Section A-Research paper
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Macro- and Microstructural Durability Investigations of Sustainable Ternary Geopolymer Concrete Paver blocks

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Abstract. With the growing infrastructure of road transport and highways, there has been a tremendous revolution in materials we use for construction of important freight corridors, expressways, access roads for villages and rural areas. The use of paving blocks, which have been in use since hundreds of years are still the foremost choice of engineers for applications in either road shoulders, pedestrians, parking lots, hangers etc. because of ease in laying. Additionally, concrete paver blocks present a less time-consuming repair and maintenance unit with ready to use properties. However, the growing need for providing sustainable materials has opened avenues for investigating environment friendly ingredients to produce these ready-made building unit. Hence, the current study attempts to reinforce the utility of geopolymer mixes by investigating durability properties of ternary geopolymer concrete along with microstructural examination. An optimum ternary blend based on previous experimental study, comprising of FA, GGBS and MK has been prepared with natural sand and foundry sand and tested in extreme environmental conditions against Sulphate attack, prolonged and rapid chloride attack to assess its performance. Reduction in strength of samples subjected to deteriorating conditions have been evaluated using destructive testing as well as non-destructive testing such as UPV Test, Rebound Hammer Test, RCP Test. The findings have also been supported with computer aided microstructural tests such as FTIR, SEM and XRD analysis. The study, through its significant findings, propose a more durable ternary geopolymer mix over conventionally used OPC based mixes for high quality precast member construction.

Keywords: Ternary geopolymer mix, Supplementary Cementitious Materials, microstructural tests, Foundry sand, Paver Blocks, Durability

1. Introduction

On a global scale, cement has been an indispensable ingredient for ever growing infrastructure industry. Given the physical and chemical processes involved in cement manufacture, energy consumption and CO_2 emissions are significant and unavoidable [1,2]. Climate studies have revealed that CO_2 emissions from construction material industry has increased 6.8 times over last two decades [3]. Therefore, finding ways to make concrete more sustainable is crucial in the fight against climate change [4,5]. Sustainable concrete reduces environmental impact throughout its entire lifecycle. This includes reducing the amount of CO_2 emissions during production, using materials that are renewable or recycled, and increasing the durability of the final product to reduce the need for replacements [6]. Research on supplementary cementitious materials (SCMs) has been crucial in decreasing carbon credits in the manufacturing of concrete since they have been shown to dramatically cut CO_2 emissions when compared to standard concrete production processes [7–10]. Additionally, SCMs have proved to improve concrete performance, such as greater durability and reduced cracking [11–19]. This minimizes the total environmental effect of concrete manufacturing by requiring less maintenance and repair [20,21].

Over time, the long-term behavior of both unary and binary geopolymer concrete (GPC) mixtures which are made by completely replacing cement with SCMs have been investigated. In 2013, researchers investigated the influence of alkali silica reactivity in a geopolymer mix based on FA. The study concludes that geopolymer mixtures are less susceptible to alkali silica reactivity than OPC-based mixtures [22]. An accelerated corrosion process was tried by adding a rebar into the mix to determine the durability behavior of FA-based GPC in marine environments. Accelerated corrosion causes specimen cracking, which indicates durability aspects [23]. Researchers have even studied the strength loss of geopolymer blends for up to eight years, demonstrating the improved durability capabilities proven under atmospheric exposure settings [24]. Binary geopolymer mixtures produced from FA and slag were tested to see how resistant they were to invasion by sodium sulphate and magnesium sulphate solutions. After 360 days, the study revealed that magnesium sulphate is much more harmful than sodium sulphate [25]. Geopolymer mixes based on a blend of pulverized fuel ash and palm oil fuel ash were evaluated for sulphate resistance by immersing them in a 5% sodium sulphate solution for one year to prove their superiority over OPC-based mixes over a longer length of time [26]. In addition, studies on fiber reinforced Slag-based geopolymer concrete have been done to investigate chloride penetration, carbonation depth, and permeability [27,28]. When exposed to sulphate attack, most durability tests found a loss greater than 20 % in compressive strength in OPC-based concrete mixtures after 90 days [26,29–32]. The behavior of alkali activated concrete in acid attack circumstances over extended periods of time has also piqued the curiosity of researchers [33]. Ongoing studies on the subject matter has also investigated the durability of with varied percentages of manufactured sand that substituted natural sand and concluded that 70% replacement by manufactured sand had good durability attributes [34]. However, this reduction in strength was seen to be much lesser in case of unary and binary geopolymer concrete mixes [26,29–31,35,36].

In general terms previous studies indicate that geopolymer mixes have potential to be a more durable solution as compared to the conventional mixes [37–42]. However, there has not been any comprehensive and definitive study deciphering the durability behavior of ternary and quaternary geopolymer concrete at ambient and increased temperatures, leaving a large potential for future research in this area. There is a scarcity of specific research on the use of geopolymerization in the production of smaller building units in the literature. Hence, the current study focusses on ascertaining the long-term behavior of ternary geopolymer concrete mix. The study promotes the scope of geopolymerization process in manufacturing of small building units like paver blocks. The usage of ternary mixes would differ in terms of durability and might provide a superior crystalline structure, making the concrete more resistant to chemical attack in harsh environmental circumstances. Many industrial byproduct materials are created by myriad industries, posing a disposal difficulty. Apart from FA and GGBS, Rice husk ash (RHA) from the rice milling industry and MK from the kaolinite clay calcination process have been described in the literature with promising results in the production of high-quality geopolymer concrete [43–46]. Considering the potential of such waste materials and their capacity to make a more durable concrete with superior properties, efforts have been undertaken to test and manufacture durable geopolymer building units.

2. Materials

The supplementary cementitious materials required as raw materials to carry out this study were procured from different industries and locations based on their availability. Class-F Fly Ash (FA) was procured from Thermal Power Plant, Khedar, Haryana. Ground Granulated Blast Furnace Slag (GGBS) was obtained from blast furnace situated in Hamirpur district, Himachal Pradesh. Rice Husk Ash (RHA) was brought from local rice mill located in Jind district of Haryana. Metakaolin (MK) and Foundry Sand

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(FS) was acquired by local vendor from Zakhira, New Delhi. Available Yamuna sand was used as Natural Sand (NS) for casting samples for the study.

2.1 Physical Characteristics

The raw materials were then tested for their physical characteristics which are tabulated in Table 1. Figure 1 also shows the particle size distribution curves of the materials. The curves clearly indicate the suitability in terms of particle size of different SCMs to produce a highly dense matrix of ternary blends fitting into the void spaces.

Table 1: Physical properties of the raw materials

S. No.	Material	Appearance		Specific Gravity
		Color	Texture	
1.	Fly Ash	Tan to Dark Grey	Smooth	1.77
2.	GGBS	Stoney Grey	Smooth-Glassy	2.53
3.	Metakaolin	Smokey White	Sticky	2.45
4.	Rice Husk Ash	Deep Grey to black	Rough Non-Sticky	2.36
5.	Natural Sand	Shiny Grey	Particulate- Rough	2.57
6.	Foundry Sand	Dirty White to Pale yellow	Particulate- Semi Rough	2.52
7.	Sodium Silicate (Na_2SiO_3- 40% Solution)	Glassy White	Sticky- Viscous	1.42
8.	Sodium Hydroxide (NaOH-14 M Solution)	Transparent	Non-Sticky	1.37

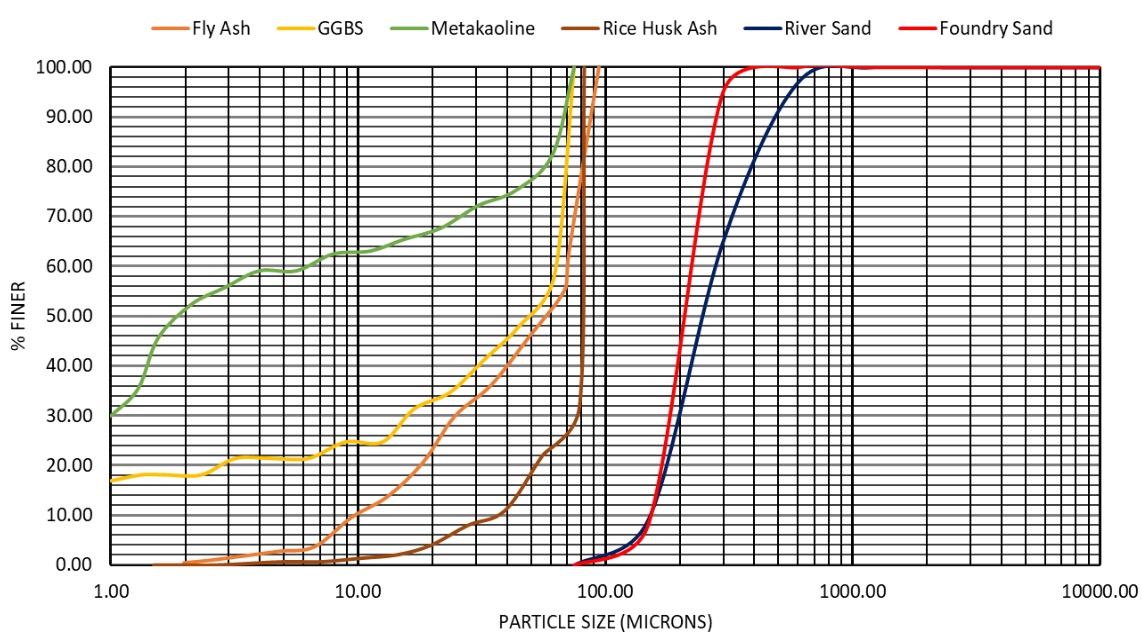


Figure 1: Grain size distribution curve of solid raw materials

2.2 Chemical Characteristics

The chemical composition of the raw materials was tested at SAIF facility, Panjab University, Chandigarh and are presented in Table 2**.** It can be inferred from the table that raw materials considered for the mix (FA, GGBS, MK) have high percentage of silica and alumina content suitable for mixing a ternary geopolymer blend. The richness of these minerals makes them an ideal raw material for the formation of Si-O-Al polymerization chains along with calcium alumino- silicate hydrate (C-A-S-H) and sodium alumino-silicate hydrate (N-A-S-H) gel. These reaction products are the key to development of high strength in geopolymer concrete even with absence of cement.

Table 2: Chemical composition of the raw materials

% Oxide	Fly Ash	GGBS	Metakaolin
SiO_2	62.19	31.99	52.50
CaO	1.97	46.86	0.04
Al_2O_3	27.15	14.54	44.40
MgO	0.40	1.05	-
Fe_2O_3	3.23	1.12	-
SO_3	0.07	-	-
TiO_2	1.06	0.54	-
Na_2O	0.30	0.23	0.24
K_2O	0.89	1.03	0.10
P_2O_5	-	-	--
S	-	0.82	-
L.O.I	1.75	1.82	0.05

3. Methodology

The methodology of the experimental program has been presented in Figure 2. After procurement and initial testing of the raw materials, they were taken into various combinations of mix proportions with 70% FA, GGBS content varying between 15-25%, MK and RHA ranging between 5-15% to find out the optimum mix with maximum characteristic compressive strength. Table 3 lists the blends taken for deciphering the optimum mix. The results which are not in purview of this manuscript presents that blend A2 shows the maximum characteristic strength and can be taken for further studies on durability aspects of ternary geopolymer mix.

For the current durability study 128 Paver Blocks of optimum blend (A2) and of grade M35 were casted and tested conforming to [47]. Grade M35 is chosen looking into the recommended use of these paver blocks for application in Pedestrian Plazas, shopping complex ramps, car parks, office driveways, housing colonies, office complexes, rural roads with low traffic volumes, local authority footways, residential roads etc. Also, paver blocks do not need any special maintenance as compared to concrete or asphalt surfaces as well as does not require curing and can be opened for traffic immediately after construction which is very likely for application of Geopolymer concrete.

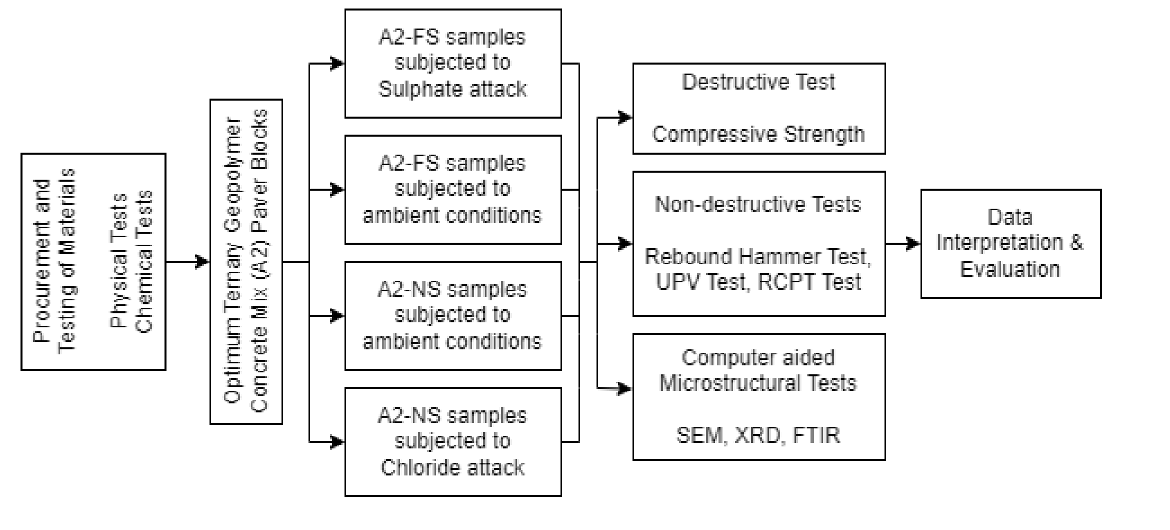


Figure 2: Flowchart depicting methodology

Table 3: Mix proportions of various blends chosen for study

S. No.	Blend	Type of Sand	Mix proportions
1.	A1-NS	Natural Sand	70% FA + 25% GGBS + 5% MK
2.	A2-NS	Natural Sand	70% FA + 20% GGBS + 10% MK
3.	A3-NS	Natural Sand	70% FA + 15% GGBS + 15% MK
4.	B1-NS	Natural Sand	70% FA + 25% GGBS + 5% RHA
5.	B2-NS	Natural Sand	70% FA + 20% GGBS + 10% RHA
6.	B3-NS	Natural Sand	70% FA + 15% GGBS + 15% RHA
7.	A1-FS	Foundry Sand	70% FA + 25% GGBS + 5% MK
8.	A2-FS	Foundry Sand	70% FA + 20% GGBS + 10% MK
9.	A3-FS	Foundry Sand	70% FA + 15% GGBS + 15% MK
10.	B1-FS	Foundry Sand	70% FA + 25% GGBS + 5% RHA
11.	B2-FS	Foundry Sand	70% FA + 20% GGBS + 10% RHA
12.	B3-FS	Foundry Sand	70% FA + 15% GGBS + 15% RHA

Out of 128 paver blocks, 64 were casted with natural sand and 64 were casted with foundry sand. The specification of the paver blocks casted are as shown in the Figure 3. The mix design of ternary GPC was done in accordance with method laid down by [48]. The mix proportions in Kg/m^3 of blend A2 with natural and foundry sand are as given in Table 4.

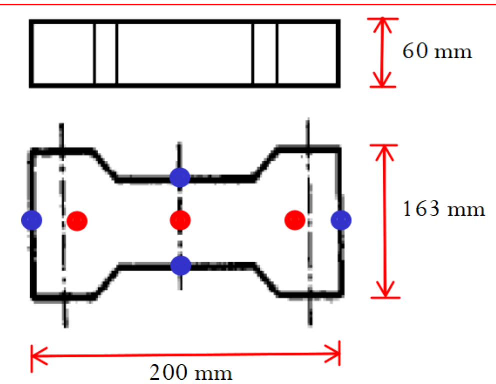


Figure 3: Specifications of Paver blocks casted

Table 4: Mix proportions (kg/m^3) of blend A2 with Natural and Foundry Sand

Blend	Fly ash	GGBS	MK	Natural Sand	Foundry Sand	Coarse Aggregates (45:55)		NaOH	Na_2SiO_3
	70:20:10					10 mm	20 mm		
Blend A2-NS	224	64	32	589.27	-	505.44	617.76	79.75	182.65
Blend A2-FS	224	64	32	-	578.50	505.44	617.76	79.75	182.65

All the samples after casting were kept for curing in oven at 80ºC for 48 hours. Post curing, all samples were checked for correctness in casted dimensions. A sample of the checks made in accordance to [47] has been shown in Table 5. After that, 64 samples comprising of 32 foundry sand samples and 32 natural sand samples were kept for ambient curing until testing on 7th, 28th, 56th and 90th day of casting. 32 foundry sand samples were kept in 5% Sodium Sulphate (Na_2SO_4) solution to test resistance to sulphate attack and 32 natural sand samples were kept in 3% Sodium Chloride (NaCl) solution to test resistance to chloride attack until testing. The nomenclature of samples taken for current study has been described in Table 6.

Table 5: Mix proportions (kg/m^3) of blend A2 with Natural and Foundry Sand

S. No.	Parameter	Result	IS Recommended Value	Tolerance	Remarks
1.	Width, *w*	160 mm	As Per Manufacturer	± 2 mm	Yes, Within the specified tolerance
2.	Length, *l*	200.67 mm	As Per Manufacturer	± 2 mm	Yes, Within the specified tolerance
3.	Thickness, *t*	59.92 mm	60 mm	± 3 mm	Yes, Within the specified tolerance
4.	Aspect Ratio, (l/t)	3.35	Maximum: 4.0	+ 0.2	Yes, Within the specified tolerance
5.	Arris/ Chamfer	0 mm	Nil	± 1 mm	Yes, Within the specified tolerance
6.	Thickness of wearing layer	6 mm	Minimum: 6.0	+ 2 mm	Yes, Within the specified tolerance
7.	Plan Area, A_{sp}	0.0286 m^2	Maximum: 0.03	+ 0.001 m^2	Yes, Within the specified tolerance
8.	Wearing Face Area, A_{sw}	0.0228 m^2	Minimum 75 percent of plan area	-1.0 %	Yes, Within the specified tolerance
9.	Squareness Face-Side Side-Side	2.00 mm 0.83 mm	Nil Nil	± 2 mm ± 2 mm	Yes, Within the specified tolerance

Table 6: Mix proportions (kg/m^3) of blend A2 with Natural and Foundry Sand

S. No.	Specimen Nomenclature	Description
1	Control NS	A2 concrete blend specimen with Natural sand kept in ambient conditions
2	Chloride NS	A2 concrete blend specimen with Natural sand subjected to Chloride attack

3	Control FS	A2 concrete blend specimen with Foundry sand kept in ambient conditions
4	Sulphate FS	A2 concrete blend specimen with Foundry sand subjected to Sulphate attack

4. Laboratory Investigations

Presently, durability properties of concrete have been assessed by checking the resistance of the samples against sulphate attack and chloride attack. These tests involve immersing the samples in sulphate and chloride solution and then test them for reduction in strength by measuring their compressive strength. This testing falls in the category of destructive tests performed on the samples. However, studies have also been done using non-destructive tests such as Ultrasonic pulse velocity test (UPV), Rebound Hammer Test which can also be used for fair assessment of concrete quality after deterioration in deleterious environment over a period of time. Rapid chloride permeability test (RCPT) was also conducted to verify the results obtained through ponding test in chloride solution. Table 7 summarizes the percentage (%) reduction in strength of various types of concrete subjected to sulphate and chloride attack.

Table 7: Summary of percentage (%) reduction in strength of various types of concrete

S. No.	Author	Type of Concrete	Reduction in Strength	
			Sulphate Attack	Chloride Attack
1.	Okoye et al. [32]	OPC Concrete	22.98 % in 90 days	9.45 % in 90 days
2.	Bhutta et al. [26]		63 % in 540 days	-
3.	Bashir & Saharan [29]		11.99 % in 28 days	-
4.	Xie et al. [30]		~20 % in 90 days	-
5.	Lingyu et al.[31]		25 % in 90 days	-
6.	Okoye et al.[32]		18.16 % in 90 days	5.87 % in 90 days
7.	Gopalakrishnan & Chinnaraju [35]	Unary GPC	-	16.95% to 40.1% in 90 days
8.	Bashir & Saharan[29]		11.54% in 28 days	-
9.	Bhutta et al. [26]	Binary GPC	~7% in 540 days	-
10.	Bashir & Saharan [29]		11.49% in 28 days	-
11.	Zhuang et al. [36]		-	11% in 90 days
12.	Xie et al. [30]		5% in 90 days	-
13.	Lingyu et al. [31]		~8.3% in 90 days	-

4.1 Resistance to Sulphate Attack

The samples after initial oven curing were kept immersed in 5 % Sodium Sulphate (Na_2SO_4) solution. The samples were taken out of the solution at their respective day of testing 30 minutes before to reach surface dry condition.

4.1.1 Destructive Testing: Reduction in Compressive Strength

The samples were then tested for their compressive strength in Compression Testing Machine of capacity 2000 KN. The variation of compressive strength of blocks are recorded in Figure 4(a). The residual strength of concrete after deterioration has also been plotted and represented in Figure 4(b).

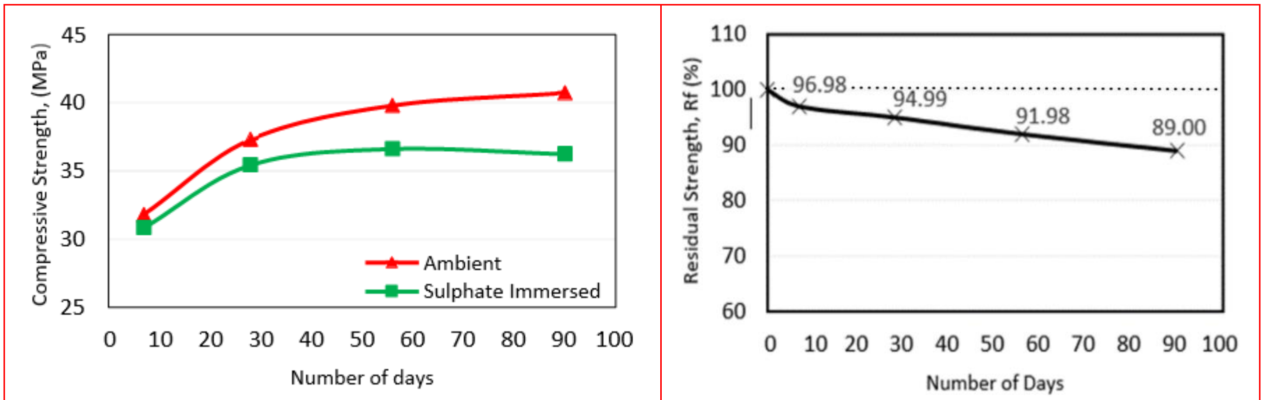


Figure 4: (a) Variation of Compressive Strength over a period of 90 days (b) Variation of Residual Strength (R_f) of concrete after deterioration with sulphate solution

The results plotted in Figure 4(a) shows a maximum reduction of 11 % over a period of 90 days in ternary GPC mix casted and kept in Sulphate solution. This explains a better resistance shown by ternary GPC mix over a reduction of approximately 24 %, 18 % and 12% by OPC concrete, Unary GPC and Binary GPC mix respectively, reported in the literature. This is due to an enhanced morphological structure seen in ternary mixes.

4.1.2 Non-Destructive Testing: Rebound Hammer Test

The Rebound Hammer readings for each paver block were taken at seven different locations as seen in Figure 3 comprising of four readings on each side face (blue dots) and three readings on the top surface of the block (red dots). The average of all these seven readings has been calculated for each paver block.

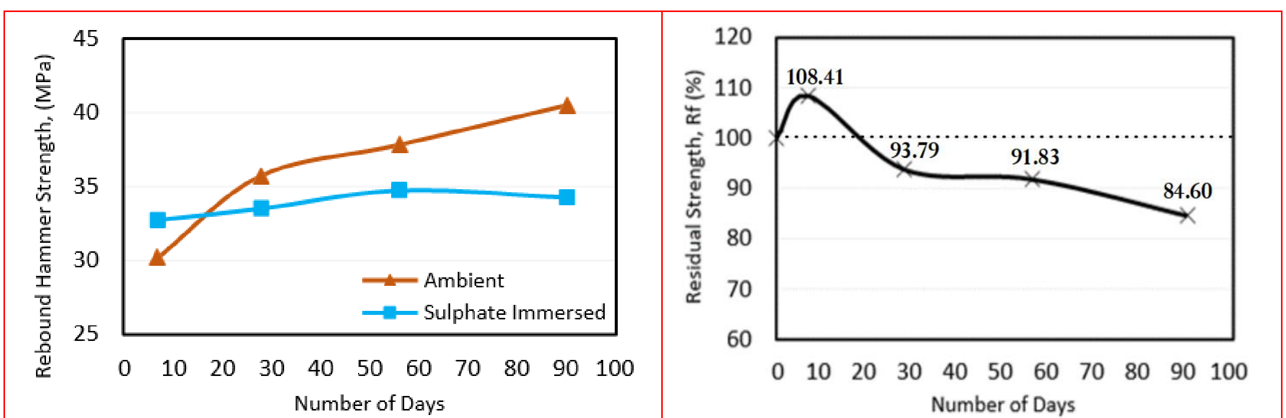


Figure 5: (a) Variation of Rebound Hammer Strength over a period of 90 days (b) Variation of Residual Strength (Rf) of concrete after deterioration with sulphate solution

On analyzing the strength obtained using rebound hammer of ambient and samples dipped in sulphate solution (Figure 5(a)), it was found that the trend followed is similar to the trend obtained in destructive testing. However, the anomaly seen in 7 days result is a mere proof of non-suitability of the correlation followed for converting rebound hammer number to compressive strength generally used for OPC mixes for GPC mix [49]. clearly defines the procedure to corelate compressive strength of concrete with rebound number during testing for different grades of concretes made. However, the present study focus on deciphering durability characteristics of a single grade of ternary concrete, making it difficult to establish such correlation in general for geopolymer mixes. The rise seen in residual strength in figure 5(b) at 7 days is also because of the anomaly observed in results.

4.1.3 Non-Destructive Testing: Ultrasonic Pulse Velocity Test

The ultrasonic pulse velocity method has been used to check the homogeneity of concrete mix, check changes in the structure of concrete which may occur with time, presence of cracks, voids and other imperfections and check the quality of concrete in relation to standard requirements. [50] recommends velocity criterion for concrete quality grading. The same is shown in Table 8.

Table 8: Velocities criterion for Concrete Quality Grading

Pulse Velocity (KM/sec)	Concrete Quality Grading
Above 4.5	Excellent
3.5 to 4.5	Good
3 to 3.5	Medium
Below 3	Doubtful
Adopted from IS 13311 (Part 1): 1992	

The results presented in Table 9 shows that ternary GPC mix conforms from medium to excellent quality concrete grade not just before but after immersion in sulphate solution also over a period of time. This supports the claim of a better morphological structure in ternary GPC mix which makes it more durable.

Table 9: Velocities in km/sec of blend A2 with Foundry sand

Parameter	7 days	28 days	56 days	90 days
Samples Immersed in 5 % Sulphate Solution				
Average Velocity	3.23	3.79	4.49	4.76
Concrete Quality Grading	Medium	Good	Excellent	Excellent
Samples kept in Ambient Surroundings				
Average Velocity	3.63	3.89	4.75	4.91
Concrete Quality Grading	Medium	Good	Excellent	Excellent

4.2 Resistance to Chloride Attack

Deterioration of strength of concrete due to attack by chloride solutions also poses a major threat to long term behavior of concrete. The current study hence checks the durability of ternary GPC mix by checking the resistance to chloride attack. For this, 50 % of natural sand samples were immersed in 3% NaCl solution for a period of up to 90 days.

4.2.1 Destructive Testing: Reduction in Compressive Strength

The destructive test done on natural sand samples immersed in chloride solution shows a maximum of 7.2% strength reduction (refer Figure 6) as compared to an average of 11.54% reduction reported for Unary GPC and 11% reduction for Binary GPC mixes. OPC mixes have also been reported in literature to show even lower residual strengths after an immersion period of up to 90 days.

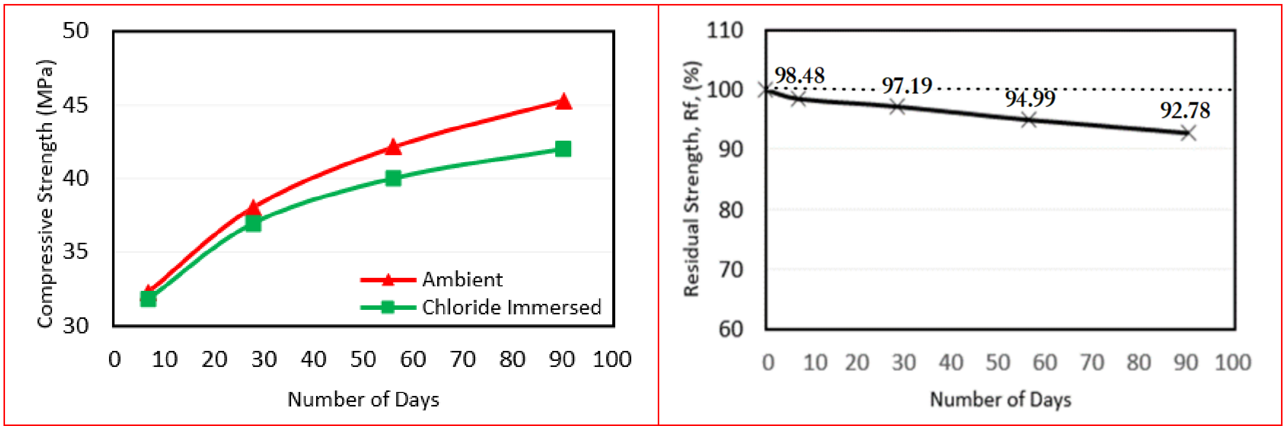


Figure 6: (a) Variation of Compressive Strength over a period of 90 days (b) Variation of Residual Strength (R_f) of concrete after deterioration with chloride solution

4.2.2 Non-Destructive Testing: Rebound Hammer Test

The results plotted in Figure 7(a) and (b) also shows a good conformity with the results reported in destructive tests. The difference in percentage (%) reduction values may be attributed to the influence of test conditions, especially the influence of binding material used for GPC mixes as stated by [49]

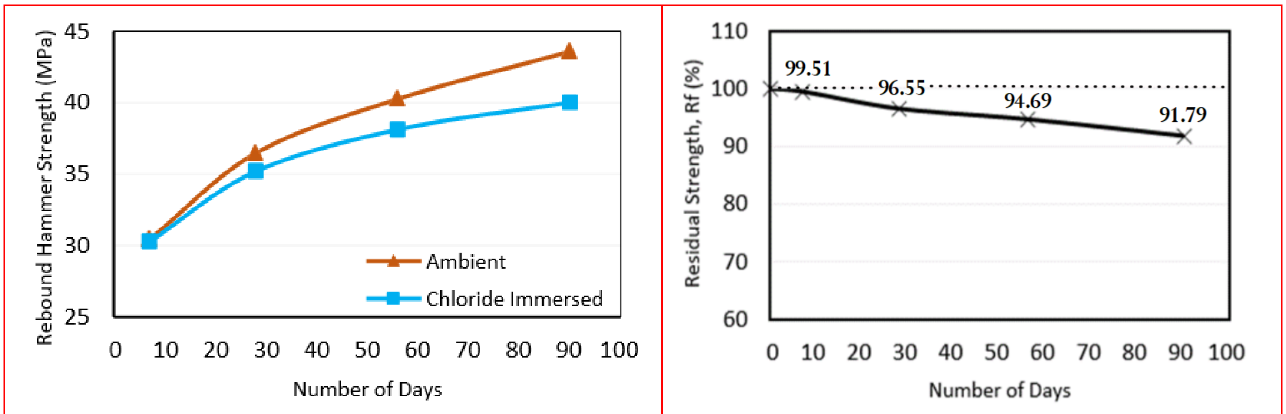


Figure 7: (a) Variation of Rebound Hammer Strength over a period of 90 days (b) Variation of Residual Strength (Rf) of concrete after deterioration with sulphate solution

4.2.3 Non-Destructive Testing: Ultrasonic Pulse Velocity Test

The UPV test results presented in Table 10 also shows almost negligible to nil effect on the microstructure of ternary GPC mix conforming between medium to excellent concrete quality grading even after up to 90 days immersion in chloride solution. The results obtained in section 4.4 (microstructural properties) support the results obtained.

Table 10: Velocities in km/sec of blend A2 with Natural Sand

Parameter	7 days	28 days	56 days	90 days
Samples Immersed in 3 % Chloride Solution				
Average Velocity	3.31	3.98	4.28	4.78
Concrete Quality Grading	Medium	Good	Good	Excellent
Samples kept in Ambient Surroundings				
Average Velocity	3.73	4.05	4.51	4.82
Concrete Quality Grading	Medium	Good	Excellent	Excellent

4.2.4 Non-Destructive Testing: Rapid Chloride Permebility Test

The rapid chloride permeability test (RCPT) was conducted in accordance to [51] which assesses resistance of concrete to chloride ions infiltration in coulombs. A constant voltage (V) of 60 Volts was supplied for 6 hours and the current travelling through the concrete cores were recorded. A core of diameter 100 mm from paver blocks of each mix containing Natural sand and Foundry sand respectively were cut for testing at 28, 56 and 90 days. The core was then fine-tuned to have a thickness of 50 mm as per the specifications of reference standard. To minimize the variation, three samples were tested, and the average value has been reported in Table 11.

The test results of both the mixes A2-NS and A2-FS were almost comparable to each other with slightly elevated values seen in foundry sand samples. This is because the test measures the movement of all ions, and not just chloride ions in the pore solution, which affects the test result. Due to source of Foundry sand, it has high content of conducting ions leading to passage of higher current through the samples. The Chloride-ions penetrability for natural sand samples was found to be low at 28 and 56 days testing which further reduced to very low category at 90 days testing. This may be due to the reason that the superficial pore structure of concrete discs clogs with foreign particles such as dust and causes the penetrability to further reduce. A similar trend in behaviour was seen in foundry sand samples with moderate, low and low penetrability at 28, 56 and 90 days of testing respectively. The results obtained however in RCPT are in concordance with the results of long-term immersion in chloride solution described in section 4.1.1. The charge passed from conventional concrete specimens as reported by [52] is between 2800 to 7000 coulombs which is high as compared to the results obtained in the current study. The standard of Chloride-ions penetrability as per [51] is shown in Table 12.

Table 11: Chloride Ion Penetrability of A2 mix casted with natural sand & foundry sand

Specimen Designation	Age of Testing	Average Charge passed	Chloride-ions

	(Days)	(Coulombs)	penetrability
A2-NS	28	1999	Low
A2-FS	28	2083	Moderate
A2-NS	56	1398	Low
A2-FS	56	1423	Low
A2-NS	90	947	Very low
A2-FS	90	1021	Low

Table 12: Chloride-ions penetrability and relation with type of concrete

Charge Passed in coulombs	Chloride-ion Penetrability (ASTM C1202)	Types of concrete [52]
>4000	High	High Alkaline-Binder ratio
2000 – 4000	Moderate	Moderate Alkaline-Binder ratio
1000 – 2000	Low	Low Alkaline-Binder ratio
100 -1000	Very Low	Latex-modified/ Internally sealed concrete
<100	Negligible	Polymer impregnated concrete

4.3 Fourier Transform Infrared Spectroscopy (FTIR)

In the current study, Figure 8-11 represents FTIR graphs obtained for four different testing regimes for the concrete mix taken. The geopolymer consists of repeating units of Si-O-Al responsible for its strength. The formation of more Si-O-Al bonds confers more strength to the geopolymer. A strong peak observed at 1007.15 cm^{-1} to 1023.14 cm^{-1} supports the formation of Si-O-Al chains and sodium alumino-silicate hydrate(N-A-S-H) and calcium alumino-silicate hydrate gel(C-A-S-H). However, if the % transmittance at these frequencies in the two specimens is compared, control NS specimen shows a transmittance of ~99.63% compared to a lesser value of ~99.91% shown by Chloride NS. The difference in % transmittance is a clear indication of deterioration of Si-O-Al chains as well as hinderance in formation of C-A-S-H and N-A-S-H gels due to attack by aqueous solution of chloride. This is in line with results obtained during strength testing of specimens under chloride attack at 90 days period. A wide peak observed at 3400 cm^{-1} corresponds to formation of H-bridge in -OH bonds indicating intrusion and subsequent action deteriorating the strength of concrete under chloride action [53,54].

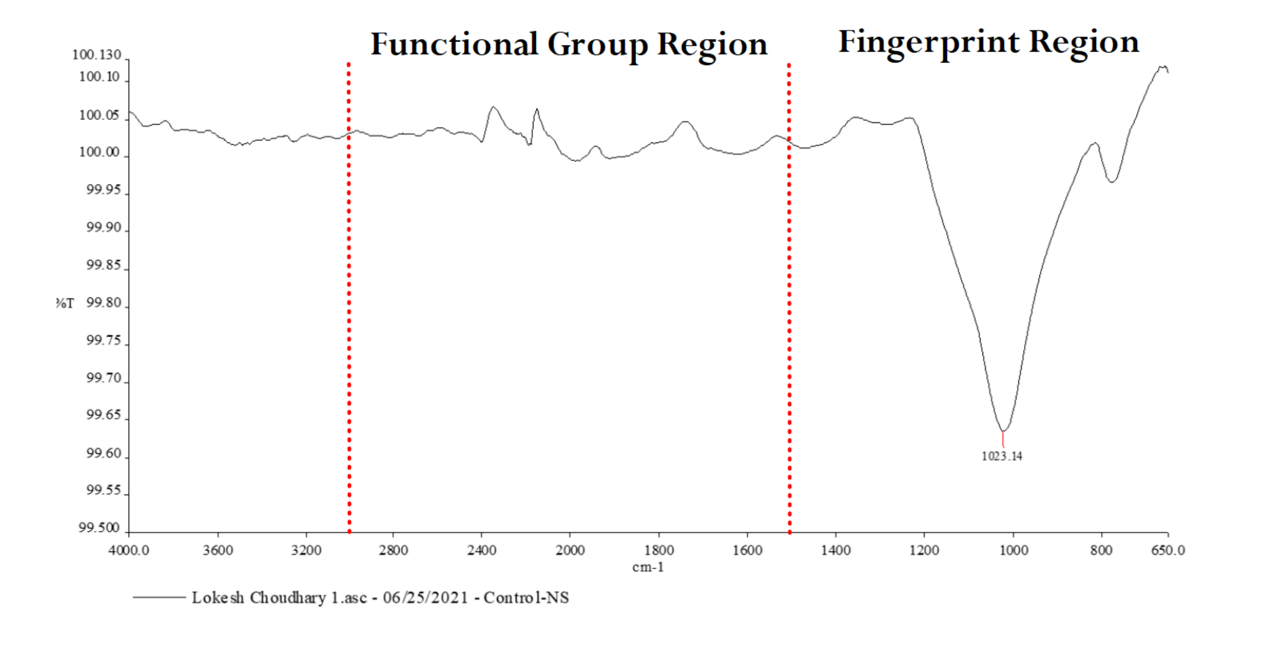


Figure 8: FTIR spectrograph of FA+GGBS+MK with NS in control condition

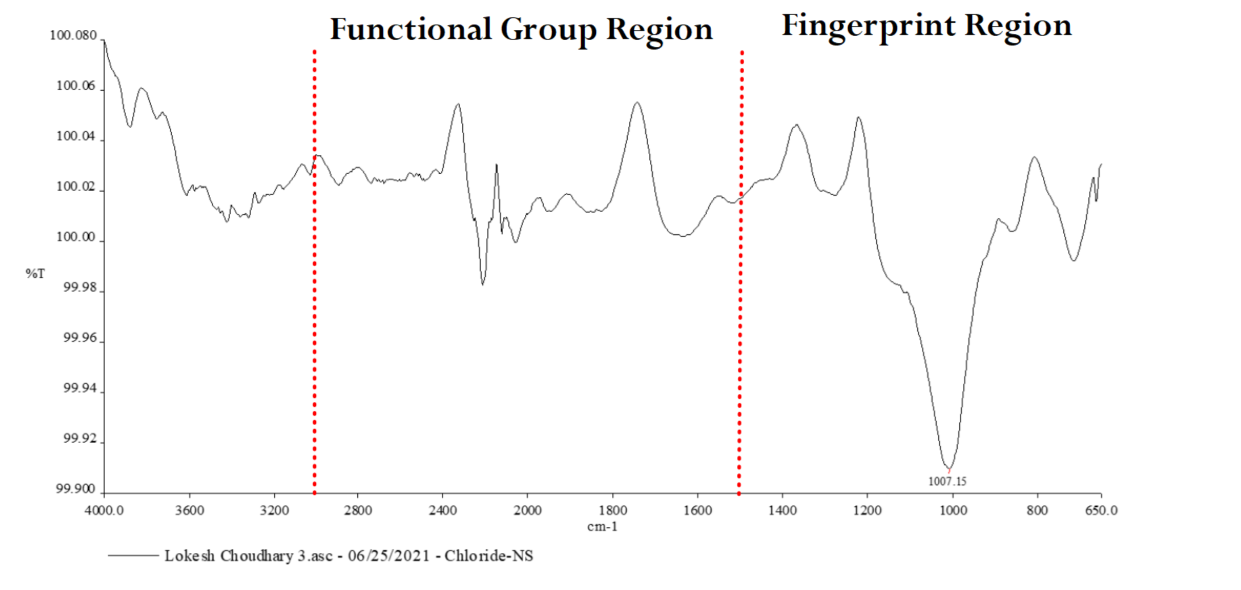


Figure 9: FTIR spectrograph of FA+GGBS+MK with NS under chloride attack

The peak obtained in the control-FS sample in the range of 1738.22 cm^{-1} reflects the characteristics of symmetric O-C-O stretching, which suggests the presence of sodium carbonate as a result of reaction between excessive sodium and atmospheric CO_2. This formation was mainly on the surface of the matrix due to prolonged exposure to carbon dioxide at atmospheric temperature. The peak cease to exist in Sulphate-FS specimen due to immersion of the sample in aqueous sulphate solution. Peaks obtained at 1010.18 cm^{-1} and 1025.05 cm^{-1} with different % transmittance is indicative of deterioration of strength as due to sulphate attack as seen in the previous case. A wide peak observed at 3400 cm^{-1} in sulphate-FS specimen again corresponds to formation of H-bridge in -OH bonds indicating intrusion and subsequent action deteriorating the strength of concrete under sulphate action.

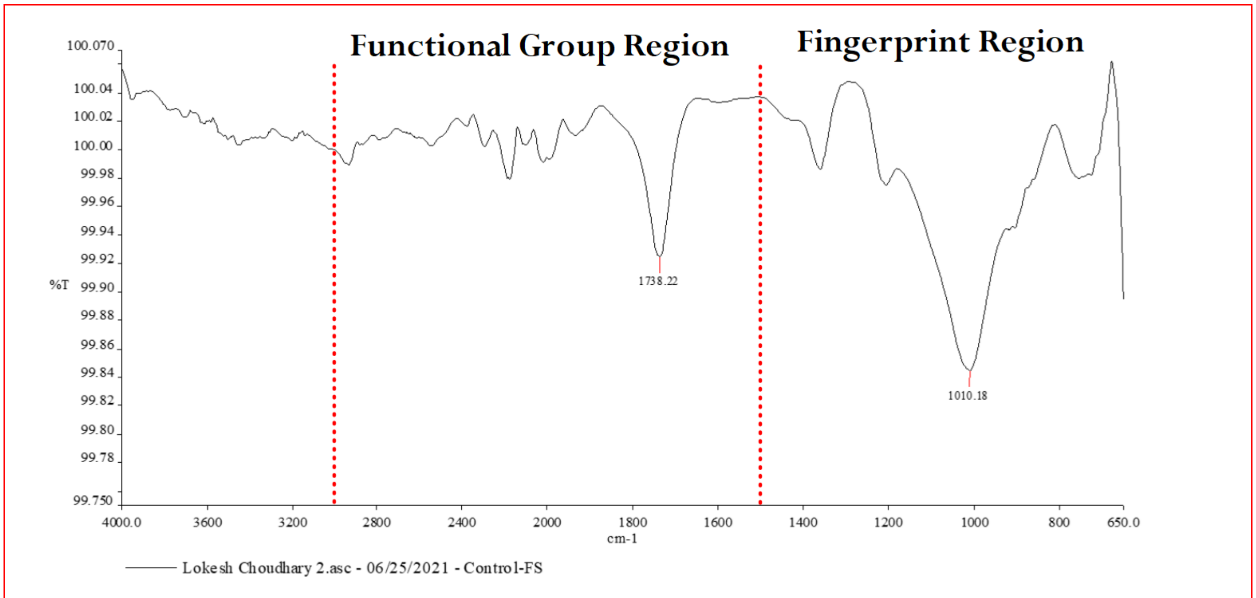


Figure 10: FTIR spectrograph of FA+GGBS+MK with FS in control condition

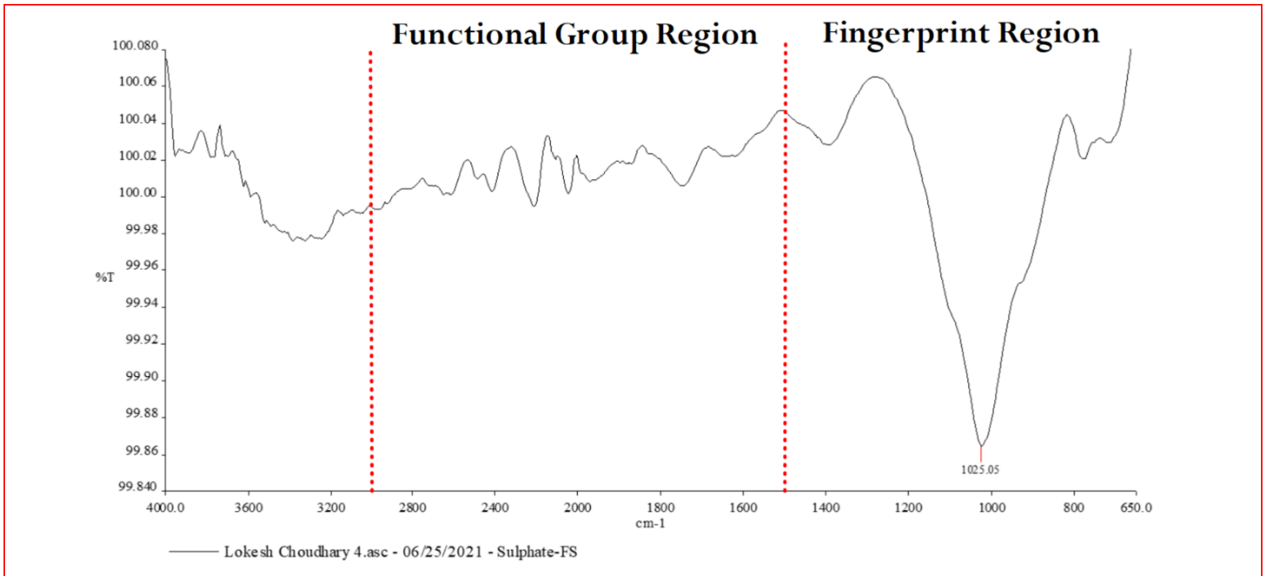
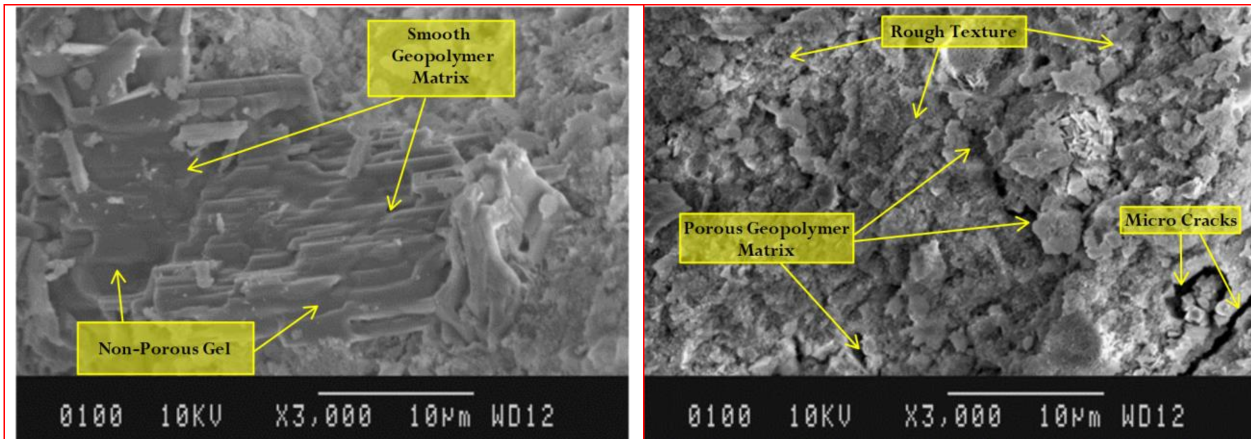


Figure 11: FTIR spectrograph of FA+GGBS+MK with FS under sulphate attack

4.4 Scanning Electron Microscope Results (SEM)

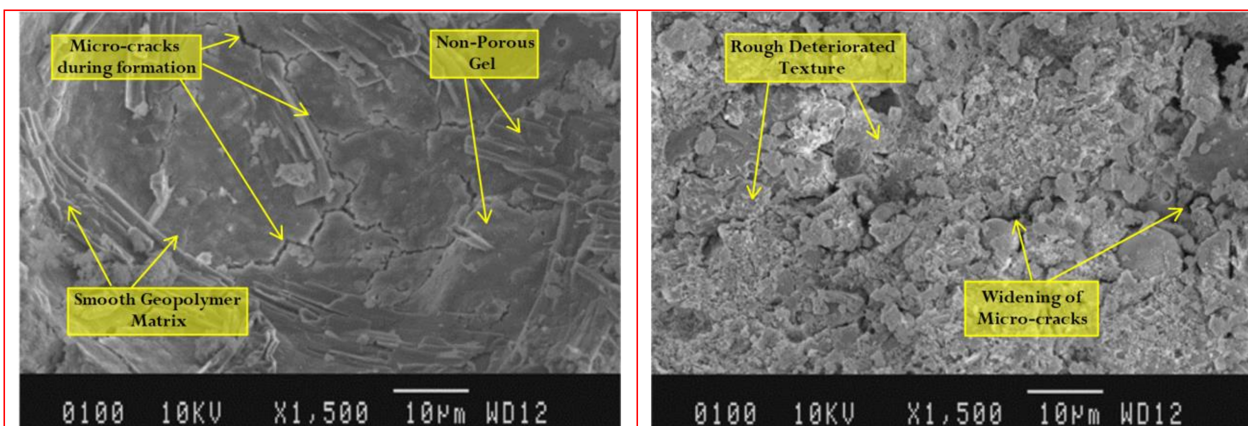
Sulfate attack of concrete is a complex process, which includes physical salt attack due to salt crystallization and chemical sulfate attack by sulfates from soil, groundwater, or seawater. Sulfate attack can lead to expansion, cracking, strength loss, and disintegration of the concrete. On observing the fragments of the specimen carefully obtained after disintegration of samples in destructive testing, under scanning electron microscope (Figure 12(a)-(b)) it is clearly seen that ingress of sulphate has made the microstructure of concrete rougher and more porous. This is a result of the expansion caused by sulphate action leading subsequently to development of cracks. The disintegration caused leads to strength loss seen in section 4.1.1. This is due to an enhanced morphological structure seen in ternary mixes.



(a) Control-FS (b) Sulphate-FS

Figure 12: SEM images of different ternary GPC blends under sulphate attack

Similar rough and porous structure due to ingress of chloride solution is seen in the SEM images observed for natural sand samples under chloride attack (Figure 13(a)-(b)). However, the effect is not that prominent as chlorides are more known to affect steel reinforcement than concrete, causing rusting and subsequent deterioration in the structure. This supports the observation of 7.2% strength reduction seen in section 4.2.1.



(a) Control-NS (b) Chloride-NS

Figure 13: SEM images of different ternary GPC blends under chloride attack

4.5 X-Ray Diffraction (XRD) Results

XRD analysis of the geopolymer samples after the exposure to Na_2SO_4 solution, did not indicate formation of any new phases formed due to a reaction with sulfate ions (Figure 14). The samples Control-

FS and Sulphate-FS contained only the phases originating from the mother sample: quartz (SiO_2), feldspar ($KAlSi_3O_8$), anhydrite ($CaSO_4$), hematite (Fe_2O_3) and mullite ($3Al_2O_3 \cdot 2SiO_2$). A similar behavior was also observed by [55]. The presence of calcite, formed as a result of carbonation during curing, was also detected.

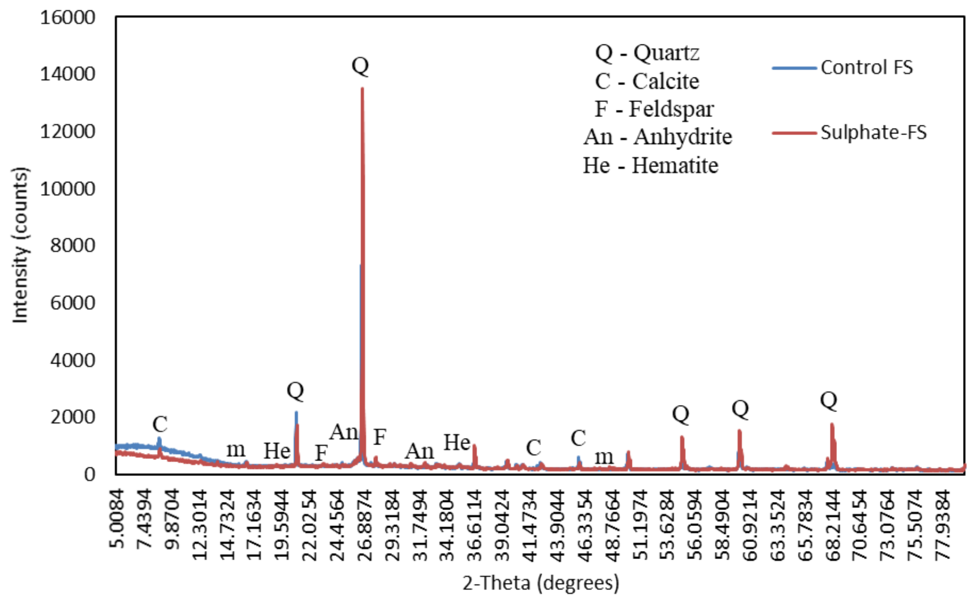


Figure 14: XRD pattern for GPC blends for control and under sulphate attack condition

On comparing the XRD curves of Control-NS and Chloride-NS specimens (Figure 15), concrete with similar age, it is observed that chloride-NS specimen form minerals bound with unreacted compounds such as calcium chloride and magnesium chloride. This proves that the binding capacity of geopolymer to bind to the ion chloride in concrete causes the chloride penetration to not produce free ions in geopolymer concrete and cause minimum deterioration. Similar results have been reported in literature for Unary GPC mixes by [56].

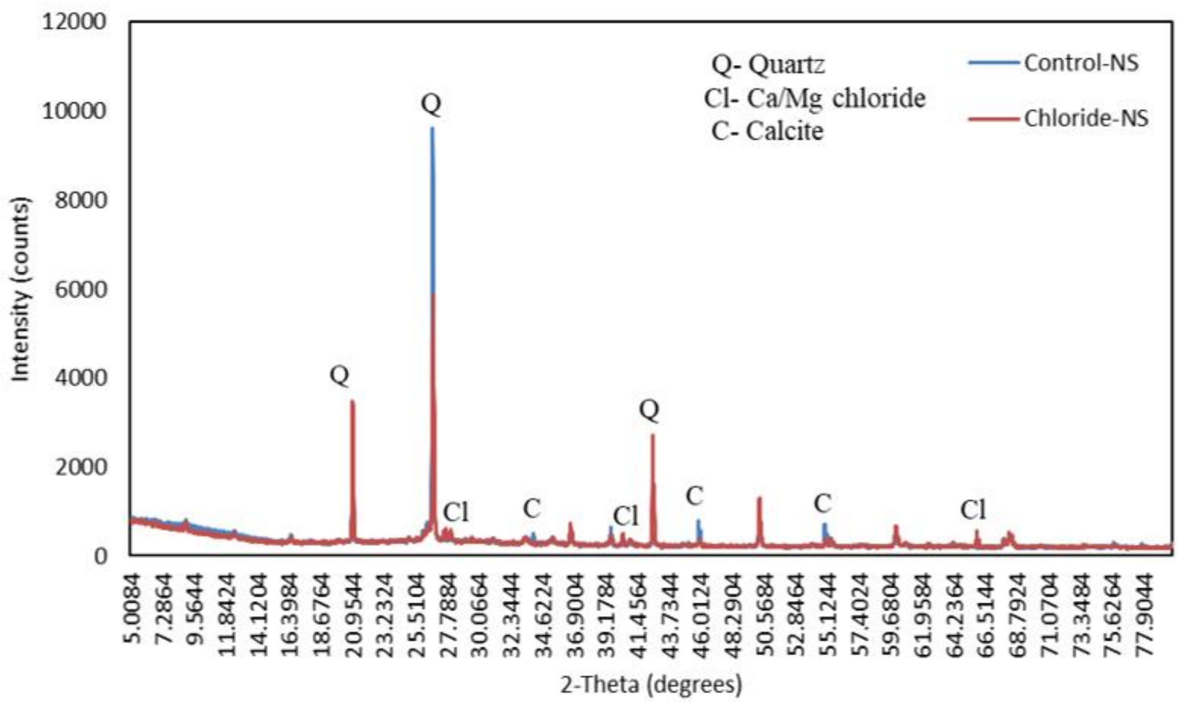


Figure 15: XRD pattern for GPC blends for control and under chloride attack condition

5. Conclusions

Following conclusions can be drawn based on the study carried out:

- Even after 90 days of immersion, foundry sand samples dipped in sulphate solution and natural sand samples immersed in chloride solution comply to good concrete quality grading. This is concluded as the highest loss of 11% Compressive strength is noticed over a period of 90 days in Ternary GPC mix with foundry sand soaked in sulphate solution as opposed to reported 24%, 18% and 12% reduction by OPC concrete, Unary GPC and Binary GPC mix. Additionally, Ternary GPC mixes with natural sand submerged in chloride solution show a maximum strength drop of 7.2%, compared to an average loss of 11.54% for Unary GPC and 11% for Binary GPC mixes.
- Rebound hammer test performed on foundry sand and natural sand samples are in good conformity with the results reported in destructive tests. Although the compressive strength of foundry sand samples stored in ambient conditions is found to be smaller than that of natural sand samples, foundry sand samples also satisfy the strength conformity requirement of [57] by a wide margin. As a result, boosting the use of foundry sand in GPC mixes can help alleviate natural resource scarcity in the coming years.
- The difference in % transmittance obtained in FTIR analysis in the range of ~1000 cm^{-1} is a clear indication of deterioration of Si-O-Al chains as well as hinderance in formation of C-A-S-H and N-A-S-H gels due to attack by aqueous solution of chloride and sulphate. This is inline with results obtained during strength testing of specimens. A wide peak observed at 3400 cm^{-1} in FTIR

analysis corresponds to formation of H-bridge in -OH bonds indicating intrusion and subsequent action deteriorating the strength of concrete under chloride and sulphate action.

- As seen in SEM images, ingress of sulphate has made the microstructure of concrete rougher and more porous. The disintegration caused leads to strength loss and explains the reduction observed in mix containing Foundry sand. A similar but less invasive observation has been made in SEM images of sample under chloride attack supporting the observation of strength reduction seen in the mix containing Natural sand.
- XRD analysis of the geopolymer samples after the exposure to the Na_2SO_4 solution did not indicate formation of any new phases formed due to a reaction with sulfate ions. The Control-FS and the Sulphate-FS specimens contained only the phases originating from the mother sample. Chloride-NS specimen form minerals bound with unreacted compounds such as calcium chloride and magnesium chloride proving minimum chloride penetration to not produce free ions in geopolymer concrete and cause deterioration proving its superiority.

Credit Author Statement

Lokesh Choudhary: Data curation, Conceptualization, Formal analysis, Investigation, Methodology, Roles/Writing: Writing-Original draft, Review and editing, Vaishali Sahu: Supervision, Roles/Writing: Review and editing, Archanaa Dongre: Supervision, Roles/Writing: Review and editing. Anu Tonk: Analysis, Review.

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Declaration of Competing Interest
The authors declare that there is no conflict of interest in any form for the present manuscript.

Data Availability Statement
The relevant data and other details concerning the present work can be shared by the corresponding author on reasonable requests.

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