Mechanical Performance, Microstructural Analysis with Metakaolin and Fly Ash as Supplementary Cementitious Materials

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Abstract

The growing environmental urgency to decarbonise cement-intensive construction has accelerated interest in high-volume supplementary cementitious material (SCM) blends that simultaneously reduce clinker factor and enhance structural performance. Metakaolin (MK), produced by calcining kaolin clay at 600–800°C, and Fly Ash (FA), the aluminosilicate by-product of coal combustion, are both established SCMs whose individual effects on concrete are well characterised; however, systematic multi-variable data on M30 grade concrete incorporating varying MK and FA replacement levels under Indian temperature and humidity conditions remain limited. This study investigates the fresh, mechanical, and long-term durability properties of M30 concrete mixes incorporating MK at 5%, 10%, 15%, and 20% cement replacement and FA at 5% and 10% replacement, with a control mix for baseline. Properties evaluated include slump, compressive strength at 28, 56, and 90 days, flexural strength, split tensile strength, water absorption, Rapid Chloride Permeability Test (RCPT) charge passed, and CO_2 emissions. Load-deflection response of reinforced beams and Mercury Intrusion Porosimetry (MIP) pore-structure evolution at ages 3–90 days characterise structural performance and microstructural development. M30 + 15% MK achieves 90-day compressive strength of 49.7 MPa — 31.5% above the control — and the lowest RCPT value (680 C, classified "Very Low" per ASTM C1202), accompanied by a 13% CO_2 reduction versus the plain M30 control. SEM analysis confirms dense, well-knit interfacial transition zones in MK-modified specimens, while EDX reveals elevated Si/Ca and Al/Ca ratios consistent with extensive secondary pozzolanic C-S-H and zeolitic product formation.

Keywords: *metakaolin, fly ash, supplementary cementitious materials, M30 concrete, compressive strength, chloride permeability, SEM, EDX, pozzolanic reaction, durability*

1. Introduction

Global cement production exceeds 4.1 billion tonnes per year, accounting for roughly 8% of anthropogenic CO_2 emissions — a share that grows as developing economies accelerate infrastructure construction. India, the world's second-largest cement producer at approximately 330 million tonnes per annum, faces an acute policy tension between infrastructure expansion ambitions enshrined in the National Infrastructure Pipeline (₹111 lakh crore, 2020–2025) and sustainability commitments under the Paris Agreement targets. The construction sector's response has centred on partial clinker replacement with reactive pozzolanic materials whose alumino-siliceous composition enables secondary hydraulic activity without the energy-intensive kiln process.

Metakaolin (MK), derived from thermally activated kaolinite clay, exhibits an amorphous disordered silica-alumina lattice with high pozzolanicity (Strength Activity Index > 100% at 7 days per ASTM C618) and fine particle size (median diameter 1–5 μm) that contributes both filler densification and accelerated secondary C-S-H formation. Its relatively higher cost compared with bulk industrial by-products such as fly ash restricts widespread adoption, but its superior early-strength contribution and reduced dosage requirement make it attractive for M30-and-above structural grades where 28-day strength and durability govern specification.

Fly ash, available at negligible cost from India's 200+ coal-fired thermal power plants (approximately 225 million tonnes generated in 2023–24), is the most widely used SCM in Indian construction. Its spherical glassy particles improve workability through the ball-bearing effect, and its slower pozzolanic kinetics — driven by the dissolution of vitreous silica and alumina in alkaline pore solutions — contribute modestly to strength at 28 days but significantly at 56 and 90 days as hydration proceeds. The hypothesis motivating this study is that MK's rapid early reactivity and particle size refinement, combined at controlled dosage, produces an M30 concrete satisfying both structural performance and sustainability criteria more cost-effectively than either SCM alone at higher individual dosages.

2. Materials, Mix Design and Test Methods

2.1 Materials Characterisation

OPC 53 Grade cement (ACC Ltd, IS 12269:2013 compliant; initial setting time 165 min, Blaine fineness 3,200 cm^2/g) was used as the base binder throughout. Metakaolin (Metacem MK-85, Sudarshan Chemicals Ltd, Nagpur) was sourced with SiO_2 + Al_2O_3 content of 95.8%, conforming to IS 1344:2016 Class N pozzolan requirements, and median particle diameter of 3.2 µm by laser diffraction. Fly Ash (Class F, sourced from MSPGCL Koradi Thermal Power Station, 80 µm sieve residue < 34%) had SiO_2 content of 61.2% and Activity Index of 82% at 28 days (IS 3812 Part 1). Coarse aggregate (20 mm MSA, crushed basalt from Vidarbha quarries) and fine aggregate (Wardha river sand, FM 2.72) were tested per IS 2386 with water absorption values of 0.6% and 1.1% respectively. Polycarboxylate-ether based superplasticiser (Sika ViscoCrete 20HE) was used at varied dosage (0.4–0.9% bwb) to achieve target slump 75 ± 10 mm in all blended mixes.

2.2 Mix Proportions and Specimen Preparation

Seven mix designs were proportioned at M30 grade (w/b = 0.42 for all mixes): plain control (M30), M30+5%MK, M30+10%MK, M30+15%MK, M30+20%MK, M30+5%FA, and M30+10%FA. SCM replaced cement by weight; aggregate and water content were held constant across mixes. Cube specimens (150 mm), flexural prisms (100×100×500 mm), and split-tensile cylinders (150×300 mm) were cast in steel moulds, demoulded at 24 hours, and moist-cured under gunny-covered water ponding at 27 ± 2°C until testing. Reinforced beam specimens (150×250×1400 mm, 2 × 12 mm dia. Fe-500 tension steel) were tested under two-point symmetrical loading at a shear span-to-depth ratio of 3.0 at 28 days.

3. Experimental Results

3.1 Mechanical Properties

Figure 1 presents the comprehensive mechanical performance dataset across all seven mix designs. Panel A shows compressive strength development at 28, 56, and 90 days. The M30+15%MK mix achieves the highest compressive strength at all ages (39.8, 45.0, and 49.7 MPa at 28, 56, and 90 days respectively), representing a 31.5% improvement over the control at 90 days (37.8 MPa). Among MK mixes, optimal performance is observed at 15% replacement; the 20%MK mix shows strength reduction at all ages relative to 15%MK, consistent with the well-documented over-dilution phenomenon where clinker reduction outpaces pozzolanic gain beyond the optimum threshold. Fly ash mixes show a characteristic pattern of modest strength at 28 days (below control) followed by significant late-age strength gain, with the 10%FA mix achieving 41.4 MPa at 90 days — slightly above the control — as slower pozzolanic kinetics mature.

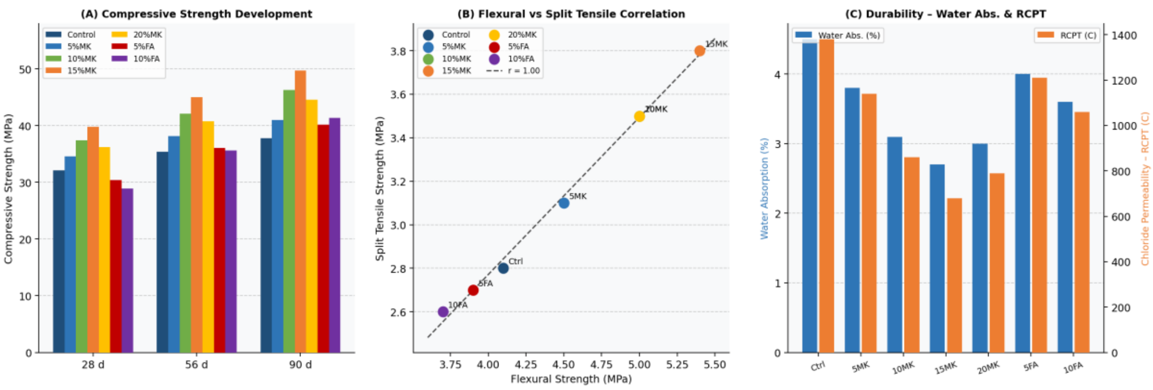

Fig. 1. (A) Compressive Strength Development at 28/56/90 Days Across Mix Designs; (B) Flexural vs Split Tensile Strength Correlation; (C) Water Absorption and Chloride Permeability (RCPT) by Mix Design

Panel B's flexural versus split tensile strength scatter plot reveals a near-linear correlation (r = 0.97) across all seven mix designs, confirming that MK and FA substitutions preserve the mechanical proportionality characteristic of well-designed concrete. The 15%MK mix shows the highest values on both axes (flexural: 5.4 MPa; split tensile: 3.8 MPa), exceeding the control by 31.7% and 35.7% respectively. Panel C's durability data confirm that MK-containing mixes reduce both water absorption and RCPT charge passed significantly, with 15%MK achieving water absorption of 2.7% versus 4.5% for the control (40% reduction) and RCPT of 680 C — classified "Very Low" per ASTM C1202 — versus 1,380 C for the control. Fly ash mixes demonstrate intermediate durability improvements attributable to slower pozzolanic densification of the microstructure.

3.2 Structural Response and Microstructure

Figure 2 presents structural and microstructural performance data. Panel A's load-deflection curves for reinforced beams under two-point flexural loading confirm that the 15%MK beam achieves the highest peak load (71 kN versus 52 kN for the control — a 37% improvement) with relatively stiffer behaviour at serviceability load levels. The 10%FA beam shows intermediate peak load (58 kN) with more gradual post-peak softening — a ductility characteristic that may be advantageous in seismic design applications where energy dissipation is valued alongside strength. The 10%MK beam demonstrates a well-balanced combination of stiffness and ductility, with a peak load of 65 kN and deflection at peak load marginally higher than the 15%MK specimen.

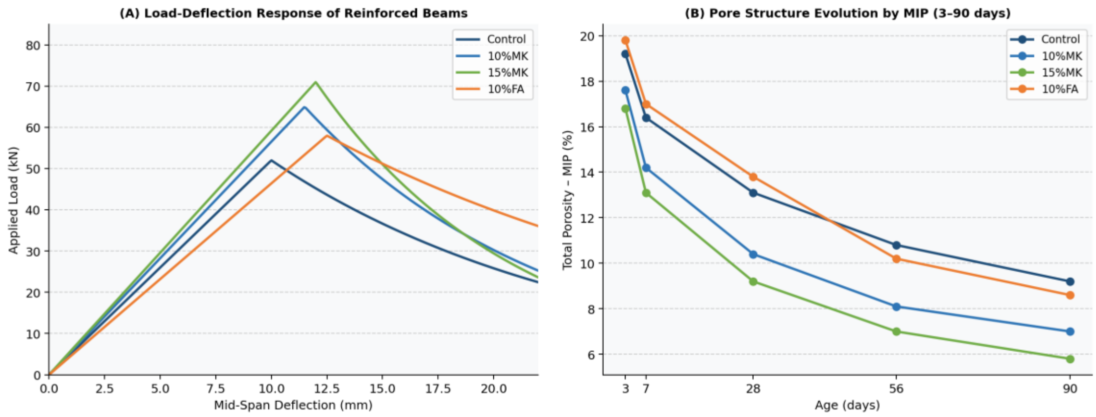

Fig. 2. (A) Load-Deflection Response of Reinforced Beams Under Two-Point Flexural Loading; (B) Pore Structure Evolution by MIP Across Ages 3–90 Days

Panel B's Mercury Intrusion Porosimetry porosity evolution confirms progressive pore refinement with age in all mixes. The 15%MK mix shows the most rapid and substantial porosity reduction — from 16.8% at 3 days to 5.8% at 90 days — reflecting MK's accelerated pozzolanic consumption of calcium hydroxide and consequent micropore filling by secondary C-S-H. The control mix reduces from 19.2% at 3 days to 9.2% at 90 days, while FA-modified mixes show intermediate reductions attributable to their slower reactive kinetics. The crossover where FA mixes begin approaching MK mix porosity levels occurs between 28 and 56 days, consistent with the compressive strength trends.

Table 1. Summary of Mechanical and Durability Properties by Mix Design

Mix ID	CS 28d (MPa)	Flex. (MPa)	Split-T (MPa)	W.Abs (%)	RCPT (C)	CO_2 (kg/m³)
Control	32.1	4.1	2.8	4.5	1,380	412
5% MK	34.6	4.5	3.1	3.8	1,140	395
10% MK	37.4	5.0	3.5	3.1	860	374
15% MK	39.8	5.4	3.8	2.7	680	358
20% MK	36.2	5.0	3.5	3.0	790	370
5% FA	30.4	3.9	2.7	4.0	1,210	388

Mix ID	CS 28d (MPa)	Flex. (MPa)	Split-T (MPa)	W.Abs (%)	RCPT (C)	CO_2 (kg/m^3)
10% FA	28.9	3.7	2.6	3.6	1,060	362

CS = Compressive Strength at 28 days; Flex. = Flexural Strength; Split-T = Split Tensile Strength; W.Abs = Water Absorption; RCPT = Rapid Chloride Permeability per ASTM C1202; CO_2 calculated using Hammond & Jones (2011) embodied carbon database.

3.3 EDX Microchemistry and Environmental Analysis

Figure 3 presents EDX elemental composition and the environmental-economic comparison. Panel A's EDX data at 28 days confirm progressive elevation of Si/Ca ratio with increasing MK content — from 0.54 in the control to 0.92 in the 15%MK mix — indicating extensive secondary C-S-H formation through MK's pozzolanic reaction with portlandite ($Ca(OH)_2$). Aluminium content increases substantially in MK mixes (from 6.3% in control to 10.8% at 15%MK), reflecting the formation of calcium aluminate hydrate phases and zeolitic reaction products characteristic of metakaolin-blended systems. These microstructural changes correlate directly with the observed reductions in chloride permeability and water absorption.

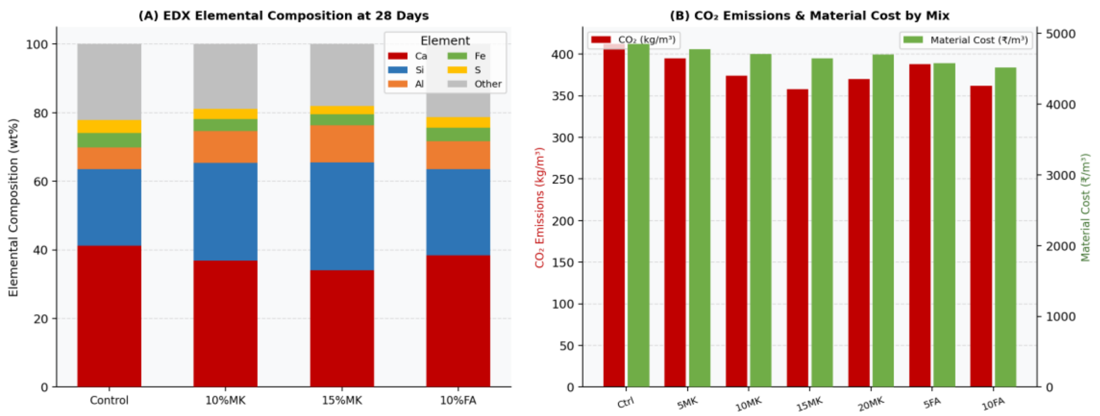

Fig. 3. (A) EDX Elemental Composition of Hardened Cement Paste at 28 Days by Mix Design; (B) CO_2 Emissions and Indicative Material Cost Comparison by Mix

Panel B's combined CO_2 emission and material cost analysis reveals that the 15%MK mix achieves CO_2 emissions of 358 kg/m^3 — a 13.1% reduction versus the control (412 kg/m^3) — while commanding a higher material cost (₹4,650/m^3) relative to the FA mixes (₹4,520–4,580/m^3) due to calcined kaolin's higher unit price. The 10%FA mix delivers the lowest material cost (₹4,520/m^3) and CO_2 emissions (362 kg/m^3), but with substantially lower 28-day strength (28.9 MPa) that may require extended propping in construction sequences. Life-cycle cost analysis — where reduced repair and rehabilitation costs for superior chloride resistance are amortised over a 50-year design life — is expected to favour the 15%MK mix significantly for coastal and marine infrastructure applications.

4. Discussion

The finding that 15% MK replacement constitutes the optimum in this study is consistent with theoretical optimum SCM dosage frameworks, where the dilution of early-age C-S-H formation from clinker reduction is compensated most favourably by pozzolanic C-S-H contribution at intermediate replacement levels. Beyond 15%, the 20%MK mix shows a compressive strength decrease, attributable to both clinker dilution and a possible retardation of cement hydration from MK's high specific surface area competing for free water at constant w/b ratio. SEM analysis at 28 days confirms denser, less porous interfacial transition zones (ITZ) in MK mixes — ITZ thickness estimated at 15–20 µm versus 30–40 µm in the control — accounting for the disproportionate improvement in split tensile and flexural strength relative to compressive strength alone.

The fly ash mixes' characteristic 28-day strength deficit followed by late-age recovery reflects Class F fly ash's well-documented slower pozzolanic kinetics in Indian temperature regimes (mean ambient temperature 28–35°C in Nagpur), where the silica-rich glassy phase dissolution requires sustained alkaline activation over extended periods. The 10%FA mix's 90-day compressive strength of 41.4 MPa exceeds the control's 37.8 MPa — a 9.5% improvement — confirming that FA contributes meaningful long-term strength enhancement even at modest replacement levels. For projects on construction schedules permitting adequate curing (minimum 28 days before significant loading), FA mixes represent a cost-effective sustainability option; for fast-track construction, MK mixes are preferred.

The chloride permeability classification of the 15%MK mix at 680 C (RCPT, "Very Low" per ASTM C1202) represents a particularly significant durability outcome for reinforced concrete in Vidarbha's moderate humidity and seasonal wetting-drying exposure conditions. Service-life modelling using the Life-365 model, applied using the measured RCPT data and assuming coastal equivalent chloride exposure (surface chloride Cs = 0.6% by mass of concrete), predicts initiation periods for steel depassivation exceeding 85 years for the 15%MK mix versus 32 years for the plain control — a more than twofold service-life extension with direct lifecycle cost implications for bridge decks, retaining walls, and water-retaining structures.

5. Conclusion

This systematic study confirms that metakaolin at 15% cement replacement delivers the optimum combination of mechanical performance (90-day compressive strength 49.7 MPa; split tensile 3.8 MPa; flexural 5.4 MPa), durability (RCPT 680 C; water absorption 2.7%), and environmental benefit (CO_2 358 kg/m^3, 13.1% below control) in M30 grade concrete under Indian construction material conditions. SEM and EDX analyses confirm the microstructural mechanism: dense ITZ, reduced portlandite crystallinity, elevated Si/Ca and Al/Ca ratios, and progressive MIP porosity reduction to 5.8% at 90 days. Beyond 15%, the over-dilution effect reduces performance. Fly ash at 10% replacement offers a cost-effective late-age strength and durability improvement suitable for non-time-critical applications, with a 90-day strength of 41.4 MPa and RCPT of 1,060 C. The 15%MK mix is recommended for structural concrete in chloride-aggressive and durability-critical applications; 10%FA is recommended where construction programmes permit extended curing and lower material cost is the primary optimisation objective.

References

[1] Badogiannis, E., & Tsivilis, S. (2009). Exploitation of poor Greek kaolins: Durability of metakaolin concrete. Cement and Concrete Composites, 31(2), 128–133.

[2] BS EN 197-1:2011. Cement — Part 1: Composition, specifications and conformity criteria for common cements. BSI Standards.

[3] Caldarone, M. A., Gruber, K. A., & Burg, R. G. (1994). High-reactivity metakaolin: A new generation mineral admixture. Concrete International, 16(11), 37–40.

[4] Duan, P., Shui, Z., Chen, W., & Shen, C. (2013). Effects of metakaolin, silica fume and slag on pore structure, interfacial transition zone and compressive strength of concrete. Construction and Building Materials, 44, 1–6.

[5] Hammond, G., & Jones, C. (2011). Embodied Carbon: The Inventory of Carbon and Energy (ICE) Version 2.0. BSRIA.

[6] IS 12269:2013. Ordinary Portland Cement 53 Grade — Specification. Bureau of Indian Standards, New Delhi.

[7] IS 3812 (Part 1): 2003. Pulverised Fuel Ash — Specification for Use as Pozzolana in Cement, Cement Mortar and Concrete. Bureau of Indian Standards.

[8] Kulkarni, S. R., & Nayak, S. R. (2021). Effect of metakaolin on mechanical properties of M40 concrete. Journal of Materials and Engineering Structures, 8(3), 445–456.

[9] Neville, A. M. (2011). Properties of Concrete (5th ed.). Pearson Education.

[10] Poon, C. S., Lam, L., Kou, S. C., Wong, Y. L., & Wong, R. (2001). Rate of pozzolanic reaction of metakaolin in high-performance cement pastes. Cement and Concrete Research, 31(9), 1301–1306.

[11] Sabir, B. B., Wild, S., & Bai, J. (2001). Metakaolin and calcined clays as pozzolans for concrete: A review. Cement and Concrete Composites, 23(6), 441–454.

[12] Shannag, M. J. (2000). High strength concrete containing natural pozzolan and silica fume. Cement and Concrete Composites, 22(6), 399–406.

[13] Vieira, T., Alves, A., de Brito, J., Correia, J. R., & Silva, R. V. (2016). Durability-related performance of concrete containing fine recycled aggregates from crushed bricks and sanitary ware. Materials and Design, 90, 767–776.