The blast furnace slag is a granulated product ground to fineness of about 370 m^2/kg .The silica fume had a density of 0.7 g/cm^3 and its SiO_2 ratio is 98.21%.

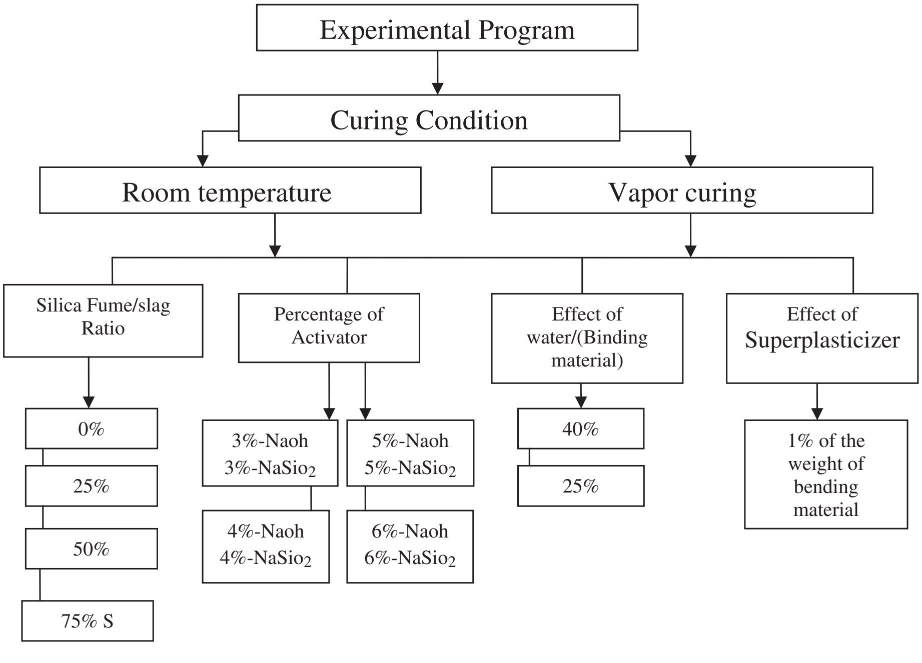


Fig. 1 Experimental program.

Table 1 Description of the mixtures.

Group	Pastes*	Slag (%)	Silica fume (%)	Activators (%)		Water (%)	Admixture (%)
				NaOH	Na_2SiO_2		
A	A1/A1v	100	0	3	3	40	0
	A2/A2v	75	25				
	A3/A3v	50	50				
	A4/A4v	25	75				
B	B1/B1v	75	25	3	3	25	0
	B2/B2v			4	4		
	B3/B3v			5	5		
	B4/B4v			6	6		
C	C1/C1v	75	25	4	4	25	1
	C2/C2v			5	5		

* Pastes A1, A2, A3, A4, B1, B2, B3, B4, C1, and C2 were cured in the room temperature while pastes A1v, A2v, A3v, A4v, B1v, B2v, B3v, B4v, C1v, and C2v were cured in the vapor cabinet.

Table 2 Chemical composition (wt%).

	Silica fume	Slag
CaO	0.10	41.45
SiO_2	98.21	34.44
Al_2O_3	0.21	13.50
Fe_2O_3	0.35	1.10
MgO	0.32	7.67
SO_3	0.30	0.20
K_2O	0.40	0.89
Na_2O	0.11	0.75

Two alkali-containing activators were used for the activation of slag, e.g., Sodium Hydroxide liquid sodium silicate. The liquid sodium silicate had a density of 1.375 g/cm^3 and a composition comprising 8.25 Na_2O, 27% SiO_2, and 64% H_2O. Superplasticizer admixture complies with ASTM C494 [13] Type F was used to reduce the mixing water and achieve acceptable and reasonable workability of the mixes. Lingosulphonate is the base chemical compound of the used superplasticizer.

2.2. Casting and curing

Liquid sodium silicate and Sodium Hydroxide were blended in 1:1 ratio and they were soluble in the mixing water. The slag was blended with silica fume and mixed in the drum mixer for 2 min in dry condition then the alkali solution with mixing water was added and the mechanical mixing was continued for another 3 min. The molds were filled by the pasts and mechanically vibrated to remove the air bubble and finely the surface of the molds was smooth using smooth trowel. Two conditions were adopted for curing the specimens. Half of the specimens were kept in the laboratory and exposed to the room temperature where the other half was cured in vapor cabinet. The specimens in the vapor cabinet were exposed to 80% relative humidity and 75 °C centigrade ambient temperature. Specimens cured in the room temperature will be refereed as "Air cured" specimens than that cured at room temperature. This is mainly due to the saturated humidity as well as the increase of curing temperature 75 °C in comparison with room temperature (25 °C). The rate of activation increases with the cures temperature.

Test technique

Compressive strength measurements of pastes were performed on compression testing machine in a load control regime with a loading rate of 2 MPa/min. Three cubes 2 cm^3 cubic moulds were tested for each data point. The specimens were tested at 1, 3, 7, and 28 days after casting. The X-ray diffraction, microscopic scan (SEM), and infrared analysis (IR) were carried out using the apparatus available at the Raw Material Institute.

3. Results

This section discuss the compressive strength test results carried out on the silica-slag activated pastes additionally, X-ray, microscopic scan (SEM), and infrared analysis (IR) were conducted to explore the hydrated products in the subsequent section.

3.1. Compressive strength behavior

3.1.1. Effects on SF/slag ratio

Tables 3 and 4 represent the compressive strength test the tested pastes. It is visible from the results that vapor results of curing significantly enhanced the compressive strength of the activated silica/slag binding material additionally; the compressive strength was increased with curing time for all pastes. The minimum recorded compressive strength at 28 days was 3.21 N/mm^2 and 4.1 N/mm^2 for pastes contained slag only and cured in air as well as vapor, respectively.

Figs. 2 and 3 illustrates the compressive strength of alkali activated slag with various propotions of silica fume/granulated slag and activation at constant values of NaOH and Na_2Sio_3 for each 3% of binding material. There two figures show the relation between the compressive strength values of cement pastes with curing time cured in 100% R.H and in atmospheric air.

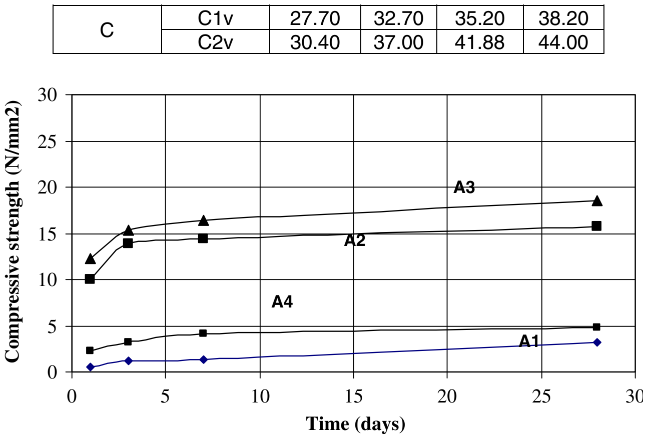
As the silica fume increases up to 50 wt% of granulated slag the compressive strength increases due to the continuous activation of the binding materials with activator forming CSH as

Table 3 Compressive strength values of air cured pastes with time.

Groups	Pastes	Compressive strength (N/mm^2)			
		1	3	7	28
A	A1	0.53	1.15	1.37	3.21
	A2	10.00	13.84	14.34	15.80
	A3	12.30	15.4	16.4	18.5
	A4	2.31	3.17	4.17	4.84
B	B1	2.00	6.00	8.80	12.80
	B2	2.93	9.30	12.50	16.90
	B3	3.07	10.41	14.30	18.70
	B4	2.10	5.10	7.55	10.65
C	C1	15.06	22.20	25.00	27.60

Table 4 Compressive strength values of vapor cured pastes with time.

Groups	Pastes	Compressive strength (N/mm^2)			
		1	3	7	28
A	A1v	1.50	2.20	2.24	4.10
	A2v	11.70	15.20	16.30	18.00
	A3v	14.30	17.10	18.80	21.42
	A4v	3.84	4.70	5.61	10.80
B	B1v	6.40	11.00	12.60	14.30
	B2v	10.80	15.60	15.65	19.90
	B3v	13.70	18.00	23.77	26.90
	B4v	5.54	10.42	11.25	12.35
C	C1v	27.70	32.70	35.20	38.20
	C2v	30.40	37.00	41.88	44.00



C	C1v	27.70	32.70	35.20	38.20
	C2v	30.40	37.00	41.88	44.00

Fig. 2 Compressive strength of air cured pastes A1, A2, A3, and A3 at different ages.

well as CASH. This is occurred in the humidity and in the atmospheric air. The increase of the silica fume up to 75 wt% of granulated slag the corresponding strength decreases. This is mainly due to the decrease of the amount of activator (NaOH, Na$_2$Sio$_3$) which were responsible about activation of the slag and SF. On the other side, the humidity chamber illustrates higher compressive values than these curved in the atmosphere air. This may be due to the continuous hydration of the activated slag in the humidity to give hydration products mainly as CSH which is the main source of strength. Curing in the atmospheric air in the laboratory at room temperature tends to evaporate some of the water filled pores which delays the hydration as well as activation therefore.

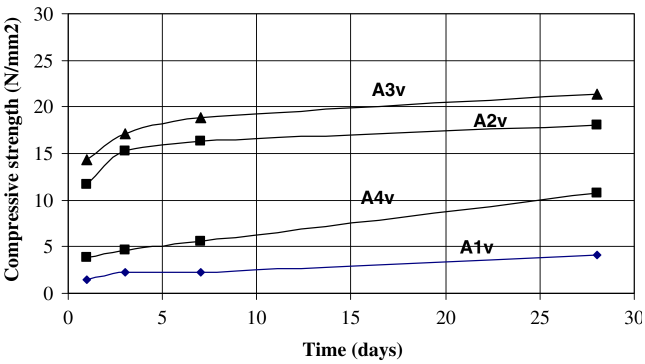


Fig. 3 Compressive strength of vapor cured pastes A1v, A2v, A3v, and A3v at different ages.

3.1.2. *Effect of amount activator*

For pastes with constant silica/slag ratio (25%) and activated with different percentages of alkali activator namely groups (B and C), the analysis of the compressive strength test results revealed the following points. This group is free from water reducer.

The compressive strength was increased with curing time regardless the percentage of the alkali activator. In addition to that, the compressive strength of pastes activated by the 5% was the highest among all other compressive strength results. The increase of activation is accompanied by the increase compressive strength up to 5 wt% and decreases at 6 wt% activator enhances the activation of the granulated slag in addition to the reaction of NaOH with silica fume forming hydration products such as CSH low CaO/SiO$_2$ ratio related mainly to the composition of slag and nature of the activator. A better understanding the effects of alkaline activators such as NaOH and Na$_2$Sio$_3$ solutions on the hydration mechanism of alkali activated slag could show to optimize the alkaline activators. As the amount of alkaline activator increase up to 6 wt% the compressive strength decreases. The increase of NaOH content leads to react with silica fume as well as granulated slag forming sodium silica hydrate with low binding properets. Also, curing at 100% R.H is more suitable than at room temperature in the atmospheric air. This is mainly due to the continuous hydration of activated slag in the saturated atmosphere. On the other side the atmospheric air tends to evaporate the free value in the activated slag which retards the hydration and the strength.

3.1.3. *Effects of super plasticizer*

The use of superplasticizer had direct effect on the quantity of mixing water which enabled the reduction of the (water/fine material) to be 25%. For paste C1 and C2 which were cured

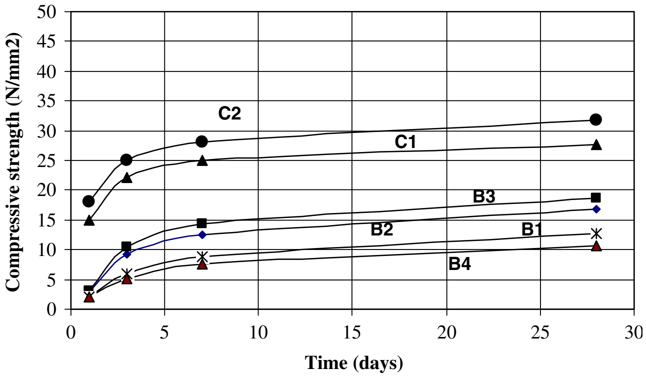


Fig. 4 Compressive strength of air cured pastes B1, B2, B3, B3, C1, and C2 at different ages.

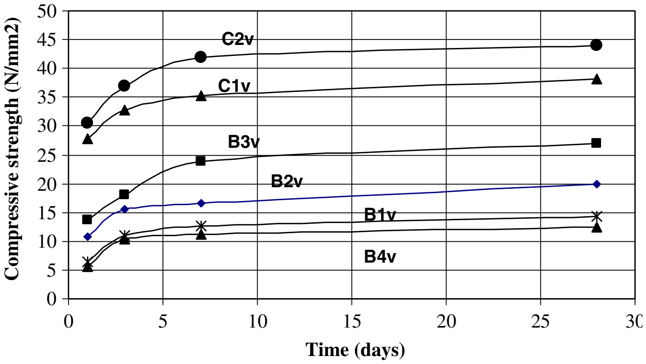


Fig. 5 Compressive strength of vapor cured pastes B1v, B2v, B3v, B3v, C1v, and C2v at different ages.

in the room temperature and activated by 8% and 10% of alkali activators, the compressive strengths at 28 days were more than the compressive strength of pastes B2 and B3 by approximately 100%. On the other hand, for vapor cured pastes the compressive strengths of pastes C1v and C2v were more than the corresponding pastes B2v and B3v by 92% and 64%, respectively.

Figs. 4 and 5 show the relation between the compressive strength of granulated slag/silica fume of activator as a function of curing time. Pastes cured in the humidity. The water reduces superplasticizer the amount of mix up water.

The compressive strength development of paste C1v (25% silica/slag ratio and 8% alkali activators) with age was relatively different than the strength development of corresponding paste B2v. The 1, 3, 7 days compressive strengths were 72.5%, 85.6%, and 92.10% respectively, from the compressive strength value at the age of 28 days. For paste C2v (25% silica/slag ratio and 10% alkali activators) the strength development at the 1, 3, 7 days were 69%, 84%, and 95.2%, respectively from the 28 days compressive strength. These results revealed that 3 days are adequate curing time to reach strength value of about 85% of the 28 days compressive strength.

Paste C2 (25% silica/slag ratio, 8% alkali activator, and cured in the room temperature) has got 28 days compressive strength more than 30 N/mm^2 where C2v which was cured in the vapor cabinet has got 28 days compressive strength about 44 N/mm^2. These two pastes represent the optimum ones among all other pastes. Chemical tests were carried out on the air cured pastes due to their promising compressive strength results.

Figs. 6 and 7 show the relation of compressive strength of alkali activated slag/silica fume.

3.2. Discussion of the chemical test results

This section discusses the X-ray, microscopic scan (SEM), and infrared analysis (IR) test results which were conducted to explore the hydrated products. It is worth to mention that the tests were carried out on air cured pastes (A1, A2, A3, and A4) and pastes (B2, B3, C1, and C2) which have showed comparable pronounced compressive strength results. The chemical analysis was restricted for the air cured pastes as this condition is used for the curing of concrete at the construction sites.

3.2.1. Crystallinity of hydration products

XRD was used to study the change in crystallinity after alkaline activation as shown in Figs. 6 and 7. It should be noted that the reactants used and most of the binders produced in this study contain a very high percentage of amorphous to semi-crystalline phases. It is difficult therefore of amorphous to semi crystalline in mix (A1, A2, A3, and A4). There is no

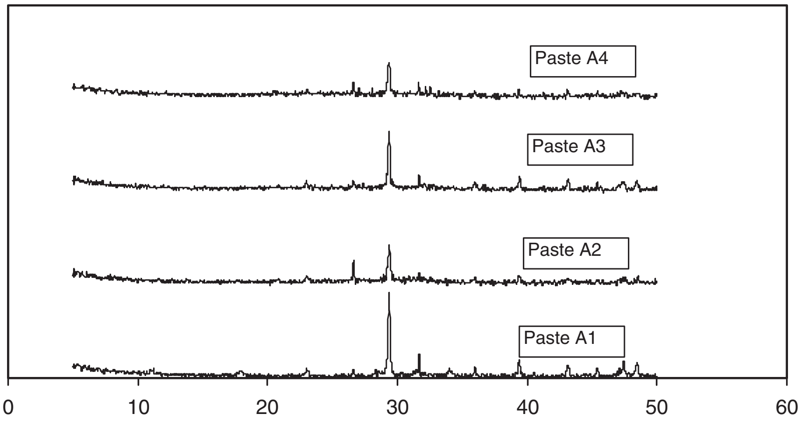


Fig. 6 X-ray test results of A1, A2, A3, and A4.

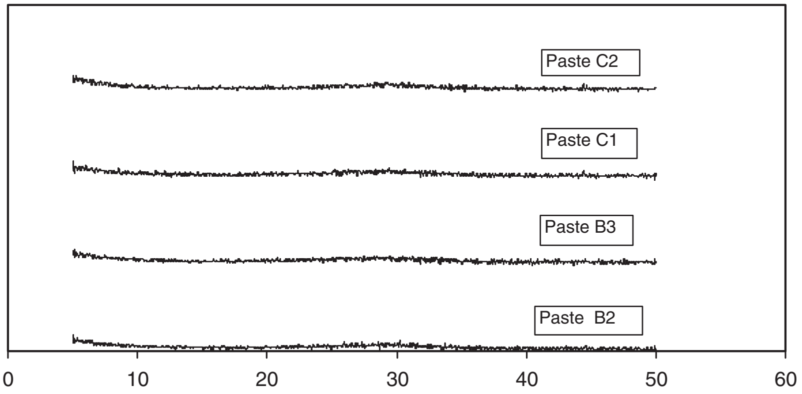


Fig. 7 X-ray test results of B2, B3, C1, and C2.

new crystalline phase formed in pastes (B2, B3, C1, and C2). Therefore, it can be concluded that crystalline CSH is not a product or it is not a dominate product formed as a result of alkaline activation of GBFS with SF under the conditions used in this investigation. This conclusion in good agreement with previous work carried out by Jaarsveld [14] which explained the phenomena by the fact that crystalline CSH is not formed in high pH (pH $\geqslant$ 14) environment. However, amorphous CSH within a geopolymeric gel could be part of the resultant product, as will be shown later in SEM.

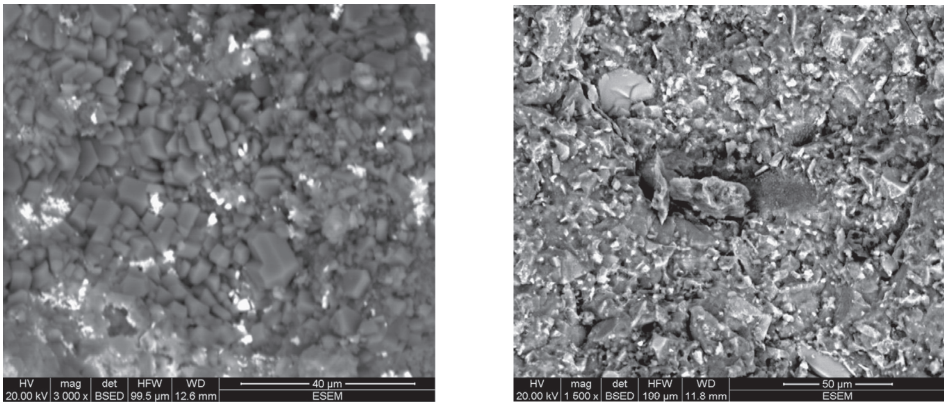
3.2.2. Microstructure of hydration products

Electron microscopy (SEM) was employed to examine the microscopic effect of pastes from GBFS + SF when activated by alkaline solution. A geopolmeric binder was formed with no phases could be identified by XRD. Fig. 8 shows a representative scanning electron micrograph of a geopolymer binder of paste B2, B3, C1, and C2 at the age of 28 days. Two separate phases were formed as a result of the alkali activation of GBFS in presence of SF. EDS analysis was conducted on the sample and it was found that the elemental composition of area X was dominated by more of silicon, calcium and oxygen and less of aluminum and sodium. The mix C1 which containing (4% NaOH + 4% water glass) + 1% superplasticizer and C2 with (5% NaOH + 5% water glass) + 1% superplasticizer were also shown in Fig. 8. The polymerization of geopolymer compound for the mix C1 and C2 are clear formed of silicon, calcium and oxygen, and aluminum and sodium.

3.2.3. Infrared analysis (IR)

Comparing IR spectra of the alkaline activation of pastes (GBFS + SF) with different ratio of alkali (NaOH + water glass as sodium silicate) solution deduced that reaction products of different nature are formed. As a consequence of the alkaline activation of slag with silica fume, a hydrated calcium silicate of gel type is formed as the main reaction product. This gel phase is differentiated from that formed in hydration of slag with silica fume and different alkali ratio. This hydrated calcium silicate is mainly constituted of imperfect structures of CH layers joint to isolated layers of $(C_9H)_4AH_{13}$ intimately mixes in their structures.

FTIR (IR) spectra of solid phases at 28 days for (A1, A2, A3, and A4) are shown in Fig. 9. The FTIR spectrum of anhydrous, the spectra were normalized at their absorption maximum and a vertical (3400–3700 cm^{-1}) detected in the three pastes for pastes (A1, A2, A3, and A4) were associated with the OH bending vibration in water, respectively denoting to $Ca(OH)_2$ and free lime are greater so the pozzolanic reaction CSH is small in mix A1 resulting smaller compressive strength. The spectra from (700–800 cm^{-1}) were bands Al–O become very weak in the spectrum slag based geopolymer; these means that six coordinate Al will transfer into the coordination in the



Paste C1 **Paste C2**

Fig. 8 Scanning electron microscope of geopolymer binder of pastes B2, B3, C1, and C2.

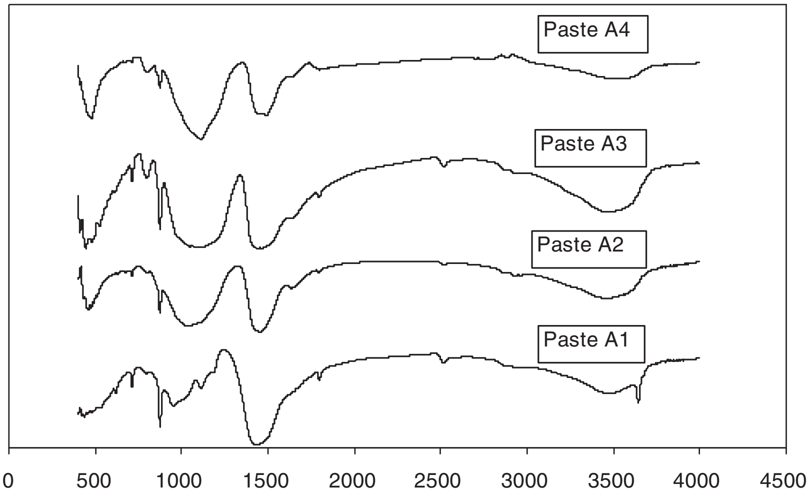


Fig. 9 IR test results of pastes A1, A2, A3, and A4.

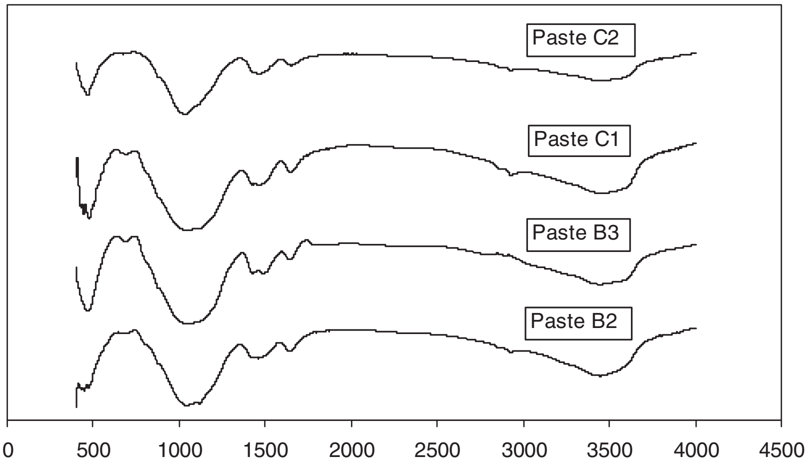


Fig. 10 IR test results of pastes B2, B3, C1, and C2.

process of hydration. The region of the 874–875 cm^{-1} evidence the presence of carbonate probably formed as a result of the hydration product in mix A1, A2, and A3 but disappear in mix A4. In mix A2 the high carbonate in spite of Al asymmetric is large, but the carbonate has more effect so the compressive strength is smaller than mix A3. In mix A3 the $CaCO_3$ was smaller than mix A2 and the hydration lower than mix A2 but the main asymmetric peak broad in uncreative peak at (456 and 438 cm^{-1}). In mix A4 which have v3(O–Si–O) bands shifts towards lower value (495–475 cm^{-1}). The vibration of Al–O bonds at 674 was observed but the vibration at 1039 cm^{-1} was observed asymmetric Si–O–Al.

FTIR spectra of pastes (B2, B3, C1, and C2) up to 28 days are shown in Fig. 10. Analysis of the figure showed that absorption bands from (3859–3459–3446) and 3447 cm^{-1} are due to stretching of OH groups and absorption from (1640–1653 cm^{-1}) are due to H-O-H. This increase in pastes (B2, B3, C1, and C2) are due to the formation of C-S-H or C-A-H which responsible to the increase of the compressive strength (19, 26, 38 and 44 $\mathrm{N/mm}^2$) and due to the $Ca(OH)_2$ and free lime is decrease gradually so the pozzolanic reaction is increase in C1 and C2 due to added the superplasticizer. The band from (670–699 cm^{-1}) is located attributed to Al–O asymmetric stretching vibration of AlO_4 groups in the slag is activated gradually leading to the decrease in the formation of carbonate in spite of Al asymmetric so the formation of carbonate has no effect resulting increase in the compressive strength due to the increase alkali media and added the superplasticizer.

4. Conclusion

Based on the properties of the used materials, results, and discussions, the following conclusion could be drawn:

1. Twenty-five percentage of silica as partial replacement of blast furnace slag is the reasonable percentage from compressive strength and economical point of views.
2. Compressive strength test results revealed that 5% of each of Sodium hydracids and Sodium Silicate are the optimum percentage of alkali activator and increasing the activators

beyond this value dramatically reduced the compressive strength.

3. Use of superplasticizer based on Lignosulphonate is recommended and cannot be avoidable to minimize the mixing water in the alkali activated slag/silica binding material.
4. Compressive strength results of vapor cured pastes was superior to the results of corresponding pastes cured at the room temperature and the 3 days of vapor curing is adequate to reach approximately 85% of the 28 days compressive strength.
5. Pastes cured in the room temperature have got comparable compressive strength values to the corresponding values of pastes cured in the vapor and the ratio of air/vapor cured pastes at the age of 28 days were in the range of 60–70%.
6. The XRD revealed that crystalline CSH is not a product or it is not a dominate product formed as a result of alkaline activation of GBFS with SF under the conditions used in this investigation.
7. The (SEM) test results showed that the polymerization of geopolymer compounds are clear formed of silicon, calcium and oxygen, and aluminum and sodium.

Acknowledgment

The researcher is grateful to the staff of ‘‘Building Materials and Quality Control Institute’’ and ‘‘Raw Material Institute’’ for their great help through the experimental work of this research especially technical Hani Abdel Rhman.

References

[1] M.F. Nuruddin, S. Qazi, N. Shafiq, A. Kusbiantoro, Compressive strength & microstructure of polymeric concrete incorporating flay ash & silica fume, Can. J. Civil Eng. 1 (1) (2010).

[2] F. Puertas, S. Martinez, S. Alonso, T. Vazquez, Alkali-activated fly ash/slag cement strength behavior and hydration products, Cem. Concr. Res. 30 (2000) 1625–1632.

[3] A. Fernández-Jiménez, A. Palomo, C. López-Hombrados, Some engineering properties of alkali activated fly ash concrete, ACI Mater. J. 103 (2) (2006) 106–112.

[4] D. Hardjito, S. Qallah, D.M.J. Sumajouw, B.V. Rangan, On the development of fly ash based geopolymer concrete, ACI Mater. J. 101 (6) (2004) 467–472.

[5] S.E. Wallh, D. Hadjito, D.M.J. Sumajouw, B.V. Rangan, Creep behavior of fly ash based geopolymer concrete, in: Proceedings of the Seventh CANMENT/ACI International Conference on Recent Advances in Concrete Technology, Las Vegas, 2004, pp. 49–59.

[6] T. Bakharev, Heat resistance of geopolymer materials prepared using class F fly ash, J. Austr. Ceram. Soc. 42 (1) (2006) 36–44.

[7] A. Katz, Microscopic study of alkali-activated fly ash, Cem. Concr. Res. 28 (2) (1998) 197–208.

[8] T. Bakharev, J.G. Sanjayan, Y. Cheng, Alkali activation of Australian slag cement, Cem. Concr. Res. 29 (1999) 113–120.

[9] J. Metso, E. Kajaus, Activation of blast furnace slag by some inorganic materials, in: First International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, vol. 2, Montbello, Canada, 1983, pp. 1059–73.

[10] K. Isozaki, S. Iwamoto, K. Nakagawa, Some properties of alkali-activated slag cement, in: Eighth International Congress on the Chemistry of Cemen, vol. 6, Rio de Janeiro, 1986, pp. 395–9.

[11] B. Talling, Effect pf curing condition on alkali-activated slag, in: Third International Conference on Fly-Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, vol. 2, Norway, 1989, SP114-72, pp. 1485–500.

[12] C.D. Atis, C. Bilim, O. Celik, O. Karahan, Influence of activator on the strength and drying shrinkage of alkali-activated slag mortar, Constr. Build. Mater. 23 (2009) 548–555.

[13] ASTM C494/C494M-05a, Standard specification for chemical admixtures for concrete, ASTM Standards 04.02 (2005).

[14] J.G.S. van Jaarsveld, J.S.J. van Deventer, Effect of the alkali metal activator on the properties of fly ash-based geopolymers, Ind. Eng. Chem. Res. 38 (1999) 3932–3941.