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Green quaternary concrete composites: Characterization and evaluation of the mechanical properties

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Industrial byproducts such as fly ash (FA), silica fume (SF), ground granulated blast furnace slag (GGBS), metakaolin (MK), and lime powder (LP), popularly known as supplementary cementitious materials (SCMs), have been extensively used in the manufacturing of cement and cement products in binary and ternary modes. In the present study, attempt has been made to develop a new sustainable green quaternary binder by partially replacing ordinary Portland cement (OPC) with different percentages of SCMs and find the optimum mix that can provide the best results in terms of mechanical as well as durability properties. The motivation is to reduce our dependency on OPC to reduce carbon foot print and utilizing these industrial byproducts for the sustainable development. Different compositions of quaternary binders were prepared and their physical, mechanical, and durability properties were studied and compared with the OPC and binary cement product pozzolanic Portland cement (PPC). The mechanical properties of concrete prepared with these OPC, PPC, and quaternary binders were also studied and it is established that the concrete mixtures prepared with quaternary binders provided better results and proved to be more economical. It is concluded that quaternary binders (a) OPC70% + FA15% + SF7.5% + GGBS7.5%, (b) OPC70% + FA15% + SF7.5% + MK7.5%, (c) 50%OPC + 30%FA + 10%SF + 10%GGBS, and (d) 50%OPC + 30%FA + 10%SF + 10%MK have produced relatively better strength, improved durability, and resistance to sulfate attack. These findings were also supported with the microstructural studies of hardened concrete of M20 grade using scanning electron microscope (SEM) and X-ray diffraction (XRD).

KEYWORDS
binary concrete, durability, green quaternary concrete, microstructure, SCMs

1 | INTRODUCTION

Concrete is one of the most versatile construction materials and it is commonly used in the construction industries due to its ability to form or adopt any shape, easy availability of the constituents, and cost effectiveness.[1] Before the advent of pozzolanic Portland cement (PPC), ordinary Portland cement (OPC) was a major constituent of the concrete to act as a hydraulic binder. Still, OPC is widely used and its manufacturing puts heavy environmental burden by emitting large amount of CO_2 in the atmosphere. It has been reported that 1 ton of cement releases 0.87 tons of CO_2.[2,3] Hence, supplementary cementitious materials (SCMs) are introduced to produce binary and ternary cements to reduce carbon footprint in cement production. PPC (binary cement) is produced by blending 30–50% of fly ash (FA) and it occupies approximately 75% of the market. In recent years, ternary binders are also produced by adding industrial byproducts such as silica fume (SF), ground granulated blast furnace slag (GGBS), or metakaolin (MK) to further reduce the CO_2 emission. These binary and ternary cement products

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not only save the required quantity of OPC but also help in recycling the industrial byproducts and improve the mechanical properties and durability of concrete produced from these binary and ternary cement. It is established that introducing less reactive pozzolan in ternary mix where there is already a more reactive SF or rice husk is available, the synergy between these pozzolans is further improved and results are more encouraging. This is called synergy effect and it is very prominent in ternary mixtures than binary mixes. SCMs such as FA, SF, GGBS, MK, and lime powder (LP) are often available as waste materials from various industrial processes and it can significantly reduce the embodied energy of concrete produced. Judicious use of these SCMs is desirable in the current scenario when lots of emphasis is given to the conservation of energy and environment in lieu of achieving civil engineering design and construction benefits.

Recent researches have also focused on preparing quaternary cement binders by addition or partial replacement of these SCMs in OPC. Previous studies[4–7] on quaternary binders have already indicated their suitability and the effect of addition of these SCMs are identified and quantified as filler effects, heterogeneous nucleation, and pozzolanic reactions based on amount and solubility of amorphous silica. Filler action involves occupying smaller pores by these finer SCMs left in the OPC and thereby producing a denser matrix and achieving improved properties. Heterogeneous nucleation is a physical process that leads to chemical activation of the hydration of OPC. In this, the particles of SCMs act as nucleation center for the hydrates and hence the hydration process.[8] SCMs contain good amount of amorphous silica and it improves the pozzolanic action between amorphous silica and calcium hydroxide/portlandite (CH) produced during hydration process to finally get non-water soluble calcium silicate hydrates (C-S-H). Due to swelling of reaction products, the density of C-S-H is much lower than CH and pure silica. From the mechanical, durability, and microstructure studies,[5,9,10] it is established that concrete so produced with the help of the quaternary binders are more resistive to all weathering actions. The amount of calcium hydroxide, which is vulnerable to chemical attack, is reduced by adding limestone fillers, blast furnace slag, and natural pozzolana, which in turn improves the resistance of concrete in aggressive environment, especially acidic due to sulfuric acid.[11] The slag has a stable and uniform chemical composition compared to FA, SF, and other natural pozzolan and therefore it is very much liked in the cement industry. Use of slag insures low heat of hydration, good resistance to acids, and sulfate attacks and provides better workability and high ultimate strength.[7,12] C-S-H hydration is further enhanced with the use of additional pozzolanic materials in the form of SCMs and it helps in giving denser matrix to concrete.[8,13]

Rodriguez-Camacho,[14] Kaid et al.,[15] Mostafa et al.,[16] and Ghrici et al.[17] have worked on SCMs and studied the behavior of fresh and hardened concrete with the use of pozzolanic materials. Natural pozzolan have been used in concrete to study its economic and environmental benefits and it was also found that the permeability of the concrete gets reduced considerably,[18–22] which is important for the corrosion protection of reinforced cement concrete (RCC). SCMs in ternary blends have shown promising results in terms of improvement in strength, durability, and reduced heat of hydration in comparison to unitary and binary blends.[23] Silica rich SCMs like GGBS, FA, and MK are considered to the most probable and well investigated cement substitutes and it has been well utilized in binary, ternary, and to some extent in quaternary blends.[24–27] FA and SF in ternary cements provide better compressive strength than binary blends. Extensive literature review suggested that synergy of binary blends (OPC + SF, OPC + FA, or OPC + GGBS) and ternary blends (OPC + GGBS + SF and OPC + FA + SF) has been well investigated and there is a need to explore synergy between quaternary blends.[11] The main objective of this research is to investigate the effects of different combinations of quaternary mix in cement concrete properties at both macro and micro level. Hence, it was proposed to investigate the synergetic effects of OPC, SF, GGBS/MK in quaternary blend by replacing different % of these SCMs with OPC and studying the mechanical properties of quaternary blend as well as concrete (M-20 grade) prepared with the quaternary blends that have shown promising results. Comparative studies are made with respect to corresponding results obtained for unitary and binary blends. The expected outcome of the study is finding the best mix proportion of SCMs with OPC for suggesting a quaternary blend that can provide favorable results for fresh and hardened concrete in terms of improving the physical and mechanical properties as well as improved durability. Microstructural studies through scanning electron microscope (SEM) and X-ray diffraction (XRD) are carried out to support the findings on sound scientific grounds.

2 | MATERIALS AND METHODS

OPC of 53 grade as per IS:8112-1989, FA as per IS:3812-2003, SF as per IS:15388-2003, GGBS, and MK in different proportion are used for the preparation of quaternary blend. Coarse aggregate (20–10 mm size with specific gravity 2.67) and fine aggregate (maximum size 4.75 mm with specific gravity 2.63) conforming to IS:456-2000 are used for the preparation of M20 grade concrete using unitary, binary, and quaternary blend as per the defined objectives of the present study. Table 1 presents the physical and chemical properties of these SCMs.

Table 2 provides information on various mix proportion of SCMs with OPC for controlled C series (100% OPC), binary F series (OPC + FA), and quaternary binders (G and M series) considered for the present study. For the

TABLE 1 Physical and chemical properties of SCMs

Description	OPC	FA	SF	BFS	MK
Physical characteristics					
Specific gravity	3.13	2.26	2.23	2.86	2.51
Blaine's fineness (cm^2/g)	2,285	3,720	16,018	3,250	8,735
Chemical compositions (%)					
CaO	67.81	2.01	1.28	36.80	1.56
SiO_2	18.58	62.32	88.31	41.55	51.48
Al_2O_3	9.92	26.18	0.89	16.21	47.83
Fe_2O_3	3.01	3.40	1.60	0.69	0.39
MnO	0.03	0.02	0.00	0.04	0.00
MgO	1.34	2.70	0.15	3.56	0.10
K_2O	0.49	0.99	1.98	0.68	0.19
Na_2O	0.23	0.06	0.40	0.20	0.07
LOI	0.88	2.98	2.00	1.09	0.56

SCMs = supplementary cementitious materials.

repeatability and reproducibility, five specimens for each trial mix composite were prepared and tested.

Compressive strength of the hardened concrete is measured as per the standard procedure given in IS:516-1959. Standard concrete cubes of dimensions 150 × 150 × 150 mm are prepared and tested in 200T capacity UTM. The rate of loading was kept as 14 N mm^{-2} min^{-1} and the compressive strength of average of three specimen showing variation within 10% were considered and reported after 7, 28, 56, 90, 180, and 265 days of curing.

Split tensile test was conducted as per IS:5816-1999 in which a cylindrical specimen of diameter 150 mm and height 300 mm was prepared and tested after 7, 28, 56, 90, 180, and 365 days of curing. The split tensile strength of average of three specimens showing variation within 10% was considered and reported.

Flexure strength was carried out as per IS:516-1959 (reaffirmed 2004) using standard 100 × 100 × 500 mm beam specimens, simply supported on an effective span of 400 mm and loaded at the third points after 7, 28, 56, 90, 180, and 365 days curing.

Durability tests were conducted for which additional concrete specimens were prepared to perform the tests like ultrasonic pulse velocity (UPV), chloride ion penetration, and sulfate expansion test.

SEM study was conducted to identify the morphological characteristics of the concrete mix prepared from quaternary binders. The test was conducted as per standard procedure established by the laboratory.

XRD method was performed to study the structure of minerals compositions and understand their properties. XRD was performed on a Bruker AXS diffractometer by employing Cu-Ka radiation in range of 2 hr = 10 to 70 maintained at 40 kV and 30 mA to detect various mineral phases. The diffraction data provided by JCPDS (International Centre for Diffraction Data, http://www.icdd.com/) was used to identify and specify mineralogical phases as present in the concrete mix prepared from quaternary blends.

TABLE 2 Various mix proportion of OPC and SCMs used for the experimental work

		Proportion of binder components (%)				
Series	Type of binders	OPC	FA	SF	GGBS	MK
C	Unitary/control	100				
Series F	Binary					
F1		70	30			
F2		50	50			
Series G	Quaternary					
G1		70	20	5	5	
G2		70	15	7.5	7.5	
G3		50	30	10	10	
G4		50	20	15	15	
G5		50	15	20	15	
Series M	Quaternary					
M1		70	20	5		5
M2		70	15	7.5		7.5
M3		50	30	10		10
M4		50	20	15		15
M5		50	15	20		15

FA = fly ash; GGBS = ground granulated blast furnace slag; MK = metakaolin; OPC = ordinary Portland cement; SCMs = supplementary cementitious materials; SF = silica fume.

3 | RESULTS AND DISCUSSION

3.1 | Workability study

As per IS:456-2000, workability can be achieved by proper placement and compaction of concrete. Workability was measured for unitary, binary, and quaternary by slump value test as per IS 1199. Super plasticizer (glenium 51) was added to make concrete in pumpable mode. High workability for M20 grade of normal concrete was achieved due to the 0.5 water–cement ratio and 2% super plasticizer. The range of slump value was in between 100 and 160 mm and it is illustrated in Table 3. For M20 grade concretes, the binary mixes showed 126 and 147 mm slump values that were higher than the corresponding values obtained for the controlled mix. It is worth mentioning that in all the cases other than controlled concrete, water–binder ratio of 0.50 was maintained and 2% super plasticizer (glenium 51) was added to achieve the slump value in between 125 and 150 mm. Due to the very high fineness of SF, the desired workability was not achieved with water. Owing to the spherical particle size of FA and less surface area of GGBS and FA compared to MK, the highest slump value was observed in the mix G3 compared to all other quaternary combinations and control mix. Entire tests were performed at ambient room temperature only. In binary concretes, the slump value increases with increase in the % FA. The quaternary concretes prepared

TABLE 3 Workability (slump) of M20 grade of quaternary concrete

Combinations	Mix series	Slump (mm)
100% control	C	112
OPC 70% + FA 30%	F1	126
OPC 50% + FA 50%	F2	147
OPC 70% + FA 20% + SF 5% + GGBS 5%	G1	139
OPC 70% + FA 15% + SF 7.5% + GGBS 7.5%	G2	140
OPC 50% + FA 30% + SF 10% + GGBS 10%	G3	157
OPC 50% + FA 20% + SF 15% + GGBS 15%	G4	149
OPC 50% + FA 15% + SF 20% + GGBS 15%	G5	144
OPC 70% + FA 20% + SF 5% + MK 5%	M1	142
OPC 70% + FA 15% + SF 7.5% + MK7.5%	M2	149
OPC 50% + FA 30% + SF10% + MK 10%	M3	151
OPC 50% + FA 20% + SF 15% + MK 15%	M4	149
OPC 50% + FA 15% + SF 20% + MK 15%	M5	146

FA = fly ash; GGBS = ground granulated blast furnace slag; MK = metakaolin; OPC = ordinary Portland cement; SF = silica fume.

with SF and GGBS as well as SF and MK showed slightly low workability due to higher surface area of SF, GGBS, and MK. The mix corresponding to [50%OPC + 30%FA + 10%SF + 10%GGBS] and [50%OPC + 30%FA + 10% SF + 10%MK] showed higher slump values when compared to all other combinations.

3.2 | Compressive strength test

Table 4 provides the compressive strength M20 grade concrete at 7, 28, 56, 90, 180, and 365 days of curing. It is seen that the compressive strength values increases with the curing time for all cases although with reduced rate of strength gain. Controlled concrete with 100% OPC attained required compressive strength as per IS:456-2000. In binary concrete (F1, F2), it was observed that the strength of the concrete reduced with increased FA percentage level from 30 to 50% which can be attributed to the properties of FA that suppress the heat of hydration of cement and in turn require longer curing period for pozzolanic reactions. In case of quaternary concretes (G and M series), compressive strength of G1, G2, G3, M1, M2, and M3 were relatively higher than the compressive strength of other mixes reported at 365 of curing period. The higher compressive strength in the above mentioned mix combinations in the quaternary concrete may be attributed to the formation of high volume of C-S-H during the hydration reaction. These findings are also supported by literature[24] in which it is confirmed that compressive strength of concrete improves not only with continuing curing for longer duration but also with the replacement of cement with pozzolanic materials and the strength values are significantly higher than the corresponding values obtained for controlled concrete at different durations of curing.

It was also observed that the higher % rate of SF at 15 and 20% makes concrete mix sticky, which reduces the fresh properties of concrete and hampers mixing and compaction process. This leads to the reduction in compressive

TABLE 4 Compressive stresngth of M20 grade of quaternary concretes

Mix (↓)	Compressive strength (N/mm^2)					
Age (days)→	7	28	56	90	180	365
C	23.97	27.6	29.9	32.08	38.9	39.01
F1	20.21	25.7	30.15	33.7	41.4	46.10
F2	17.93	21.41	24.8	26.93	32.11	35.40
G1	22.01	30.64	37.34	39.2	45.2	49.90
G2	23.46	31.09	38.1	39.67	46.7	51.20
G3	25.65	35.08	40.28	45.9	54.9	59.20
G4	19.05	22.22	26.34	37.27	39.16	43.94
G5	13.89	18.1	30.39	33.21	34.19	39.73
M1	20.19	39.44	44.93	46.21	52.16	58.39
M2	20.18	38.9	45.2	47.19	55.9	61.80
M3	20.29	39.54	46.18	48.56	57.2	63.90
M4	28.4	39.22	47.67	50.21	52.02	55.31
M5	27.09	29.8	38.9	41.02	46.79	49.20

strength and it was observed in G4, G5, M4, and M5 mixes. These mixes cannot be applicable to make concrete for heavy construction work.

3.3 | Split tensile strength

Table 5 summarizes the results of split tensile strength test of controlled, binary, and quaternary concrete and it can be observed that the strength increases with time due to continued pozzolanic reactions. The study reported that split tensile strength increases with increase in the FA content.[11] Although the study was conducted on binary blend, the similar results are obtained for quaternary blend. In the present study, series G1, G2, G3, and M2 for quaternary concrete syndicate higher tensile strength and G3 showed the highest value. It was also observed that quaternary binders having higher silica content due to presence of SF, GGBS, and MK show lower rate of strength gain with time. For quaternary concretes, as compared to 50% replacement level of OPC, 30% replacement of OPC

TABLE 5 Split tensile strength of concrete prepared from controlled, binary, and quaternary cement binders

Mix (↓)	Split tensile strength (N/mm^2)					
Age (days) →	7	28	56	90	180	365
C	2.4	2.97	3.5	3.79	3.98	4.01
F1	2.56	3.01	3.7	3.9	4.18	4.23
F2	2.66	3.12	3.89	4.1	4.29	4.56
G1	2.98	3.13	3.45	4.12	4.36	4.69
G2	3.1	3.29	3.94	4.18	4.32	4.60
G3	2.65	3.04	3.25	4.19	4.58	4.89
G4	2.66	3.12	3.34	3.45	3.51	3.55
G5	2.68	3.27	3.45	3.49	3.59	3.56
M1	2.89	3.12	3.49	3.98	4.21	4.39
M2	2.99	3.28	3.87	4.13	4.38	4.51
M3	2.45	2.99	3.53	3.8	3.99	4.10
M4	2.39	2.9	3.51	3.88	4.14	4.17
M5	2.48	2.89	3.52	3.89	4.13	4.18

shows better tensile strength development due to lower silica content. Reduction in the split tensile strength has been observed with corresponding increase in SF.[28] Also, it was concluded that split tensile strength of concrete does not increase significantly with replacement of very high percentage of SF.[29] It was observed that G4, G5, M4, and M5 mix quaternary combinations do not show much tensile strength due to the higher percentage of silica in the quaternary concrete.

3.4 | Flexural strength

Table 6 summarizes the flexural strength of unitary, binary, and quaternary concretes at 7, 28, 56, 90, 180, and 365 age days of curing. Test results indicate that flexural strength of the binary and quaternary concretes increases with time due to continued pozzolanic reaction. Quaternary mix G3 and M3 have shown the best flexure strength among all other combinations. Fifty percent of replacement of OPC with SCMs observed good strength compared to 30% replacement of OPC. Binary concrete with 50% FA does not show much flexural strength, but with 30% FA it has shown good effect and at the age of 365 days, the obtained flexural strength is higher than the controlled concrete.

It was also observed that the quaternary concrete combinations G1, G2, G3, M1, M2, and M3 have shown pronounced effect on flexural strength compared to controlled concrete. Higher percentage of silica content in concrete demanded more water and it leads to decrease in flexural strength. This observation was observed in G4, G5, M4, and M5 due to higher silica in quaternary mix combinations.

3.5 | Ultrasonic pulse velocity

UPV test is a nondestructive test of concrete to evaluate the quality of concrete and its matrix. The test is majorly used for finding defects or voids inside the concrete. The travel time of pulse over the predetermined length of travel is used to estimate the pulse velocity which directly indicates the quality of interior concrete. If a void, cavity or crack is present inside, the travel length of the pulse increases thereby reducing the pulse velocity. Hence, in principle, higher the pulse velocity better the concrete quality inside. Whitehurst (1951) has classified concretes in the following categories as (a) excellent, (b) good, (c) doubtful, (d) poor, and (e) very poor for the corresponding UPV values obtained as 4,500 m/s and above 3,500–4,500 m/s, 3,000–3,500 m/s, 2,000–3,000 m/s, and 2,000 m/s or below.

Table 7 provides the UPV values recorded for all mix proportions at different age of curing. It can be noted that UPV values ranged from 3,510 to 6,128 m/s and based on the above mentioned criteria, all the concrete mixes can be classified as good or excellent category. The maximum UPV was recorded 5,649 and 6,128 m/s for the mix G3 and M3, respectively.

TABLE 6 Flexural strength of concrete prepared with controlled, binary, and quaternary cement blends

Mix (↓)	Flexural strength (N/mm^2)					
Age (days) →	7	28	56	90	180	365
C	2.8	3.9	4.2	4.22	4.23	4.24
F1	2.02	3.0	3.33	4.09	4.62	4.65
F2	1.62	2.02	2.23	2.25	2.38	2.39
G1	3.28	4.42	5.23	5.82	5.83	5.89
G2	4.43	5.38	6.37	6.65	6.73	6.8
G3	5.03	6.65	7.12	7.78	8.02	8.03
G4	3.39	4.28	5.0	5.20	5.21	5.24
G5	2.82	3.36	4.43	4.67	4.72	4.76
M1	4.52	5.02	5.58	6.18	6.67	7.08
M2	4.82	5.65	6.08	6.68	7.03	7.08
M3	5.0	5.96	6.69	7.68	7.70	7.73
M4	3.36	4.48	5.65	5.71	5.73	5.74
M5	3.61	4.08	5.39	5.48	5.50	5.13

TABLE 7 Ultrasonic pulse velocity of concrete prepared with controlled, binary, and quaternary mixes

Mix (↓)	Pulse velocity (m/s)					
Age (days) →	7	28	56	90	180	365
C	3,287	3,342	3,568	3,982	4,147	4,793
F1	3,458	3,889	4,046	4,432	4,821	5,122
F2	3,448	3,628	3,893	3,974	4,579	5,269
G1	3,729	3,998	4,198	4,487	4,856	5,347
G2	3,838	3,977	4,342	4,749	4,991	5,377
G3	4,288	4,494	4,839	5,110	5,498	5,649
G4	4,129	4,378	4,658	4,992	5,228	5,556
G5	4,118	4,347	4,682	5,189	5,280	5,556
M1	4,007	4,438	5,203	5,399	5,422	5,689
M2	4,258	4,567	5,317	5,398	5,872	5,893
M3	4,175	4,332	5,119	5,349	5,583	6,128
M4	4,294	4,301	4,992	5,242	5,365	5,493
M5	4,158	4,190	4,378	4,739	5,084	5,259

UPV = ultrasonic pulse velocity.

3.6 | Chloride ion penetration test

Table 8 summarizes the results of the chloride penetration test (for permeability value) conducted as per ASTM C 1202-05, on concrete specimen prepared with controlled, binary, and quaternary cement binders. It can be observed that the quaternary concretes give better results when compared to the binary concretes. In quaternary concrete, the presence of FA along with other two SCMs in the quaternary blends, yielded higher reduction in the permeability compared to the binary blends. Reduction in total charge value designates the better resistance of chloride ion penetration and lower permeability. The lower chloride permeability of the quaternary concrete with high volume of SCMs is a result of dense microstructure and impermeable structure. Literature also suggests that denser matrix due to pozzolanic reactions of FA, SF, GGBS, and MK fill the available pores and results in significant reduction in the permeability values.[30–33]

TABLE 8 Chloride ion penetration values obtained for concrete prepared from controlled, binary, and quaternary blends

Mix (↓) Age (days) →	Chloride ion penetration test (C)			
	28	90	180	365
C	5,698	4,931	4,702	4,274
F1	2093	1,182	1,029	928
F2	1,082	982	898	820
G1	976	549	428	359
G2	854	424	326	281
G3	388	163	139	112
G4	329	134	109	98
G5	221	109	102	96
M1	958	761	549	482
M2	590	441	398	346
M3	316	115	105	87
M4	218	118	89	80
M5	220	112	83	79

From Table 8, it was observed that quaternary concrete provides better resistance to chloride ion penetration compared to binary and controlled concrete. At the age of 365 days, the total charged passed reduction was 78 and 80.8% in binary concrete mix F1 and F2 with respect to controlled concrete. Also, the charged pass reduced 91.6, 93.4, 97.3, 97.70, 97.75, 88.72, 91.90, 97.96, 98.12, and 98.15% in G1, G2, G3, G4, G5, M1, M2, M3, M4, and M5 mix combinations, respectively, compared to controlled concrete. From the results, it can be concluded that OPC with [FA + SF + GGBS] and [FA + SF + MK] together reacts well and provides better results in quaternary concrete compared to unitary and binary.

3.7 | Sulfate expansion

Table 9 shows compilation of results for the resistance to sulfate attack for M20 grade of concrete for different binders at various ages of curing. Percentage expansion was determined for all the mix combinations cured in 5% Na_2SO_4 + 3% MgSO4 solutions. It can be noted that resistance to sulfate attack increases with the partial replacement of cement by SCMs. For longer curing period, the ability of concrete to resist sulfate attack improves. Quaternary binder concretes provide better results than the binary binder and control concretes. The results obtained in the present study are in consistent with the previous findings which states that resistance to sulfate attack is improved by adding pozzolanic materials.[34–37] Improvement in resistance to sulfate attack is attributed to the reduced amount of calcium hydroxide, which is most vulnerable to sulfate attack. Results show that M4 has the highest resistance to sulfate attack.[38–40] The use of SCMs such as FA, GGBS, SF, and MK in different percentage of quaternary mix combinations has improved the resistance of sulfate attack because of the reduction of calcium hydroxide, which is the most susceptible to sulfate attack. These findings are also supported by the study which revealed that the high volume of pozzolan provides excellent functional properties due to its synergetic effect.[41]

TABLE 9 Sulfate expansion test conducted on concrete prepared from controlled, binary, and quaternary blends

Mix (↓) Age (days) →	Sulfate expansion (%)			
	56	90	180	365
C	0.28	0.36	0.52	0.68
F1	0.082	0.089	0.13	0.22
F2	0.059	0.068	0.096	0.14
G1	0.049	0.076	0.091	0.13
G2	0.062	0.084	0.097	0.12
G3	0.079	0.087	0.094	0.10
G4	0.082	0.097	0.099	0.15
G5	0.074	0.082	0.093	0.099
M1	0.056	0.065	0.089	0.096
M2	0.049	0.053	0.068	0.084
M3	0.063	0.071	0.078	0.088
M4	0.059	0.063	0.074	0.082
M5	0.068	0.075	0.081	0.085

From the studies it is concluded that the best proportions of quaternary binder in the concretes are (a) OPC70% + FA15% + SF7.5% + MK7.5%, (b) OPC70% + FA15% + SF7.5% + GGBS7.5%, (c) OPC50% + FA30% + SF10% + MK10%, and (d) OPC50% + FA30% + SF10% + GGBS10%. A microstructural study of concrete has been performed for the above binders and results were compared with the controlled concrete with 100% OPC.

3.8 | Microstructural study

3.8.1 | XRD studies

XRD studies were performed on those samples in which the compressive strengths were significantly high as compared to the other mixes. Two quaternary mix specimens having 7.5% (G2) and 10% (G3) GGBS and other two quaternary mix specimens having 7.5% (M2) and 10% (M3) MK were selected for the XRD analysis. The XRD diffraction pattern of the control specimen (100% OPC) is shown in Figure 1. The XRD diffraction patterns showed evidence that the presence of majority of crystalline phases of quartz and anorthite

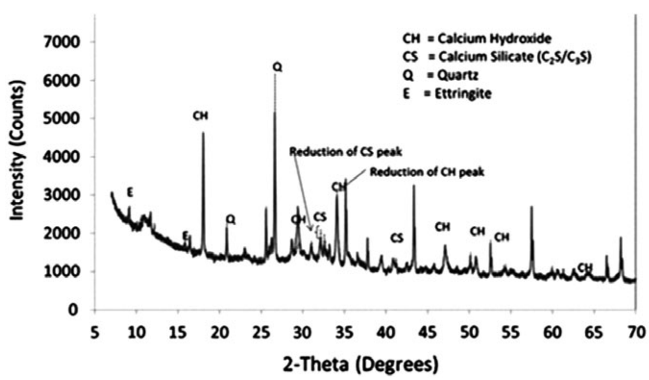

FIGURE 1 X-ray diffraction (XRD) pattern for M20 control specimen (100% ordinary Portland cement [OPC])

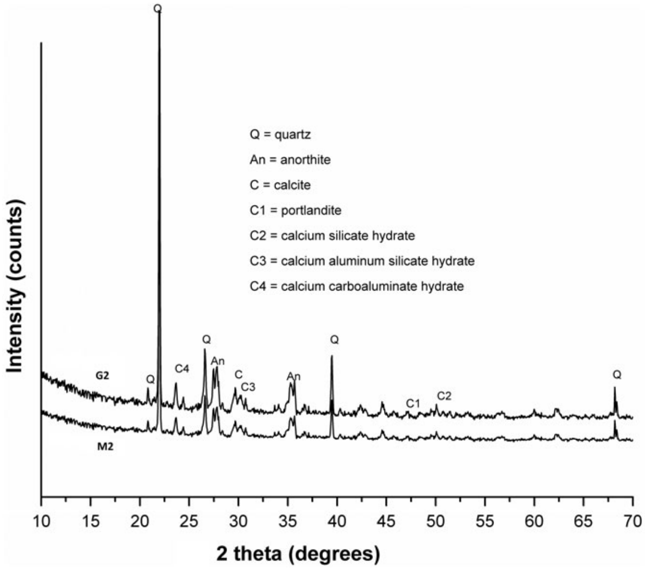

FIGURE 2 X-ray diffraction (XRD) of OPC70% + FA15% + SF7.5% + GGBS7.5% [G2] and OPC70% + FA15% + SF7.5% MK7.5% [M2]

(calcium aluminum silicate). The mineralogical alternations taking place due to the hydration processes were also identified as C-S-H (calcium silicate hydrate) and C-A-S-H (calcium aluminum silicate hydrate).

The XRD patterns in Figures 2 and 3 show sharp peaks of quartz that reflects the partly non reacted particles of FA and SF. The low-intensity peaks of calcium silicate hydrate (C-S-H), calcium aluminum silicate hydrates (C-A-S-H), and portlandite were also observed, which confirms the formation of cementitious compounds. However, it is very difficult to identify the peaks of CSH and CASH, but some of

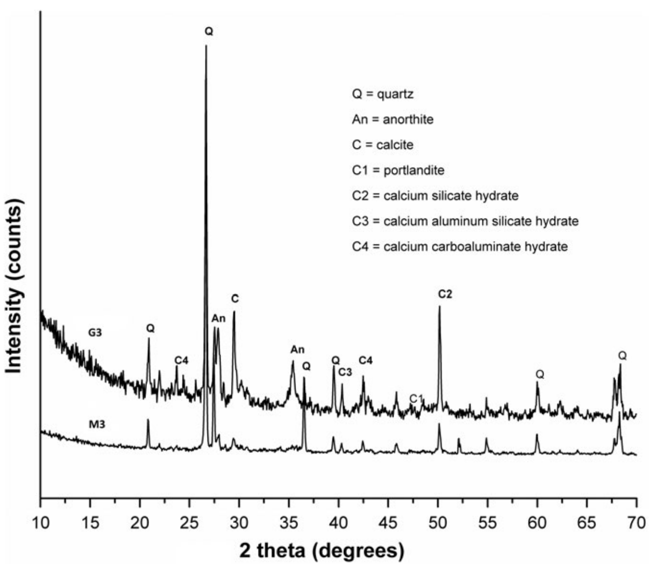

FIGURE 3 X-ray diffraction (XRD) of OPC50% + FA30% + SF10% + GGBS10% [G3] and OPC50% + FA30% + SF10% MK10% [M3]

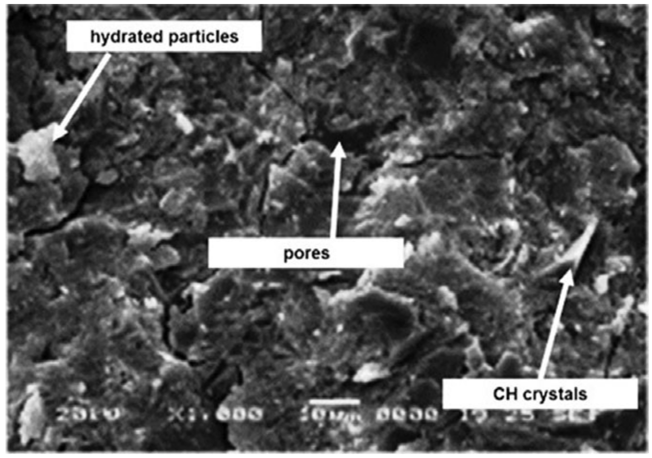

FIGURE 4 Scanning electron microscopic (SEM) image of 100% control concrete

the previous studies have also indicated the observance of these peaks.[42,43] In case of MK, an additional peak at 2θ equal to 36° is also observed. MK consists of significant

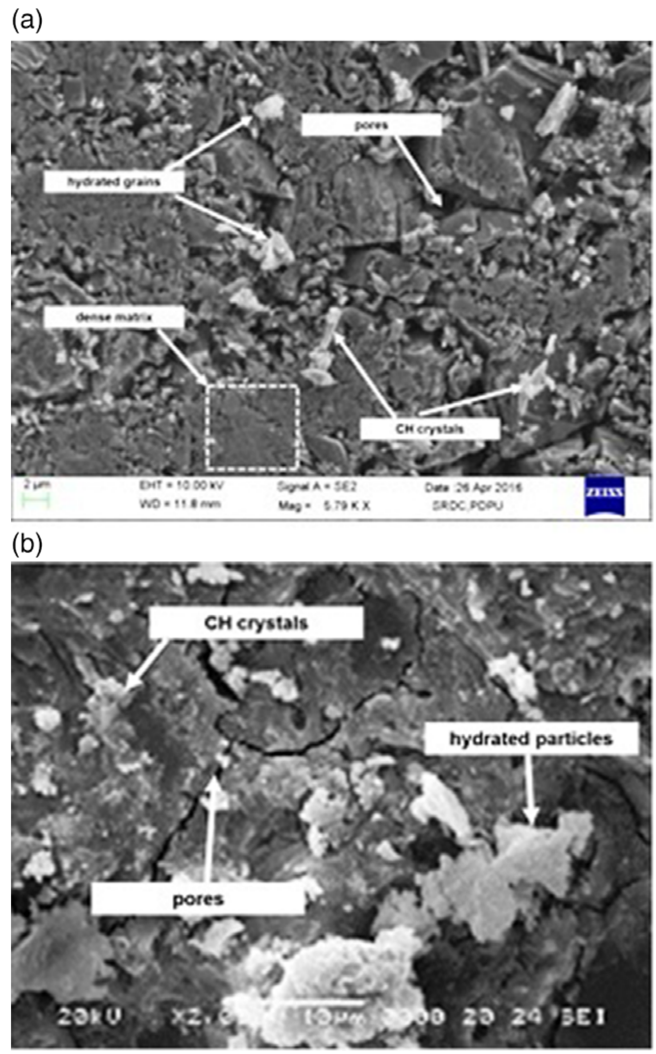

FIGURE 5 Scanning electron microscopic (SEM) photograph of (a) OPC70% + FA15% + SF7.5% + GGBS7.5% and (b) OPC70% + FA15% + SF7.5% + MK7.5%

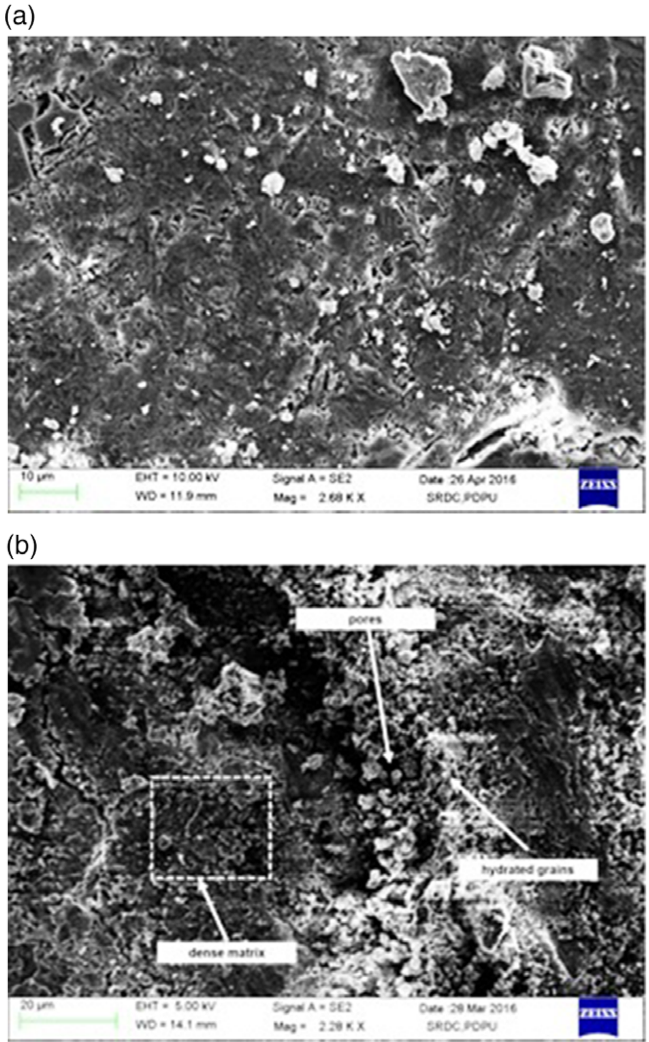

FIGURE 6 Scanning electron microscopic (SEM) photograph of (a) OPC50% + FA30% + SF10% + GGBS10% and (b) OPC50% + FA30% + SF10% + MK10%

amount of silica and alumina, which helps in the formation of calcium aluminum silicate hydrate. At 2θ equal to 50°, the specimen containing GGBS shows a very sharp peak, which may be due to presence of quartz. However, at the same 2θ angle, the MK sample shows less pronounced peak of C-S-H formed as a result of the dissolution of the quartz. In addition, calcite and calcium carboaluminate hydrate peaks are also detected due to their formation along with cementitious compounds. The XRD results support the compressive strength test results where in 50% OPC + 30% FA + 10% SF + 10% GGBS (G3) and 50% OPC + 30% FA + 10% SF + 10% MK (M3) were found to attain higher strengths as well. The formation of ettringite in the XRD diffraction patterns of any of the samples was not observed. This may be due to the very low sulfate content in the specimen.

3.8.2 | SEM studies

SEM studies were performed to analyze the microstructures of various combinations. Figure 4 shows the SEM image of 100% controlled concrete, whereas Figures 5 and 6 show SEM images of selected combinations shows best performances in terms of both strength and durability. As shown in Figure 6a,b with the replacement of 30% of cement by SCMs like FA, SF, and GGBS/MK, the microstructure shows a very dense matrix. It is obvious that as the matrix is denser, it reduces the pores and improves the contact between the aggregates. Supplementary materials like SF and MK are very fine particles and when they are replaced with cement, they can easily occupy the available void spaces thereby reducing the pores. Due to this the chances of formation of micro-cracks are also reduced.

4 | CONCLUSION

1. The quaternary concretes containing SCMs achieved excellent strength, durability, and a dense microstructure. It indicates that by using SCMs high to very high strength concrete can be obtained by utilizing several industrial byproducts. Therefore, quaternary concretes can be safely used for construction purposes and its application may reduce our dependency on OPC.
2. The findings indicate that the quaternary combinations are more effective as compared to binary combination. The synergetic effects were observed when more than one SCMs in concrete were utilized. Also, the SF, GGBS and MK were able to fulfill all the mechanical and durability properties of concrete. Therefore, utilization of SCMs in concrete may help to reduce the burden on natural raw materials used in OPC.
3. Based on the comprehensive study of physical, mechanical, and microstructural properties of the quaternary mixes, the following quaternary binder mixes can be suggested for utilization in the construction industry, that is, (a) OPC70% + FA15% + SF7.5% + GGBS7.5% and (b) OPC50% + FA30% + SF10% + GGBS10%.
4. The acute shortage of raw materials for the manufacture of OPC as well as PPC can be fulfilled by the utilization of quaternary binders. It will not only reduce the overall construction cost but also promote the application of industrial byproducts in the construction practices.

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