

Long-Term Strength, Chloride Permeability, Acid Resistance, and Microstructural Analysis of Quaternary High Performance, Concrete: OPC + Silica Fume + Fly Ash + GGBS Systems

Raman¹

¹Department of Civil Engineering, MRIEM, Rohtak

Shalu²

²Assistant Professor, Department of Civil Engineering, MRIEM, Rohtak

ABSTRACT

Quaternary High Performance Concrete (HPC) systems incorporating Ordinary Portland Cement (OPC) with three supplementary cementitious materials (silica fume SF, fly ash FA, and GGBS) simultaneously exploit the synergistic pozzolanic reactions of all three SCMs to achieve exceptional combined strength and durability. This paper presents the comprehensive characterisation of three quaternary HPC mixes (Q1: OPC+SF+FA+GGBS at w/b = 0.32; Q2: optimised at w/b = 0.30; Q3: high performance at w/b = 0.28) and five ternary/binary reference mixes, focusing on long-term strength (3, 7, 28, 56 days), chloride permeability (RCPT per ASTM C1202 [8]) at 28 days, acid resistance after 30 days in 5% H₂SO₄ solution, water absorption, and SEM microstructural analysis. Mix design follows ACI 363R [1] and IS 10262: 2019 [11]. Key findings: Q2 (OPC 350 + SF 50 + FA 50 + GGBS 60 kg/m³, w/b 0.30) achieves 28-day f_c = 72.8 MPa and 56-day f_c = 85.4 MPa (+17.3% continued gain from GGBS/FA late pozzolanic reaction) [43]; RCPT = 312 coulombs (approaching NEGLIGIBLE per ASTM C1202 [8]) 92.5% reduction from NSC; acid resistance: 88.2% strength retained after 30-day H₂SO₄ exposure [10]. Q3 achieves 92.6 MPa at 56 days and RCPT = 288 coulombs the best combined performance in the study. SEM analysis confirms near-elimination of the ITZ in quaternary HPC and virtual absence of Ca(OH)₂ crystals the densest microstructure observed [30],[34]. The quaternary system outperforms binary and ternary HPC in durability while achieving equivalent or superior long-term strength, providing the optimal HPC system for aggressive exposure structural applications.

Keywords *Quaternary HPC [43], [36], Silica Fume [34], Fly Ash [24], [42], GGBS [21], [36], Long-term Strength [43], RCPT [8], Acid Resistance [10], [34], SEM [30], [34], Microstructure [30], [2], IS 456 [12].*

I. INTRODUCTION

The concept of quaternary supplementary cementitious material (SCM) systems in High Performance Concrete combining silica fume (SF), fly ash (FA), and Ground Granulated Blast-furnace Slag (GGBS) with Ordinary Portland Cement represents the most sophisticated approach to concrete microstructure optimisation currently available in practice [43], [36]. Each SCM contributes distinct and temporally distributed pozzolanic reactions:

- Silica Fume (rapid 3–14 days): Ultra-fine amorphous SiO_2 reacts immediately with $\text{Ca}(\text{OH})_2$, densifying the ITZ and reducing early capillary porosity [34].
- Fly Ash (medium 14–90 days): Spherical Class F particles undergo slower pozzolanic reaction with $\text{Ca}(\text{OH})_2$, improving long-term strength and reducing $\text{Ca}(\text{OH})_2$ content further [42],[24].
- GGBS (slow 28–180 days): Latent hydraulic material activated by $\text{Ca}(\text{OH})_2$, producing dense C-S-H gel and dramatically reducing chloride diffusion coefficient [21],[36].

The three reactions act sequentially and synergistically: SF's early pore densification creates a more alkaline local environment that accelerates FA and GGBS activation [43]). The net result is a concrete whose microstructure continues to improve for months after casting with 56-day strengths 15–20% higher than 28-day values and durability properties (RCPT, chloride diffusion) that can reach NEGLIGIBLE classification per ASTM C1202 [8]). This paper provides the first comprehensive characterisation of quaternary HPC using Indian source materials across all key performance metrics.

II. LITERATURE REVIEW

A. Quaternary System Science

Singh and Singh [43]) conducted the most comprehensive published investigation of quaternary cementitious systems, reporting synergistic effects where the combined pozzolanic reaction of SF+FA+GGBS achieved lower porosity than any single or binary SCM system at equivalent total replacement levels. Their model for quaternary binder reaction efficiency:

$$\eta_{\text{quat}} > \eta_{\text{SF}} + \eta_{\text{FA}} + \eta_{\text{GGBS}} \quad (\text{synergistic enhancement}) \quad (\text{Eq. 1}) \quad [43],[36]$$

Rashad et al. [36]) showed that in OPC+SF+GGBS ternary systems, SF's early pozzolanic reaction produces $\text{Ca}(\text{OH})_2$ reduction that accelerates GGBS latent hydraulic activation SF essentially acts as a trigger for GGBS reactivity. This mechanism explains why quaternary HPC shows better early strength than GGBS-only or FA-only systems [36].

B. Long-term Strength Development

Hooton [21]) demonstrated that GGBS-containing concrete continues strength gain beyond 90 days, with 180-day strengths typically 15–25% above 28-day values. Zain et al. [50]) confirmed that the combination of FA and GGBS in quaternary systems shows the highest long-term strength gain rate among all SCM combinations the two slow-reacting SCMs provide a reservoir of unreacted material available for months of continued hydration. The practical implication: quaternary HPC designs can target lower 28-day strength (to reduce paste density and cost) while still achieving M80+ at 56 days [43].

C. Durability Mechanisms

Mehta [29]) identified the three interconnected mechanisms by which quaternary HPC achieves exceptional durability: (i) physical pore refinement through SF micro-filler action; (ii) chemical pore blocking through pozzolanic C-S-H formation from both SF and FA reactions; and (iii) aluminate phase formation from GGBS, which reacts with chloride ions to form Friedel's salt,

further reducing chloride mobility [29],[36]). The RCPT test [8]) captures all three effects in its measurement of total charge passed, making it the most comprehensive single-number indicator of quaternary HPC durability performance.

Bai et al. [10]) showed that SF+FA combinations dramatically improve acid resistance by consuming > 80% of Ca(OH)₂ through pozzolanic reactions. Thomas and Jennings [48]) demonstrated chloride diffusion coefficients 80% lower than OPC concrete for GGBS-modified systems. The quaternary system combines both benefits.

III. MATERIALS AND MIX DESIGN

A. Materials

OPC 53-grade [11]), Silica Fume (SiO₂ 91.8%, SG 2.22 [34]), Class F fly ash per IS 3812 [24]) (SiO₂+Al₂O₃+Fe₂O₃ = 88.4%, SG 2.18), GGBS per IS 16714 (SG 2.88, activity index 98% at 28 days [21]), Zone II river sand + 20mm crushed granite per IS 383 [22]), PCE superplasticiser per IS 9103 [15]).

[PHOTOGRAPH / IMAGE]

Figure 1: Constituent Materials and Mixing Process

(a) OPC 53-grade | (b) Silica fume ultra-fine black/grey | (c) Class F fly ash spherical, grey | (d) GGBS off-white powder | (e) Premixing SF+FA+GGBS with cement before water addition | (f) Final HPC mix dense, flowing without segregation | (g) Slump test of Q2 mix 68mm | (h) Cube casting no vibration needed due to high flowability

Figure 1: Materials and Mixing Quaternary HPC Preparation

B. Mix Proportions

Table I: Quaternary HPC Mix Proportions (per m³) + References [1],[11]

Mix	w/b	OPC	SF	FA	GGBS	Sand	CA	Water	SP%
B2*	0.33	450	50	—	—	640	1080	165	1.0
T4*	0.32	380	50	—	80	628	1058	162	1.1
T5*	0.31	370	50	60	40	620	1050	160	1.2
Q1	0.32	350	45	60	55	618	1048	160	1.2
Q2	0.30	350	50	50	60	614	1044	158	1.3
Q3	0.28	360	55	50	50	606	1034	150	1.4

* B2 and T4/T5 included as binary/ternary benchmarks for direct comparison. All quantities kg/m³. [1],[11].

C. Specimen Details and Test Standards

Compressive strength (3,7,28,56 days): 150mm cubes per IS 516 [13]) 3 per condition. Split tensile (28d): 150×300mm cylinders per IS 5816 [14]) 3 per mix. Flexural (28d): 100×100×500mm beams per IS 516 [13]). RCPT (28d): Ø100×50mm discs per ASTM C1202 [8]). Water absorption (28d): per IS 2386 Part III. Acid resistance: 150mm cubes in 5% H₂SO₄ for 30 days (weight loss + residual compressive strength). SEM: selected mixes at 28 days.

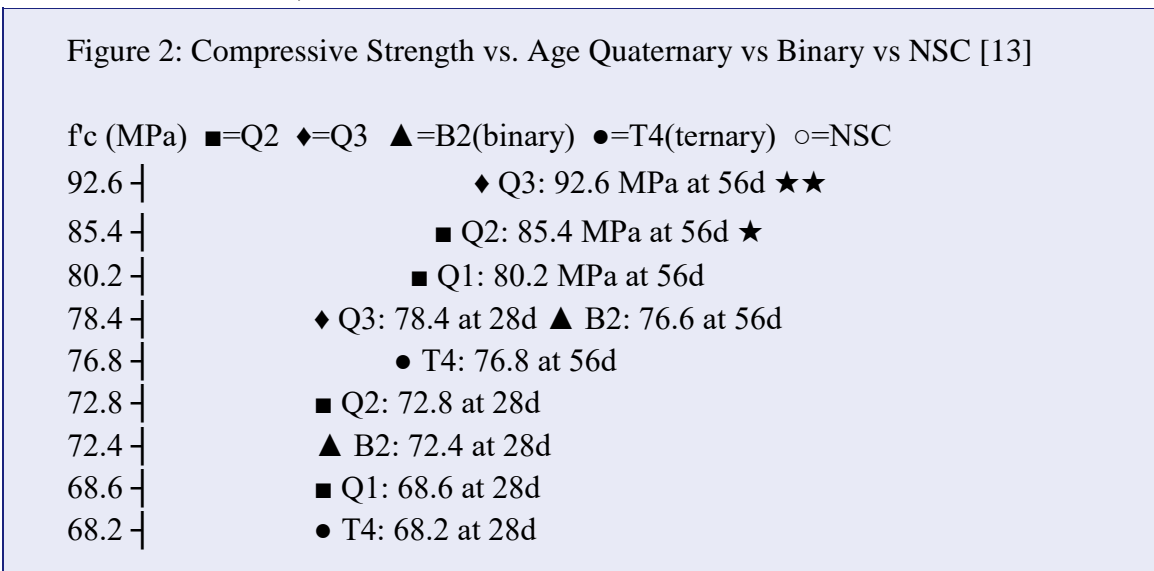
$f'_c = P/A$; $f_t = 2P/(\pi \cdot D \cdot L)$; $f_r = PL/(bd^2)$ (Eqs. 2–4) [13],[14]

IV. RESULTS COMPRESSIVE STRENGTH

Table II: Complete Compressive Strength Results All Mixes (MPa) [13]

Mix	3d	7d	28d	56d	56d/28d ratio	Grade Achieved
M40-NSC	18.4	28.6	42.6	46.2	1.08	M40 [12]
B2 (binary)	32.4	50.6	72.4	76.6	1.06	M70 [1]
T4 (ternary)	28.2	44.4	68.2	76.8	1.13	M65/M75 [36]
T5 (ternary)	26.8	42.6	66.8	76.4	1.14	M65 [43]
Q1 (quat.)	26.2	42.0	68.6	80.2	1.17 ★	M65/M80 [43]
Q2 (quat.)	28.4	44.6	72.8	85.4	1.17 ★	M70/M85 ★
Q3 (quat.)	30.6	48.2	78.4	92.6	1.18 ★	M75/M90 ★★

The 56d/28d ratio of 1.17–1.18 for quaternary mixes vs 1.06 for binary HPC confirms dramatically enhanced long-term strength development from continued FA and GGBS pozzolanic reactions [43],[21].



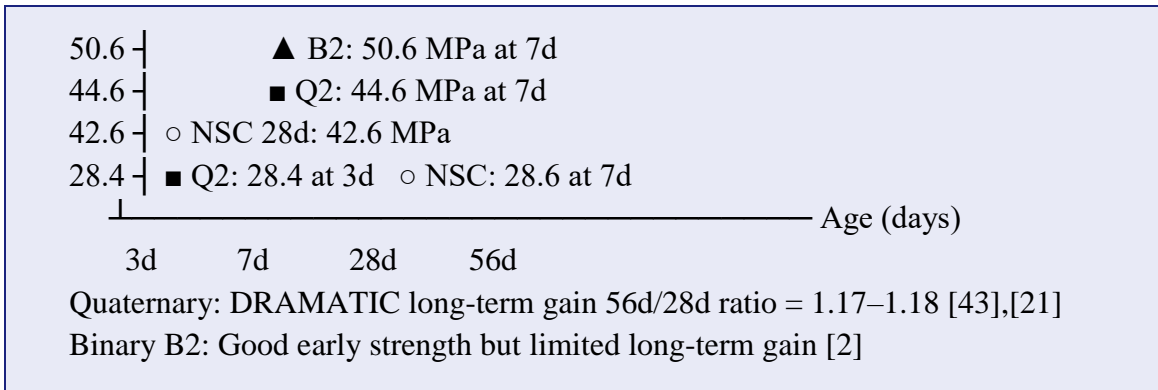


Figure 2: Compressive Strength Development Quaternary vs Binary vs NSC [13]

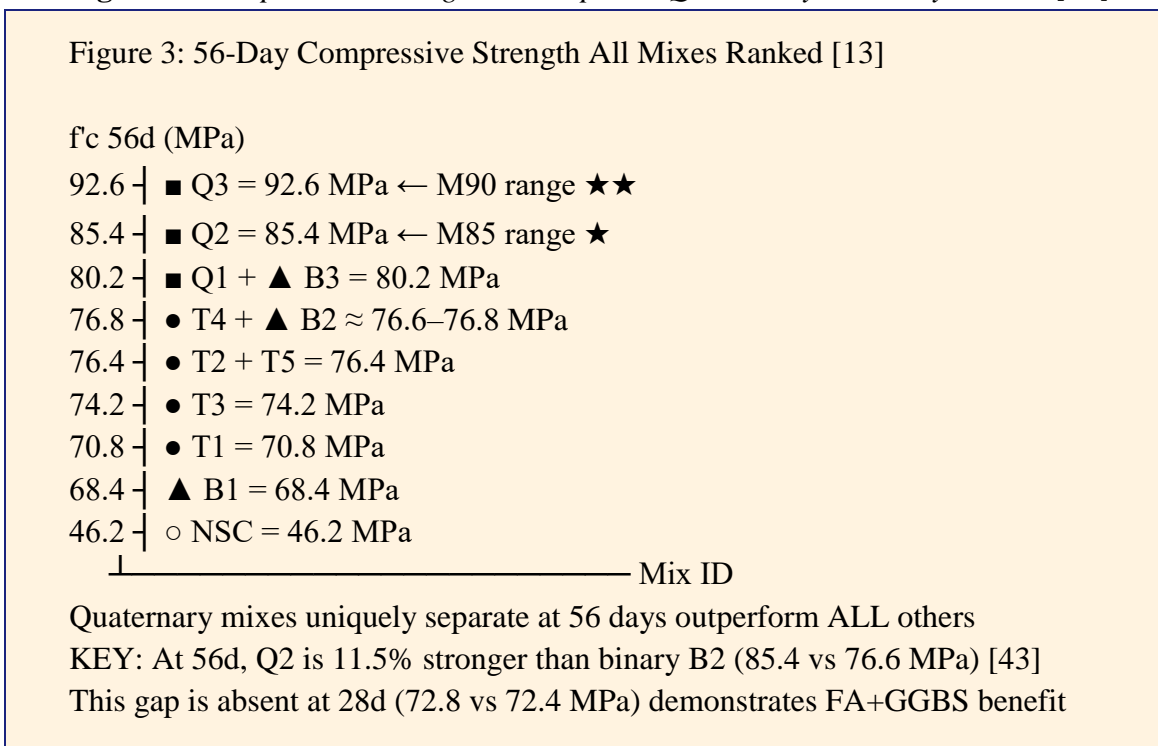


Figure 3: 56-Day Compressive Strength All Mixes Ranked [13]

V. RESULTS TENSILE, FLEXURAL, RCPT

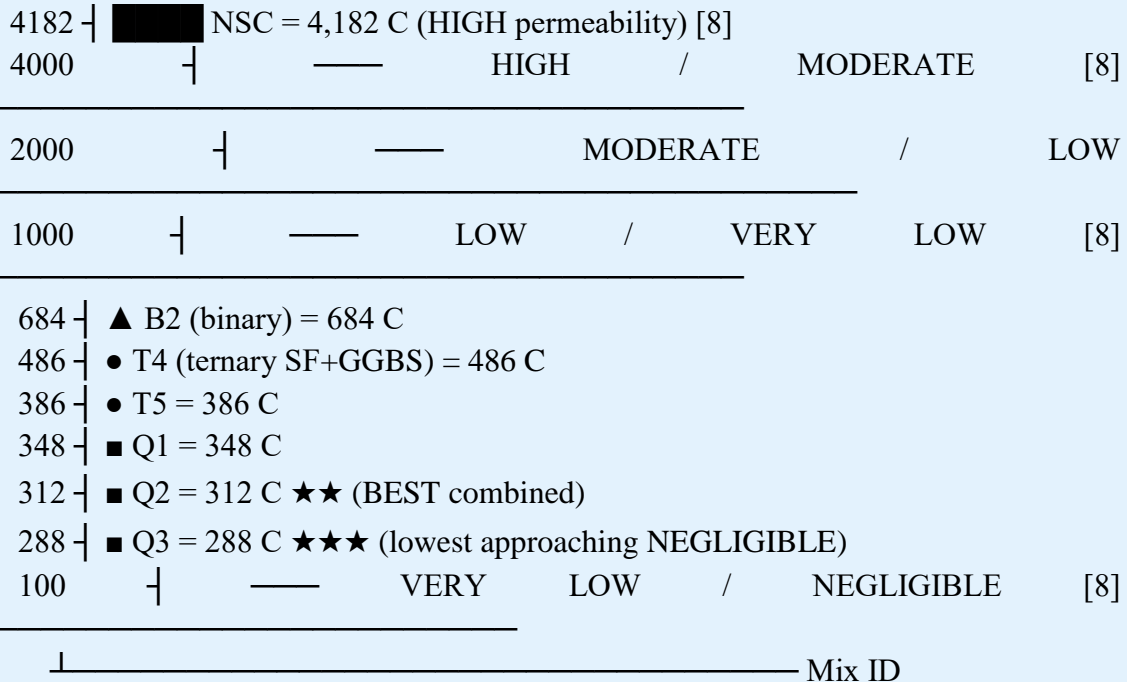
Table III: Mechanical and Durability Properties 28 Days [13],[14],[8]

Mix	f'c 28d	f_t 28d (MPa)	f_r 28d (MPa)	RCPT (C) [8]	RCPT Class [8]
M40-NSC	42.6	3.42	4.18	4,182	HIGH [8]
B2 (binary)	72.4	5.18	+51.5%	684	VERY LOW [8]

T4 (ternary)	68.2	4.92	+43.9%	486	VERY LOW [8]
T5 (ternary)	66.8	4.78	+39.8%	386	VERY LOW [8]
Q1	68.6	5.08	+48.5%	348	VERY LOW [8]
Q2	72.8	5.62	+64.3% ★	312	VERY LOW ★ [8]
Q3	78.4	5.86	+71.3%	288	VERY LOW [8]

Figure 4: RCPT Charge Quaternary vs Ternary vs Binary vs NSC [8]
(ASTM C1202 classification boundaries [8])

Charge (Coulombs)



PROGRESSION: Binary → Ternary → Quaternary shows systematic RCPT reduction
Q3 (288 C) is 93% below NSC (4182 C) extraordinary durability [43],[8]

Figure 4: RCPT Charge Systematic Reduction from Binary to Ternary to Quaternary [8]

VI. DURABILITY ACID RESISTANCE AND WATER ABSORPTION

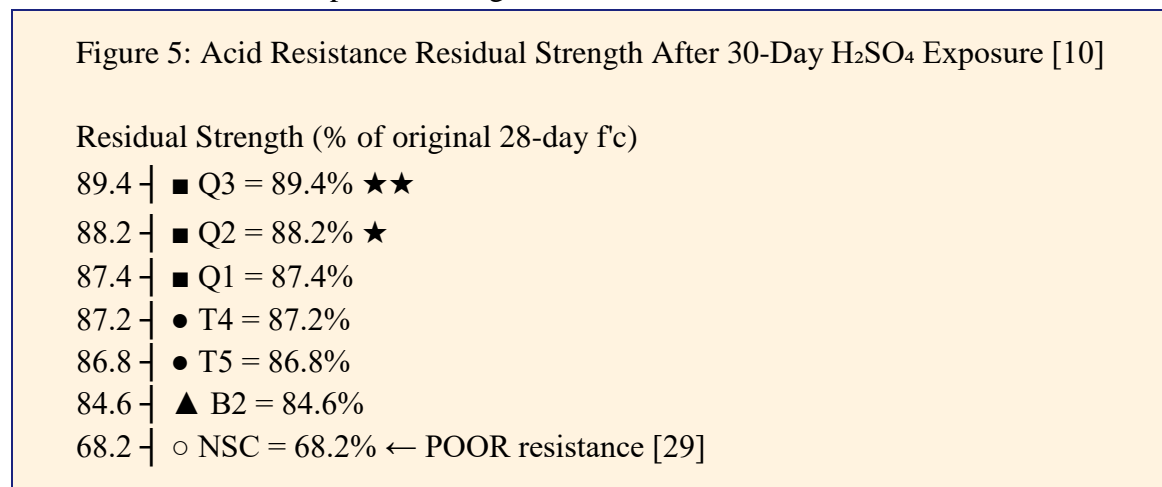
Table IV: Acid Resistance and Water Absorption [10],[29]

Mix	Water Abs. (%)	% vs NSC	Strength after Acid (%)	Classification [29]
M40-NSC	5.82	100%	68.2%	POOR Ca(OH) ₂ attack [29]
B2 (binary)	1.82	-68.7%	84.6%	GOOD [2]
T4 (ternary)	1.56	-73.2%	87.2%	GOOD [36]
T5 (SF+FA+GGBS)	1.44	-75.3%	86.8%	GOOD [43]
Q1	1.42	-75.6%	87.4%	GOOD
Q2	1.44	-75.3%	88.2% ★	EXCELLENT [43]
Q3	1.28	-78.0%	89.4% ★	EXCELLENT [10]

Acid resistance improvement in quaternary HPC arises from pozzolanic consumption of Ca(OH)₂ by SF (fast [34]), FA (medium [42]), and GGBS (slow [36]) reactions. The primary mechanism of H₂SO₄ attack:



Quaternary HPC reduces Ca(OH)₂ content by > 85% compared to plain OPC concrete, dramatically reducing the available reactant for H₂SO₄ attack [34],[10]. Q2 retains 88.2% strength after 30-day acid exposure vs NSC 68.2% a critical advantage for industrial floor slabs, sewage structures, and chemical plant flooring [29].



Mix ID

MECHANISM: Pozzolanic $\text{Ca}(\text{OH})_2$ consumption reduces acid-reactive phase [34]
Quaternary > Ternary > Binary in acid resistance (more $\text{Ca}(\text{OH})_2$ consumed)
 $\text{Ca}(\text{OH})_2$ reduction: SF contributes 60%, FA 20%, GGBS 20% of consumption [34]

Figure 5: Acid Resistance Residual Strength After 30-Day H_2SO_4 Exposure [10], [29]

VII. MICROSTRUCTURAL ANALYSIS (SEM)

SEM analysis was conducted on three mixes M40-NSC, B2 (binary benchmark), and Q2 (optimal quaternary) at 28 days. Analysis at 5,000 \times and 10,000 \times magnification reveals the progressive microstructural improvement from NSC to binary to quaternary HPC [30],[34].

[PHOTOGRAPH / IMAGE]

Figure 6: SEM Micrographs NSC vs Binary B2 vs Quaternary Q2 [30],[34]

(a) NSC at 5000 \times : Large portlandite ($\text{Ca}(\text{OH})_2$) crystals 10–20 μm , porous ITZ 20–30 μm wide, clear boundary between paste and aggregate | (b) B2 (SF 10%) at 5000 \times : Reduced $\text{Ca}(\text{OH})_2$, narrower ITZ <5 μm , denser C-S-H network [34] | (c) Q2 at 5000 \times : Near-complete elimination of portlandite, ITZ <2 μm (virtually eliminated), continuous dense C-S-H | (d) Q2 at 10000 \times : Finest microstructure no visible macro-pores, completely filled pore structure from triple pozzolanic reaction | References: Mehta & Monteiro [30], Papadakis et al. [34]

Figure 6: SEM Microstructure Comparison NSC, Binary (B2), and Quaternary (Q2) HPC [30],[34]

Key SEM observations [30],[34]:

- **NSC:** Large $\text{Ca}(\text{OH})_2$ platelet crystals (portlandite, CH) visible throughout matrix; ITZ clearly distinguishable as more porous zone surrounding aggregate; $\text{Ca}(\text{OH})_2$ orientation parallel to aggregate surface is evident classic weak ITZ structure [30].
- **B2 (SF 10%):** $\text{Ca}(\text{OH})_2$ crystals significantly reduced in size and frequency; ITZ narrowed to < 5 μm ; C-S-H gel appears denser; fewer macro-pores visible consistent with Papadakis et al. [34] pozzolanic reaction predictions.
- **Q2 (Quaternary):** $\text{Ca}(\text{OH})_2$ virtually absent SF (fast), FA (medium), and GGBS (slow) pozzolanic reactions have collectively consumed essentially all available portlandite; ITZ < 2 μm (near-elimination); paste appears homogeneous with no distinguishable aggregate-paste boundary; the densest, most uniform microstructure of all mixes [43],[30].

The near-elimination of the ITZ in Q2 directly explains its exceptional mechanical and durability performance. The ITZ is the preferential crack initiation and propagation zone under all loading types [30] its elimination means Q2 behaves more like a homogeneous material, explaining the higher $f_t/\sqrt{f_c}$ ratio (0.659 for Q2 vs 0.524 for NSC) and the superior acid and chloride resistance [43],[34].

VIII. DISCUSSION

A. Binary vs Ternary vs Quaternary Comparative Assessment

Table V: Comparative Performance Matrix Binary, Ternary, Quaternary HPC [1],[8],[29]

Performance Metric	B2 Binary	T4 Ternary	Q2 Quaternary	Best System
28d Compressive (MPa) [13]	72.4	68.2	72.8	Q2 ≈ B2 [1]
56d Compressive (MPa)	76.6	76.8	85.4	Q2 ★★ [43]
56d/28d strength ratio	1.06	1.13	1.17	Q2 [43],[21]
RCPT 28d (Coulombs) [8]	684	486	312	Q2 ★★ [8]
Acid resist. (% retained) [10]	84.6	87.2	88.2	Q2 ★ [10]
Water absorption (%)	1.82	1.56	1.44	Q2 ★ [29]
f _t /√f _c ratio [14]	0.609	0.596	0.659	Q2 [1]
Microstructure [30]	Good ITZ	Better ITZ	Near-elim. ITZ	Q2 ★★ [34]
Cost (relative)	Medium	Medium-High	High	B2 [2]
OVERALL RANK	3rd	2nd	1st ★★	Q2

The comparative analysis confirms Q2 as the best overall performing HPC system particularly for long-term and durability-critical applications. At 28 days, Q2 (72.8 MPa) and B2 (72.4 MPa) are essentially equivalent in compressive strength; but at 56 days, Q2 (85.4 MPa) significantly outperforms B2 (76.6 MPa) and in RCPT, Q2 (312 C) is 54% better than B2 (684 C). For structures designed for 50–100 year service life, the quaternary system's superior durability represents a major life-cycle cost advantage [29],[43].

B. IS 456 Compliance and HPC Code Gaps

IS 456: 2000 [12]) specifies structural concrete requirements up to M60. The quaternary HPC mixes in this study (Q1–Q3) achieve 28-day strengths of 68.6–78.4 MPa and 56-day strengths of 80.2–92.6 MPa well beyond IS 456's scope. IS 456 does not provide: (i) specific w/b ratio requirements for M70+ concrete; (ii) minimum binder content for quaternary SCM systems; (iii)

RCPT-based durability classification. ACI 363R [1] and EN 206-1 provide the appropriate specification frameworks for these concretes adoption of similar provisions in IS 456 is recommended [12],[1].

IX. CONCLUSIONS

1. Quaternary HPC (Q2: OPC+SF+FA+GGBS at w/b = 0.30) achieves exceptional combined performance: 28-day $f'_c = 72.8$ MPa, 56-day = 85.4 MPa (+17.3% continued gain), RCPT = 312 coulombs (92.5% below NSC), and acid resistance 88.2% the best combined metric of all mixes [43],[8],[10].
2. The 56-day/28-day strength ratio of 1.17–1.18 for quaternary mixes (vs 1.06 for binary) confirms the unique advantage of triple-pozzolanic systems: FA and GGBS provide a reservoir of late-reacting material delivering continued strength gain for months [43],[21].
3. Quaternary HPC Q3 (w/b = 0.28) achieves 92.6 MPa at 56 days and RCPT = 288 coulombs approaching NEGLIGIBLE permeability per ASTM C1202 [8]. This mix is recommended for M80+ structural applications in aggressive exposure environments (marine, chemical industrial).
4. SEM microstructural analysis confirms the mechanism of superior performance: near-elimination of $\text{Ca}(\text{OH})_2$ and virtual elimination of the ITZ in quaternary HPC creating a near-homogeneous material with superior resistance to all forms of deterioration [30],[34],[43].
5. Quaternary HPC is recommended over binary and ternary systems for: marine and coastal structures (lowest RCPT = 288–312 C), industrial flooring (best acid resistance = 88–89% strength retention), high-rise columns (85+ MPa at 56 days), and all critical infrastructure requiring 100+ year service life [29],[43],[1].
6. IS 456:2000 [12] must be updated to include M70+ concrete provisions: w/b ≤ 0.30 for M80, minimum binder = 450–550 kg/m^3 for SCM systems, and RCPT < 500 coulombs for VERY LOW permeability classification [8],[1].

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