

Report for end-semester evaluation of CE 499

Influence of mix parameters on mechanical, microstructural, and durability properties of geopolymer mortar

Submitted

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CERTIFICATE

It is certified that the work contained in the project report entitled “**Influence of mix parameters on mechanical, microstructural, and durability properties of geopolymer mortar**”, by **Nameet** (Roll No. 200104065) has been carried out under my supervision and that this work has not been submitted elsewhere for the award of a degree or diploma.

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ABSTRACT

The objective of this study is to investigate the effect of source materials, alkaline solution, and admixed chloride and sulphate salts i.e., NaCl (NC), Na₂SO₄ (NS), MgSO₄ (MS), NC plus NS, and NC plus MS on flowability, compressive strength, chloride content, sulphate ion concentration and microstructural properties of geopolymer mortar (GPM). The GPM mixes were made with different proportions of ground granulated blast furnace slag (BFS) and fly ash. The alkaline solution used was a mixture of sodium hydroxide solution (6 M and 10 M) and sodium silicate solution. The flow table test was conducted on fresh GPM to measure the flowability. The compressive strength test was carried out on GPM cubes of size 50 mm at the age of 7, 28, and 90 days. In addition, chloride contents (i.e., total chloride, free chloride, and bound chloride) and sulphate ion concentration of salt added GPM mixes were also evaluated. The microstructural investigations on GPM were carried out by XRD analysis and FESEM analysis. From the obtained results, the flow index (%) increased with fly ash content, and reduced with increase in NaOH solution molarity. The compressive strength of GPM mixes mostly increased with BFS content, molarity of NaOH solution, and age. The strength of control GPM was mostly higher than salt admixed GPM mixes at lower molarity of NaOH solution, whereas at higher NaOH solution molarity, the mixes admixed with NC plus NS showed greater strength than all other GPM mixes. The increase in BFS content and molarity of NaOH solution mostly resulted in reduction in free chloride content and increase in bound chloride content. The sulphate ion concentration was reduced with increase in BFS content, and an opposite variation was observed with increase in molarity of NaOH solution. The results of XRD analysis showed greater formation of geopolymeric compounds and C-S-H gel (as indicated by their peak intensity) with increase in BFS content and molarity of NaOH solution. The peak intensity of C-S-H gel was lower in the mixes added with MS alone or along with NC than that added with NS alone or along with NC, which may be due to the effect of decalcification of C-S-H gel in the presence of Mg²⁺ ion. The FESEM micrographs showed less denser microstructure in GPM admixed with MS than that admixed with NS.

Keywords: Geopolymer mortar; Ground granulated blast furnace slag (BFS); Fly ash; Chloride; Sulphate; Compressive strength; Microstructure.

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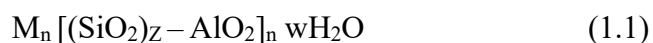
Introduction

1.1. General

Concrete is the second most used material after water on the earth. Cement is one of the primary constituents, typically associated with the production of conventional concrete. It is well known that the production of one ton of cement releases one ton of carbon dioxide (CO₂) into the atmosphere. To overcome this problem, different alternate binding materials have been developed and one such emerging material that has gained interest in the scientific community is alkali activated material which is also termed as geopolymer binders [1,2]. Researchers have utilized different industrial by-products such as fly ash, ground granulated blast furnace slag, silica fume, etc., as a partial or full replacement of cement in the production of concrete through alkali activation [3]. Among different alkali activators, the combination of sodium hydroxide (NaOH) solution and sodium silicate (Na₂SiO₃) solution was commonly used in the production of geopolymer binders.

1.2 Geopolymerization mechanism

The polymerization process of geopolymer binders mainly includes four stages: (i) dissolution: the Si–O and Al–O bonds are broken in the aluminosilicate materials under the action of the alkali activator, and the Si–O and Al–O tetrahedral monomers are released; (ii) diffusion: dissolved Si–O and Al–O tetrahedral monomers diffuse into the reaction system. According to the principle of chemical equilibrium, the silicon and aluminium concentrations decrease on the particle surface owing to the diffusion, and the dissolution process continues, (iii) polycondensation: Si–O and Al–O tetrahedra form amorphous -Si-O-Al-O- structures through polymerization, and (iv) hardening: dehydration reaction occurs, forming a hardened geopolymer with high mechanical strength [4]. The geopolymer structure was given by Prof. J. Davidovits, which is shown in equation (1.1) [5,6].



where, M is an alkali metal cation; n represents the degree of polycondensation; w represents the number of chemically bound water molecules; z represents the silicon-to-aluminium ratio (Si/Al), which is 1, 2, or 3. The structures of the aluminosilicates are divided into three forms as per the Z value, which are illustrated in Fig. 1.1 [6].

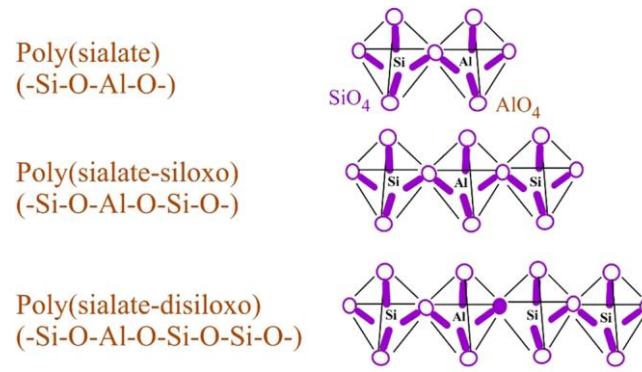


Fig. 1.1 Different types of aluminosilicate structures (1989) [6]

1.3 Properties of geopolymer composites

Geopolymer composites generally exhibit inferior fresh properties compared to OPC based composites. This is due to the higher viscous nature of silicate components present in the geopolymers [7]. Wong et al. investigated the fresh properties of fly ash based geopolymer mortar by varying the sodium silicate (Na_2SiO_3) solution to the sodium hydroxide (NaOH) solution, and concentration of NaOH solution. The authors found that the increase in sodium silicate solution to the sodium hydroxide solution, and concentration of NaOH solution reduced the flowability of fly ash based geopolymer mortars [8]. According to experimental results, utilizing geopolymer binders in place of ordinary Portland cement (OPC) in several applications significantly increased both compressive strength and resistance to sulfuric acid [9]. The performance of geopolymer binders depends on several factors which included type and size of precursor, concentration of alkaline activator solution, mix design, curing conditions etc. The increase in fineness of precursor material and molarity of alkaline solution improved the strength properties due to increase in specific surface area and increased polymerization rate, respectively [10]. The geopolymer composites cured at high temperatures showed better performance due to more stable crosslinked aluminosilicate polymer structure [11]. Generally, geopolymer composites made of 100% fly ash required curing at elevated temperatures due to slow polymerization reaction. However, this limitation can be overcome by replacing fly ash with calcium rich material such as ground granulated blast furnace slag [12]. When compared to OPC composites, geopolymer composites exhibits superior mechanical properties and offers greater resistance towards chemical attack. Additionally, water absorption, sorptivity, and porosity have a positive impact on the durability characteristics in ambient curing environments [13]. Verma et al [14]. stated that the fineness of fly ash, concentration of alkaline liquid, ratio of alkaline solutions, and ratio of fly ash to the

alkaline solution affects the properties of geopolymer composites. From the literature, it was found that the effect of variation in proportions of fly ash and BFS, and variation in concentration of sodium hydroxide solutions on mechanical properties of geopolymer mortar made with fly ash and BFS were studied [15–17].

1.4 Durability studies on geopolymer composites

Before the implementation of geopolymer composites in practical conditions, it is very much important to investigate its behaviour towards aggressive environment which include chloride and sulphate ions. These ions can ingress into the geopolymer composites either from internal source such as concrete ingredients, or external source such as marine conditions. Bakharev [18] investigated the durability of fly ash based geopolymers against the acetic acid and sulphuric acid solutions. The authors reported that the strength of fly ash based geopolymers were drastically reduced when exposed to sulphuric acid solutions as compared to the acetic acid solutions. Zhu et al. [19] compared the chloride penetration resistance of alkali activated fly ash composites with OPC based composites, when exposed to saturated NaCl solutions. The authors reported that the alkali activated fly ash composites exhibited superior chloride resistance when compared with OPC based composites.

Literature Review

2.1 General

In this chapter, the review of previous research works carried out on different properties of geopolymer composites is presented.

Lee and Lee [2] investigated the effect of slag proportion, concentration of NaOH solution and mass ratio of sodium silicate (SS) to sodium hydroxide (SH) ratio (SS/SH) solution on setting time, workability, compressive strength, and split tensile strength of alkali activated fly ash-slag concrete cured under room temperature. The fly ash-slag alkali activated concrete mixes were made with varying slag replacement level at 10%, 15%, 20%, 25%, and 30% (by mass of the total binder), NaOH solution concentration was varied at 4 M, 6 M and 8 M. Further, the SS/SH ratio was varied at 0.5, 1, and 1.5. For evaluation of compressive strength, cylindrical specimens (size: 100 mm diameter and 200 mm height) were prepared and tested at 3, 7, 14, 28 and 56 days. The result showed, increase in slag content, concentration of NaOH solution, and SS/SH ratio led to reduction in setting time of alkali-activated fly ash-slag paste. The compressive strength at 28 days was increased with increase in slag content, except in case of slag at 25% and 30%. The compressive strength of alkali-activated fly ash-slag (70%:30%) concrete decreased, due to the formation of a crack induced by the shrinkage of the paste in concrete.

Hager et al. [20] have investigated the microstructure and mechanical properties of geopolymer mortars made of fly ash and ground granulated blast furnace slag, and cured at room temperature and elevated temperatures (200, 400, and 800°C). The fly ash was replaced with ground granulated blast furnace slag at 0, 10, 30, and 50% by weight. The authors have used sodium silicate solution as alkaline solution. The mortars were prepared with a sand to binder of 1.5, the ratio of alkaline solution to binder was 0.45, and water to binder weight ratio taken was 0.3. The authors have concluded that the addition of slag resulted in higher mechanical strength. In addition, the mortar specimens when subjected to 800°C showed lower strength. From microstructural observation, the authors have reported that the fly ash geopolymer mortars showed better behavior when cured at high temperature.

H. Liu et al. [21] have investigated the impact of different alkali activators on the setting time of Class F fly ash paste, and also investigated the compressive strength and microstructure of

paste by using FT-IR. The different alkaline activators that are used are sodium hydroxide (NaOH) solution, sodium silicate solution (Na_2SiO_3) solution, and a combination of NaOH and Na_2SiO_3 solutions. The authors have also investigated the influence of anhydrous borax as a retarder at varying dosages (5%, 10%, 15%, 20%, and 25% by fly ash mass). Cubes of 50 mm size were prepared and cured at 75°C in chamber with water bath for compressive strength test at 1 and 3 days. From the results, the authors have concluded that the setting time was extended with increased NaOH dosage when using combination of NaOH and Na_2SiO_3 solutions. Further, they reported that the addition of 10% and 15% borax to NaOH solution significantly extended setting time, but other dosages had less impact. The prolonged setting time with borax was due to the formation of $[\text{BO}_4^-]$ tetrahedron in Class F fly ash, which was observed by authors from FT-IR analysis. The authors have concluded that the borax's retarding effect was weakened with higher alkali concentration, and the compressive strength was decreased with addition of borax when compared with the mixtures without borax.

Ryu et al. [22] have investigated the mechanical properties of fly ash-based geopolymer concrete with different alkaline activators. The alkaline activators used in this study were sodium hydroxide (NaOH) solution at a concentration of 6 M, 9 M, and 12 M, and mixture of NaOH solution (9 M) along with sodium silicate (Na_2SiO_3) solution. Mortar cubes of 50 mm size were prepared for compressive strength test, and cylinders of 100 mm diameter and 200 mm height were prepared for split tensile strength test. The authors have also carried out microstructure studies i.e., X-ray diffraction (XRD) analysis, scanning electron microscope (SEM), and energy dispersive X-ray analysis (EDS) analyses. The authors have reported that the increase in molarity of NaOH solution led to increase in the compressive strength and split tensile strength. Further, it was found that the mixes made with mixture NaOH solution and Na_2SiO_3 solution had attained higher strength than mix made with NaOH solution. From the microstructural investigations, the authors concluded that the concrete mixes made with both NaOH solution and Na_2SiO_3 solution showed denser microstructure than the mixes made with NaOH solution.

Elyamany et al. [23] have investigated the setting time, compressive strength, and flexural strength at the age of 7 days of geopolymer mortars prepared with different binders. The geopolymer mortars were made with different proportions of fly ash, ground granulated blast furnace slag, and silica fume i.e., 100% fly ash, 50% FA with 50 % slag, and 50% FA with 35 % slag and 15 % silica fume. The alkaline solution used was a combination of sodium hydroxide (NaOH) solution and sodium silicate (Na_2SiO_3) solution. The concentration of

NaOH solution was varied at 10 M, 12 M, 14 M, and 16 M. The geopolymer mortars were made with different alkaline solution to binder ratios i.e., 0.35, 0.4, 0.45, and 0.50. The mortar specimens were cured at 30°C, 60°C, and 90°C. Cubes of 70 mm size were made for compressive strength test, and prisms of size 40 mm × 40 mm × 160 mm were made for flexural strength test. The authors have also conducted scanning electron microscope (SEM) as part of microstructure studies. From the results, the authors have reported that the increase in curing temperature led to increase in compressive strength and flexural strength of geopolymer mortars. In addition, the mortar mixes with fly ash, slag and silica fume had attained higher strength than other mixes. The increase in molarity of NaOH solution had enhanced the compressive strength and flexural strength of geopolymer mortar mixes. Further, the compressive strength and flexural strength decreased with increase in alkaline solution to binder ratio. SEM micrographs show that the mortar mix with fly ash, slag, and silica fume had denser microstructure compared to that of mortar mix with fly ash, and mix with fly ash and slag.

Nazari et al. [24] have studied the compressive strength and microstructure of boroaluminosilicate geopolymer pastes made of fly ash. The authors have prepared anhydrous borax by heating borax decahydrate at 150°C for 30 min and further heated at 300°C for 15 hours, and mixed with NaOH solution. The authors have used this solution for the preparation of fly ash based boroaluminosilicate geopolymer. The mixes were made with different alkaline activator (NaOH plus anhydrous borax) to binder ratios i.e. 0.75, 0.80, 0.85, and 0.90. Cubes of 50 mm size were prepared and tested for compressive strength test at the age of 3, 7, 28 and 90 days. The microstructure studies i.e., scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FT-IR). The authors reported that the compressive strength was increased with increase in ratio of alkaline activator to binder ratio. Additionally, the authors did not observe any micro cracks in the pastes made of boroaluminosilicate geopolymers while conducting the SEM analyses. Further, from FT-IR analysis, the authors have identified additional bond i.e. B-O bond in boroaluminosilicate geopolymer paste, and it was not present in aluminosilicate geopolymer.

Somna et al. [25] have studied the compressive strength and microstructural properties of ground fly ash based geopolymer paste. The authors have used sodium hydroxide (NaOH) solution as an alkaline solution. The molarity of NaOH solution was varied at 4.5 M, 7 M, 9.5 M, 12 M, 14 M, and 16.5 M. The ratio of NaOH solution to fly ash was taken as 0.3. The fly ash and NaOH solution were mixed for five minutes, and the samples of geopolymer paste

were casted into cylindrical mould (size: 30 mm diameter and 60 mm height). The samples were maintained in a controlled environment at a temperature of 25 to 28°C till the day of testing. The compressive strength of geopolymer paste specimens was assessed at 7, 14, 28, 42, and 60 days. The authors have carried out X-ray diffraction (XRD) analysis, scanning electron microscope (SEM) analysis, and energy dispersive spectroscopy (EDS) analysis as part of microstructural studies. The authors have found that the highest compressive strength was attained in the pastes made of 14 M NaOH solution. Additionally, they reported that the compressive strength was increased with age. From microstructural investigations, the authors have found that the alkali activation of ground fly ash has occurred at room temperature. Further, they concluded that the ground fly ash can be used for preparation of geopolymers at room temperature.

Lee and Deventer [26] investigated the effects of inorganic salt contamination (KCl , K_2CO_3 , CaCl_2 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, MgCO_3 , and $\text{Mg}(\text{OH})_2$) on the strength and durability of geopolymer paste made with fly ash and kaolin, and alkaline solution used was mixture of 15 M KOH s and sodium silicate solutions. The strength and microstructure of the geopolymer pastes were studied by performing compressive strengths, Fourier-transform transmission infrared spectroscopy (FTIR) spectra, X-ray diffraction (XRD), and scanning electron microscopy coupled with energy dispersive spectrometer (SEM-EDS) analysis at different ages (7, 21, 90, 80, and 270 days). The authors reported that the addition of salt led to deterioration of geopolymers, due to the effect of hydrolytic attack on aluminosilicate gel. Further, from microstructural investigations, they stated that the amorphous aluminosilicate precipitates were detected in the deteriorated samples.

2.2 Objectives of present study

The objective of the present research work are as follows:

- To study the flowability and compressive strength of geopolymer mortar (GPM) made with different proportions of ground granulated blast furnace slag (BFS) and fly ash, different concentrations of sodium hydroxide solution and admixed with chloride and sulphate salts.
- To investigate the durability and microstructural properties of BFS-fly ash based geopolymer mortar.

Experimental Work

3.1 General

In this chapter, the materials used in the preparation of ground granulated blast furnace slag (BFS) and fly ash (FA) based geopolymer mortar (GPM) mixes, and the tests conducted on the GPM are presented.

3.2 Materials

3.2.1 Material details and mix proportions

For the preparation of geopolymer mortar (GPM), the precursor materials used are ground granulated blast furnace slag (BFS) and fly ash (FA). The alkali solution used was a mixture of sodium hydroxide (NaOH) solution, and sodium silicate (Na_2SiO_3) solution. The geopolymer mortar was designed for a wet density of 2125 kg/m^3 , and the mass ratio of alkaline solution to binder content was taken as 0.5. The fine aggregate used in the preparation of GPM mixes was locally available river sand confirming to Zone II as per IS 383:2021 [27] that had a specific gravity of 2.65. The proportions and quantities of geopolymer mortar mixes are given in Table 3.1.

Table 3.1 Proportions and quantities of geopolymer mortar

BFS (%)	Fly ash (FA) (%)	Molarity of NaOH Solution	SS/SH ratio	Binder (kg/m ³)		Alkaline solution (kg/m ³)	Sand (kg/m ³)
				BFS	FA		
85	15	6 M	1.45	578	102	340	1105
		10 M					
65	35	6 M		442	238		
		10 M					

SS: Sodium silicate solution, SH: Sodium hydroxide solution

3.2.2 Source of chloride and sulphate ions

In the present study, sodium chloride (NaCl) was used as the source of chloride ions, and sodium sulphate (Na_2SO_4), and magnesium sulphate (MgSO_4) were used as the source of sulphate ions while preparing the salt admixed GPM mixes. In addition, to study the combined

effect of chloride and sulphate ions, the combination of NaCl with Na₂SO₄, and NaCl with MgSO₄ were also admixed during the preparation of salt admixed GPM mixes. The concentrations of admixed salts in the GPM mixes are given in Table 3.2.

Table 3.2 Details of admixed salts in GPM mixes

Admixed salt with concentration	Abbreviation
3.5% sodium chloride (NaCl)	3.5NC
7% sodium sulphate (Na ₂ SO ₄)	7NS
7% magnesium sulphate (MgSO ₄)	7MS
3.5% NaCl with 7% Na ₂ SO ₄	3.5NC with 7NS
3.5% NaCl with 7% MgSO ₄	3.5NC with 7MS

3.3 Preparation of GPM mixes

Initially, the alkaline solution was prepared for the preparation of GPM mixes. The preparation of alkaline solution involves dissolving the NaOH pellets in laboratory tap water as per the required molarity, i.e. 6 M and 10 M, 48 hours before the preparation of GPM mixes. After 24 hours, the Na₂SiO₃ solution was added to the NaOH solution. In case of salt admixed GPM mixes, the salts i.e., NaCl, Na₂SO₄, and MgSO₄ of different concentrations, as mentioned above, by mass of geopolymer solids were added to the alkaline solution prior to the preparation of mixes. During preparation of GPM mixes, the dry mixing of source materials and fine aggregate was carried out in a mortar mixer. Subsequently, the alkaline solution was added, and the mixing was continued to obtain a homogeneous mix. Then, flow table test was conducted on the fresh geopolymer mortar mix. Subsequently, the fresh mortar mix was placed in cube moulds of size 50 mm in 2 layers, and each layer was tamped 25 times with a tamping rod followed by vibration for 10–15 seconds on a vibrating table. After 24 hours of casting, the geopolymer mortar (GPM) cubes were demoulded and left to ambient laboratory condition till the day of testing.

3.4 Test methods

3.4.1 Flowability of GPM

The freshly prepared geopolymer mortar (GPM) flowability was measured by conducting the flow table test as per the procedure given in ASTM C 1437-20 [28]. The mould was lubricated with oil and then placed at centre of the flow table. The freshly prepared GPM mix was filled

in two layers, and each layer was tamped for 20 times with a tamping rod. The additional material was struck off, the top surface was levelled and the table was cleaned with a dry cloth. Then, the mould was lifted and flow table was dropped for 25 times within a duration of 15 seconds. To measure the flow value of the GPM mix, the diameter of the mortar spread was measured along four lines inscribed on top surface of the flow table. The average of these four measurements is the flow value of the GPM mix. The flow index was evaluated using the following equation.

$$FI (\%) = \frac{A}{B} \times 100 \quad (3.1)$$

Where, $FI (\%)$ is the flow index, A is the average of four measurements of mortar spread minus the inner diameter of base of the mould, and B is the inner diameter of base of the mould.

3.4.2 Compressive strength test on GPM

The compressive strength test of GPM mixes was carried out on 50 mm cubes in a compression testing machine at the age of 7, 28, and 90 days. Three replicate cubes from a given mortar mix were tested, and the average value was noted as the compressive strength value of that GPM mix. It may be noted that the salt admixed GPM mixes were tested at the age of 28 and 90 days.

3.4.3 Free chloride content and total chloride content in GPM

After strength test, the GPM specimens were further ground in a crusher, and passed through 75 μm sieve. This powder was used to evaluate the free chloride and total chloride contents in salt admixed GPM mixes. The chloride contents were evaluated by using automatic potentiometric titrator (maker: Metrohm, model: 848 Titrino plus). For evaluation of free chloride content, 4 gram GPM powder and 40 ml distilled water was taken into a beaker and thoroughly mixed by a magnetic stirrer and simultaneously heated on hot plate till boiling. Then, the solution was allowed to cool to the room temperature. Thereafter, free chloride content was evaluated by titrating with 0.1 M AgNO_3 solution in automatic potentiometric titrator. For the evaluation of total chloride content, 4 gram GPM powder and 40 ml of HNO_3 solution (1 N concentration) was thoroughly mixed in a beaker by a magnetic stirrer (without any heating). Thereafter, total chloride content was evaluated by titrating with 0.1 M AgNO_3 solution in the automatic potentiometric titrator. Subsequently, bound chloride content was evaluated by subtracting free chloride content from total chloride content. The free, total, and bound chloride contents are expressed as % by mass of geopolymer mortar.

3.4.4 Evaluation of sulphate ion concentration in GPM

To evaluate the sulphate ion concentration in GPM mixes, initially, the aqueous pore solution was prepared from the salt added GPM mixes. For this purpose, the GPM powder passing through 75 μm sieve was mixed with distilled water at a mass ratio of 1:1. The mixing was performed with a magnetic stirrer for a period of 20 minutes. Subsequently, the solution was heated and stirred on a hot plate for another 20 minutes. Thereafter, the solution was allowed to cool to the room temperature and then filtrated through Whatman no.1 filter paper. The sulphate ion concentration was then evaluated by using turbidimetric method as per the procedure given in Standard methods for the examination of water and waste water prescribed by American Public Health Association (APHA) [29].

3.4.5 Microstructural investigations on GPM

3.4.5.1 XRD analysis of GPM

The GPM powder sample (passing through 75 μm sieve) was used for investigating the microstructure of geopolymer mortar through X-ray diffraction (XRD) analysis. The analysis was carried out in X-ray diffractometer (Rigaku SmartLab 9 kW model) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The GPM powder sample was scanned from $5^\circ 2\theta$ to $65^\circ 2\theta$ at a step size of $0.03^\circ 2\theta$.

3.4.5.2 FESEM analysis of GPM

The morphology of GPM mixes was investigated by conducting Field emission scanning electron microscope (FESEM) by using FESEM instrument: ZEISS (model: Gemini). Carbon tape was mounted on the stub, then the GPM powder sample was placed on carbon tape, and a thin layer of gold coating was applied by sputtering method. The FESEM analysis was operated with in-lens mode.

Results and Discussion

4.1 General

In this chapter, the flowability of control and salt admixed GPM mixes, compressive strength, chloride contents, sulphate ion concentration, XRD, and FESEM analyses of GPM mixes made with different replacement levels of ground granulated blast furnace slag (BFS) and fly ash, and different molarity of NaOH solution are presented and discussed.

4.2 Flow index (%) of geopolymmer mortar

The flow index (%) of control and salt admixed geopolymmer mortar made with different proportions of ground granulated blast furnace slag (BFS) and fly ash (FA), and different concentrations of NaOH solution are depicted in Fig. 4.1. From this figure, it is inferred that the flow index increased with increase in fly ash content regardless of molarity of NaOH solution and type of admixed salt. This is due to the increase in the amount of spherical fly ash particles that resulted in higher flowability of GPM mixes [30]. Further, it was observed that the flow index mostly reduced with increase in concentration of NaOH solution regardless of fly ash content and type of admixed salt (Fig. 4.1). This is due to the greater amount of solids present in the GPM mixes made with 10 M NaOH solution than that made with 6 M NaOH solution.

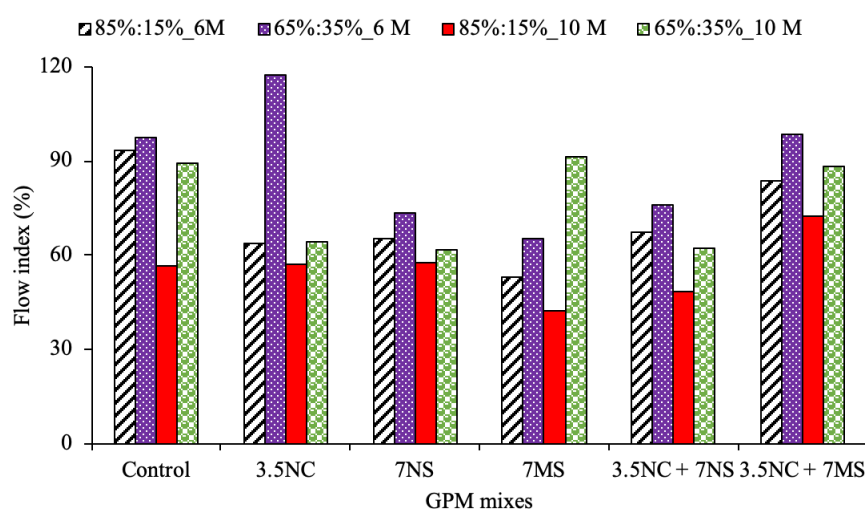


Fig. 4.1 Flow index (%) of control and salt admixed geopolymmer mortar mixes

From Fig. 4.1, it was observed that the GPM mixes admixed with Na_2SO_4 mostly showed higher flow index as compared to the mixes admixed with MgSO_4 . However, in case of GPM mixes admixed with combined chloride and sulphate salts, it was observed that the GPM mixes admixed with NaCl plus MgSO_4 had higher flow index than the mixes admixed with NaCl plus Na_2SO_4 regardless of fly ash content and molarity of NaOH solution (Fig. 4.1). Further, between chloride, and composite chloride plus sulphate salt admixed mixes, the flow index was mostly higher in case of NaCl admixed GPM mixes when compared with NaCl plus Na_2SO_4 admixed GPM mixes. However, mostly opposite variation in flow index was observed between NaCl , and NaCl plus MgSO_4 admixed GPM mixes. Further, the flowability as indicated by flow index was mostly higher in case of composite chloride plus sulphate salt admixed GPM mixes as compared to GPM mixes admixed with only sulphate salt irrespective of cation type associated with sulphate ions (Fig. 4.1). The variation in flow index was mostly unsystematic between control and salt admixed GPM mixes as observed from Fig. 4.1. This could be due to the effect of presence of chloride and sulphate ions that altered the particle mobility in salt admixed GPM mixes.

4.3 Compressive strength of GPM

The compressive strength of control GPM mixes at the age of 7 days made with different proportions of BFS and fly ash, and different molarity of NaOH solution is shown in Fig. 4.2. In addition, the compressive strength of control and salt admixed GPM mixes at the age of 28 and 90 days are illustrated in Fig. 4.3. From Figs. 4.2 and 4.3, it was observed that the GPM mixes made with higher BFS content mostly showed higher compressive strength than the mixes made with lower BFS content regardless of molarity of NaOH solution, type of admixed salt, and age. This is attributed to the increase in calcium content present in BFS that led to more formation of calcium based geopolymer gel [31] and C-S-H gel thereby resulting in formation of denser microstructure and enhanced compressive strength at higher BFS content. From Figs. 4.2 and 4.3, the compressive strength of GPM mixes mostly increased with increase in molarity of NaOH solution regardless of BFS content, type of admixed salt, and age. This is due to the effect of greater leaching of silica and alumina from the precursor materials at higher molarity of NaOH solution that led to formation of denser geopolymer matrix, which increased the compressive strength of GPM mixes [32].

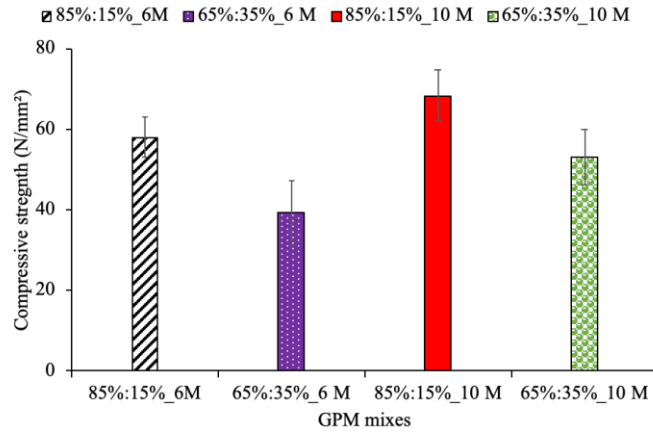


Fig. 4.2 Compressive strength of control GPM mixes at the age of 7 days.

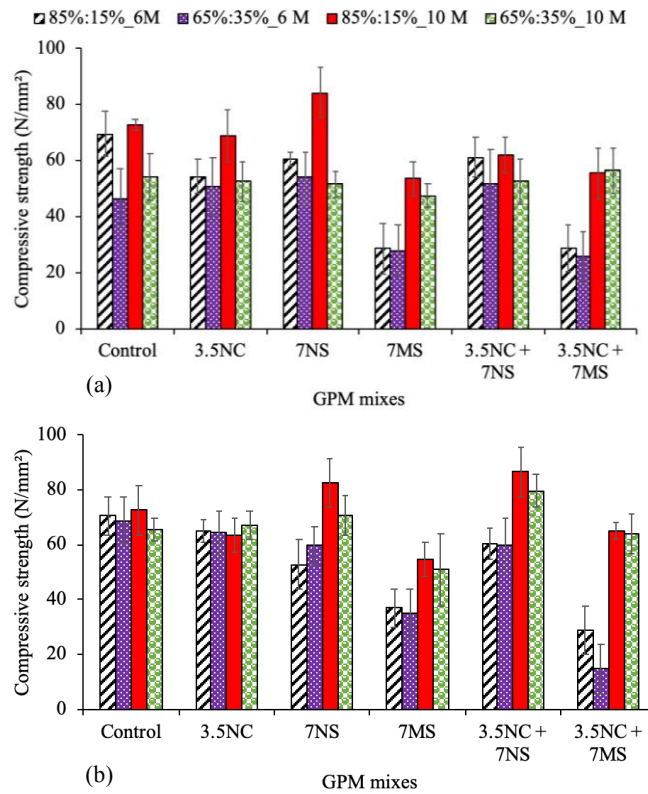


Fig. 4.3 Compressive strength of control and salt admixed GPM mixes, (a) at the age of 28 days, and (b) at the age of 90 days.

In case of GPM mixes made with 6 M NaOH solution, the compressive strength was mostly higher in control GPM mixes than that of salt admixed GPM mixes regardless of BFS content and age (Fig. 4.3). In case of GPM mixes made with 10 M NaOH solution, the compressive strength was mostly lower in control mixes than the GPM admixed with Na₂SO₄, and NaCl plus Na₂SO₄. However, the strength of control GPM was higher than the mixes admixed with NaCl, MgSO₄, and NaCl plus MgSO₄ regardless of BFS content and age. The lower compressive strength of GPM mixes admixed with NaCl than control mixes could be due to the effect of crystallization of NaCl in geopolymer matrix, which resulted in obstruction of

geopolymerization reaction to certain degree. From Fig. 4.3, it was observed that the GPM mixes admixed with Na_2SO_4 showed higher compressive strength than that admixed with MgSO_4 regardless of BFS content, and molarity of NaOH solution. In the same line, the GPM mixes admixed with NaCl plus Na_2SO_4 mostly showed higher compressive strength when compared with that admixed with NaCl plus MgSO_4 . Further, the GPM mixes admixed with only NaCl showed higher strength than that admixed with NaCl plus MgSO_4 . The lower strength of GPM mixes in the presence of MgSO_4 might due to the effect of Mg^{2+} ion associated with the sulphate that led to decalcification of C-S-H gel [33], and resulted in formation of less denser microstructure. Further, it may be noted that the variation in compressive strength of GPM mixes admixed with only NaCl was found to be unsystematic when compared with the mixes admixed with NaCl plus Na_2SO_4 regardless of BFS content, molarity of NaOH solution, and age as observed from Fig. 4.3. The mixes admixed with NaCl plus Na_2SO_4 mostly showed higher strength than mixes admixed with only Na_2SO_4 . Similarly, the mixes admixed with NaCl plus MgSO_4 mostly exhibited higher strength than mixes added with only MgSO_4 . This indicates formation of comparatively denser microstructure due to pore filling effect of reaction products formed in the GPM admixed with composite chloride plus sulphate salts than that admixed with only sulphate salt (irrespective of cation type). From Fig. 4.3, it was observed that the compressive strength of GPM mixes mostly increased with increase in age regardless of BFS content, molarity of NaOH solution, and type of admixed salt. This is due to the effect of greater extent of geopolymerization reaction at later ages.

4.4 Chloride content in GPM mixes

The free chloride, total chloride, and bound chloride contents of salt admixed GPM mixes are shown in Fig. 4.4. From this figure, it was observed that the variation in total chloride content with BFS content was found to be unsystematic. Further, the free chloride content mostly reduced and the bound chloride content mostly increased with increase in BFS content irrespective of molarity of NaOH solution, type of admixed salt, and age. This might be due to the formation of more amount of N-(C)-A-S-H gel and C-S-H gel in GPM mixes made with 85% BFS than the mixes made with 65% BFS, which resulted in greater physical binding of chloride ions on these gels [34]. From Fig. 4.4, the GPM mixes made with 10 M NaOH solution mostly showed higher total chloride content than the mixes made with 6 M NaOH solution. This is attributed to addition of more amount of NaCl in GPM mixes made with 10 M NaOH solution as NaCl was added as percentage of geopolymer solids content where solids present

in NaOH solution is part it. Further, free chloride content mostly decreased and bound chloride content mostly increased with increase in molarity of NaOH solution regardless of BFS content, type of admixed salt, and age. This is due to the effect of higher extent of geopolymerization reaction in GPM mixes made at higher NaOH solution concentration that led to formation of more amount of geopolymeric gels, thereby resulting in greater physical binding of chloride ions.

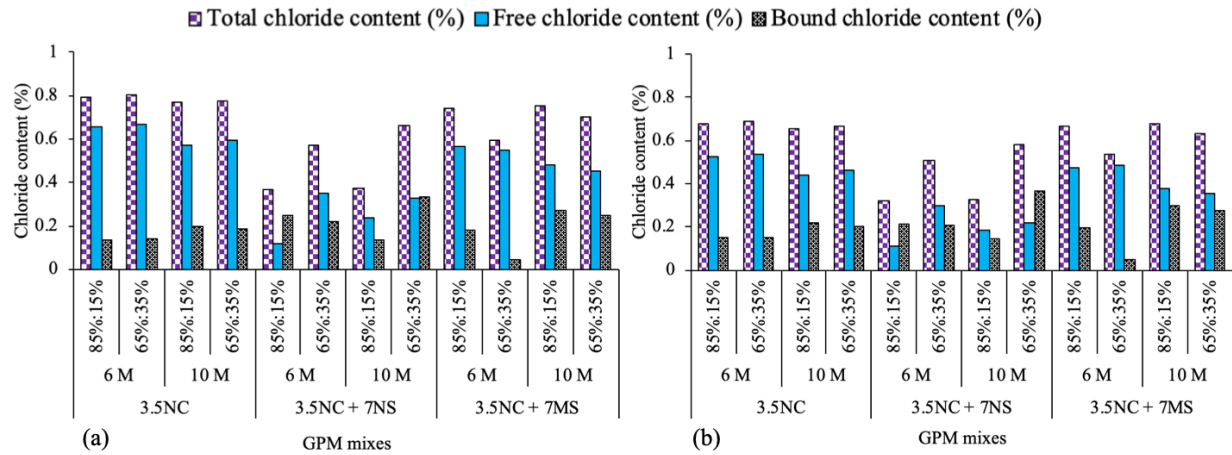


Fig. 4.4 Chloride contents (%) of GPM mixes evaluated at different ages, (a) at 28 days, and (b) at 90 days.

From Fig. 4.4, the total chloride and free chloride contents were mostly higher in GPM mixes admixed with only NaCl than the mixes admixed with NaCl plus MgSO_4 followed by the mixes admixed with NaCl plus Na_2SO_4 regardless of BFS content, molarity of NaOH solution, and age. Further, the GPM mixes admixed with NaCl plus Na_2SO_4 mostly showed higher bound chloride content than the mixes admixed with NaCl plus MgSO_4 followed by the mixes admixed with NaCl. The lower free chloride content in the conjoint presence of chloride and sulphate salts might be due to the competing effect of sulphate ions with chloride ions that led to lower free chloride content in the aqueous pore solution of GPM admixed with both chloride and sulphate salts. The lower bound chloride content in GPM mixes admixed with NaCl plus MgSO_4 as compared to NaCl plus Na_2SO_4 is due to the effect of decalcification of C-S-H gel in presence of Mg^{2+} ion, which resulted in lower physical binding of chloride ions [33], thereby increasing the free chloride content in GPM mixes admixed with NaCl plus MgSO_4 when compared with NaCl plus Na_2SO_4 . From Fig. 4.4, it was observed that the total chloride and free chloride content were reduced, and the bound chloride content mostly increased with age irrespective of BFS content, molarity of NaOH solution, and type of admixed salt. This is due to the effect of continuation of geopolymerization process with age from 28 to 90 days that led

to formation of more amount of binding gels, which led to greater physical binding of chloride ions with these gels.

4.5 Sulphate ion concentration in GPM mixes

The sulphate ion concentration of salt added GPM mixes made with different BFS proportions and molarity of NaOH solution at the age of 28 and 90 days are illustrated in Fig. 4.5. From this figure, it was observed that the sulphate ion concentration was reduced with increase in BFS content regardless of molarity of NaOH solution, type of admixed salt, and age. This is attributed to increase in calcium content with increase in BFS content that resulted in formation of greater amount of N-(C)-A-S-H gel and C-S-H gel [34], which in turn led to greater physical adsorption of sulphate ions onto these gels. From Fig. 4.5, it was observed that the sulphate ion concentration mostly increased with increase in molarity of NaOH solution irrespective of BFS content, type of admixed salt, and age. This might be due to addition of more amount of sulphate salt as a result of higher solids content in 10 M NaOH solution than 6 M NaOH solution.

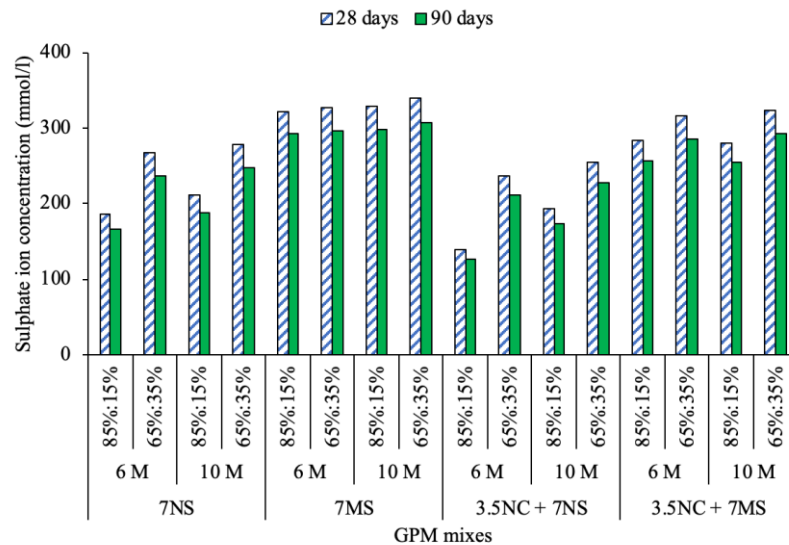


Fig. 4.5 Sulphate ion concentration of salt admixed GPM mixes at the age of 28 and 90 days.

From Fig. 4.5, it was observed that the sulphate ion concentration was greater in the aqueous pore solution of GPM admixed with MgSO_4 than that admixed with Na_2SO_4 . Same variation was observed between the GPM mixes admixed with NaCl plus MgSO_4 , and NaCl plus Na_2SO_4 regardless of BFS content, molarity of NaOH solution, and age. This might be due to decalcification of C-S-H gel in the presence of Mg^{2+} ion [33], which resulted in lower adsorption of sulphate ions on C-S-H gel in GPM mixes admixed with MgSO_4 . The sulphate ion concentration was greater in aqueous pore solution of GPM admixed with only sulphate

salt when compared with that admixed with composite chloride and sulphate salts regardless of type of cation associated with the sulphate ion (Fig. 4.5). This may be ascribed to the competing effect of chloride ions with sulphate ions, which resulted in lower sulphate ion concentration in the pore solution of GPM added with composite chloride and sulphate salts than that admixed with only sulphate salt. From Fig. 4.5, it was observed that the sulphate ion concentration was decreased with increase in age irrespective of BFS content, molarity of NaOH solution, and type of admixed salt. The continued geopolymerization reaction with age resulted in formation of more amount of binding gels that led to greater physical adsorption of sulphate ions on these gels during later age.

4.6 Microstructural investigations on GPM mixes

4.6.1 XRD analysis of GPM mixes

The XRD spectra of GPM mixes at the age of 7, 28, and 90 days are illustrated in Figs. 4.6, 4.7, and 4.8 respectively. From these figures, the crystalline phases of quartz and mullite were identified in all the XRD spectra, which indicates the presence of partially reacted fly ash particles. In addition, the semi crystalline peaks corresponding to hydrotalcite at $10.5^\circ 2\theta$, nepheline at $27.1^\circ 2\theta$, anorthoclase at $27.5^\circ 2\theta$, albite at $28.02^\circ 2\theta$, calcite along with calcium silicate hydrate (C-S-H) gel at $29.5^\circ 2\theta$, and aragonite at $45.8^\circ 2\theta$ were identified in all GPM mixes. The formation of nepheline and albite indicates the existence of N-A-S-H gel [35] and N-(C)-A-S-H gel [36] respectively. In case of GPM mixes admixed with chloride, and chloride plus sulphate salts, the peak related to halite (NaCl) was identified at $31.7^\circ 2\theta$. Further, the peak related to gypsum was identified at $33.35^\circ 2\theta$ in the GPM mixes admixed with sulphate, and chloride plus sulphate salts.

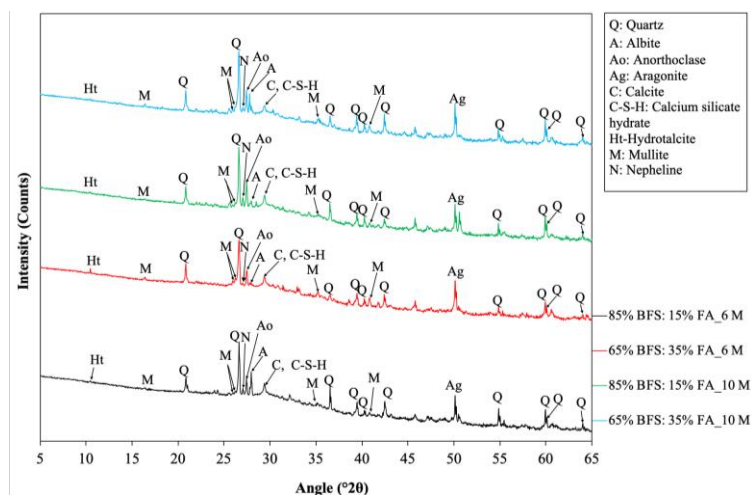


Fig. 4.6 XRD spectra of control GPM mixes at the age of 7 days.

From Fig. 4.6, the peak intensity of albite varied unsystematically with BFS content. However, the peak intensity related to nepheline, anorthoclase, and C-S-H gel in the XRD spectra increased with increase in BFS content regardless of molarity of NaOH solution at the age of 7 days. The more formation of geopolymer gel and C-S-H gel at higher BFS content as indicated by the XRD spectra led to higher compressive strength (Fig. 4.1). From Figs. 4.7 and 4.8, it was observed that the variation in peak intensity of nepheline and anorthoclase was found to be unsystematic with BFS content at the age of 28 and 90 days. However, the peak intensity of albite and C-S-H gel mostly increased with BFS content regardless of molarity of NaOH solution and type of admixed salt at both ages. The increase in calcium oxide content at higher BFS content resulted in more formation of calcium based binding gels i.e., albite and C-S-H gel in GPM made with 85% BFS content than the mixes made with 65% BFS content. Thus, greater formation of these gels resulted in higher compressive strength (Fig. 4.3) and more physical binding of chloride ions, thereby reducing the free chloride content and increasing the bound chloride content with increase in BFS content (Fig. 4.4). Further, the variations in the formation of albite and C-S-H gel with BFS content as indicated by the XRD spectra is in line with the variations in sulphate ion concentration (Fig. 4.5) of GPM.

From Fig. 4.6, it was observed that there was unsystematic variation in the peak intensity of albite and C-S-H gel with molarity of NaOH solution at the age of 7 days. However, the peak intensity of nepheline and anorthoclase increased with increase in molarity of NaOH solution irrespective of BFS content. The greater formation of nepheline and anorthoclase resulted in attaining higher compressive strength of GPM mixes made with 10 M NaOH solution than 6 M NaOH solution at the age of 7 days (Fig. 4.2). At the age of 28 days, the variations in the peak intensity of nepheline and C-S-H gel were found to be unsystematic. However, the peak intensity of anorthoclase and albite mostly increased with molarity of NaOH solution regardless of BFS content and type of admixed salt (Fig. 4.7). At the age of 90 days, the peak intensity of nepheline, anorthoclase, albite, and C-S-H gel were mostly increased with increase in molarity of NaOH solution (Fig. 4.8). This is due to the effect of more leaching of silica and alumina species from the precursor materials in the presence of 10 M NaOH solution as compared to 6 M NaOH solution that enhanced the reaction between these species and alkaline solution [37], which resulted in greater formation of these geopolymeric compounds and C-S-H gel. As a result, the compressive strength increased (Fig. 4.3) and the physical binding of chloride ions was greater in GPM mixes made with higher molarity of NaOH solution. This

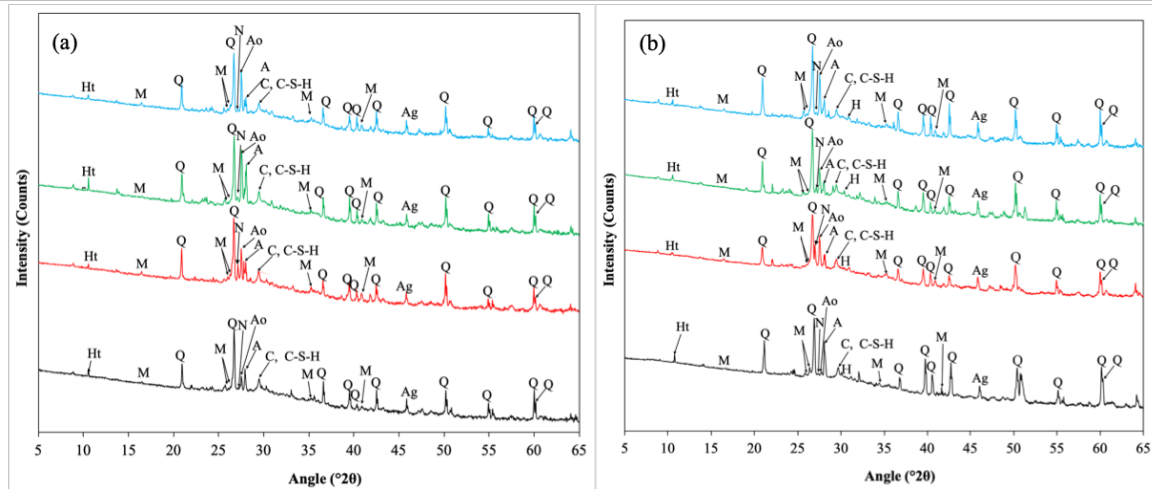
led to lower free chloride content and higher bound chloride content of GPM with increase in molarity of NaOH solution (Fig. 4.4).

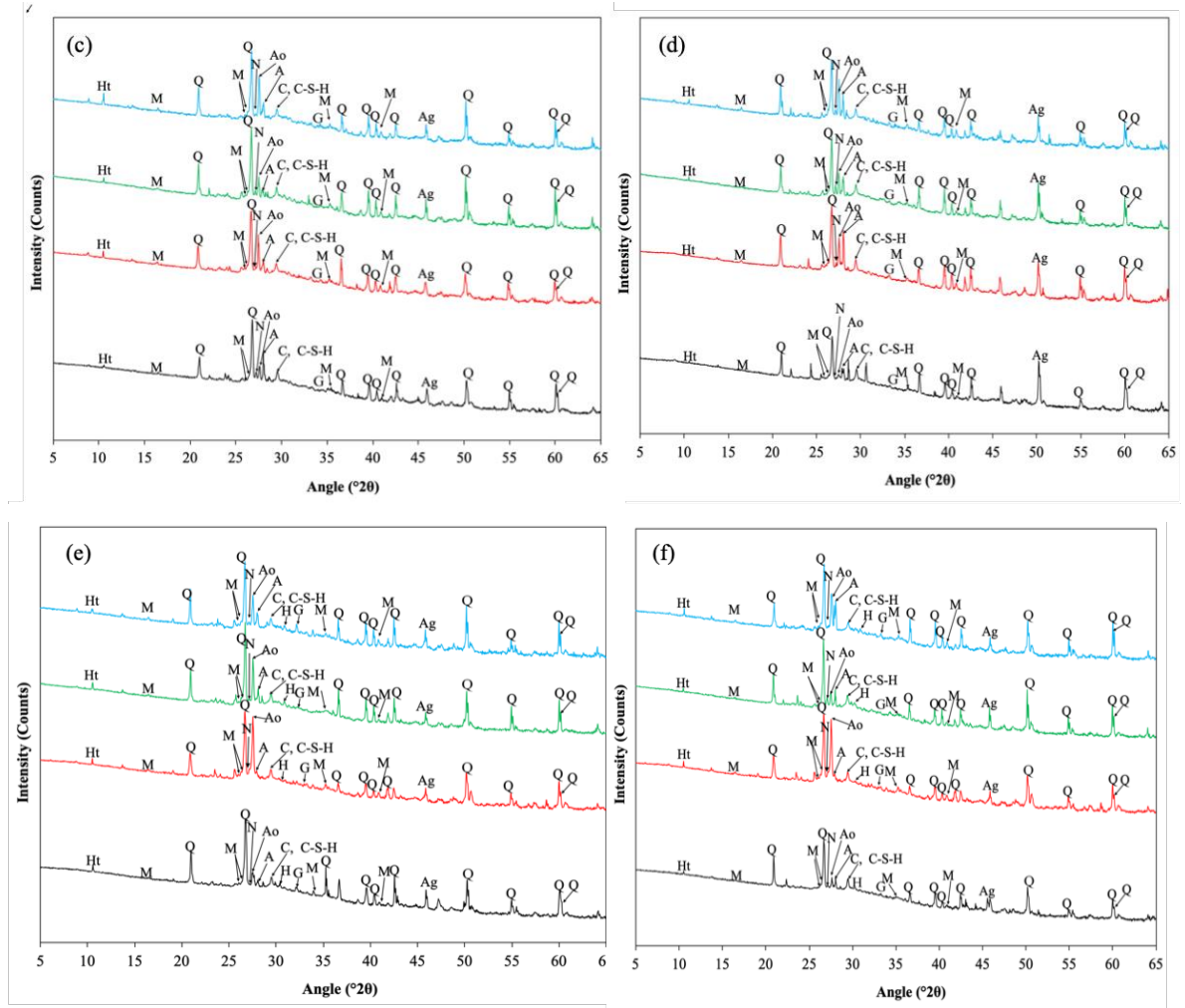
In case of GPM mixes made with 6 M NaOH solution, the variations in peak intensity of nepheline, anorthoclase, and C-S-H gel were found to be unsystematic in control GPM mixes when compared with salt added GPM mixes. However, the peak intensity of albite was mostly higher in control GPM mixes than salt added GPM mixes (Figs. 4.8 and 4.9) irrespective of BFS content and age. This indicates that the greater formation of albite played a dominant role in attaining higher compressive strength of control GPM mixes than salt added GPM mixes (Figs. 4.3). In case of GPM mixes made with 10 M NaOH solution, the peak intensity of the geopolymeric compounds and C-S-H gel were unsystematic between control and salt admixed GPM mixes (Figs. 4.8 and 4.9). In case of salt added GPM mixes, the peak intensity of anorthoclase and C-S-H gel were mostly lower in the GPM mixes admixed with MgSO_4 than the mixes admixed with Na_2SO_4 . Similar variation related to peak intensity of anorthoclase and C-S-H gel was observed between GPM mixes admixed with NaCl plus MgSO_4 and that admixed with NaCl plus Na_2SO_4 . Further, the peak intensity of anorthoclase and C-S-H gel were mostly lower in GPM mixes admixed with NaCl plus MgSO_4 than that admixed with NaCl regardless of BFS content, molarity of NaOH solution, and age. The lower peak intensity of C-S-H gel may be due to the effect of Mg^{2+} ion associated with sulphate that led to decalcification of C-S-H gel [33] in the GPM mixes admixed with MgSO_4 alone or along with NaCl. This resulted in reduction of compressive strength of GPM mixes in the presence of MgSO_4 or in conjoint presence with NaCl (Fig. 4.3). Further, the GPM mixes admixed with only MgSO_4 mostly showed lower peak intensity of anorthoclase and C-S-H gel than NaCl plus MgSO_4 . The peak intensity of anorthoclase and C-S-H gel in the XRD spectra were mostly higher in GPM mixes admixed with NaCl plus Na_2SO_4 than that admixed with only Na_2SO_4 followed by only NaCl. This is in line with the variation in compressive strength of GPM mixes (Fig. 4.3).

From the XRD spectra shown in Figs. 4.7 and 4.8, it was observed that the peak intensity of halite was found to be unsystematic, and the gypsum peak intensity mostly increased with BFS content regardless of NaOH solution concentration, type of admixed salt and age. The increase in calcium content in BFS might have led to greater formation of gypsum. The peak intensity of halite and gypsum were mostly decreased with increase in molarity of NaOH solution irrespective of BFS content, type of admixed salt and age (Figs. 4.7 and 4.8). This is due to greater formation of binding gels in GPM made with higher molarity of NaOH solution that

led to more physical adsorption of chloride ions (Fig. 4.4). Further, the increase in molarity of NaOH solution might have resulted in higher pH value of GPM mixes made with 10 M NaOH solution than 6 M NaOH solution. This increase in pH values led to lower formation of gypsum in GPM mixes made with 10 M NaOH solution than 6 M NaOH solution [38]. The peak intensity of halite was unsystematic with type of admixed salt (NaCl, NaCl plus Na₂SO₄ and NaCl plus MgSO₄) regardless of BFS content, NaOH solution concentration, and age. From Figs. 4.7 and 4.8, it was observed that the peak intensity of gypsum was mostly higher in GPM mixes admixed with Na₂SO₄ than that admixed MgSO₄. The similar trend was observed in GPM mixes admixed with composite chloride and sulphate salts irrespective of BFS content, molarity of NaOH solution, and age. This might be due to the effect of cation type associated with sulphate ion that influenced the formation of gypsum. The GPM mixes admixed with composite chloride plus sulphate salts showed lower peak intensity of gypsum when compared with the mixes admixed with only sulphate salt regardless of BFS content, molarity of NaOH solution, type of cation associated with sulphate ion, and age (Figs. 4.7 and 4.8). This might be due to the presence of NaCl that altered the formation of gypsum. From Figs. 4.6 to 4.8, it was observed that the peak intensity of albite, nepheline, and C-S-H gel mostly increased with age regardless of BFS content, molarity of NaOH solution, and type of admixed salt. This is due to the effect of continued geopolymerization process with age, which resulted in formation of more amount of binding gels. As a result, the compressive strength mostly increased (Figs. 4.2 and 4.3), and the free chloride content (Fig. 4.4) and sulphate ion concentration (Fig. 4.5) reduced with age.

—85% BFS: 15% FA_6 M —65% BFS: 35% FA_6 M —85% BFS: 15% FA_10 M —65% BFS: 35% FA_10 M

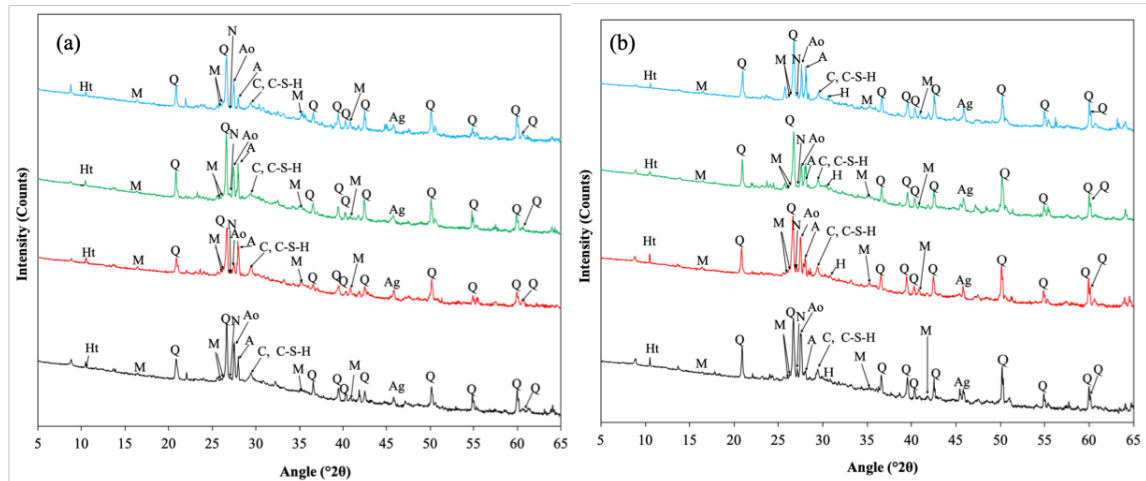


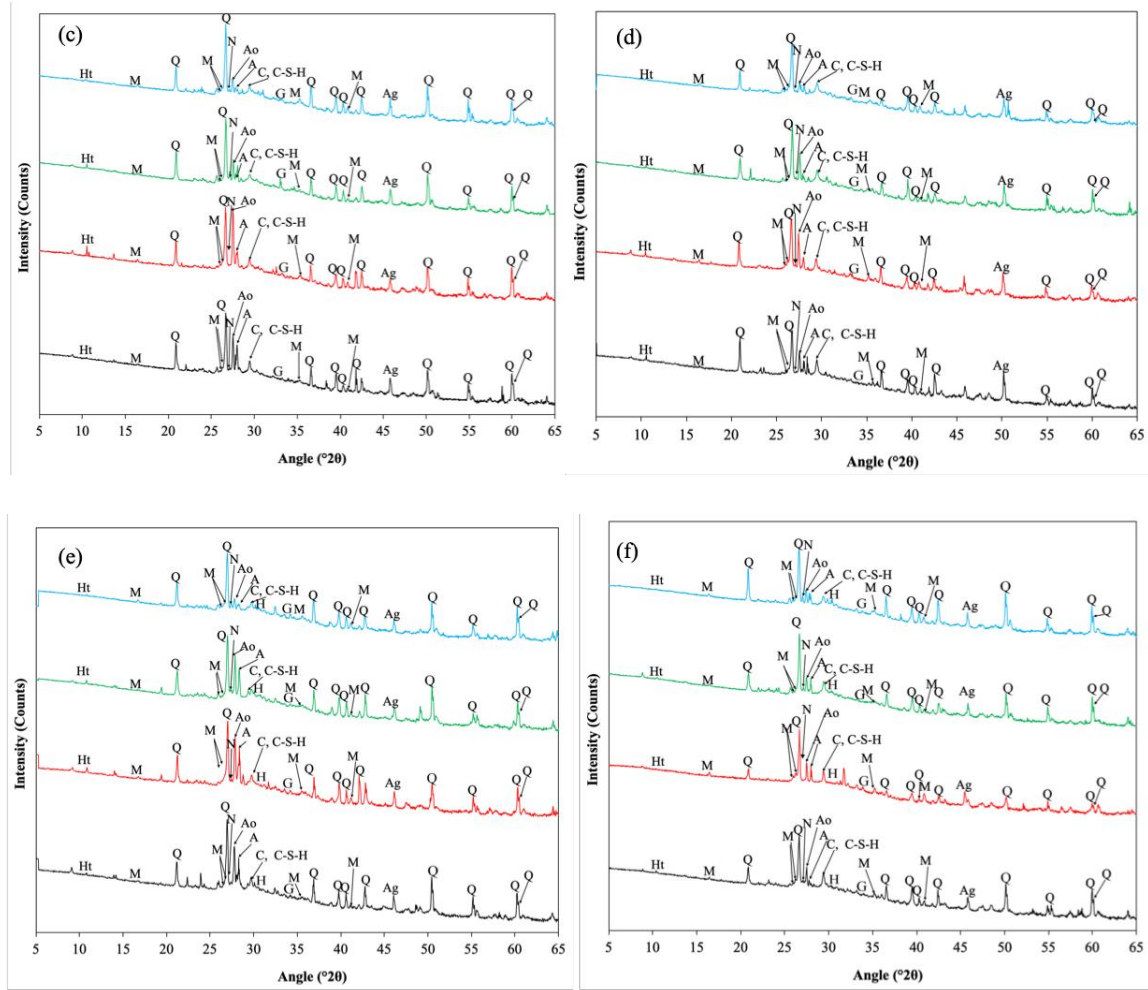


Q: Quartz, A: Albite, Ao: Anorthoclase, Ag: Aragonite, C: Calcite, C-S-H: Calcium silicate hydrate, G: Gypsum, H: Halite Ht: Hydrotalcite, M: Mullite, N: Nepheline

Fig. 4.7 XRD spectra of GPM at the age of 28 days, (a) control mixes, (b) mixes admixed with 3.5% NC, (c) mixes admixed with 7% NS, (d) mixes admixed with 7% MS, (e) mixes admixed with 3.5% NC plus 7% NS, and (f) mixes admixed with 3.5% NC plus 7% MS.

—85% BFS: 15% FA_6 M —65% BFS: 35% FA_6 M —85% BFS: 15% FA_10 M —65% BFS: 35% FA_10 M





Q: Quartz, A: Albite, Ao: Anorthoclase, Ag: Aragonite, C: Calcite, C-S-H: Calcium silicate hydrate, G: Gypsum, H: Halite Ht: Hydrotalcite, M: Mullite, N: Nepheline

Fig. 4.8 XRD spectra of GPM at the age of 90 days, (a) control mixes, (b) mixes admixed with 3.5% NC, (c) mixes admixed with 7% NS, (d) mixes admixed with 7% MS, (e) mixes admixed with 3.5% NC plus 7% NS, and (f) mixes admixed with 3.5% NC plus 7% MS.

4.6.2 FESEM analysis

The FESEM micrographs of control GPM mixes at the age of 90 days are illustrated in Fig. 4.9. Further, the FESEM micrographs of BFS-FA (85%:15%) based GPM mixes made with 10 M NaOH solution and admixed with different salts, at the age of 90 days are shown in Fig. 4.10. From these figures, the morphology of GPM mixes indicated the presence of partially reacted BFS and fly ash particles along with the formation of geopolymer gel and C-S-H gel. In addition, halite and gypsum crystals were observed in GPM mixes admixed with chloride and sulphate salts (Fig. 4.10). The presence of halite is due to the crystallization of NaCl in GPM mixes, and the formation of gypsum is due to the reaction between calcium present in

BFS and sulphate ion from the admixed salt. The presence of halite and gypsum was also substantiated with the XRD spectra of salt added GPM mixes (Figs. 4.7 and 4.8).

From Fig. 4.9, it was observed that the control GPM mixes prepared with 85% BFS showed denser microstructure comprising of more amount of geopolymer gel and C-S-H gel when compared with GPM mixes made with 65% BFS content regardless of molarity of NaOH solution. This is consistent with the results of XRD analysis where increase in BFS content led to more formation of albite and C-S-H gel (as indicated by their peak intensity in the XRD spectra shown Fig. 4.8). From Fig. 4.9, the FESEM micrographs indicated more compact microstructure of GPM made with 10 M NaOH solution when compared with that made with 6 M NaOH solution. This is substantiated with the results of XRD analysis at the age of 90 days, where there was more formation of geopolymer gel and C-S-H gel at higher molarity of NaOH solution as indicated by the peak intensity of nepheline, anorthoclase, albite, and C-S-H gel in the XRD spectra (Fig. 4.8).

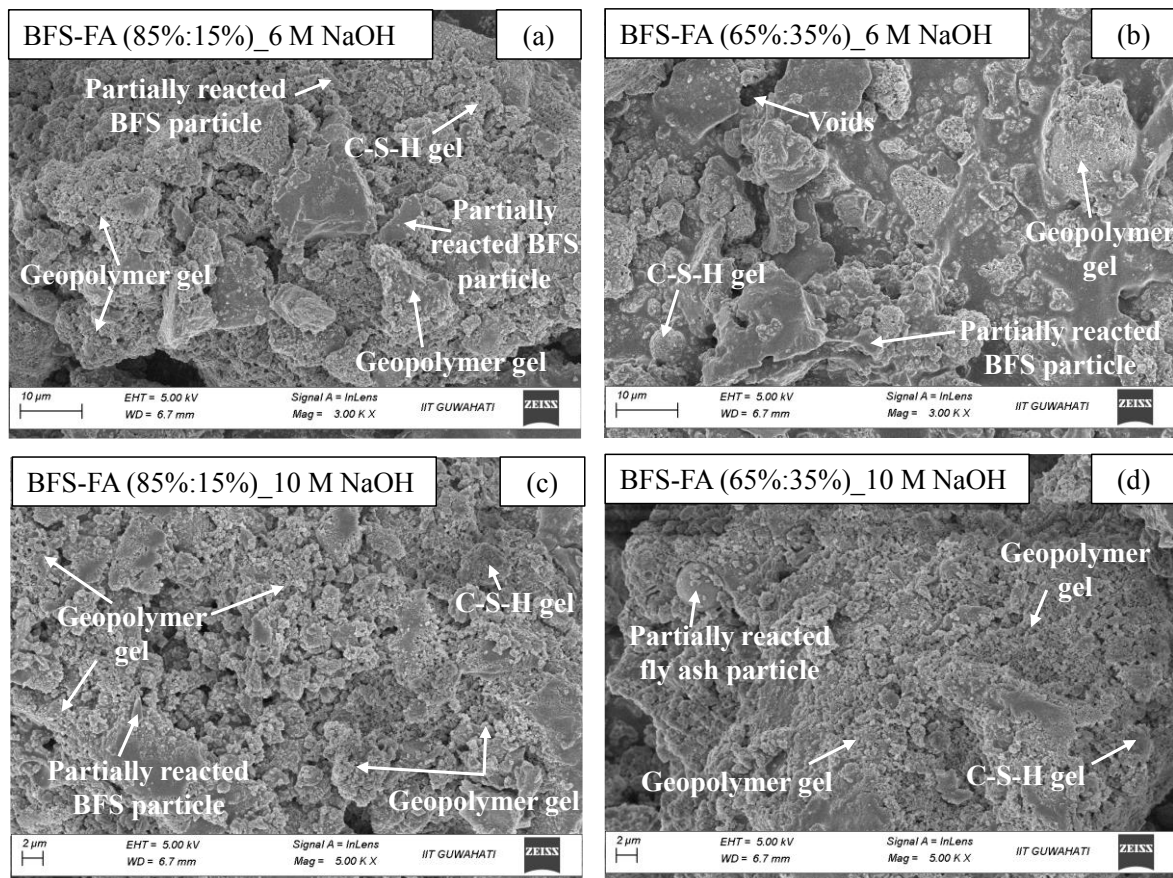


Fig. 4.9 FESEM micrographs of control GPM mixes made with, (a) BFS-FA (85%:15%) at 6 M NaOH solution, (b) BFS-FA (65%:35%) at 6 M NaOH solution, (c) BFS-FA (85%:15%) at 10 M NaOH solution, and (d) BFS-FA (65%:35%) at 10 M NaOH solution.

From Fig. 4.10, it was observed that the GPM mix admixed with 3.5% NaCl plus 7% Na₂SO₄ showed comparatively denser microstructure with presence of more amount of geopolymer gel and C-S-H gel than the GPM mix admixed with 7% Na₂SO₄ followed by the mixes admixed with other salts. This is consistent with the XRD analysis where the peak intensity of anorthoclase and C-S-H gel were mostly higher in the GPM added with NaCl plus Na₂SO₄ than that admixed with other salts (Fig. 4.8). Further, it can be observed that the GPM mix admixed with 7% MgSO₄ showed porous microstructure. This indicates that the presence of Mg²⁺ ion resulted in decalcification of C-S-H gel [33], which is in line with the XRD analysis where the peak intensity of C-S-H gel was lower in the GPM admixed with MgSO₄ (Fig. 4.8). These observations are in line with the variation in compressive strength of GPM mixes at the age of 90 days (Fig. 4.3 (b)).

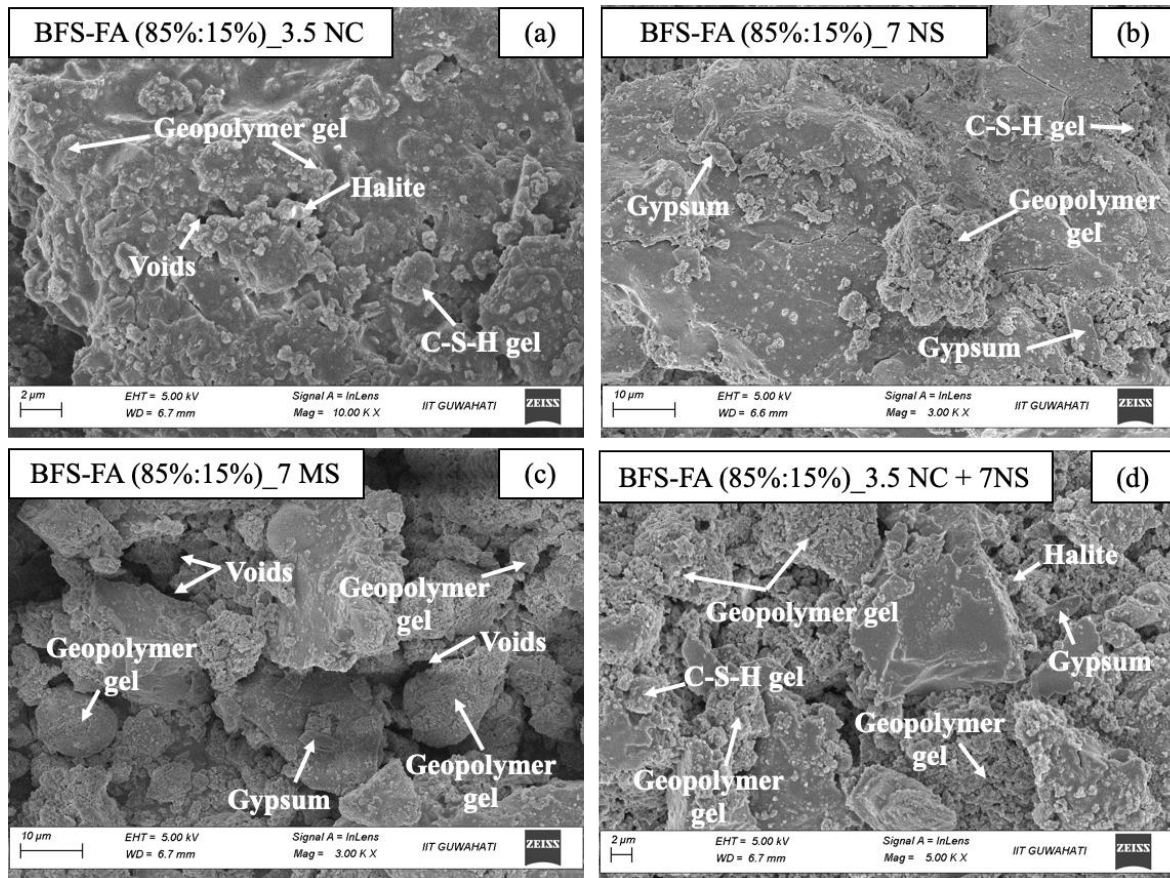


Fig. 4.10 FESEM micrographs of GPM mixes made with BFS-FA (85%:15%), 14 M NaOH solution and admixed with, (a) 3.5% NC, (b) 7% NS, (c) 7% MS, and (d) 3.5% NC + 7% NS.

Conclusions and Future scope of work

5.1 General

In this chapter, the conclusions obtained from the present work are presented.

5.2 Conclusions

The conclusions obtained from the present work are as follows:

- The flowability of GPM increased with fly ash content and decreased with concentration of NaOH solution. The admixed salts altered the workability of GPM mixes, and the variation was found to be unsystematic with control GPM mix.
- The increase in BFS content and molarity of NaOH solution resulted in higher compressive strength of GPM mixes. Further, the compressive strength of GPM mixes was increased with age.
- The addition of salts in GPM mixes made with 6 M NaOH solution led to decrease in strength in most of the cases when compared with control GPM mix. In case of 10 M NaOH solution, the strength of GPM admixed with NaCl (NC) plus Na₂SO₄ (NS) was greater than control GPM followed by other salt added GPM mixes. Further, the GPM mixes exhibited lower compressive strength in the presence of MgSO₄ (MS) when compared with Na₂SO₄.
- The free chloride content was mostly reduced and the bound chloride content was mostly increased with increase in BFS content and NaOH solution concentration. The variation in free chloride content was: NC > NC plus MS > NC plus NS, and there was opposite variation in bound chloride content with admixed salt type.
- The sulphate ion concentration was reduced with increase in BFS content, whereas it was increased with increase in molarity of NaOH solution. The GPM mixes admixed with MgSO₄ alone or along with NaCl showed higher sulphate ion concentration than that admixed with Na₂SO₄ alone or along with NaCl.
- From the XRD analysis, the increase in BFS content led to increase in peak intensity of albite and C-S-H gel in GPM mixes. In addition, the increase in concentration of NaOH solution led to greater formation of geopolymeric gels and C-S-H gel at the age of 90 days as indicated by their peak intensity in the XRD spectra. These observations are consistent with the variations in compressive strength and chloride content of GPM mixes.

- The XRD spectra of salt added GPM mixes showed more formation of anorthoclase and C-S-H gel (as indicated by their peak intensity) in the GPM mixes added with NaCl plus Na₂SO₄ than that added with Na₂SO₄ followed by NaCl. The presence of MgSO₄ in GPM mixes resulted in reduction in peak intensity of C-S-H gel, which is attributed to the decalcification of C-S-H gel in the presence of Mg²⁺ ions. These observations from XRD analysis are corroborated with the variations in compressive strength of salt admixed GPM mixes.
- The FESEM micrographs showed formation of denser microstructure in GPM mixes made with higher BFS content and higher molarity of NaOH solution. The GPM admixed with MgSO₄ showed less denser microstructure as compared to that admixed with Na₂SO₄.

5.3 Future scope of work

- The present research work can be carried out on geopolymer mortar made with only fly ash.
- The present research work can be extended to geopolymer mortar exposed to chloride and composite chloride-sulphate solutions.

References:

- [1] H. Ulugöl, A. Kul, G. Yıldırım, M. Şahmaran, A. Aldemir, D. Figueira, A. Ashour, Mechanical and microstructural characterization of geopolymers from assorted construction and demolition waste-based masonry and glass, *J. Clean. Prod.* 280 (2021) 124358.
- [2] N.K. Lee, H.K. Lee, Setting and mechanical properties of alkali-activated fly ash/slag concrete manufactured at room temperature, *Constr. Build. Mater.* 47 (2013) 1201–1209.
- [3] I. Hager, M. Sitarz, K. Mróz, Fly-ash based geopolymer mortar for high - temperature application—Effect of slag addition, *J. Clean. Prod.* 316 (2021) 128168.
- [4] P. Zhang, Z. Gao, J. Wang, J. Guo, S. Hu, Y. Ling, Properties of fresh and hardened fly ash/slag based geopolymer concrete: A review, *J. Clean. Prod.* 270 (2020) 122389.
- [5] J. Davidovits, Geopolymers: inorganic polymeric new materials. *J. Therm. Anal. Calorim.* 37(8) (1991) 1633-1656.
- [6] T. Srividya, P.R. Kannan Rajkumar, M. Sivasakthi, A. Sujitha, R. Jeyalakshmi, A state-of-the-art on development of geopolymer concrete and its field applications, *Case Stud. Constr. Mater.* 16 (2022) e00812.
- [7] Alhawati, Musab, A. Ashour, G. Yildirim, A. Aldemir, M. Sahmaran. Properties of geopolymers sourced from construction and demolition waste: A review. *J. Build. Eng.* 50 (2022) 104–104.
- [8] C.L. Wong, K.H. Mo, U.J. Alengeram, Y.S. Poh, Mechanical strength and permeation properties of high calcium fly ash-based geopolymer containing recycled brick powder, *J. Build. Eng.* (2020) 101655.
- [9] Ch.V. Reddy, L.S. Reddy, Experimental Research on Behaviour of Geopolymer mortar in compression, *J. Xidi. Univ.* 14 (2020) 3958–3963.
- [10] C. Kuenzel, L. Li, L. Vandeperre, A.R. Boccaccini, C.R. Cheeseman, Influence of sand on the mechanical properties of metakaolin geopolymers, *Constr. Build. Mater.* 66 (2014) 442–446.
- [11] T. Bakharev, Resistance of geopolymer materials to acid attack, *Cem. Concr. Res.* 35 (2005) 658–670.

- [12] M.M.A. Abdullah, H. Kamarudin, H. Mohammed, I. Khairul Nizar, A.R. Rafiza, Y. Zarina, The relationship of NaOH molarity, $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, fly ash/alkaline activator ratio, and curing temperature to the strength of fly ash-based geopolymer, in: *Adv. Mat. Res.* (2011) 1475–1482.
- [13] E. Hewayde, M. Nehdi, E Allouche, G. Nakhla, Effect of geopolymer cement on microstructure, compressive strength and sulphuric acid resistance of concrete, *Mag. Concr. Res.* 58 (5) (2006) 321–331.
- [14] M. Verma, K. Upreti, P. Vats, S. Singh, P. Singh, N. Dev, D. Kumar Mishra, B. Tiwari, Experimental Analysis of Geopolymer Concrete: A Sustainable and Economic Concrete Using the Cost Estimation Model, *Adv. Mater. Sci. Eng.* (2022) 7488254.
- [15] J. Shang, J.G. Dai, T.J. Zhao, S.Y. Guo, P. Zhang, B. Mu, Alternation of traditional cement mortars using fly ash-based geopolymer mortars modified by slag, *J. Clean. Prod.* 203 (2018) 746–756.
- [16] H. Zhu, Z. Zhang, Y. Zhu, L. Tian, Durability of alkali-activated fly ash concrete: Chloride penetration in pastes and mortars, *Constr. Build. Mater.* 65 (2014) 51–59.
- [17] S. Vinod Maruti, Properties of geopolymer cement mortar and blocks with calcium carbonate, *Mater. Today.* 24 (2020) 1518-1524.
- [18] T. Bakharev, Resistance of geopolymer materials to acid attack, *Cem. Concr. Res.* 35 (2005) 658–670.
- [19] H. Zhu, Z. Zhang, Y. Zhu, L. Tian, Durability of alkali-activated fly ash concrete: Chloride penetration in pastes and mortars, *Constr. Build. Mater.* 65 (2014) 51–59.
- [20] I. Hager, M. Sitarz, K. Mróz, Fly-ash based geopolymer mortar for high-temperature application – Effect of slag addition, *J. Clean. Prod.* 316 (2021) 128168.
- [21] H. Liu, J.G. Sanjayan, Y. Bu, The application of sodium hydroxide and anhydrous borax as composite activator of class F fly ash for extending setting time, *Fuel.* 206 (2017) 534–540.
- [22] G.S. Ryu, Y.B. Lee, K.T. Koh, Y.S. Chung, The mechanical properties of fly ash-based geopolymer concrete with alkaline activators, *Constr. Build. Mater.* 47 (2013) 409–418.
- [23] H.E. Elyamany, A.E.M. Abd Elmoaty, A.M. Elshaboury, Setting time and 7-day strength of geopolymer mortar with various binders, *Constr. Build. Mater.* 187 (2018) 974–983.

- [24] A. Nazari, A. Maghsoudpour, J.G. Sanjayan, Characteristics of boroaluminosilicate geopolymers, *Constr. Build. Mater.* 70 (2014) 262–268.
- [25] K. Somna, C. Jaturapitakkul, P. Kajitvichyanukul, P. Chindaprasirt, NaOH-activated ground fly ash geopolymer cured at ambient temperature, *Fuel*. 90 (2011) 2118–2124.
- [26] W.K.W. Lee, J.S.J. Van Deventer, The effects of inorganic salt contamination on the strength and durability of geopolymers, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 211(2002) 115–126.
- [27] BIS (Bureau of Indian standard), IS 383:2021. Coarse and fine aggregate for concrete—Specification. (2021), New Delhi, India.
- [28] ASTM, C1437. Standard test method for flow of hydraulic cement mortar. C1437 (2007).
- [29] Standard Methods for the Examination of Water and Waste water, American Public Health Association, 19th edition (1999).
- [30] P.S. Deb, P. Nath, P.K. Sarker, The effects of ground granulated blast-furnace slag blending with fly ash and activator content on the workability and strength properties of geopolymer concrete cured at ambient temperature, *Mater. Des.* 62 (2014) 32–39.
- [31] P. Nath, P.K. Sarker, Effect of GGBFS on setting, workability and early strength properties of fly ash geopolymer concrete cured in ambient condition, *Constr. Build. Mater.* 66 (2014) 163–171.
- [32] S. Hanjitsuwan, S. Hunpratub, P. Thongbai, S. Maensiri, V. Sata, P. Chindaprasirt, Effects of NaOH concentrations on physical and electrical properties of high calcium fly ash geopolymer paste, *Cem. Concr. Compos.* 45 (2014) 9–14.
- [33] W.G. Valencia Saavedra, D.E. Angulo, R. Mejía de Gutiérrez, Fly ash slag geopolymer concrete: Resistance to sodium and magnesium sulfate attack, *J. Mater. Civ.* 28 (2016) 04016148.
- [34] R. Shrivastava, B.R. Paramkusam, S.B. Dwivedi, Strength and durability performance of geopolymer binder of ambient cured alkali-activated MSW rejected waste and GGBFS mixes, *Environ. Sci. Pollu. Res.* 29 (2022) 30521–30536.

- [35] D. Sha, F. Wang, B. Wang, B. Pan, Microstructural and mechanical properties of a high-strength geopolymer based on coal-based synthetic natural gas slag cured at ambient temperature, *J. Clean. Prod.* 430 (2023) 139657.
- [36] S. Çelikten, M. Sarıdemir, İ. Özgür Deneme, Mechanical and microstructural properties of alkali-activated slag and slag + fly ash mortars exposed to high temperature, *Constr. Build. Mater.* 217 (2019) 50–61.
- [37] G. Nagalia, Y. Park, A. Abolmaali, P. Aswath, Compressive Strength and Microstructural Properties of Fly Ash–Based Geopolymer Concrete, *J. Mater. Civ.* 28 (2016). 04016144.
- [38] K. Liu, M. Deng, L. Mo, Influence of pH on the formation of gypsum in cement materials during sulfate attack, *Adv. Cem. Res.* 27 (2015) 487–493.