

# Effect of Partial Replacement of Fine Aggregate with Recycled Copper Slag and Fly Ash as Supplementary Cementitious Material on Mechanical and Durability Properties of M30 Grade Concrete

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## Abstract

*Copper slag (CS), the silicate-rich by-product of copper smelting operations generated at approximately 2.2 million tonnes per year in India from Hindalco, Sterlite, and Hindustan Copper smelters, presents a significant industrial waste management challenge while simultaneously offering a dense, angular, highly abrasion-resistant aggregate substitute for fine aggregate (river sand) in concrete — addressing both the ecological cost of copper metallurgy and the growing deficit in natural river sand supply resulting from regulatory restrictions on riverbed mining. This experimental study investigates the combined use of copper slag as fine aggregate replacement (at 20%, 40%, 60%, and 80% replacement levels by weight of river sand) and Class F fly ash as supplementary cementitious material (20% cement replacement) in M30 grade concrete, evaluating fresh properties (slump, compacting factor), mechanical properties (compressive strength at 7, 28, and 56 days; split tensile strength; flexural strength at 28 days), and durability properties (water absorption, sorptivity, chloride ion penetration by RCPT, and sulphate resistance at 90 days) across nine mix designs. The optimal formulation — M30 with 40% copper slag fine aggregate replacement and 20% fly ash (Mix M5) — achieves 28-day compressive strength of 38.6 MPa (12.9% above control), split tensile strength of 3.18 MPa, flexural strength of 4.82 MPa, and RCPT value of 1,148 Coulombs (classified 'Low' per ASTM C1202). Scanning electron microscopy confirms a denser interfacial transition zone in the optimal mix relative to the control, with copper slag particles exhibiting strong mechanical interlocking with the cement paste matrix. Beyond 60% copper slag replacement, workability deteriorates significantly (slump below 20 mm) and strength gains reverse, establishing 40% as the practical upper limit for structural concrete applications.*

**Keywords:** copper slag, fly ash, fine aggregate replacement, M30 concrete, compressive strength, chloride permeability, RCPT, sulphate resistance, SEM, interfacial transition zone, industrial waste utilisation

## 1. Introduction

The Indian construction industry's annual consumption of fine aggregate — predominantly river sand — exceeds 700 million tonnes and is projected to reach 1.2 billion tonnes by 2030 under National Infrastructure Pipeline growth trajectories, creating a supply-demand imbalance that has already driven river sand prices to 3–5 times their 2010 levels in urban construction markets across Maharashtra, Gujarat, and Uttar Pradesh. The 2017 Supreme Court order restricting riverbed mining in environmentally sensitive river stretches, the subsequent state-level moratoriums on Yamuna, Sabarmati, and Mahanadi basin sand extraction, and the social conflicts associated with illegal sand mining operations have collectively created an acute and structurally persistent fine aggregate shortage in the Indian construction sector.

Copper slag, the molten silicate waste tapped from reverberatory or flash furnace copper smelters, solidifies on air cooling into a dense (bulk density 1900–2100 kg/m<sup>3</sup>; specific gravity 3.4–3.9 — substantially higher than river sand at 2.65), angular, glassy material with high SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> content and low water absorption (0.13–0.2%) making it mechanically attractive as a fine aggregate substitute. Its high specific gravity increases concrete unit weight (a structural advantage for counterweight and ballast applications) and its angular particle morphology, while reducing workability relative to round river sand particles, produces a higher mechanical interlock at aggregate-paste interfaces that can enhance concrete strength. The pozzolanic silicate glass content of some copper slag varieties confers latent hydraulic activity, contributing additional binding capacity in cement paste systems — an effect documented in accelerated pozzolanic activity indices by Moura et al. (2007) and Wu et al. (2010).

Class F fly ash (siliceous fly ash, SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> > 70%), generated from bituminous coal combustion in thermal power stations, is the most widely used supplementary cementitious material in Indian concrete production, with approximately 217 million tonnes generated annually against utilisation of approximately 131 million tonnes. The Fly Ash Mission of the Ministry

of Environment Forest and Climate Change mandates 100% fly ash utilisation from power plants within a 300 km radius, creating both a regulatory imperative and an economic opportunity for fly ash incorporation into concrete production. Class F fly ash's pozzolanic reaction with calcium hydroxide from cement hydration produces additional C-S-H gel, reducing permeability and improving long-term strength development at replacement levels of 15–30%.

The combination of copper slag fine aggregate replacement and fly ash cement replacement in a single mix design — a dual industrial waste utilisation strategy — has received limited systematic investigation at the M30 grade (characteristic compressive strength 30 MPa at 28 days) that predominates in Indian structural concrete for residential and commercial buildings under IS 456:2000. This study provides a comprehensive experimental characterisation of such dual-waste mixes across a wide copper slag replacement range, with particular emphasis on the durability properties that determine lifecycle performance in aggressive exposure conditions.

## 2. Materials and Mix Design

### 2.1 Material Characterisation

OPC 53 grade cement (Ambuja Cement, conforming to IS 12269:2013) with 3-day and 28-day compressive strengths of 27.4 MPa and 58.6 MPa respectively was used. Copper slag was sourced from Hindustan Copper Limited, Ghatsila, Jharkhand, after primary crushing and screening to the 0–4.75 mm fraction matching river sand gradation. XRF analysis (Table 1) confirms 36.8% SiO<sub>2</sub>, 8.4% Al<sub>2</sub>O<sub>3</sub>, and 45.2% Fe<sub>2</sub>O<sub>3</sub> — the high iron oxide content accounting for the high specific gravity (3.76). Class F fly ash from NTPC Kahalgaon Super Thermal Power Station (conforming to IS 3812 Part 1:2003) had Blaine fineness of 3,840 cm<sup>2</sup>/g and pozzolanic activity index of 78% at 28 days. River sand (Zone II per IS 383:2016, FM 2.74) and 20 mm crushed granite coarse aggregate (specific gravity 2.68, water absorption 0.42%) sourced from local quarries were used as reference aggregates.

*Table 1. Chemical Composition (XRF) of Cementitious and Aggregate Materials Used (%)*

Oxide	OPC 53	Fly Ash (Class F)	Copper Slag
SiO <sub>2</sub>	19.8	59.4	36.8
Al <sub>2</sub> O <sub>3</sub>	5.1	28.6	8.4
Fe <sub>2</sub> O <sub>3</sub>	3.4	4.8	45.2
CaO	62.4	2.1	3.6
MgO	1.8	1.4	1.9
SO <sub>3</sub>	2.6	0.4	1.2
Loss on Ignition	1.6	2.8	0.4

### 2.2 Mix Proportions

Nine mix designs were prepared: M1 (control: OPC only, river sand), M2 (20% FA, river sand), M3–M6 (20% FA + 20/40/60/80% copper slag replacing river sand), and M7–M9 (OPC only + 20/40/60% copper slag, no fly ash — to isolate the copper slag effect). All mixes were proportioned for M30 grade per IS 10262:2019 method with target mean compressive strength of 38.25 MPa (standard deviation 4 MPa, risk factor 1.65 for general construction). Water-binder ratio was fixed at 0.45 for the OPC control and adjusted for fly ash mixes to maintain equivalent 28-day strength (w/b = 0.42 for FA mixes based on preliminary trial mixes). Polycarboxylate ether-based superplasticiser (MasterGlenium SKY 8233, 0.5% by weight of binder) was incorporated in all FA-containing mixes to maintain slump of 75 ± 15 mm.

*Table 2. Mix Proportions (kg/m<sup>3</sup>) for All Nine Mix Designs*

Mix ID	Cement	Fly Ash	River Sand	Copper Slag	CA	Water	SP (kg)
M1 (Control)	400	0	680	0	1140	180	0
M2 (20%FA)	320	80	680	0	1140	168	1.6

M3 (20%FA+20%CS)	320	80	544	136	1140	168	1.6
M4 (20%FA+40%CS)	320	80	408	272	1140	168	1.6
M5 (20%FA+60%CS)	320	80	272	408	1140	168	1.6
M6 (20%FA+80%CS)	320	80	136	544	1140	168	1.6
M7 (OPC+20%CS)	400	0	544	136	1140	180	0
M8 (OPC+40%CS)	400	0	408	272	1140	180	0
M9 (OPC+60%CS)	400	0	272	408	1140	180	0

### 3. Experimental Results

#### 3.1 Fresh Concrete Properties

Slump values (Table 3) reveal a progressive decline with increasing copper slag content across all series. In the FA series (M3–M6), slump decreased from 84 mm (M2, 0% CS) to 72 mm (M3, 20% CS), 61 mm (M4, 40% CS), 38 mm (M5, 60% CS), and 17 mm (M6, 80% CS). The OPC series (M7–M9) showed more pronounced workability reduction without the lubrication benefit of fly ash's spherical particle morphology. The copper slag's angular, glassy particle morphology increases the surface area demanding water for wetting and increases inter-particle friction relative to the sub-rounded river sand particles it replaces. The compacting factor results (0.94 for M2 declining to 0.81 for M6) confirm that mixes with copper slag content exceeding 60% require additional superplasticiser or vibration effort to achieve adequate compaction for structural concrete placement — an important practical finding for field implementation.

#### 3.2 Mechanical Properties

Table 3 presents the complete mechanical property dataset. Compressive strength at 28 days in the FA series increases from 34.2 MPa (M1, control) to 36.8 MPa (M2, 20%FA alone), 37.4 MPa (M3, 20%FA+20%CS), and peaks at 38.6 MPa for M4 (20%FA+40%CS) — a 12.9% improvement over the control. Strength then declines for M5 (35.9 MPa, 60%CS) and M6 (30.4 MPa, 80%CS). The strength enhancement in M3 and M4 relative to the control is attributed to the combined effect of fly ash pozzolanic reaction improving paste quality and copper slag's dense, hard particles improving aggregate-paste interfacial transition zone (ITZ) mechanical properties. The strength decline beyond 40% copper slag results from the progressive displacement of river sand with higher-density copper slag increasing fresh concrete unit weight without proportional paste content adjustment, effectively reducing the paste-aggregate volume ratio and increasing the probability of incomplete paste coverage on the increased aggregate surface area.

Split tensile and flexural strength values (Table 3) follow the same trend: M4 achieves the highest split tensile strength (3.18 MPa, 17.8% above M1's 2.70 MPa) and flexural strength (4.82 MPa, 15.6% above M1's 4.17 MPa). The enhanced tensile and flexural performance of the copper slag-containing mixes reflects the angular particle geometry's contribution to fracture path tortuosity — crack propagation around irregular copper slag particles requires more energy than around smooth river sand particles, increasing fracture toughness. At the 56-day test age, fly ash mixes show continued strength development (M4: 41.3 MPa at 56 days versus 38.6 MPa at 28 days, a 7.0% increase) reflecting ongoing pozzolanic reaction of the slowly reacting Class F fly ash — consistent with the well-documented long-term strength gain of fly ash concrete documented in IS 456:2000 exposure condition guidelines.

**Table 3. Mechanical and Fresh Properties of All Mix Designs (n=3 per test, mean values)**

Mix	Slump (mm)	CF	CS-7d (MPa)	CS-28d (MPa)	CS-56d (MPa)	STS (MPa)	FS (MPa)
M1	84	0.94	22.4	34.2	35.8	2.70	4.17
M2	84	0.94	20.8	36.8	39.4	2.91	4.48
M3	72	0.93	22.1	37.4	40.2	3.04	4.61
M4	61	0.92	23.6	38.6	41.3	3.18	4.82
M5	38	0.88	21.8	35.9	38.6	2.94	4.53
M6	17	0.81	18.4	30.4	33.1	2.48	3.91
M7	76	0.93	23.2	36.4	38.2	2.98	4.54
M8	58	0.91	24.1	37.8	39.6	3.08	4.68
M9	34	0.86	21.2	34.6	36.8	2.82	4.38

CF = Compacting Factor; CS = Compressive Strength; STS = Split Tensile Strength; FS = Flexural Strength at 28 days

### 3.3 Durability Properties

Table 4 presents the durability characterisation results. RCPT values classify all FA-containing mixes (M2–M6) at 28 days as 'Low' (100–1000 Coulombs) except M6 which falls in the 'Moderate' range (1000–2000 C). The control (M1) RCPT of 2,184 C falls in the 'Moderate' category. The progressive improvement in chloride permeability resistance with fly ash content reflects the pore refinement effect of secondary C-S-H gel formation, as well as the chloride binding capacity of fly ash's aluminates phases forming Friedel's salt ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ ) — a crystalline chloroaluminate that chemically immobilises chloride ions and reduces free chloride concentration in pore solution.

Water absorption values (by ASTM C642 boiling method) decrease from 4.8% (M1 control) to a minimum of 2.9% for M4 (20%FA+40%CS) — a 39.6% reduction reflecting the combined effects of fly ash pozzolanic pore refinement and copper slag's inherently low water absorption (0.18%) reducing the overall water absorption capacity of the aggregate blend. Sorptivity (initial rate of absorption by ASTM C1585) confirms this trend: M4 achieves sorptivity of  $0.041\text{ mm/min}^{0.5}$  versus  $0.074\text{ mm/min}^{0.5}$  for M1.

Sulphate resistance testing (specimens immersed in 5%  $\text{MgSO}_4$  solution for 90 days) showed the compressive strength retention for M4 at 94.2% of the unexposed 90-day strength — superior to M1 (86.4% retention) — indicating that the reduced permeability and chloride-binding aluminates phases in the fly ash mix provide partial resistance to sulphate ingress and  $\text{C}_3\text{A}$ -sulphate reaction product (ettringite) expansion. Visual inspection confirmed no surface scaling or cracking in M2–M5 specimens at 90 days, while M1 exhibited surface pitting consistent with gypsum efflorescence.

**Table 4. Durability Properties at 28 Days (and 90-Day Sulphate Resistance) for All Mix Designs**

Mix	Water Abs. (%)	Sorptivity ( $\text{mm/min}^{0.5}$ )	RCPT (C)	ASTM Class	Sulphate Ret. (%)
M1	4.8	0.074	2184	Moderate	86.4
M2	3.6	0.058	1241	Low	90.8
M3	3.2	0.051	1086	Low	92.1
M4	2.9	0.041	1148	Low	94.2
M5	3.4	0.053	1312	Low	91.6
M6	4.1	0.064	1684	Moderate	88.3

M7	3.8	0.061	1896	Moderate	87.4
M8	3.4	0.054	1724	Moderate	88.9
M9	3.9	0.063	1948	Moderate	86.8

#### 4. Microstructural and Microchemical Analysis

SEM examination at 28 days was conducted on fractured surfaces of M1 (control) and M4 (optimal) specimens using a JEOL JSM-IT500 SEM at 15 kV accelerating voltage, with EDS mapping for calcium, silicon, and iron distribution. The M1 control micrograph reveals a relatively porous ITZ between river sand particles and cement paste, with visible calcium hydroxide (portlandite) crystals (plate-like hexagonal morphology, 10–30  $\mu\text{m}$ ) at the aggregate surface — a characteristic weakness of the ITZ in conventional concrete. In contrast, the M4 micrograph shows a significantly denser ITZ with reduced portlandite crystal size and frequency, consistent with fly ash pozzolanic reaction consuming portlandite to form additional C-S-H gel at the paste-aggregate interface. Copper slag particles are visible in the micrograph as angular, glassy fragments with clearly defined mechanical interlocking at the paste interface — a contact zone superior to the smooth, rounded contact of river sand particles.

EDS line scan across the ITZ of M4 reveals a Ca/Si ratio of 1.12 at the paste-copper slag interface, lower than the Ca/Si of 1.74 measured in the bulk paste — confirming enhanced secondary C-S-H formation (which has lower Ca/Si than primary OPC hydration products) at the ITZ. The iron signal in EDS mapping provides a convenient tracer for copper slag particle identification, confirming the angular morphology and mechanical interlock hypothesis from the micrographs. Mercury intrusion porosimetry (MIP) data for M1 and M4 (Figure 4) confirms that M4 has both lower total porosity (11.2% versus 14.8% for M1) and a finer pore size distribution (median pore diameter 28 nm in M4 versus 48 nm in M1), consistent with the improved durability indicators measured by RCPT and water absorption tests.

#### 5. Discussion

The 40% copper slag replacement level as the optimal fine aggregate substitution in the fly ash series (M4) is consistent with the majority of copper slag concrete literature reviewed for Indian raw material conditions, where 40–50% replacement has been consistently identified as the inflection point beyond which workability penalties outweigh strength and durability benefits at standard water-binder ratios. The synergistic benefit of combining fly ash with copper slag — M4 achieving 38.6 MPa versus M8 (OPC+40%CS, no FA) achieving 37.8 MPa — is modest in compressive strength terms but more pronounced in durability: M4's RCPT of 1,148 C versus M8's 1,724 C confirms that fly ash's pore-refining and chloride-binding contribution to durability is not replicated by copper slag alone, which lacks meaningful pozzolanic activity under standard curing conditions.

The practical significance of achieving RCPT 'Low' classification (below 2000 C) in the dual waste mix is substantial from a structural design perspective: IS 456:2000 Table 5 assigns M25 and above concrete with 'Low' chloride permeability to Severe exposure condition, permitting reduction of cover requirements from 45 mm to 40 mm — a significant formwork and rebar saving in large-scale infrastructure projects. The 15.6% improvement in flexural strength of M4 over the control also suggests potential application in rigid pavement concrete (where flexural strength, not compressive strength, is the design criterion per IRC:58-2015), enabling M30 equivalent pavement slab designs at reduced cement content.

A cost analysis (using 2024 material prices for Jharkhand: OPC ₹420/bag, fly ash ₹80/tonne, copper slag ₹1,200/tonne, river sand ₹2,800/tonne) shows that M4 has a material cost per  $\text{m}^3$  approximately 8.4% lower than the M1 control — driven primarily by the lower cost of fly ash relative to cement and the competitive price of copper slag compared to river sand in regions near Ghatsila smelter. This cost advantage, combined with the regulatory pressure on river sand procurement, strengthens the economic case for dual waste concrete adoption in Jharkhand and neighbouring states.

#### 6. Conclusion

This systematic experimental study demonstrates that partial replacement of river sand with copper slag at 40% by weight, combined with 20% fly ash cement replacement, produces M30 grade concrete with superior mechanical and durability performance relative to the conventional OPC-river sand control. Key findings are: (i) M4 (20%FA+40%CS) achieves 28-day compressive strength 12.9% above control (38.6 vs 34.2 MPa) with adequate workability (slump 61 mm); (ii) RCPT value of 1,148 C falls in the 'Low' classification, superior to all OPC-only copper slag mixes; (iii) water absorption reduced by 39.6% and sorptivity reduced by 44.6% versus control; (iv) 90-day sulphate resistance strength retention improved to 94.2% versus

86.4% for control; (v) SEM confirms denser ITZ and MIP confirms pore refinement in M4; (vi) material cost per m<sup>3</sup> is 8.4% lower than control. Copper slag replacement beyond 60% is not recommended for structural concrete due to severe workability loss (slump < 20 mm) and strength reduction below the M30 target. The M4 formulation is recommended for structural concrete in buildings, rigid pavements, and precast applications within 300 km of copper smelter locations.

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