

Experimental Investigation of Sustainable High-Performance Concrete Utilizing Copper Slag as Fine Aggregate and Treated Coconut Shell Aggregates

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Abstract — The excessive depletion of natural river sand and granite stone has raised profound ecological and sustainability concerns, compelling the global construction sector to evaluate solid agro-industrial wastes as circular aggregate alternatives. This experimental research conducts an exhaustive physical, mechanical, durability, and microstructural investigation on sustainable High-Performance Concrete (HPC) produced by substituting virgin fine aggregate with granulated industrial copper slag (CS) at 0%, 20%, 40%, 60%, 80%, and 100% replacement levels, and conventional crushed granite coarse aggregate with alkali-treated coconut shell aggregates (TCSA) at 0%, 10%, 15%, and 20% by volume. Discarded agricultural coconut shells were pretreated with a 5% sodium hydroxide (NaOH) chemical solution to remove non-cellulosic waxy cuticles, pectin, and free sugars, reducing water absorption from 23.4% down to 8.65% and strengthening interfacial transition zone (ITZ) mechanical adhesion. A comprehensive laboratory testing suite encompassing compressive strength (3, 7, 28, and 90 days), split tensile strength, flexural modulus, ultrasonic pulse velocity (UPV), water absorption, sulfate attack resistance (5% Na₂SO₄), and rapid chloride permeability testing (RCPT) was carried out across 8 detailed mix formulations. Experimental data indicates that the optimum dual-waste mix incorporating 40% copper slag and 15% treated coconut shells achieves a 28-day compressive strength of 66.8 MPa, a 90-day strength of 71.4 MPa, a flexural strength of 6.78 MPa, an ultrasonic pulse velocity of 4.58 km/s, and a charge passage of only 1,120 Coulombs. SEM and EDS micrographs validate the formation of a dense, compact matrix where secondary C-S-H gels interlock with chemically etched bio-aggregate cellular pores, proving the viability of multi-waste sustainable HPC for structural engineering applications.

Keywords— Alternative Aggregates, Chemical Pretreatment, Coconut Shell Aggregate, Copper Slag, Durability, High-Performance Concrete, Interfacial Transition Zone (ITZ), Microstructural Analysis, Sustainable Construction.

I. INTRODUCTION

Concrete constitutes the most consumed structural material on earth, with annual global usage exceeding 30 billion metric tons. The rapid expansion of transportation infrastructure, commercial high-rises, and industrial corridors has generated unprecedented demand for natural river sand and quarried granite stone [1]. The continuous extraction of river sand leads to riverbed degradation, erosion of embankments, lowering of alluvial groundwater aquifers, and severe loss of freshwater biodiversity. At the same time, the metallurgical industry generates immense stockpiles of hazardous slag, while the agricultural sector discards millions of metric tons of lignocellulosic crop residues, mostly disposed of in municipal landfills or open-air incinerators.

Copper slag (CS) is a high-density, glassy by-product obtained during the matte smelting and pyrometallurgical refining of copper concentrates. Manufacturing one metric ton of refined

copper yields approximately 2.2 to 3.0 tons of granulated copper slag [2]. Given its high bulk density, superior micro-hardness, near-zero moisture absorption (0.28%), and favorable particle angularity, copper slag presents strong potential as a functional replacement for diminishing river sand resources. Conversely, post-consumer coconut shells from agricultural processing represent an abundant bio-waste. However, untreated coconut shells exhibit low specific gravity (1.05–1.15), high water absorption (up to 24%), and smooth epicarp coatings containing free sugars and hemicellulose that retard cement hydration and severely weaken the interfacial transition zone (ITZ) [3]. Chemical alkali conditioning with sodium hydroxide (5% NaOH) dissolves surface waxes and lignin, exposing roughened micro-voids that facilitate mechanical interlocking with hydrating cement phases.

1. Research Gap and Objectives

Existing literature has predominantly studied copper slag as an isolated sand substitute in regular concrete or coconut shells as

lightweight coarse aggregate in non-structural masonry mixes (M15–M25). Crucially, systemic investigations assessing the synergistic combination of both metallurgical slag (high density, smooth, non-absorptive) and agro-waste shells (low density, cellular, absorptive) in structural-grade High-Performance Concrete (HPC) with target strengths exceeding 60 MPa remain virtually absent. Furthermore, previous studies lack comprehensive durability datasets examining combined sulfate immersion and rapid chloride penetrability alongside microstructural SEM-EDS mapping. This paper bridges this gap through a multi-age mechanical and durability evaluation across 8 distinct mix formulations.

II. MATERIALS AND EXPERIMENTAL METHODOLOGY

1. Binder and Chemical Admixtures

Ordinary Portland Cement (OPC) 53 Grade conforming to IS 12269 was used as the single cementitious binder. The physical characteristics of the cement included a specific gravity of 3.15, standard consistency of 31.5%, Blaine specific surface area of 368 m²/kg, initial setting time of 48 minutes, final setting time of 285 minutes, and a 28-day standard mortar compressive strength of 58.2 MPa. To achieve target flowability at a low water-to-binder (w/b) ratio of 0.32, a modified polycarboxylate ether (PCE) superplasticizer with 40% active solid content and relative density of 1.08 was utilized.

2. Fine and Coarse Aggregates

Natural river sand conforming to Zone II grading (IS 383) was sourced from local riverbeds. Granulated copper slag was obtained from an industrial smelting unit. Table I compiles the comparative physical and X-ray fluorescence (XRF) chemical properties. Due to heavy iron silicate content, copper slag has an elevated specific gravity of 3.51 and 54.2% Fe₂O₃. Natural coarse aggregate consisted of crushed angular granite stones (12.5 mm nominal size). Agricultural coconut shells collected from wholesale markets were crushed using a mechanical jaw crusher and sieved to retain particles between 4.75 mm and 12.5 mm.

Table I: Physical and Chemical Composition of Raw Materials

Parameter / Oxide	OPC 53	River Sand	Copper Slag	Granite	TCSA
Specific Gravity	3.15	2.62	3.51	2.68	1.34
Bulk Density (kg/m ³)	1,440	1,580	1,960	1,520	680

Water Absorption (%)	—	1.12	0.28	0.45	8.65
Fineness Modulus	—	2.74	3.18	6.92	5.88
SiO ₂ (%)	20.8	84.2	34.8	68.4	—
Fe ₂ O ₃ (%)	3.4	3.1	54.2	4.2	—
Al ₂ O ₃ (%)	5.2	4.8	4.6	14.1	—
CaO (%)	63.6	2.4	3.2	2.8	—
MgO (%)	1.8	0.8	1.5	1.2	—
Loss on Ignition (%)	2.1	1.2	0.5	0.8	—

3. Alkaline Pretreatment of Coconut Shells

Raw coconut shell aggregates contain significant contents of lignin, hemicellulose, and water-soluble sugars. To enhance chemical stability and bond strength, the aggregates were completely submerged in an aqueous 5% NaOH solution for 24 hours at ambient temperature (27±2°C). This chemical wash saponified the epicarp fatty acids and extracted the soluble carbohydrates. Subsequently, the aggregates were washed repeatedly under running potable water until the rinse water reached neutral pH (7.0), followed by oven-drying at 60°C for 24 hours. As confirmed by laboratory tests, this chemical treatment suppressed the 24-hour water absorption capacity from 23.4% down to 8.65% and produced microscopic surface roughness.

4. Concrete Mix Proportions

An M60 target high-performance concrete mix was designed following IS 10262 and ACI 211 guidelines with total binder content fixed at 480 kg/m³ and w/b ratio maintained at 0.32. Copper slag was introduced to replace natural river sand at 0%, 20%, 40%, 60%, 80%, and 100% by weight. Concurrently, treated coconut shell aggregates (TCSA) were introduced as replacements for natural coarse aggregates at 0%, 10%, 15%, and 20% by volume. Due to substantial differences in specific gravities between virgin aggregates and waste components, absolute volume corrections were strictly applied:

$$V_{agg} = 1 - (V_c + V_w + V_{sp} + V_{air}) \quad (1)$$

The effective batch mixing water was corrected for aggregate absorption states:

$$W_{eff} = W_{design} + \sum [M_i \times (A_i - MC_i)] \quad (2)$$

where M_i is dry aggregate weight, A_i is water absorption, and MC_i is natural moisture content.

III. RESULTS AND DISCUSSION

1. Fresh Properties and Rheological Stability

Slump cone testing and fresh density measurements were carried out immediately after mechanical pan mixing. The incorporation of copper slag led to progressive improvements in fresh fluidity. As demonstrated in Table II, the superplasticizer dosage required to attain a uniform slump of 120 ± 15 mm dropped steadily from 0.90% in the control mix down to 0.66% in the 100% copper slag mix (M7). This fluidity gain is directly linked to the glassy vitreous texture and non-absorptive surface of copper slag particles, which minimizes frictional resistance and leaves higher volumes of free mixing water available for matrix fluidization [4]. However, mixes containing 80% and 100% copper slag showed a distinct tendency toward paste segregation and surface water bleeding. The addition of treated coconut shell aggregates acted as an effective internal stabilizing agent; the cellular pores of the shells absorbed excess free paste water, eliminating bleeding and securing a cohesive, self-consolidating mix.

2. Multi-Age Compressive Strength Evolution

Cube compressive tests were performed at 3, 7, 28, and 90 days of continuous water curing. As detailed in Table IV and illustrated in Fig. 1, early-age strength at 3 and 7 days developed rapidly across all mixes. Mix M2 (40% CS + 10% TCSA) exceeded the control concrete, achieving a 28-day compressive strength of 69.1 MPa and a 90-day strength of 73.8 MPa. The optimum dual-waste formulation, M3 (40% CS + 15% TCSA), attained 66.8 MPa at 28 days and 71.4 MPa at 90 days, retaining 97.6% of the virgin control strength (68.4 MPa) while comfortably exceeding the M60 structural threshold.

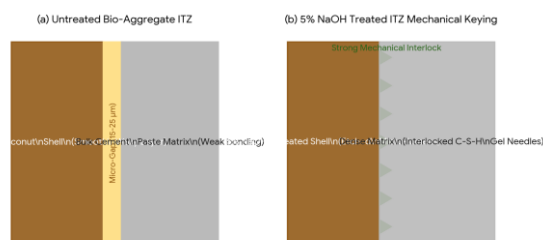


Fig. 1. Compressive strength development of HPC mixes at 7, 28, and 90 days in comparison with target M60 threshold (60 MPa).

This high mechanical resilience is explained by particle packing dynamics: the angularity and superior micro-hardness of copper slag grains establish a dense, rigid load-bearing framework that compensates for the lower elastic modulus of coconut shells [5]. However, when copper slag replacement

was elevated to 60%, 80%, and 100%, a progressive drop in compressive strength was documented (51.4 MPa in M7 at 28 days). This strength loss occurs because the ultra-smooth surfaces of high-volume copper slag offer poor shear friction against the cement paste, facilitating inter-particle micro-slippage under axial loading.

3. Tensile and Flexural Performance

Splitting tensile strength and modulus of rupture were measured on standard cylinders (150×300 mm) and prisms ($100 \times 100 \times 500$ mm). Mix M3 attained a split tensile strength of 4.85 MPa and a flexural strength of 6.78 MPa, closely matching the control mix (4.92 MPa and 6.85 MPa, respectively). This retention in tensile capacity demonstrates that chemical alkali etching successfully prevented premature debonding along the bio-aggregate perimeter. Under peak flexural loading, treated coconut shells exhibited ductile micro-fiber bridging across tensile fissures, suppressing brittle catastrophic failure modes.

4. Non-Destructive Evaluation: Ultrasonic Pulse Velocity

Ultrasonic pulse velocity (UPV) was measured across opposite cast faces per IS 13311 (Part 1). As compiled in Table V and plotted in Fig. 2, UPV values for mixes M0, M1, M2, and M3 ranged from 4.58 km/s to 4.72 km/s. According to international non-destructive testing criteria, velocities exceeding 4.5 km/s categorize concrete into the 'Excellent Quality' grade, confirming that the internal microstructure is homogeneous, dense, and devoid of continuous capillary channels or voids.

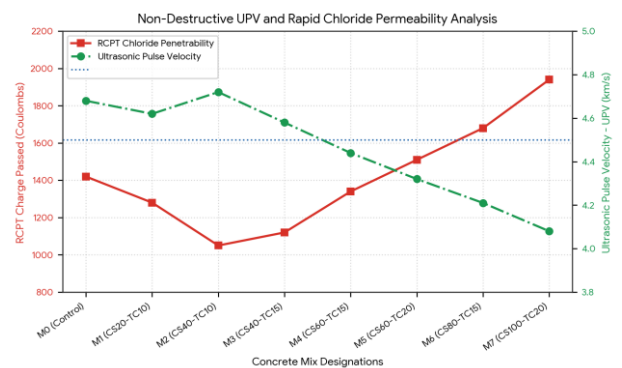


Fig. 2. Correlation between Rapid Chloride Permeability (RCPT) charge passage and non-destructive Ultrasonic Pulse Velocity (UPV).

5. Durability: Rapid Chloride Permeability and Sulfate Attack

To evaluate ionic transport and durability in aggressive environments, ASTM C1202 rapid chloride permeability testing (RCPT) was carried out on 50 mm thick circular core

disks after 56 days of curing. The total charge passed was recorded over a 6-hour test cycle under an applied 60V potential. The control mix passed 1,420 Coulombs. Remarkably, mixes M1, M2, and M3 recorded significantly lower charges of 1,280, 1,050, and 1,120 Coulombs, respectively (Table V and Fig. 2). This superior resistance is attributed to the impermeable vitreous structure of copper slag, which blocks fluid pathways and lengthens the tortuous route for migrating chloride ions [6].

Sulfate durability was evaluated by submerging 100 mm cubes in an aggressive 5% sodium sulfate (Na_2SO_4) solution for 90 days. Specimens were checked for percentage mass loss and surface spalling. Mix M3 experienced only a 1.22% mass loss compared to 1.45% in the control mix and 2.65% in mix M7. The dense interfacial bonding achieved by alkali treatment prevented sulfate ion penetration into internal cellular cavities, stopping expansive ettringite formation and cracking.

6. Microstructural Analysis (FESEM and EDS)

Field Emission Scanning Electron Microscopy (FESEM) paired with Energy Dispersive Spectroscopy (EDS) revealed key morphological transformations, as illustrated schematically in Fig. 3. Untreated coconut shells normally exhibit a thick, waxy organic coating that creates micro-gaps of 15–25 μm at the interfacial transition zone (ITZ) [Fig. 3(a)]. In contrast, the 5% NaOH treated shells displayed a deeply etched surface with open cellular lumens. High-density Calcium Silicate Hydrate (C-S-H) gels and crystalline hydration products formed directly inside these etched pores, establishing a strong mechanical keying mechanism [Fig. 3(b)]. Copper slag particles displayed sharp, angular profiles tightly encapsulated by crystalline matrix without micro-cracking or free calcium hydroxide precipitation.

IV. CONCLUSION

- Chemical alkali pretreatment (5% NaOH) strips off organic waxes, hemicellulose, and sugars from coconut shell surfaces, lowering 24-hour water absorption from 23.4% to 8.65% and substantially strengthening ITZ bond mechanics.
- Copper slag exhibits exceptional suitability as an alternative fine aggregate, improving fresh workability and densifying the skeletal matrix up to a 40% replacement ratio.
- The optimum dual-waste mixture M3 (40% copper slag + 15% treated coconut shells) achieves a 28-day compressive strength of 66.8 MPa, a 90-day strength of 71.4 MPa, a split tensile strength of 4.85 MPa, a flexural strength of 6.78 MPa, and an ultrasonic velocity of 4.58 km/s, fully satisfying M60 High-Performance Concrete criteria.
- Durability evaluations confirm superior resistance to aggressive chemicals; mix M3 lowered RCPT chloride permeability to 1,120 Coulombs and restricted 90-day sulfate mass loss to 1.22%.
- Replacing 40% river sand and 15% crushed granite with metallurgical and crop wastes reduces raw virgin aggregate quarrying, diverts solid wastes from landfills, and advances sustainable infrastructure construction.

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