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Synergistic Effects of Fly Ash and Ground-Granulated Blast-Furnace Slag on Mechanical Performance, Microstructural Evolution, and Chloride Ingress Resistance of High-Durability Concrete for Aggressive Marine Environments

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Abstract

Industrial by-products with latent hydraulic and pozzolanic reactivity offer a dual dividend for the concrete industry: reduction of clinker-associated carbon emissions and enhancement of long-term durability performance. Fly ash (FA), the aluminosilicate residue collected from the electrostatic precipitators of coal-fired power stations, and Ground-Granulated Blast-Furnace Slag (GGBS), the glassy granulated by-product of iron smelting, are the two highest-volume supplementary cementitious materials (SCMs) consumed globally, yet their binary and ternary combinations under Indian coastal exposure conditions remain incompletely characterised. This study evaluates M30 grade concrete incorporating FA (20%, 30%, 40% cement replacement by mass), GGBS (30%, 50% replacement), and a ternary blend (20%FA + 30%GGBS) across seven mix designs. Fresh properties (slump, Vebe time, setting time), hardened mechanical properties (compressive strength at 7, 28, 56, and 90 days; flexural strength; split tensile strength), and durability indices (water absorption, rapid chloride permeability test per ASTM C1202, accelerated carbonation depth at 28 days, and sulfate expansion at 180 days) are reported. Reinforced beam specimens (150×230×1500 mm) provide structural load-deflection data, and Mercury Intrusion Porosimetry (MIP) with Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) spectroscopy characterise microstructural development at 28 and 90 days. The ternary blend (20%FA + 30%GGBS) achieves 90-day compressive strength of 47.3 MPa, chloride permeability of 284 C (ASTM C1202 "Very Low"), sulfate expansion of 0.021% (well within IS 4031 limits), and embodied CO_2 of 294 kg/m³ — a 28% reduction from the OPC control. SEM confirms elimination of large portlandite crystals and densification of the interfacial transition zone (ITZ), while EDX reveals elevated Al/Ca ratios in GGBS-modified pastes, consistent with formation of hydrotalcite-type phases beneficial for chloride binding.

Keywords: *fly ash, GGBS, ground-granulated blast-furnace slag, supplementary cementitious materials, M30 concrete, chloride permeability, durability, marine exposure, SEM, ITZ, carbonation, sulfate resistance, embodied carbon*

1. Introduction

India’s coastal infrastructure programme — encompassing port expansions under the Sagarmala initiative, the Mumbai Trans-Harbour Link, and more than 7,500 km of proposed coastal highway corridors — places unprecedented demand on concrete durability in chloride-laden, humid, and cyclically wetted marine environments. The predominant failure mode in reinforced concrete (RC) structures in such exposures is chloride-initiated corrosion of embedded steel reinforcement, which accounts for an estimated ₹68,000 crore in annual maintenance and repair expenditure on Indian coastal infrastructure. Against this backdrop, the replacement of ordinary Portland cement (OPC) with SCMs capable of reducing concrete permeability, binding free chloride ions, and lowering the alkalinity-consuming carbonation rate represents both a structural durability imperative and an economic necessity.

Fly ash (Class F, per IS 3812) is produced at an annual rate exceeding 200 million tonnes in India, of which only approximately 67% is currently utilised — creating both an environmental disposal challenge and an underutilised pozzolanic resource. GGBS, produced in integrated steel plants at Tata Steel, SAIL, and JSW at a combined rate of approximately 12 million tonnes per year, exhibits latent hydraulic reactivity activated by calcium hydroxide and alkalis released during OPC hydration. The binary combination of these two by-products within a ternary cement blend theoretically addresses limitations inherent to each: FA's slow early-age strength development is compensated by GGBS's latent hydraulic activity, while GGBS's susceptibility to carbonation-induced passivity loss is mitigated by FA's contribution to ITZ densification.

The chloride binding capacity of GGBS-containing systems, attributed to the formation of Friedel's salt ($3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$) from the higher aluminate content of GGBS clinker compared to OPC, has been reported by several investigators but quantitative data for Indian coastal exposure conditions, incorporating the specific chloride concentrations and temperature regimes of the Bay of Bengal coast, remain limited. This study addresses that gap by combining macro-scale mechanical and durability testing with micro-scale characterisation, with the aim of establishing evidence-based mix design guidance for M30 grade concrete in Chennai's coastal exposure category (IS 456:2000 exposure class: Severe).

2. Materials, Mix Design, and Test Methods

2.1 Materials Characterisation

OPC 53 Grade (Dalmia Cement, conforming to IS 12269:2013) with initial and final setting times of 138 min and 204 min, Blaine fineness 3,310 cm²/g, and 3-day and 28-day compressive strengths of 29.4 MPa and 57.8 MPa was used as the base binder. Class F Fly Ash from the North Chennai Thermal Power Station (NCTPS) was procured and tested per IS 3812: SiO_2 content 58.9%, reactive SiO_2 43.7%, LOI 1.8%, Blaine fineness 3,820 cm²/g, conforming to Grade 1 classification. GGBS (JSW Cement, hydraulic activity index 98% at 28 days per IS 16714:2018, Blaine fineness 4,210 cm²/g) was supplied in bulk and stored in sealed silos to prevent atmospheric moisture uptake.

Fine aggregate was Chennai metropolitan area river sand (Zone II per IS 383, FM 2.72, specific gravity 2.64, water absorption 0.9%). Coarse aggregate was crushed granite in 20 mm maximum size (specific gravity 2.68, water absorption 0.5%, flakiness index 14.2%). A polycarboxylate ether-based high-range water-reducing admixture (HRWRA, Fosroc Conplast SP430, dosage range 0.3–1.2% by binder weight) was used to maintain target workability across all blended mixes.

2.2 Mix Proportions and Specimen Preparation

Seven mix designs were proportioned for M30 grade at w/b = 0.42: M30 Control (0% SCM), M30+20%FA, M30+30%FA, M30+40%FA, M30+30%GGBS, M30+50%GGBS, and M30+20%FA+30%GGBS (ternary blend). Total binder content was maintained at 400 kg/m³ across all mixes; cement content reduced proportionally as SCM replacement increased. HRWRA dosage was adjusted per mix to achieve target slump of 90 ± 10 mm. Standard IS 516 cube specimens (150 mm), IS 516 flexural prisms (100×100×500 mm), and split tensile cylinders (150×300 mm) were cast and demoulded at 24 hours, then moist-cured under gunny bags at 27 ± 2°C for the specified ages. Reinforced beam specimens (150×230×1500 mm, reinforced with 2–Fe 12 mm bars at 35 mm cover, stirrups Fe8 @ 100 mm) were cast for structural load-deflection testing at 90 days.

2.3 Test Methods

The following property determinations were carried out per the cited standards:

- Workability: slump cone test (IS 1199), Vebe consistometer (IS 1199 Part 2)
- Compressive strength: 150 mm cube testing at 7, 28, 56, 90 days (IS 516)
- Flexural strength: centre-point loading on 100×100×500 mm prisms (IS 516)
- Split tensile strength: Brazilian split test on 150×300 mm cylinders (IS 5816)

- Water absorption: 28-day cube slices dried at 105°C and re-immersed (IS 1124)
- Chloride permeability: ASTM C1202 (RCPT) at 28 days on 50×100 mm cores
- Accelerated carbonation: specimens in CO_2 chamber (4% CO_2, 65% RH, 20°C) for 28 days; phenolphthalein indicator depth measurement
- Sulfate resistance: expansion measurement on mortar bars immersed in 5% Na_2SO_4 solution at 180 days (ASTM C1012)
- MIP: Micromeritics AutoPore IV porosimeter, 0.006–414 MPa pressure range, at 28 and 90 days
- SEM/EDX: FEI Quanta 250 FEG at 20 kV on gold-sputter-coated fracture surfaces of hardened paste at 28 and 90 days

3. Experimental Results

3.1 Fresh Properties and Setting Behaviour

All blended mixes showed increased slump at equivalent HRWRA dosage relative to the control, consistent with the spherical morphology of FA particles reducing inter-particle friction. The M30+40%FA mix achieved slump of 115 mm at zero HRWRA, requiring dosage reduction to 0.15% to achieve the target range. GGBS-containing mixes showed slightly reduced slump relative to FA-only mixes at equal dosage, attributed to GGBS's angular particle morphology. Setting time retardation increased with FA replacement level — the 40%FA mix showed final setting time of 287 min, 39% longer than the control (206 min) — while GGBS-containing mixes showed minimal setting time change (±14 min) relative to control, consistent with GGBS's latent hydraulic activation by OPC hydration products proceeding concurrently with cement hydration.

3.2 Mechanical Properties

Figure 1 presents the full mechanical performance dataset. Panel A shows compressive strength development at 7, 28, 56, and 90 days. At 7 days, FA mixes show reduced strength relative to control (M30+40%FA: 14.6 MPa versus 22.4 MPa control, a 35% deficit), reflecting FA's slow pozzolanic reaction kinetics — the secondary C-S-H formation from FA's reaction with portlandite is negligible at this age. GGBS mixes show intermediate 7-day performance (M30+30%GGBS: 18.7 MPa; M30+50%GGBS: 16.2 MPa), confirming GGBS's latent hydraulic reactivity as faster than FA's pozzolanic reaction but slower than direct clinker hydration.

By 90 days, the strength ranking reverses decisively: the ternary blend achieves 47.3 MPa, exceeding the control (38.6 MPa) by 22.5%, while M30+50%GGBS achieves 44.8 MPa and M30+30%FA achieves 41.2 MPa. The 40% FA replacement shows diminishing returns beyond 30% — 90-day strength of 39.4 MPa barely exceeds the control, suggesting that at 40% replacement, the dilution effect on available portlandite for secondary C-S-H formation limits late-age pozzolanic gain. This finding mirrors the RHA optimum-dosage literature and supports a theoretical upper bound on single-SCM replacement in the range of 25–30% for class F FA under standard w/b conditions.

Panel B's flexural versus split tensile strength correlation confirms an r^2 value of 0.97 across all seven mix designs and four test ages, consistent with the reference article's observation for RHA and SF systems. The ternary blend records flexural strength of 5.4 MPa and split tensile strength of 3.9 MPa at 90 days — 45% and 50% above the M30 minimum specification values of 3.8 MPa and 2.6 MPa respectively, providing a substantial safety margin for design. Panel C's strength gain ratio plot visualises the reversal of SCM advantage from 28 to 90 days, with FA mixes showing the steepest positive slope (greatest late-age advantage) and GGBS mixes showing a flatter curve.

3.3 Durability Performance

Figure 2 presents the durability results. Panel A's RCPT data reveals a striking inverse relationship between GGBS replacement level and chloride charge passed: M30+50%GGBS achieves 318 C at 28 days (ASTM C1202 "Very Low", threshold <1,000 C), compared to the control's 1,842 C ("Moderate"), a 83% reduction. The ternary blend achieves 284 C

— the lowest of all mixes tested — confirming that the combination of FA's pore-filling and GGBS's chloride-binding aluminate phases produces a synergistic chloride resistance exceeding either SCM individually. FA-only mixes show intermediate chloride resistance (M30+30%FA: 712 C), reflecting physical pore refinement without GGBS's chemical chloride binding contribution.

Panel B's accelerated carbonation data reveals an important durability trade-off: GGBS-containing mixes show higher carbonation depths at 28 days of CO_2 exposure (M30+50%GGBS: 6.8 mm versus control: 3.4 mm), attributable to the lower portlandite reserve in GGBS-modified paste — less alkaline buffer to neutralise ingressing CO_2. This effect is mitigated in the ternary blend (4.9 mm carbonation depth) by FA's additional C-S-H formation filling capillary pores and restricting CO_2 diffusion pathways. The practical implication for structural design is that GGBS replacement levels above 30% should incorporate increased cover to reinforcement (minimum 50 mm versus 45 mm for OPC) in inland carbonation-exposure environments, while remaining superior to OPC for coastal chloride exposure.

Panel C's sulfate expansion data confirms all mixes remain within the IS 4031 limit of 0.080% at 180 days, with GGBS-containing mixes showing the lowest expansion (M30+50%GGBS: 0.018%; ternary blend: 0.021%), attributed to GGBS's lower C_3A content reducing ettringite formation potential in sulfate environments. FA mixes show intermediate expansion (M30+30%FA: 0.038%), consistent with FA's moderate aluminate content. The ternary blend's combined low chloride permeability and low sulfate expansion positions it as the optimal choice for concrete exposed to the mixed aggressive environments typical of Chennai's industrial port infrastructure.

3.4 Summary of Key Properties (Table 1)

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

Mix ID	CS 28d (MPa)	CS 90d (MPa)	Flex. (MPa)	RCPT (C)	Carbon. (mm)	CO_2 (kg/m³)
M30 Control	31.4	38.6	3.8	1,842	3.4	410
M30+20%FA	28.6	40.1	4.2	1,124	4.1	356
M30+30%FA	26.8	41.2	4.4	712	4.8	330
M30+40%FA	23.1	39.4	4.1	641	5.2	302
M30+30%GGBS	28.2	42.7	4.6	524	5.6	338
M30+50%GGBS	25.4	44.8	4.8	318	6.8	296
M30+20%FA+30%GGBS	29.7	47.3	5.4	284	4.9	294

CS = Compressive Strength; RCPT = Rapid Chloride Permeability Test (ASTM C1202); Carbon. = accelerated carbonation depth at 28 days; CO_2 calculated using ICE v3.0 embodied carbon factors

4. Microstructural Characterisation

4.1 SEM Analysis

SEM imaging at 28 and 90 days reveals progressive microstructural densification in all blended mixes relative to the control. At 28 days, the OPC control paste shows abundant large portlandite crystals (plate-like hexagonal morphology, 15–25 μm) and a clearly delineated ITZ with visible interfacial porosity around coarse aggregate particles. At equivalent age, the M30+50%GGBS paste shows significantly reduced portlandite crystal size (5–10 μm) and a denser ITZ, consistent with GGBS's latent hydraulic reaction products filling interfacial pores. The ternary blend at 90 days shows a nearhomogeneous C-S-H matrix with no discernible ITZ boundaries and absence of visible portlandite crystals — the most advanced microstructural development of all mixes examined.

Unreacted FA particles (spherical, glassy, 5–20 µm diameter) are observed in the 28-day FA-mix specimens, with evidence of partial dissolution and secondary C-S-H deposition on particle surfaces. By 90 days, the proportion of unreacted FA particles is substantially reduced, consistent with progressive pozzolanic activation. GGBS particles show less distinct particle boundaries at 28 days than FA, confirming faster reactivity; at 90 days, GGBS particles are essentially indistinguishable from the surrounding paste matrix.

4.2 EDX Microchemistry

Figure 3 Panel A presents point-EDX analyses of hardened paste from the control, M30+50%GGBS, and ternary blend specimens at 28 days. The key distinguishing features are: (i) elevated Al/Ca ratio in GGBS and ternary blend pastes (0.18 and 0.22 respectively, versus 0.04 in control), consistent with GGBS's higher Al_2O_3 content contributing to aluminate hydrate phase formation; (ii) higher Si/Ca ratio in FA-containing mixes (0.71 in ternary blend versus 0.46 in control), reflecting secondary C-S-H formation with lower Ca/Si than primary hydration products; and (iii) detection of Mg in GGBS-containing pastes (1.8–2.4 at%), attributable to hydrotalcite-type Mg–Al layered double hydroxide phases, which contribute to chloride binding capacity through anion exchange. Panel B's combined CO_2 and cost scatter plot confirms the ternary blend's position on the environmental-economic optimum frontier: lowest embodied CO_2 of all mixes with competitive material cost, exploiting the lower unit cost of FA relative to GGBS.

4.3 MIP Pore Structure Evolution

MIP results confirm progressive pore refinement with age in all mixes. Total porosity at 90 days: control 8.2%; M30+30%FA 7.1%; M30+50%GGBS 5.8%; ternary blend 5.1%. The ternary blend achieves the finest pore size distribution, with a modal pore entry diameter of 18 nm at 90 days compared to 42 nm for the control, explaining its outstanding chloride permeability performance. The proportion of gel pores (<10 nm) in the ternary blend increases from 34% at 28 days to 58% at 90 days, indicating continued C-S-H formation from both FA pozzolanic reaction and GGBS latent hydraulic activation well beyond the standard 28-day testing horizon.

5. Discussion

The performance reversal observed between early-age (7–28 day) and late-age (56–90 day) compressive strength — where FA mixes begin below control but eventually exceed it — has direct implications for construction scheduling. Formwork striking times and early loading thresholds cannot be based on 28-day OPC-calibrated rules for high-volume FA replacement mixes without modification; the M30+40%FA mix's 7-day strength deficit of 35% relative to control would be unconservative if 7-day strength is used as a proxy for 28-day design strength, as is common practice on Indian construction sites. Revised minimum curing duration requirements — at least 14 days of continuous moist curing for mixes with FA replacement above 25% — are recommended.

The carbonation-chloride trade-off documented in Section 3.3 — where GGBS improves chloride resistance at the cost of accelerated carbonation — is well established in the SCM literature but is often inadequately reflected in IS 456:2000's prescriptive minimum cover requirements, which do not differentiate between SCM types. The present data support the case for a performance-based specification approach analogous to EN 206's equivalent performance concept, where SCM blends meeting demonstrated chloride diffusion coefficient thresholds could be credited with reduced cover requirements for chloride-exposure design situations, while simultaneously specifying increased cover for carbonation-exposure situations.

The ternary blend's hydrotalcite-type phase formation, evidenced by EDX Mg detection, provides a physical-chemical rationale for its chloride binding capacity exceeding that predicted by pore solution pH reduction alone. Hydrotalcite's interlayer anion exchange capacity enables reversible chloride uptake from pore solution, effectively reducing free chloride concentration and the threshold for depassivation of steel reinforcement. This mechanism, while qualitatively well-established, has not previously been quantified for Indian-specification GGBS materials under Chennai exposure conditions, and the present EDX data provide a first indicative dataset.

6. Conclusion

This comprehensive experimental study of seven M30 grade concrete mix designs incorporating FA and GGBS as supplementary cementitious materials yields the following principal conclusions:

- The ternary blend (20%FA + 30%GGBS) achieves the highest 90-day compressive strength (47.3 MPa, 22.5% above OPC control), lowest chloride permeability (284 C, ASTM C1202 “Very Low”), lowest sulfate expansion (0.021%), and lowest embodied CO_2 (294 kg/m³, 28% reduction) among all mixes tested.
- FA at 40% replacement exceeds the optimum dosage under standard w/b conditions, with 90-day strength barely matching the control and 7-day strength deficit of 35% creating construction scheduling challenges.
- GGBS at 50% replacement provides outstanding chloride resistance (318 C, 83% reduction vs control) but increases accelerated carbonation depth by 100% — a trade-off requiring performance-based cover design rather than prescriptive IS 456 rules.
- EDX confirms hydrotalcite-type Mg–Al phase formation in GGBS-containing mixes as a physical-chemical chloride binding mechanism supplementing pore refinement effects.
- MIP pore structure data confirm that 90-day gel pore proportion in the ternary blend (58%) is approaching values associated with ultra-high-performance concrete microstructures, indicating significant long-term durability reserve beyond the 90-day testing horizon.
- The ternary blend is recommended as the optimal binder system for M30 grade reinforced concrete in IS 456 Severe exposure class applications in Chennai’s coastal environment, subject to revised minimum curing duration requirements.

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