



Experimental and microstructural assessment of ternary blended geopolymer concrete with different Na₂SiO₃-to-NaOH volume ratios

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Abstract

The concrete manufactured by using geopolymer technology is considered to be sustainable and economical. The production of geopolymer concrete helps in converting industrial by-product materials into a valuable product. Compared to OPC concrete, geopolymer concrete has superior strength properties. The advantage of using geopolymer concrete is that it is environment-friendly, has low production cost and protects the available natural resources by utilizing industrial by-products and consuming less embodied energy. The ternary blended, low-molarity (2M) geopolymer concrete is manufactured using fly ash, ground granulated blast furnace slag and alccofine, with M-sand as fine aggregate. The present study aimed to find the optimum ratio of Na₂SiO₃ to NaOH of geopolymer concrete based on the strength and microstructural characterization through scanning electron microscopy/energy-dispersive X-ray spectroscopy, X-ray powder diffraction, Fourier-transform infrared spectroscopy, kinetic ratios and thermogravimetric analysis/differential scanning calorimetry. The results revealed that the Na₂SiO₃-to-NaOH ratio of 1.5 had a significant increase in the polymerization of geopolymer concrete, which, in turn, resulted in better compressive strength and microstructural features than the other ratios. Although the results of the study are encouraging regarding the use of ternary blended geopolymer concrete by effective utilization of industrial waste products through an environment-friendly route, they also provide a sustainable and economical route for handling the industrial by-products currently generated in various countries. Additionally, it was found that the use of low molarity (2M) and Na₂SiO₃-to-NaOH ratio of 1.5 reduced the risk involved in handling the alkaline solution.

Keywords Geopolymer concrete · Na₂SiO₃ · NaOH · Alkaline solution · Microstructure

Introduction

Ordinary portland cement (OPC) is a widely used construction material owing to its availability, ease in operation, cost-effectiveness and better mechanical as well as durability properties [1]. Infrastructure development is growing at a fast pace to meet the urban demand, and, hence, the demand for cement has increased. The current annual production of cement is 2.8 billion tonnes per year and is expected to increase by 4 billion tonnes per year [2]. Moreover, it is estimated that the global demand for cement will increase

up to 5.5 Gt/year by 2050 [3]. The production of cement is associated with carbon dioxide (CO₂) emissions, which is responsible for global warming. This is because cement is an energy-intensive material that consumes the available natural resources and liberates 0.8 tonnes of CO₂ for each tonne of cement production [4, 5]. Furthermore, with the growth of industrialization, the by-products have increased and are at present abundantly available in India. These by-products require a large area of land for safe disposal, which, in turn, had a huge impact on the environment and land usage. The by-products, such as fly ash, ground granulated blast furnace slag (GGBFS), alccofine and rice husk ash, are pozzolanic and can be used as supplementary cementitious materials in partial replacement to cement [6]. Therefore, there is an urgent need for researchers to find alternative binders to replace or reduce the usage of cement in concrete as well as utilize the industrial by-products so as to make the environment pollution free. In 1970, Prof. Joseph Davidovits, a French scientist, developed geopolymer concrete by using

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the aluminosilicate material by activating with alkaline solution. The efficiency of geopolymer concrete depends on the alkaline activator, the sources of the aluminosilicate material and the adopted curing condition [7]. The development and effective use of geopolymer materials will reduce greenhouse gas emissions by 80% and overcome the issues associated with OPC production and the unregulated disposal of industrial by-products by recycling them for geopolymer manufacturing [8]. The industrial by-products such as fly ash, GGBFS, alccofine, silica fume, palm oil fuel ash and rice husk ash are rich in silica and alumina and can be effectively used in the production of geopolymer. Geopolymers are synthesized from the aluminosilicate species dissolved in the presence of alkaline solution to form a three-dimensional polymeric ring structure of Si–O–Si and Si–O–Al [9]. Geopolymer is proved to have superior properties to OPC, such as higher early strength, faster setting time, longer term of durability, greater acid and fire resistance, lower thermal conductivity and lower shrinkage [7, 10]. In previous studies, most of the researchers used heat curing to complete the geopolymerization reaction for the fly ash-based geopolymer [11]. For instance, Kumar et al. [12] observed a slower development of strength and longer setting times at ambient temperature curing for fly ash-based geopolymer. This is considered to be a limitation for geopolymer concrete in site conditions as it restricts the production of precast elements. Therefore, to widen the applications of geopolymer concrete in the construction industry, most of the researchers blended fly ash with GGBFS. Incorporating GGBFS improved the setting times and compressive strength at ambient temperature curing due to high calcium content [13]. The main reaction product that formed for the fly ash-based geopolymer concrete was alkali silicate hydrate, while for the GGBFS it was calcium silicate hydrate gel (C–S–H) [14]. The use of alccofine enhanced the early age strength and microstructure of geopolymer concrete [15]. The properties of geopolymer were influenced by the source and type of materials [16], the molarity of NaOH [17], the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio [18], the binder/aggregate ratio [19], the solids-to-liquids ratio [20] and the curing temperature.

In this study, an experimental and microstructural investigation was carried out on the ternary blended, low-molarity (2M) geopolymer concrete with different Na_2SiO_3 -to-NaOH ratios of alkaline solution. The binder materials considered were fly ash, GGBFS and alccofine. The optimal combination of the Na_2SiO_3 -to-NaOH volumetric ratio was

determined based on the compressive strength and microstructure of the geopolymer concrete. To understand the morphology, elemental composition, phase composition, structural nature and thermal stability analysis, the microstructural characterization was performed through scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX), X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR) and thermogravimetric analysis/differential scanning calorimetry (TGA/DSC). Moreover, cost analysis was conducted in order to examine the economic perspective of geopolymer concrete due to a change in the ratios of alkaline solution.

Materials

The following materials were used for the synthesis of ternary blended, industrial by-products-based geopolymer concrete.

Fly ash

In this study, Class F fly ash ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$) (ASTM C618) was procured from the Kakatiya Thermal Power Project (KTPP), Telangana, India. The chemical composition of fly ash was determined by XRF, which is mentioned in Table 1. The SEM and EDS images of fly ash in Fig. 1 show that the particles of fly ash are spherical. This spherical shape of fly ash provides high workability and is used to synthesize geopolymer [21].

Ground granulated blast furnace slag (GGBFS)

Ground granulated blast furnace slag (GGBFS) was procured from the Astrra Chemical, Chennai, India. GGBFS is a by-product of iron ore industries; it mainly consists of calcium, magnesium silica and alumina. The chemical composition of GGBFS from XRF is presented in Table 1. The SEM and EDS images of GGBFS in Fig. 1 show that the particle shape of GGBFS is angular. Moreover, GGBFS is amorphous and poorly crystalline.

Alccofine 1203

Alccofine 1203 is an industrial by-product obtained from Counto Microfine Products Pvt. Ltd. Alccofine 1203 is a

Table 1 Chemical composition of binder material

Binder	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	MgO	Na_2O	So_3	Others
Fly ash	57.3	23.4	6.73	6.21	1.99	1.84	1.14	0.235	0.60	0.55
GGBFS	32.99	14.5	0.18	40.91	0.33	0.66	7.73	0.25	1.84	0.61
Alccofine 1203	36.5	21.5	1.18	32.2	–	–	6.1	–	1.2	1.32

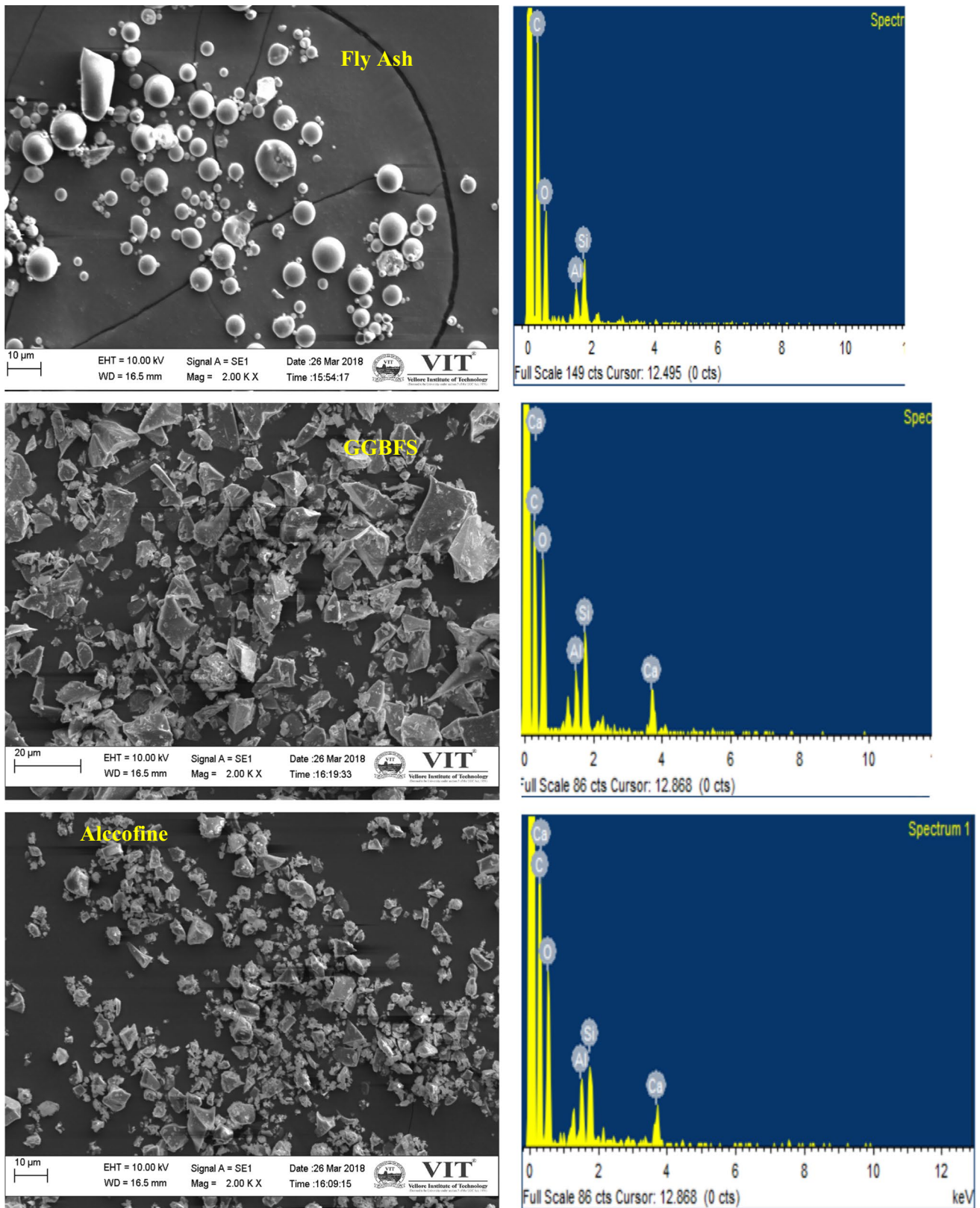


Fig. 1 SEM and EDS analyses of fly ash, GGBFS and Alccofine 1203

low-calcium silicate and ultra-fine supplementary cementitious material used in concrete in order to improve its workability and compressive strength. The chemical properties of alccofine are mentioned in Table 1. The SEM and EDS images of alccofine in Fig. 1 show that the particle shape of the alccofine 1203 is angular. Adding alccofine 1203 in concrete modifies the fresh and hardened properties.

Aggregates

M-sand is a by-product of the granite crushing plant. The M-sand used in this study was obtained from a local supplier in Vellore. The shape of M-sand is angular, and it has a rougher surface texture than the natural river sand. The sieve analysis of M-sand was conducted as per IS 383-1970, reaffirmed 2007, which confirmed that the M-sand belongs to zone II and the fineness modulus is 3.2. Moreover, the coarse aggregates used are passed through 20 mm and retained at 12.5 mm sieve. The aggregates were of surface-saturated dry condition (SSD).

Alkali activating solution/alkaline solution

Alkaline solution with industrial by-products (i.e., sources materials) binds the fine and coarse aggregates to form a geopolymer concrete. Sodium-based alkaline solution was prepared in the laboratory a day prior to its use. The alkaline solution is the combination of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH). The industrial-grade sodium hydroxide pellets with 98% purity were dissolved in distilled water of the desired low-molarity (2M) NaOH solution. The SiO_2 -to- Na_2O ratio of Na_2SiO_3 was 2.28 with chemical compositions $\text{Na}_2\text{O} = 14.30$ wt%, $\text{SiO}_2 = 32.62\%$ wt% and $\text{H}_2\text{O} = 53.08$ wt%. The role of sodium silicate is to enhance the polymerization process with industrial by-products [22]. The alkaline solutions considered in this study with respect to different Na_2SiO_3 -to-NaOH volume ratios were 0.5, 1, 1.5, 2 and 2.5.

Curing

The inorganic amorphous geopolymer concrete can attain strength effectively in the presence of heat curing. The geopolymer concrete specimens after casting are placed at ambient temperature, i.e., at a temperature of 28–30 °C until the test age of 7 and 28 days.

Superplasticizer

Geopolymer concrete is stickier and more viscous than OPC concrete due to the addition of higher viscous alkaline solution than water. Naphthalene-based superplasticizer is used as a superplasticizer in order to improve the workability of the ternary blended geopolymer concrete.

Preparation and casting of geopolymer concrete

In this study, five geopolymer mixes with different Na_2SiO_3 -to-NaOH ratios of the alkaline solution were prepared as shown in Table 2. The alkaline-to-binder ratio was fixed at 0.45. The preparation of fresh geopolymer concrete samples was similar to that of OPC concrete, as demonstrated in the previous works of Lloyd and Rangan [23] and Parveen [24]. Table 2 presents the mix proportions of geopolymer concrete. In order to prepare the geopolymer concrete, all the desired quantities of fly ash, GGBFS and alccofine were mixed for 2 min. Then, the fine and coarse aggregates were added to the dry mix until the mix was uniform. This was continued by adding the premixed alkaline solution for the next 4 min. Afterward, superplasticizer (2% of binder wt%) and additional water (10% of binder wt%) were added during the mixing [25]. The mixing process continued until the homogeneous fresh mix was attained. After that, the freshly mixed geopolymer concrete was filled into 100-mm cube molds in three layers, as per IS 516. The specimens with geopolymer concrete were compacted by

Table 2 Mix proportions of geopolymer concrete with different Na_2SiO_3 /NaOH ratios

Materials (units)	Mix 0.5 (kg/m ³)	Mix 1 (kg/m ³)	Mix 1.5 (kg/m ³)	Mix 2 (kg/m ³)	Mix 2.5 (kg/m ³)
Fly ash	140.07	140.07	140.07	140.07	140.07
GGBFS	175.12	175.12	175.12	175.12	175.12
Alccofine	35.03	35.03	35.03	35.03	35.03
FA	769.8	769.8	769.8	769.8	769.8
CA	1204	1204	1204	1204	1204
Na_2SiO_3	52.54	78.81	94.57	105.08	112.50
NaOH	105.08	78.15	63.05	52.54	45.03
Superplasticizer	7	7	7	7	7
Water	35.02	35.02	35.02	35.02	35.02

Corresponding mix Na_2SiO_3 -to-NaOH ratio is indicated in () at respective mix numbers

using the vibrating table in order to remove the entrapped air, and the caste specimens were allowed to dry for a rest period of 24 h at room temperature. After the rest period, the specimens were demolded and placed in room temperature until they attained the age of testing. For each mix, six specimens were cast and the compressive strength of the samples was tested at 7 and 28 days, which was followed by microstructural characterization.

Test methods

Workability

The workability of freshly mixed geopolymer concrete with different ratios of Na_2SiO_3 to NaOH was determined by using the slump cone test. The slump cone test was conducted on freshly mixed geopolymer concrete, in accordance with IS 1199: 1959. The slump value was measured as the vertical difference between the top of the mold and the top center of the collapsed concrete sample. Moreover, the slump value was measured with the graduated tapping rod of a diameter of 16 mm.

Compressive strength

The compressive strength of ternary blended, low-molarity geopolymer samples was examined according to IS 516. The compressive strength test was done at 7 and 28 days on the ambient cured samples in a compression testing machine (CTM) with a capacity of 2000 kN, at a loading rate of 2.5 kN/s. The compressive strength was determined by using the following formula:

$$\text{Compressive strength} = \frac{\text{Failure load of the specimen}}{\text{surface area of the specimen}}$$

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS)

SEM and EDS were performed on the geopolymer samples cured at ambient temperature for 28 days in order to observe the changes in their microstructure upon changing the Na_2SiO_3 -to-NaOH ratio in the alkaline solution. Prior to the image acquisition, all the samples were oven-dried and sputter-coated with gold and palladium. The magnification for the SEM and EDX was 2000 \times times at the voltage of 20 kV.

Powder X-ray diffraction analysis (XRD)

The powder X-ray diffraction analysis was conducted in order to identify the mineral phases of geopolymer concrete with different ratios of Na_2SiO_3 to NaOH cured at ambient temperature for 28 days. The analysis was conducted at VIT Vellore using the BRUKER, the D8 ADVANCE instrument. The samples were analyzed in the range of 0° – 90° of 2θ and at an interval of 0.5° . The phases of the sample were identified by comparison with the global database by using the X'Pert HighScore Plus software.

Fourier-transform infrared spectroscopy (FT-IR) analysis

The FT-IR spectroscopy analysis (Shimadzu, IRAffinity-1) was conducted in order to collect the spectra of geopolymer concrete samples in the range of 4000 – 400 cm^{-1} at a resolution of 8 cm^{-1} . Moreover, FT-IR was performed at low-molarity geopolymer concrete samples that were ambient cured for 28 days.

Thermogravimetric analysis (TGA) and differential scanning curves (DSCs)

The TGA and DSC measurements were performed with STD Q-600 in order to find the mass loss in the geopolymer concrete samples in the temperature range of ambient to 800°C , with a heating rate of 10°C per minute and under an inert atmosphere of nitrogen. The samples

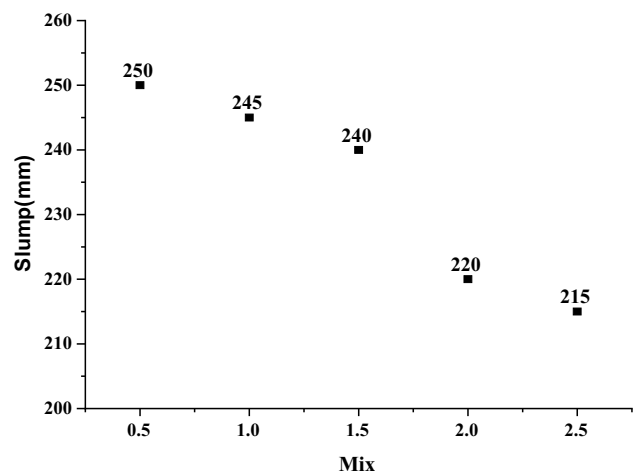


Fig. 2 Workability of geopolymer concrete different Na_2SiO_3 -to-NaOH ratios of alkaline solution

(ambient cured for 28 days) were ground to a fine powder so as to ensure the thermal equilibrium (Fig. 2).

Results and discussion

Workability of geopolymer concrete mixes

The workability of geopolymer concrete was ensured in accordance with the IS 1199: 1959 in a manner similar to that of OPC concrete. The slump values of all the mixes are mentioned in Fig. 2. From the results, it can be seen that the mix with the ratio of 0.5 had the highest slump of 250 mm, while the mix with the ratio of 2.5 had the lowest slump of 215 mm. It is also observed from Table 2 that with an increase in the Na_2SiO_3 -to- NaOH ratio, the Na_2SiO_3 increased and made the mix more viscous, and due to this the slump decreased. From this, it is evident

that the alkaline solution in the mix plays a dominant role in the workability of fresh geopolymer concrete. In the present study, with an increase in the Na_2SiO_3 -to- NaOH ratio from 0.5 to 2.5, the slump of the ternary blended geopolymer concrete decreased from 250 to 215 mm. Similar observations were reported by Nath and Sarker [13], i.e., with an increase in Na_2SiO_3 -to- NaOH ratio from 1.5 to 2.5, the slump values also reduced from 245 to 230. Similar kind of results has been reported by Nath et al. [13].

Compressive strength and the importance of kinetic ratios in geopolymer concrete

Table 3 shows the results related to the compressive strength of low-molarity geopolymer concrete with different Na_2SiO_3 -to- NaOH ratios. It can be observed that the mix with the ratio of 0.5 had the lowest compressive strength (25.73 MPa at 7 days and 29 MPa at 28 days),

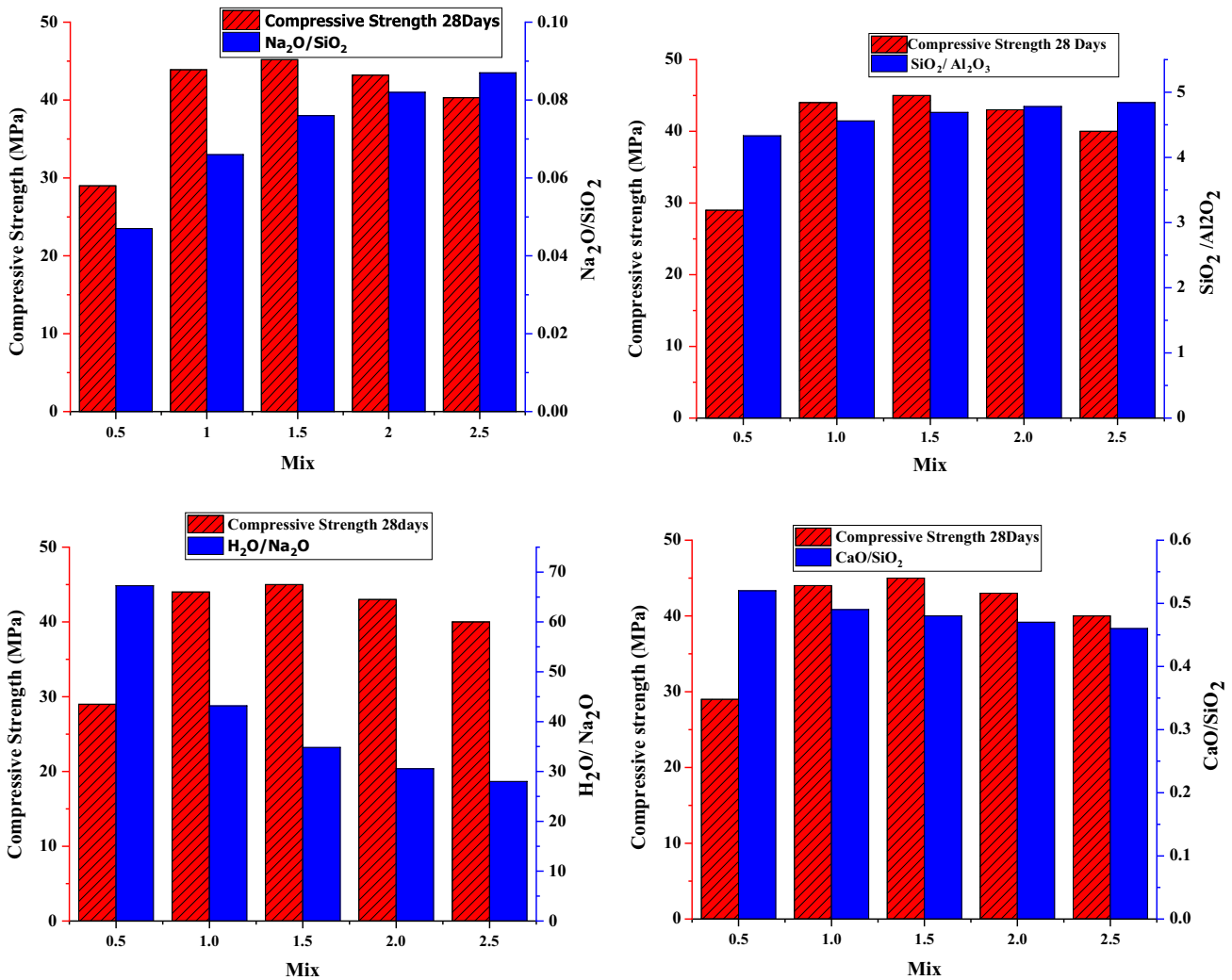


Fig. 3 Effect of compressive strength and kinetic ratios with different Na_2SiO_3 -to- NaOH mixes

Table 3 Compressive strength and kinetic reactions of geopolymer concrete

Mix	7 days (MPa)	SD	28 days (MPa)	SD	SiO ₂	Al ₂ O ₃	H ₂ O	Na ₂ O	Na ₂ O/SiO ₂	SiO ₂ /Al ₂ O ₃	H ₂ O/Na ₂ O	CaO/SiO ₂
0.5	26	3.21	29	2.5	2795	644	8979	133	0.047	4.33	67.25	0.52
1	41	2.92	44	0.96	2938	644	8383	194	0.066	4.56	43.18	0.49
1.5	41	1.8	45	3.55	3023	644	8026	230	0.076	4.69	34.82	0.48
2	42	3.56	43	0.68	3080	644	7786	254	0.082	4.78	30.56	0.47
2.5	40	0.3	41	0.61	3121	644	7615	272	0.087	4.84	27.99	0.46

SD standard deviation

while the mix with the ratio of 1.5 had the highest compressive strength (41 MPa at 7 days and 45.2 MPa at 28 days). This indicates that with an increase in the Na₂SiO₃-to-NaOH ratio from 0.5 to 1.5, the compressive strength increased due to an increase in the geopolymerization reactions [26]. Furthermore, with an increase in the ratio from 1.5 to 2.5, the compressive strength decreased. The decrease in compressive strength was due to the increased silicate solution, which hindered the geopolymerization. Similar kind of results has been reported by Deba [27].

Figure 3 shows that with an increase in the Na₂SiO₃-to-NaOH ratio from 0.5 to 2.5, the SiO₂/Al₂O₃ and Na₂O/SiO₂ ratios increased and the H₂O/Na₂O, CaO/SiO₂ ratios decreased. Moreover, Table 3 shows that there was an increase in SiO₂ and Na₂O and a decrease in H₂O with an increase in the Na₂SiO₃-to-NaOH ratio. The increased SiO₂/Al₂O₃ and Na₂O/SiO₂ ratios (4.69 and 0.76, respectively) for the mix with the Na₂SiO₃-to-NaOH ratio of 1.5 improved the dissolution of Si and Al from the binder materials to form Si–O–Si and Si–O–Al oligomers and yielded the highest compressive strength of 45 MPa [28]. Furthermore, with an increase in the Na₂SiO₃-to-NaOH ratio from 1.5 to 2.5, the SiO₂/Al₂O₃ and Na₂O/SiO₂ ratios increased to 4.84 and 0.87 and the compressive strength reduced to 41 MPa. The increased SiO₂ and Na₂O contents obstructed the formation of oligomers and, subsequently, geopolymerization [29].

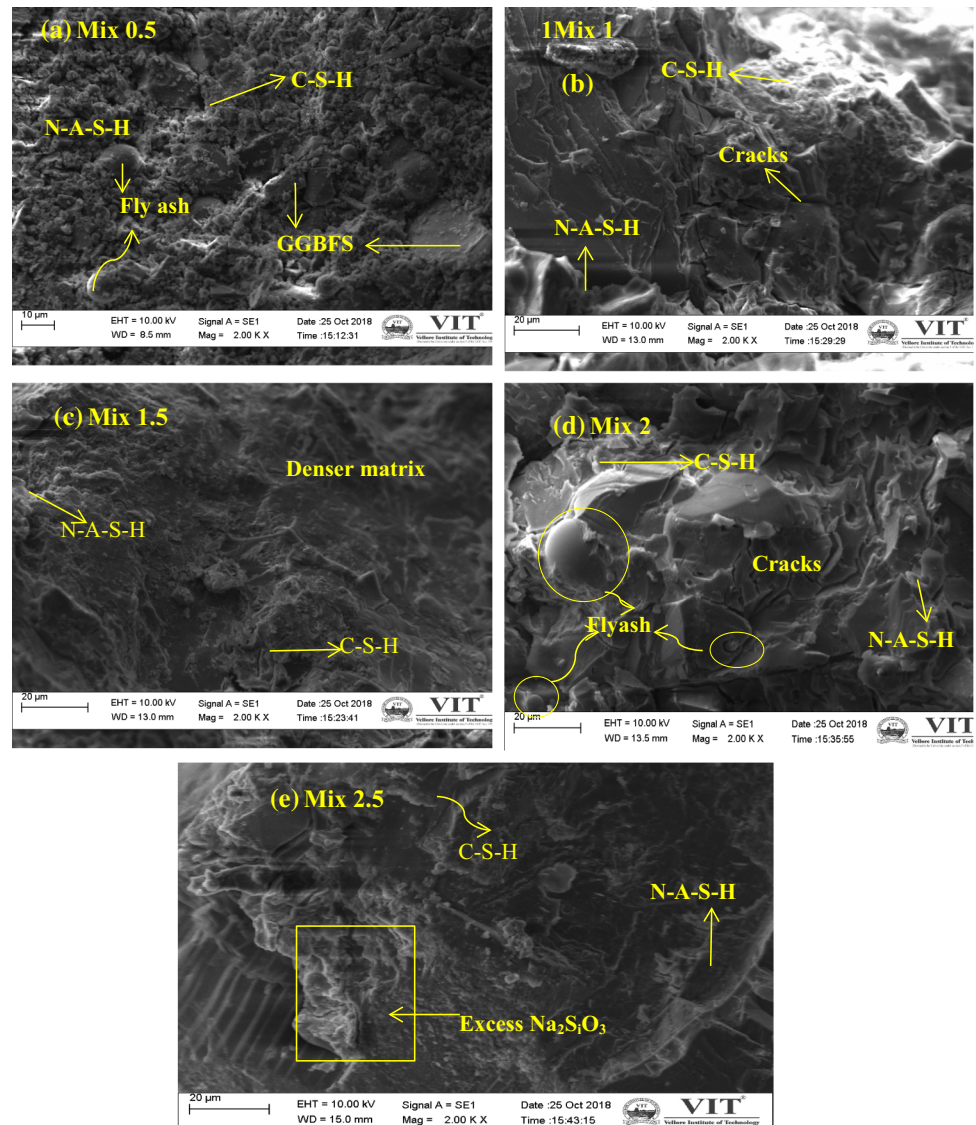
Table 3 shows the kinetic ratios of H₂O/Na₂O and CaO/SiO₂ decreased with an increase in the Na₂SiO₃-to-NaOH ratio. The H₂O/Na₂O ratio plays a key role during and after the geopolymerization. The H₂O/Na₂O ratio helps in the dissolution of binder and facilitates the transfer of ions. The mix with the ratio of 1.5, with the H₂O/Na₂O ratio of 38.82, attained the highest compressive strength. The presence of higher H₂O/Na₂O ratio improved the dissolution of Si and Al of binder materials but hindered the polymerization, resulting in a weak bond formation. The effective reaction of CaO and SiO₂ formed the calcium silicate hydrate (C–S–H) gel as a strength-developing

compound. From the results, the optimum ratio of CaO/SiO₂ was observed to be 0.48, which attained the highest compressive strength of 45 MPa at 28 days.

Scanning electron microscopy (SEM)

Figure 4 represents the SEM micrographs of ternary blended, low-molarity geopolymer concrete cured at ambient temperature for 28 days. The study was conducted upon different Na₂SiO₃-to-NaOH ratios of alkaline solution, with other parameters unchanged. In the mix 0.5, unreacted fly ash and GGBFS particles were clearly seen and did not take part in the geopolymerization due to insufficient Na₂SiO₃ solution [30, 31]. The poor bonding between the binder and aggregates was observed, which, in turn, resulted in weak matrix formation and low compressive strength. With an increase in the ratio to 1, the silicate content in the matrix was increased and formed a denser matrix by forming the C–S–H and N–A–S–H. Moreover, the small cracks were observed on the surface that weakens the structure at later ages, thereby decreasing the compressive strength of geopolymer concrete [32]. Furthermore, with an increase in the Na₂SiO₃-to-NaOH ratio to 1.5, the geopolymer matrix appeared to be a denser, more compacted and more non-porous structure due to the formation of strength-developing compounds, C–S–H and N–A–S–H gels. Low NaOH and high Na₂SiO₃ improved the bonding between the binder and aggregates, which helped in arresting the cracks and was responsible for the higher compressive strength of 45.2 MPa. With further increase in the Na₂SiO₃-to-NaOH ratio to 2, the excess Na₂SiO₃ solution with few fly ash particles was left unreacted, with fine cracks developing in it, resulting in strength reduction [31]. With a further increase in the Na₂SiO₃-to-NaOH ratio to 2.5, the compressive strength reduced because excess Na₂SiO₃ solution hindered the geopolymerization.

Fig. 4 SEM images of geopolymer concrete with different Na_2SiO_3 -to- NaOH ratios



EDS characterization

Totally, five samples of ternary blended, low-molarity geopolymer concrete specimens were cured at an ambient temperature for 28 days. The collected concrete samples were finely powdered and oven-dried for 3 h at 100 °C. Figure 5 and Table 4 present the quantitative elemental analysis by the weight percentage of different geopolymer mixes. The EDAX result shows that Si, Al, Na, Ca and O are the dominant elements identified in all the geopolymer mixes with different Na_2SiO_3 -to- NaOH ratios. The dissolution of silica and alumina in the binder material played a key role in the formation of the geopolymer system. Fly ash and GGBFS had an approximately similar rate of dissolution of Si and Al [33]. The Si/Al ratio for different Na_2SiO_3 -to- NaOH ratios was between 3.29 and 2.3. Increasing the Na_2SiO_3 content in the geopolymer

mixes, the percentage of silicate, sodium and water varied. With increasing the Na_2SiO_3 -to- NaOH ratio in the mixes from 0.5 to 1.5, the Si/Al ratio decreased from 3.29 to 2.30. The decrease in the Si/Al ratio was due to the rapid dissolution of alumina from the binder materials. The dissolution of alumina was higher than the silica in the early ages of geopolymerization [34]. With an increase in the Na_2SiO_3 -to- NaOH ratio from 1.5 to 2.5, Si/Al ratio increased significantly from 2.3 to 2.9. This was due to a decrease in the dissolution and polycondensation of aluminosilicate gel in the geopolymer systems. In addition to this, an increase in the Na_2SiO_3 solution hindered the geopolymerization with excess water in the mixes. Moreover, there was an insufficiency of sodium ion at higher Na_2SiO_3 -to- NaOH ratios for balancing the covalent bonding. The presence of calcium in the GGBFS reacted with the silicate to form calcium silicate hydrate (C–S–H) gel,

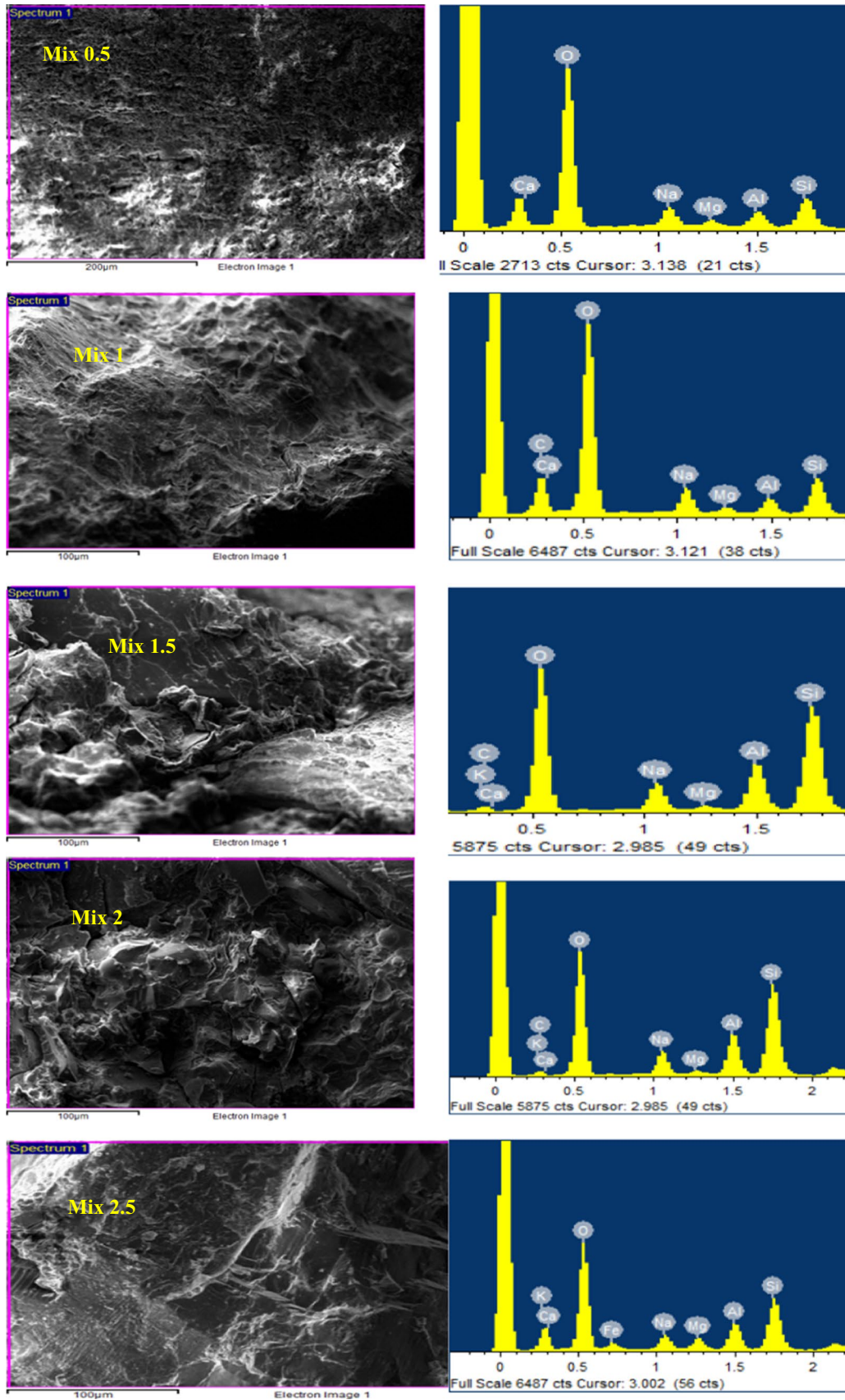
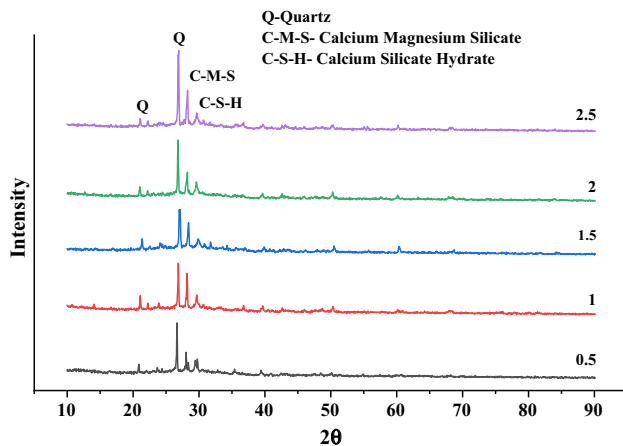


Fig. 5 EDS images of geopolymer concrete with different ratios of Na_2SiO_3 to NaOH

Table 4 Quantitative elemental analysis of ternary blended geopolymer concrete at 28 days

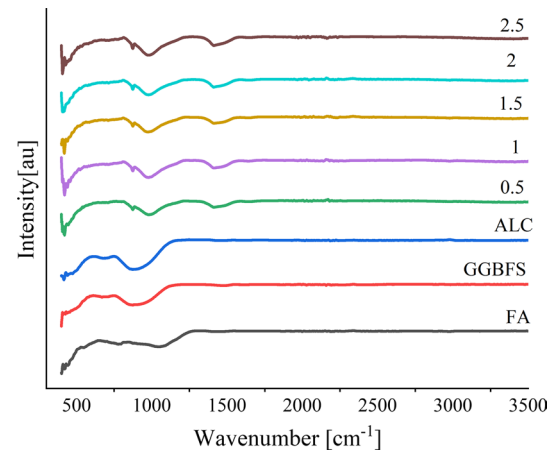
Mix	O	Na	Mg	Al	Si	Ca	Si/Al	Ca/Si
0.5	50.38	5.02	1.18	4.16	13.72	16.58	3.29	1.20
1	54.91	5.14	1.55	5.44	14.79	18.20	2.71	1.02
1.5	47.16	3.86	2.66	6.74	15.55	6.97	2.30	0.44
2	50.67	5.19	0.57	8.73	24.51	2.86	2.80	0.11
2.5	53.82	5.43	0.99	8.60	25.53	4.16	2.90	0.16

**Fig. 6** XRD diffractograms of geopolymer concrete with different Na_2SiO_3 -to- NaOH ratios

which is a strength gain compound in the geopolymer system at an ambient temperature. Table 4 shows that the mix with the ratio of 0.5 had the highest Si/Al ratio of 3.29, which resulted in the lowest compressive strength of 29 MPa at 28 days, while the mix with the ratio of 1.5 had the lowest Si/Al ratio, which resulted in the highest compressive strength of 45.2 MPa at 28 days.

Powder X-ray diffraction (XRD)

The samples were collected from the core of the crushed cubes after 28 days of compressive strength. In total, five different volume ratios of $\text{Na}_2\text{SiO}_3/\text{NaOH}$ -based geopolymer concrete samples, which were oven-dried fine powder samples, were analyzed. Figure 6 demonstrates that approximately 95% were amorphous phases and responsible for the geopolymerization, while only 5% were crystalline phases and not involved in the geopolymerization [35]. The crystalline and semicrystalline phases were observed between the 20° and 30° of 2θ , which indicated the formation of calcium silicate hydrate (C–S–H). All the ternary blended geopolymer samples were ambient cured and exhibited the same crystalline phases of quartz ($2\theta = 26.67^\circ$; $Q = \text{SiO}_2$ as per JCPDS Number 88-2488), calcium magnesium silicate ($2\theta = 28.04^\circ$; C–M–S as per JCPDS Number 84-1743) and calcium silicate hydrate ($2\theta = 28.043^\circ$; C–S–H as per JCPDS Number

**Fig. 7** FT-IR spectra of geopolymer specimens with different Na_2SiO_3 -to- NaOH ratios

89-6458), even though there was a difference in the alkaline solutions' ratio. In all the samples, the highest crystalline peak was observed at quartz ($2\theta = 26.67^\circ$; $Q = \text{SiO}_2$). The presence of quartz was confirmed through the EDAX and FT-IR analysis. Figure 5 shows that with an increase in the Na_2SiO_3 -to- NaOH content, the crystalline peak of quartz increased. These results were in correlation with the existing results of the Class C fly ash-based geopolymer concrete [36]. Moreover, the presence of C–S–H was confirmed through FT-IR and responsible for the strength development in the slag-based geopolymer concrete.

FT-IR

The Fourier-transform infrared spectroscopy analysis was conducted in order to find the degree of geopolymerization and the reaction products formed in the geopolymer concrete. Figure 7 shows the FT-IR spectra of ternary blended, low-molarity geopolymer concrete, with M-sand as the fine aggregate cured in an ambient temperature for 28 days. The geopolymer concrete was manufactured with different Na_2SiO_3 -to- NaOH ratios of alkaline solution, with other parameters as constant. The vibrations identified in all the mixes were at the same bandwidth intensities, although there were different alkaline activator ratios. The main absorption bandwidths were observed

at 420.48, 445.46, 873.75, 979.84, 1411.89, 1641.42 and 3323.35 cm^{-1} (Fig. 7). The bandwidth between 420.48 and 455.20 cm^{-1} was identified in the ternary blended geopolymer concrete mixes with different alkaline activator Na_2SiO_3 -to- NaOH ratios due to the bending vibrations of the Si–O–Si bonds of the tetrahedral groups. Similar kind of results was observed with fly ash- and palm oil fuel ash-based geopolymer mortar in the study of Ranjbar et al. [37]. The intensity around the bandwidths of 873.75 and 979.8 cm^{-1} corresponds to the asymmetric stretching vibrations of the Si–O–Si or Si–O–Al. In fact, these are the strongest bands in the geopolymer concrete. It is notable that with an increase in the alkaline ratio from 0.5 to 1.5, the band at 979.84 decreased, and with an increase from 1.5 to 2.5, the alkaline ratio bandwidth increased. The intensity variation of this band is indicative of the variation in the sodium aluminosilicate polymer chain length. The Al/Si ratio defines the exact position of this band in geopolymer concrete [38]. The bandwidth of around 950–980 cm^{-1} was due to the formation of calcium silicate hydrate gel in the paste that was activated [39]. Similar kind of results was observed in the study by Salih et al. [40]. The band was observed at 1411.89 cm^{-1} in all the mixes, which was due to the carbonate asymmetric stretching vibrations (O–C–O). This is attributed to the reactions of the sodium hydroxides with the atmosphere’s CO_2 . Similar results were identified in the study by Panias et al. [41]. These bands shifted toward frequencies lower than those of fly ash (1417.68 cm^{-1}), GGBFS

(1481.33 cm^{-1}) and alccofine 1203 (1456 cm^{-1}). The wide bands of 1641.42 cm^{-1} and 3323.57 cm^{-1} were observed in all the mixes of ternary blended geopolymer concrete. Their vibration was owing to the bending vibrations of O–H–O bands and the stretching of OH^{-1} , respectively. These bands were related to the presence of water during the geopolymerization reaction of NaOH , activated with the binder materials [17]. These bands did not appear in fly ash, GGBFS and alccofine 1203.

TGA and DSC

The thermogravimetric analysis was performed on geopolymer concrete samples with different Na_2SiO_3 -to- NaOH ratios. The powder samples were collected from the core of the cube after 28 days of compressive strength test. All the geopolymer samples are having similar patterns. A gradual mass loss was observed in all the samples, with an increase in the rate of temperature. The mass loss was due to the loss of moisture and change in the chemical structure within the geopolymer concrete. From Fig. 8a, b, the first phenomena in the DSC curve at 100 °C were an exothermic peak corresponding to a mass loss in the TGA curve. The mass loss at this temperature was due to the evaporation of free and absorbed interstitial water in the geopolymer samples [42]. The second phenomenon in the DSC curve at 550 °C was an endothermic peak corresponding to a mass loss in the TGA curve. The mass loss at this temperature was due to the escape of the structural water and hydroxyl groups of Si–O

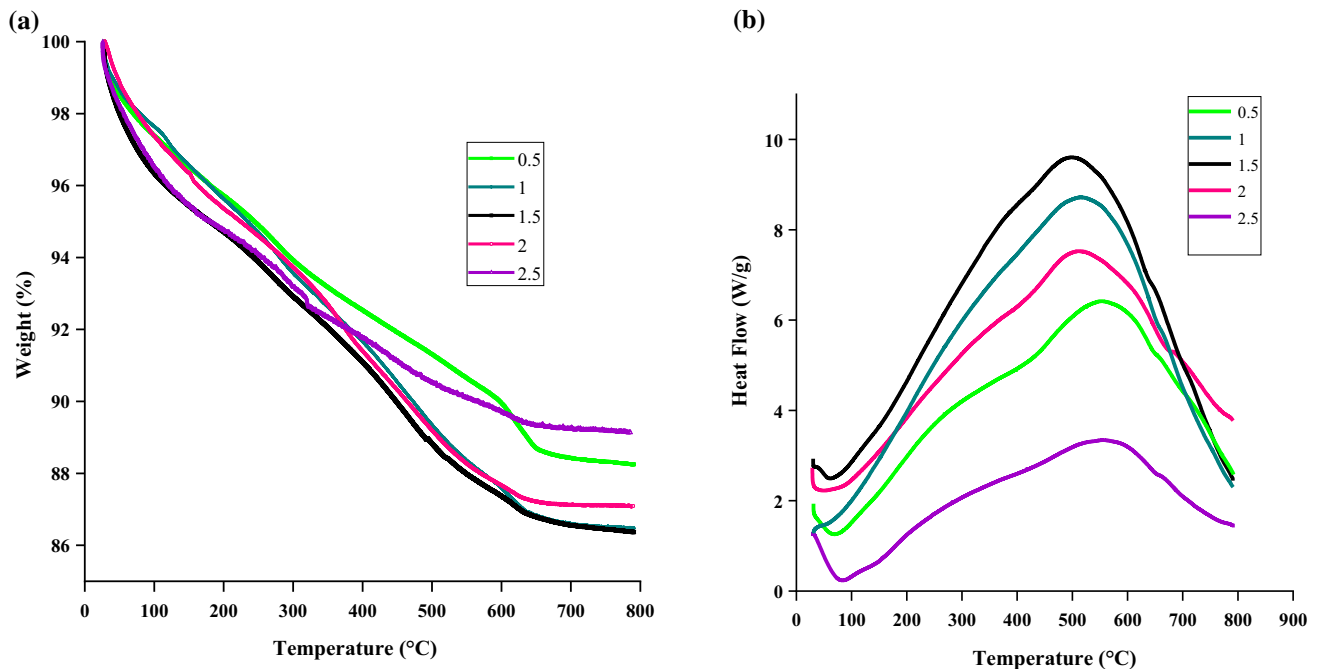


Fig. 8 a, b The TGA and DSC analysis of geopolymer concrete with different Na_2SiO_3 -to- NaOH ratios

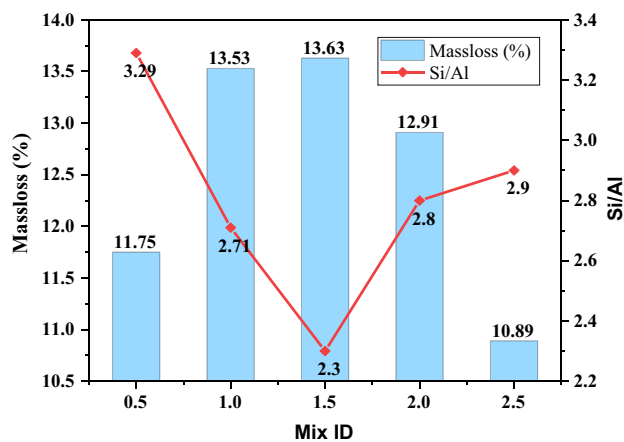


Fig. 9 Mass loss versus Si/Al ratio

and Al–O. The mass loss at this stage was approximately 2%. Similar kind of results was observed by Aliabdo et al. [43]. From the TGA observations, it can be seen that the geopolymer concrete had a mass loss, especially in the mix with the ratio of 0.5, at a temperature of 650 °C owing to the decarbonation of by-products such as CaCO_3 and NaCO_3 . The excess alkaline solution present in the geopolymer mix reacted with the CO_2 to form Ca and Na carbonates [44], and this was confirmed by the FT-IR. The major mass loss in the geopolymer concrete with M-sand at 28 days was due to the escape of water from the matrix. Mass loss of the samples cured at an ambient temperature was more at shorter curing ages and could be reduced by long-term curing.

Figure 9 demonstrates that with an increase in the Na_2SiO_3 -to-NaOH ratio from 0.5 to 1.5, the mass loss increased, and with a further increase in the Na_2SiO_3 -to-NaOH ratio from 1.5 to 2.5, the mass loss decreased. The values of the mass loss values are mentioned in Fig. 8. Moreover, with an increase in the Na_2SiO_3 -to-NaOH ratio, the sodium, water and silicate content increased. The mix with the Na_2SiO_3 -to-NaOH ratio of 1.5 had the lowest Si/Al ratio of 2.3 and the highest mass loss of 13.63%, while the mix with the Na_2SiO_3 -to-NaOH ratio of 0.5 had the highest Si/Al ratio of 3.29 and the mass loss of 11.75%. Similar kind of results has been reported by Nath et al. [8].

Cost analysis of the different molar ratios of geopolymer concrete

Na_2SiO_3 , NaOH and superplasticizer were the commercial materials used in this study. Previous researchers conclude that the geopolymer concrete is more economical than the OPC concrete [45]. The rate of geopolymerization depends on Na_2SiO_3 and NaOH, and these materials are considered to

Table 5 Detailed rate of the materials (per cubic meter) used in geopolymer concrete

Material (M^3)	Cost (rupees)	Cost (\$)
Fly ash	72	1
GGBFS	5700	79.72
Alcofine	14,300	200
Coarse aggregate	1065	14.89
Fine aggregate (M-sand)	600	8.39
Sodium silicate	14,000	195.80
Sodium hydroxide	52,500	734.26
Superplasticizer	36,000	503.49

be approximately 70% of the overall cost of the geopolymer concrete. In the present study, the cost analysis for 1 m^3 of geopolymer concrete was conducted with different Na_2SiO_3 and NaOH ratios. Table 5 presents the cost of the materials used in geopolymer concrete per cubic meter of the materials. The cost of geopolymer concrete mainly depended on the Na_2SiO_3 -to-NaOH ratio of the alkaline solution.

The cost comparison of 1 m^3 of geopolymer concrete was calculated based on the quantities of the materials (Table 2). Table 6 demonstrates that with an increase in the Na_2SiO_3 -to-NaOH ratios, the cost of geopolymer concrete increased. For the mix with Na_2SiO_3 -to-NaOH ratio 0.5, the manufacturing cost was 2598.77 rupees, while for the mix with Na_2SiO_3 -to-NaOH ratio 1.5, which showed the highest compressive strength, the production cost was 2898.98 rupees. Similarly, the production cost was calculated for the ratios 1, 2 and 2.5 as 2786.41, 2928.88 and 2988.81 rupees, respectively.

Conclusion

The effective utilization of the industrial by-products in geopolymer concrete makes the concrete superior to OPC concrete, with properties such as being more eco-friendly and cost-effective. This shows the way for the safe disposal of industrial by-products, which otherwise requires a large area of land. Hence, the development of geopolymer concrete can fulfill the future need for concrete.

- The compressive strength of ternary blended geopolymer concrete increased with an increase in the Na_2SiO_3 -to-NaOH ratio from 0.5 to 1.5, and the percentage increase in the compressive strength was 55.86. Furthermore, with an increase in the ratio from 1.5 to 2.5, the compressive strength reduced, and the percentage decrease in the compressive strength was 11.4. The mix with the ratio of 1.5 attained the highest compressive strength of 45.2 MP. Additionally, the optimum kinetic

Table 6 Details of the cost comparison of the different geopolymers concrete mixes per cubic meter of concrete (m³)

Materials	Mix 0.5		Mix 1		Mix 1.5		Mix 2		Mix 2.5	
	Cost rupees	Cost \$	Cost rupees	Cost \$	Cost rupees	Cost \$	Cost rupees	Cost \$	Cost rupees	Cost \$
Fly ash	8.40	0.11	8.40	0.11	8.40	0.11	8.40	0.11	8.40	0.11
GGBFS	350.24	4.89	350.24	4.89	350.24	4.89	350.24	4.89	350.24	4.89
Alccofine	175.15	2.44	175.15	2.44	175.15	2.44	175.15	2.44	175.15	2.44
Fine aggregate	307.92	4.30	307.92	4.30	307.92	4.30	307.92	4.30	307.92	4.30
Coarse aggregate	878.9	12.29	878.9	12.29	878.9	12.29	878.9	12.29	878.9	12.29
Sodium silicate	472.86	6.61	709.33	9.92	851.20	11.90	945.77	13.22	1013.23	14.17
Sodium hydroxide	195.3	2.73	146.475	2.04	117.175	1.63	52.5	0.73	45	0.62
Superplasticizer	210	2.93	210	2.93	210	2.93	210	2.93	210	2.93
Total cost	2598.77	36.34	2786.41	38.92	2898.98	40.49	2928.88	40.91	2988.84	41.75

ratios contributing to the highest compressive strength, SiO₂/Al₂O₃, Na₂O/SiO₂, H₂O/Na₂O and CaO/SiO₂, were 4.69, 0.07, 34.82 and 0.48, respectively.

- The decline in the slump values was observed with an increase in the Na₂SiO₃-to-NaOH ratio. Moreover, the decline in the slump values reduced the workability of the geopolymer concrete. The decline was due to the increase in the viscosity Na₂SiO₃ in the mixes. The rheological behavior of geopolymer concrete was entirely different from the OPC concrete. Geopolymer concrete with GGBFS required high slump values.
- The Na₂SiO₃-to-NaOH ratio has a significant effect on the geopolymer matrix formation. From the SEM/EDS, the mix with the ratio of 1.5 had the denser matrix. The denser matrix was due to the additional dissolution and polycondensation of the calcium aluminosilicate precursors from the binder materials. An increase in the Na₂SiO₃-to-NaOH ratio promotes the hydrolysis of the silica and alumina species of the binder materials and provides additional silicate anions to react with Ca²⁺ so as to form the calcium silicate hydrate (C–S–H) gel. The presence of C–S–H was confirmed through EDX, XRD and FT-IR.
- The FT-IR spectroscopy shows that an increase in the Na₂SiO₃-to-NaOH ratio can have undeniable influences on the formation of geopolymer products. The Na₂SiO₃ had a significant role in the gel homogeneity of geopolymer compounds, and the vibration peaks varied with the change in the ratio.
- From the TGA and DSC curves, it was observed that with an increase in the Na₂SiO₃-to-NaOH ratio, the weight loss increased to a ratio of 1.5 and then decreased to a ratio of 2.5. All the mixes had 75% of the total weight loss at a temperature of below 200 °C due to the evaporation of water.

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