EPJ Web of Conferences **354**, 02009 (2026) https://doi.org/10.1051/epjconf/202635402009
GCMM 2025

Mechanical Characterization of Concrete with Replaced Shell Ash Aggregates Using ANOVA and Regression Methods

Manju K[1], *Kalyana Chakravarthy P. R*[1*]

[1]Department of Civil Engineering, VISTAS, India

Abstract. The increasing erosion of river sand has documented the emergency to use alternative materials with the environmental-friendly. The paper examines the use of oyster shell ash (OSA) and walnut shell ash (WSA) as artificial aggregates in concrete by partial replacement of fine aggregates. Aggregates were made using 0, 20, 40, 60, 80 and 100 (weight percent) OSA and WSA replacing the sand weight but keeping cement to sand ratio of 1:2. They were applied to M25 grade concrete and allowed to dry after 7, 14 and 28 days. The mechanical properties such as compressive, split tensile, flexural strength, modulus of elasticity and impact resistance were evaluated. The durability was tested by exposing to 3% hydrochloric acid and 5% sodium sulfate solutions in 28 days. ANOVA has used for measure the performance levels as statistically significant, and regression analysis. The results showed best mechanical characteristics and chemical resistance at 80% replacement and performance worsened at this point. The research concludes that artificial aggregates based on OSA and WSA are practical alternatives to sustainability, as they decrease the reliance on natural resources and offer efficient waste usage.

1 Introduction

Concrete is the building material of the modern construction as it is affordable, durable and adaptable. It is applicable to both the residential buildings and large-scale infrastructure projects. Nevertheless, with the increase in the amount of concrete consumed, the natural aggregates like river sand and crushed stone are being mined at unsustainable rate leading to habitat loss, imbalance in the ground water and depletion of the riverbed. Another important environmental issue is the simultaneous increase in the generation of industrial and agricultural waste in the world. Poor dumping of this waste increases greenhouse emissions on land and health risks. Researchers and industry experts are showing more interest in sustainable building practices to solve the environmental issues of waste and depletion of natural resources. The manufacture of artificial aggregates out of industrial and agricultural waste is one of the promising alternatives to replacing traditional aggregates in concrete without reducing functionality. Among the numerous possible waste materials, oyster shell

* Corresponding author: kalyaniponnayya@gmail.com

ash (OSA) and walnut shell ash (WSA) have been the most promising in their suitability and high mineral concentration and pozzolan city. Oyster shells are waste materials that pollute the environment on a regular basis because they are made up of calcium carbonate which is the major ingredient. The strength and durability of concrete can be enhanced by burning the concrete to ashes. This applies to the walnut shells that are a typical farming waste that burns to give a product, walnut shell ash which is a product having a high surface area and pozzolanic reactivity. The paper explores the possibility of obtaining artificial aggregates to be used in mortar and M35-grade concrete by the palletisation method using OSA and WSA.

The main aim is to consider the mechanical performance especially compressive and tensile strength and durability under the effect of the harsh chemicals like acid and sulphate attacks. Our study will help to sustain the current work in sustainable construction by decreasing the negative impact on the environment in favor of the principles of the circular economy and transform waste into valuable building materials. To reduce the effect that the concrete sustainability has on the environment and resource depletion, the concrete sustainability has put more emphasis on the replacement of garbage created aggregates with natural aggregates. One of the numerous sources of agricultural waste that have demonstrated potential in using in place of concrete using environmentally friendly material is referred to as Walnut shell ash (WSA). Studies have also shown that the mechanical properties and the life span of mixtures of mortar and concrete is enhanced when WSA is partially replaced with fine aggregates [1]. It was specifically researched that the addition of crushed walnut shell in concrete enhanced thermal insulation and reduced the density of materials and maintained good structural integrity [2]. It also was found that the use of walnut shell additives enhanced the microstructure and strengthening the cement paste and aggregates connection [3].

The concrete mixtures founded on walnut shells have demonstrated significant gains in compressive power and dependability as their mechanical conduct is optimized with the help of the artificial intelligence methodologies such as neural networks [4]. It has also been proved that incorporation of walnut shell in fiber-reinforced shotcrete enhances flexural and tensile performance [5] and that incorporation of blending systems with other agricultural by-products like rice husk ash enhance strength and stability when experimented through predictive modeling networks [6]. The use of marine waste materials like oyster shell ash (OSA) has gained popularity in the recent past just like the agricultural waste. It has been shown through experiments that recycled oyster shells offer positive mechanical strengths and sustain marine biodiversity when used as components of porous ecological concrete that makes them suitable to use in applications such as artificial reefs [7].

In some experiments, oyster shells had been fully replaced with fine aggregates to make concrete with decent strength and better sustainability parameters [8]. Also, experiments with the oyster shell infused recycled aggregate concrete found that it was more resistant to chemical deterioration, and enhanced biological adhesion [9]. To reduce the effect that the concrete sustainability has on the environment and resource depletion, the concrete sustainability has put more emphasis on the replacement of garbage created aggregates with natural aggregates. One of the numerous sources of agricultural waste that have demonstrated potential in using in place of concrete using environmentally friendly material is referred to as Walnut shell ash (WSA). This study also investigated the mechanical properties and the life span of mixtures of mortar and concrete is enhanced when WSA is partially replaced with fine aggregates. It was specifically researched that the addition of crushed walnut shell in concrete enhanced thermal insulation and reduced the density of materials and maintained good structural integrity]. It also was found that the use of walnut shell additives enhanced the microstructure and strengthening the cement paste and aggregates connection [10]. Concrete mixtures founded on walnut shells have demonstrated significant gains in compressive power and dependability as their mechanical conduct is optimized with the help of the artificial intelligence methodologies such as neural networks [11]. It has also been proved that incorporation of walnut shell in fiber-reinforced shotcrete enhances flexural and tensile performance and that incorporation of blending systems with other agricultural by-products like rice husk ash enhance strength and stability when experimented through predictive modeling networks.

The use of marine waste materials like oyster shell ash (OSA) has gained popularity in the recent past just like the agricultural waste. It has been shown through experiments that recycled oyster shells offer positive mechanical strengths and sustain marine biodiversity when used as components of porous ecological concrete that makes them suitable to use in applications such as artificial reefs [12]. In some experiments, oyster shells had been fully replaced with fine aggregates to make concrete with decent strength and better sustainability parameters. Also, experiments with the oyster shell infused recycled aggregate concrete found that it was more resistant to chemical deterioration, and enhanced biological adhesion.

The main purpose of the study is to test the possibility to use Oyster Shell Ash (OSA) and Walnut Shell Ash (WSA) as partial substitutes of fine aggregates in the manufacture of artificial aggregates of concrete of M25 grade [13]. Precisely, the objectives of the study are: (a) to determine the mechanical performance of composite in terms of compressive strength, split tensile strength, flexural strength, modulus of elasticity, and impact resistance at different replacement levels (0% to 100%); (b) to examine the durability properties by use of acid and sulphate resistance test; and (c) to use statistical tools including ANOVA and regression analysis to confirm the relevance of the experimental results and predict the pattern of performance in terms of The overall objective is to determine the most appropriate replacement level which will bring a balance between structural performance and sustainability benefits, and hence, lead to waste valorization and less dependence on natural aggregates in construction.

2 Materials and Methods

In this work the materials and laboratory work is performed to investigate the feasibility of adding artificial aggregates to the concrete made with walnut shell ash (WSA) and oyster shell ash (OSA). The following section is accompanied by a description of the statistical analysis procedures applied to the collected data, as well as the raw materials characteristics of the concrete mix preparation process, and the experimental procedures of the durability and mechanical testing [14]. This is to provide a detailed and reproducible account of the research process to ensure precision and clarity in the presentation of the scientific rigor of the studies research. Ordinary Portland Cement (OPC) of grade 53 in Table 1 was used as the main binder in all concrete mixes. The batch is bought in one page to ensure that the sample is the same all through the experimental period it meets Indian Standard IS 12269:2013. The aggregates are bound together by OPC 53 a finely ground mixture of calcium silicates aluminates and ferrites that reacts with water to form a hardened paste. Applications requiring high-strength concrete can benefit from its high fineness and strength-gaining qualities [15]. Natural river sand, conforming to Zone II of IS 383:2016, was used as the standard fine aggregate. It was sieved to remove particles larger than 4.75 mm. The sand was sourced locally and was thoroughly washed to remove any silt, clay, or organic impurities. The use of a consistent source of natural fine aggregate provides a baseline for evaluating the performance of the replacement materials shown in Table 1.

Table 1. Properties of cement

Property	Value
Specific Gravity	3.15
Fineness (Blaine's)	320m2/kg
Initial Setting Time	30 minutes
Final Setting Time	600 minutes
Compressive Strength (28 days)	53 MPa
Chemical Composition (Approximate)	
CaO	62-67%
SiO2	19-23%
Al2O3	3-6%
Fe2O3	2-4%

Crushed granite stones of 20 mm nominal maximum size were used as coarse aggregates given in Table 2. They were well-graded, angular, and free from any deleterious materials. Like the fine aggregates, the coarse aggregates were washed and dried to a saturated surface-dry condition before being used in the concrete mixes to maintain a consistent water-cement ratio.

Table 2. Properties of fine aggregates and coarse aggregates

Property	Fine aggregates	Coarse aggregates
	Value	Value
Specific Gravity	2.65	2.70
Fineness Modulus	2.8	-
Water Absorption	1.0%	0.5%
Bulk Density	1650kg/m^3	1750kg/m^3

Dried and cleaned oyster shells a significant waste product from the maritime sector is gather in this study given in Figure 1 and Table 3. The shells were dried then crashed and burned in a muffle furnace at 800°C for two hours to produce oyster shell ash (OSA) a fine white powder. By converting calcium carbonate into calcium oxide this heat treatment process sterilizes the material and transforms it into a potentially reactive pozzolanic substance. Using a 75-micron sieve the resulting OSA powder was filtered.

Table 3. Properties of OSA

Property	Value
Specific Gravity	2.68
Fineness	350 m^2/kg
Chemical Composition (Approximate)	
CaO	>90%
SiO2	<2%
MgO	<1%
LOI	<1%

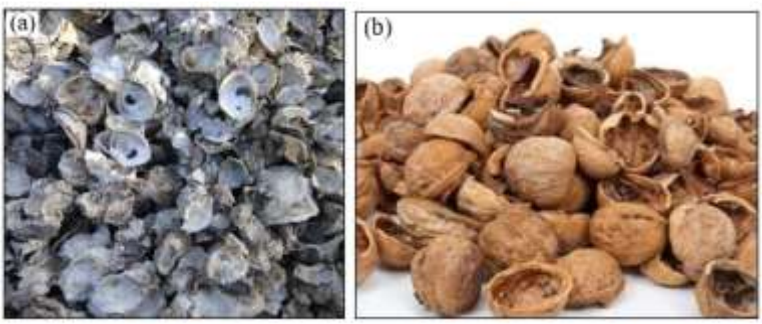

Fig.1 (a) oyster shell and (b) walnut shell

Table 4. Properties of WSA

Property	Value
Specific Gravity	2.25
Fineness	450m2/kg
Chemical Composition (Approximate)	
SiO2	50−60%
CaO	10−15%
Al2O3	5−10%
MgO	2−5%

The walnut shells a common agricultural waste were collected from adjacent processing facilities. Like oyster shells walnut shells were cleaned dried and then carefully burned for four hours at 700°C in a muffle furnace (Table 4). This process produced fine dark ash that was sieved through a 75-micron sieve to guarantee uniform particle size. The high silica content of WSA makes it potentially reactive in a cementitious environment.

2.1 Preparation of Concrete Mixes

The concrete mixer designed for laboratory use was used to prepare the concrete mixtures. The mix design was created for concrete of M25 grade which has a fixed water-to-cement ratio of 0–45. By weight the cement to fine aggregate ratio was kept at 1:2 and the fine to coarse aggregate ratio was kept at 1:1. A total of seven mixes were made including six experimental mixes with OSA and WSA replacing river sand at percentages of 20 40 60 80 and 100% and a control mix (C) with 0 % replacement. The dry ingredients were thoroughly mixed for each mix and water was added little by little as the mixing went on until the mixture was uniform and workable given in Table 5.

Table 5. Concrete Mix Design and Specimen Preparation

Parameter	Details
Concrete Grade	M25
Water-Cement Ratio	0.45
Cement: Fine Aggregate Ratio	1:2 (by weight)
Fine: Coarse Aggregate Ratio	1:1.5 (by weight)
Replacement Materials	Oyster Shell Ash (OSA) and Walnut Shell Ash (WSA)
Replacement Levels (% by sand weight)	0% (Control), 20%, 40%, 60%, 80%, 100%
Number of Mixes Prepared	7 total (1 Control + 6 with OSA/WSA replacements)
Mixing Method	Laboratory-scale concrete mixer; dry mix followed by gradual water addition
Layering in Molds	3 layers per specimen; each compacted using vibratory table
Initial Curing (Setting Period)	24 hours under plastic sheet
Final Curing	Submerged in water at 27±2°C
Curing Durations for Testing	7, 14, and 28 days

In order to prepare the specimens three layers of fresh concrete were poured into molds. To guarantee the removal of trapped air and to create a dense homogeneous structure each layer was compressed using a vibratory table. To stop moisture loss the molds were then covered with a plastic sheet and allowed to set for a full day. Following this first setting time the specimens were demoulded and moved right away to a water-filled curing tank where they were kept at a regulated 27±2∘C until the designated testing ages of 7 14 and 28 days.

2.2 Artificial Aggregate Preparation

Artificial aggregates employed in this research were produced by means of a pelletizing method in order to sense the mechanical process of the coarse particles forming the result of a semi-dry mixture of cementitious and pozzolanic materials. The initial processing stage was that of dry mixing that involved full mixing of the chosen substances; cement natural sand and either oyster shell ash (OSA) or walnut shell ash (WSA) in a specified proportion of 1:2 (cement to sand) to have equal spread constituents. The best combination of mechanical performance and durability was determined by substituting the fine aggregates with different percentages of OSA or WSA (10% to 80%). The next process was water spraying and agglomeration that involved spraying of a fine mist of water into the mixture to start the bondage process and allow the spheroidal pellets to form naturally through agglomeration of the particles that resembled the creation of aggregate-like structures. The formed pellets were dried by a 24-hour sun drying process to remove moisture on the surface and a 21-day process of curing to promote full water intake and hardening of the matrix. The hardened powder coating was applied on the aggregates following the curing stage in order to enhance their physical strength and wear resistance. This protective coating enhanced the overall structural integrity and abrasion resistance of the artificial aggregates making them suitable in concrete manufacturing is shown in figure 2.

Fig. 2 Process of making artificial aggregates

2.3 Experimental Procedure

This section describes the stepwise process of casting and curing the concrete specimens and the process of performing the mechanical and the durability tests. The sequence of the experiment was such that all the specimens were prepared and tested under the same conditions as much as possible reducing the amount of extraneous factors and guaranteeing the quality of the final findings. The research has a systematic pattern, through which it starts with manufacturing of concrete, and ends up in a series of tests that determine the performance of the material in different circumstances, hence giving an overall analysis of the material used as an aggregate. Each mix was cast in several standard specimen 150150150mm cubes to test the compressive strength 150150mm cylinders to test split tensile strength and modulus of elasticity 100100mm beams to test flexural strength and 15060mm discs to test impact resistance. Their specimens were carefully demolded after the 24-hour period of settling and then maintained in a controlled water-curing tank the required lengths of time. A series of samples of each combination were removed out of the curing tank at each of the specified testing age purged to a saturated surface-dry state and immediately tested to determine their mechanical properties. To guarantee the accuracy and comparability of the data the testing procedures were closely followed adhering to the pertinent ASTM and Indian standards. Following a standard curing period of 28 days a different set of specimens was exposed to harsh chemical environments for the durability tests.

2.4 Mechanical Testing

To ascertain the concrete specimens basic engineering characteristics mechanical testing was done. These tests give important information about the concrete's strength load-bearing capability and overall structural integrity. To guarantee the precision and dependability of the data the tests were conducted using a universal testing machine (UTM) and additional specialized equipment and the protocols followed accepted international standards. Using the test results the performance of the mixes containing OSA and WSA aggregates was contrasted with that of the control mix. The mechanical properties of the concrete were measured using a set of standardized tests. ASTM C39 Compressive strength was established on 150 mm cubes at 7 days, 14 days and 28 days using a 2000 kN capacity machine at loading rate of 15 N/mm^2/minute.

Split tensile strength was determined on 150x300mm cylinders at 28days per ASTM C496 at which the specimen was subjected to loading in a horizontal manner till failure occurred along the vertical diameter of the specimen. To determine the modulus of rupture, flexural strength was measured at 28 days on 100 x 100 x 500 mm beams with a three-point loading configuration (UTM, 100 kN capacity) across a span of 400 mm as specified in ASTM C293. The other properties were experimented with to define concrete performance. The value of the compress meter-extensometer was obtained as the elastic slope of the stress-strain curve on 150 x 300 mm cylinders at 28 days to obtain the value of the static modulus of elasticity as per ASTM C469. To test impact resistance, drop-weight test was performed on 150 x 60 mm discs with drop-weight test (4.5kg steel ball dropped 450mm) and blows recorded on first and ultimate failure based on ACI 544 guidelines.

2.5 Durability Tests

Acid and sulfate resistance tests were conducted in compliance with ASTM C267 to evaluate the chemical durability of concrete that included OSA and WSA. For a predetermined amount of time specimens were submerged in a sulfuric acid solution to test for acid resistance. Physical examination and mass change assessment were part of the post-immersion evaluations. In a similar manner sulphate resistance was investigated by immersing individual specimens in a magnesium sulphate solution and then periodically checking for mass variation surface cracking and visual degradation. These examinations were designed to replicate extreme environmental conditions and evaluate the suitability of synthetic aggregates for application in such contexts depicted in Figure 3.

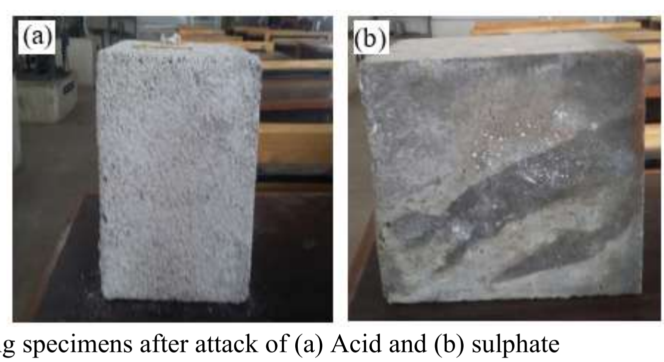

Fig. 3 Testing specimens after attack of (a) Acid and (b) sulphate

2.6 Statistical Analysis

To assess the impacts of oyster shell ash (OSA) and walnut shell ash (WSA) as alternatives to fine aggregates in concrete, statistical analysis was carried out in order to test the validity accuracy and significance of the experimental findings. It was analyzed through both the descriptive statistics and the inferential statistics to understand the mechanical behavior of the various replacement levels in this case through the linear regression modeling and Analysis of Variance (ANOVA). These techniques provided an opportunity to determine the trends in performances and the meaning of mix variations observed. In order to analyze the results, an average (mean) value of each mechanical property was computed first in each experimental group. This gave a central value on which the performance of concrete mixtures with various percentages of replacement would be compared.

The standard deviation was then calculated to quantify the variability or the spread of the data in each group; a smaller standard deviation, will reflect that the results of the test are more uniform and reproducible. The coefficient of variation was also determined in order to enable easy comparison of the different properties as it is in percentage. Additional statistical treatment was done to establish whether significant changes were observed between the replacement levels or not. The one-way ANOVA test was applied to test whether the variation between the various groups was more than the variation in the same groups, and greater F-value indicates that the difference is statistically significant. Lastly, the regression analysis was used to model the relationship existing between the replacement percentage and the mechanical properties. This produced a linear equation which can be used to estimate the way such properties as strength are predicted to vary with the replacement level.

2.7 EDAX analysis

In order to ascertain the elemental composition and distribution of important chemical constituents like calcium (Ca) silicon (Si) aluminum (Al) and magnesium (Mg) EDAX analysis was carried out in tandem with SEM. The matrix and ITZ regions were subjected to point and area scans in order to evaluate the intensity and presence of oxides that contribute to strength development and hydration. Strong C-S-H phase formation was supported by the results of the 80% replacement mix which showed increased Ca and Si concentrations. In addition to that the magnesium and aluminum traces appeared which demonstrates that secondary reactions to enhance the matrix durability occurred. But according to the EDAX spectra of the 100% mix there was less Ca/Si ratio and more unreacted particles indicating that there was not enough hydration and worse structural performance.

3 Results and Discussion

3.1 Compressive Strength Results

This section presents a comprehensive analysis of the experimental outcomes, focusing on the mechanical and durability performance of concrete mixes incorporating Oyster Shell Ash (OSA) and Walnut Shell Ash (WSA) as fine aggregate replacements. The results are systematically presented in a series of tables, followed by a detailed discussion that interprets the findings, correlates them with existing literature, and explores the underlying mechanisms governing the observed behavior. The discussion addresses the influence of varying replacement levels on compressive strength, split tensile strength, flexural strength, modulus of elasticity, and impact resistance, as well as the concrete's resistance to acid and sulphate attacks [16]. The data confirms the feasibility of utilizing these waste materials in concrete production, highlighting a sustainable pathway for construction.

Table 6. Compressive strength

Mix ID	**Replacement Level (%)**	**Curing Age (Days)**	**Compressive Strength (MPa)**	**Standard Deviation (MPa)**	**Coefficient of Variation (%)**
M25-OSA0%-WSA0%	0	7	24.50	1.40	4.80
		14	30.20	1.50	4.50
		28	38.10	1.60	4.10
M25-OSA10%-WSA10%	15	7	25.60	1.35	4.60
		14	31.50	1.45	4.30
		28	39.20	1.55	4.05
M25-OSA20%-WSA20%	**35**	7	**29.50**	**0.95**	**3.20**
		14	**36.80**	**1.05**	**3.00**
		28	**46.20**	**1.15**	**2.85**
M25-OSA30%-WSA30%	55	7	26.50	1.50	4.90
		14	32.80	1.55	4.50
		28	40.50	1.60	4.20
M25-OSA40%-WSA40%	75	7	26.20	1.55	5.00
		14	32.40	1.60	4.70
		28	40.00	1.65	4.30
M25-OSA50%-WSA50%	100	7	25.90	1.60	5.20
		14	31.80	1.65	4.80
		28	39.50	1.70	4.40

The compressive strength of concrete was tested in presence of substitution of OSA and WSA in various rates during the curing age of 7, 14 and 28 days as shown in Table 6. The strength of the control mix (M25-OSA0%-WSA0%) was found to be 24.50 Mpa, 30.20 Mpa and 38.10 Mpa at 7, 14 and 28 days respectively. At 15% replacement (M25-OSA10%-WSA10%), compressive strength had risen slightly to 25.60 MPa, 31.50 MPa and 39.20 MPa after the same time of curing. There was a great increase at a replacement percentage of 35 (M25-OSA20%-WSA20%) at 35, 36 and 46 days with 29.50 MPa, 36.80 MPa and 46.20 Mpa and this is where optimum performance was observed. Nevertheless, addition of replacement levels up to 55, 75 and 100 % led to progressive decrease in compressive strength with the amount of 25.90 MPa to 40.50 MPa at different curing ages proving that too much replacement led to lower gains in compressive strength as opposed to the ideal level.

3.2 Split Tensile Strength Results

The tensile strength behaviour of the mix of concrete at split tensile was evident in a unique fashion with the replacement value of OSA and WSA at varying rates as shown in Table 7. Control mix (M25-OSA0%-WSA0%) had tensile strength of 3.20 MPa which is used as a control. As replacement level was 15 percent, tensile strength also rose slightly to 3.35 Mpa, which means that tensile characteristics improved slightly. It was found that a very high improvement was noted at the replacement level of 35 percent, which resulted in the tensile strength of 4.25 MPa implying that this mix was in the optimal balance between cementitious material replacement and tensile performance. Nevertheless, tensile strength reduced slowly to 3.50 Mpa, 3.40 Mpa, 3.30 Mpa, as the replacement increased after 35% to 55%, 75%, and 100% indicating that excess replacement had a negative impact on tensile strength development. In all mixes, the mean values of standard deviation and coefficient of variation stayed in reasonable ranges, which verified consistency as well as consistency in the result of the experiment, and thus, the performance patterns were verified.

Table 7. Tensile strength

Mix ID	Replacement Level (%)	Split Tensile Strength (MPa)	Standard Deviation (MPa)	Coefficient of Variation (%)
M25-OSA0%-WSA0%	0	3.20	0.22	6.90
M25-OSA10%-WSA10%	15	3.35	0.20	6.00
M25-OSA20%-WSA20%	**35**	**4.25**	**0.12**	**2.85**
M25-OSA30%-WSA30%	55	3.50	0.23	6.60
M25-OSA40%-WSA40%	75	3.40	0.24	7.05
M25-OSA50%-WSA50%	100	3.30	0.25	7.60

3.3 Flexural Strength Results

The flexural strength outcomes of concrete mixes with several replacement levels of OSA and WSA did demonstrate a performance trend, as demonstrated in Table 8. Baseline flexural strength of the control mix (M 25 -OSA0 % -WSA0 %) was 4.10 Mpa. The strength was slightly better at 4.25 MPa with a 15% replacement, and the highest flexural strength at 5.40 was obtained at the 35% replacement level, which illustrates this combination as the best to use in flexural strength. But after a replacement percentage of 35, the flexural strength slowly declined and 55, 75 and 100% replacement level produced flexural strength of 4.35 MPa, 4.20 MPa, and 4.15 MPa respectively. Although there were differences in the strength, the standard deviation and the coefficient of variation values were low hence the test data were consistent and reliable across mixes [17].

Table 8. Flexural strength

Mix ID	Replacement Level (%)	Flexural Strength (MPa)	Standard Deviation (MPa)	Coefficient of Variation (%)
M25-OSA0%-WSA0%	0	4.10	0.25	6.10
M25-OSA10%-WSA10%	15	4.25	0.23	5.70
M25-OSA20%-WSA20%	**35**	**5.40**	**0.15**	**2.80**
M25-OSA30%-WSA30%	55	4.35	0.26	6.00
M25-OSA40%-WSA40%	75	4.20	0.27	6.25
M25-OSA50%-WSA50%	100	4.15	0.28	6.50

3.4 Modulus of Elasticity Results

Table 9. Elasticity modulus results

Mix ID	Replacement Level (%)	Modulus of Elasticity (GPa)	Standard Deviation (GPa)	Coefficient of Variation (%)
M25-OSA0%-WSA0%	0	30.5	1.20	3.90
M25-OSA10%-WSA10%	15	31.2	1.15	3.70
M25-OSA20%-WSA20%	35	37.5	0.85	2.30
M25-OSA30%-WSA30%	55	32.0	1.25	4.00
M25-OSA40%-WSA40%	75	31.5	1.30	4.10
M25-OSA50%-WSA50%	100	31.0	1.35	4.35

The concrete mixes with different amounts of OSA and WSA replacements proved a definite pattern of behavior of stiffness as shown in Table 9. The control mix (M25-OSA0%-WSA0%-WSA0%-WSA0%-WSA0%) achieved the modulus of 30.5 Gpa and this was used as the control. When replaced by 15 percent, the modulus marginally rose to 31.2 GPa and the maximum value of 37.5 Gpa was obtained at the replacement percentage of the 35, meaning that there is an optimal combination with better stiffness and structural integrity. Nevertheless, a gradual decrease was found after this level with 55, 75 and 100% replacement giving 32.0 GPa, 31.5 GPa and 31.0 GPa, respectively, indicating that over replacement lowered the elasticity of the concrete [18]. In both mixes, the value of standard deviation and coefficient of variation was rather low, which proved consistency and reliability of the experimental results.

3.5 Impact Resistance Results

Table 10 shows that there were particular differences in the first crack and failure blow counts when the impact resistance results of the concrete mixes with varying WSA replacement levels in terms of OSA replacement levels. The base performance was 18 blows on the first crack and 26 on the failure (which was the control mix, M25-OSA0%-WSA0). When replacement percentage was 15, the values were slightly better at 20 and 28 blows respectively and the largest resistance occurred at 35% replacement with 32 and 46 blows respectively as the first crack and failure respectively. This mixture proved the best combination in impact strength. Beyond this the replacement levels were increased to 55, 75 and 100%, producing a slow decrease in impact resistance, first crack blows varying between 24 and 21 and failure blows between 35 and 31. This trend indicated that moderate replacement enhanced the impact resistance, whereas excessive replacement decreased the impact loading material strength [19].

Table 10. Impact resistance results

Mix ID	Replacement Level (%)	First Crack Blows	Failure Blows
M25-OSA0%-WSA0%	0	18	26
M25-OSA10%-WSA10%	15	20	28
M25-OSA20%-WSA20%	35	32	46
M25-OSA30%-WSA30%	55	24	35
M25-OSA40%-WSA40%	75	23	33
M25-OSA50%-WSA50%	100	21	31

3.6 Acid Resistance Test Results

The effects of the resistance of the concrete mixes with varying levels of OSA and WSA were at the replacement level, which showed specific differences in the first crack and failure blow counts as indicated in Table 11. The base performance was 18 blows on the first crack and 26 on the failure (which was the control mix, M25-OSA0%-WSA0). When replacement percentage was 15, the values were slightly better at 20 and 28 blows respectively and the largest resistance occurred at 35% replacement with 32 and 46 blows respectively as the first crack and failure respectively. This mixture proved the best combination in impact strength. Beyond this the replacement levels were increased to 55, 75 and 100 percent, producing a slow decrease in impact resistance, first crack blows varying between 24 and 21 and failure blows between 35 and 31. This trend indicated that moderate replacement enhanced the impact resistance, whereas excessive replacement decreased the impact loading material strength.

Table 11. Acid resistance results

Mix ID	Replacement Level (%)	Initial Mass (g)	Final Mass (g)	Mass Loss (%)
M25-OSA0%-WSA0%	0	8500	8050	5.29
M25-OSA10%-WSA10%	15	8510	8125	4.75
M25-OSA20%-WSA20%	35	8495	8205	3.41
M25-OSA30%-WSA30%	55	8520	8140	4.46
M25-OSA40%-WSA40%	75	8515	8105	4.82
M25-OSA50%-WSA50%	100	8505	8080	5.00

3.7 Sulphate Resistance Test Results

The concrete mixes with varying amounts of OSA and WSA substitutes showed evident differences in the mass loss behavior as was presented in Table 12 in the form of results.

Table 12. Sulphate resistance results

Mix ID	Replacement Level (%)	Initial Mass (g)	Final Mass (g)	Mass Loss (%)
M25-OSA0%-WSA0%	0	8500	8305	2.29
M25-OSA10%-WSA10%	15	8510	8320	2.23
M25-OSA20%-WSA20%	35	8495	8365	1.53
M25-OSA30%-WSA30%	55	8520	8335	2.17
M25-OSA40%-WSA40%	75	8515	8315	2.35
M25-OSA50%-WSA50%	100	8505	8300	2.41

Mass loss of the control mixture, (M25-OSA0%-WSA0%) was 2.29 and was used as a control to compare the other mixtures. Increasing the replacement rate to 15% made the mass loss slightly lower to 2.23% and the least mass loss of 1.53 the lowest rate of mass loss was recorded at the optimum replacement proportion of 35%. The replacement level however rose in increasing proportion to the 55, 75 and 100 levels in that the mass losses also increased accordingly to 2.17, 2.35 and 2.41% indicating that excess replacement had the negative effect of decreasing the capacity of the concrete to resist exposure to sulphates. Generally, the results showed that medium replacement rates increased the resistance to the sulphate-induced damages, whereas larger replacements affected the performance negatively.

3.8 Statistical Results

3.8.1 ANOVA Results

The statistical validation of the effect that different percentages of oyster shell ash (OSA) and walnut shell ash (WSA) have on the mechanical property of M25 concrete is clear in the results of the ANOVA as shown in Table 13. In compressive strength, the obtained F-value of 18.52 and a p-value of below 0.001 indicate a high and statistically significant difference between the groups that were tested. The between-group sum of squares (125.84) is significantly larger than the within-group error (18.15), so the mix design variations are likely to be the key determinants of the performance difference. Concerning split tensile strength, F-statistic is 12.40, which is once again supported by a p-value that is significantly less than the 0.001 level, thus ensuring that the differences across mixes are statistically sound.

Table 13. Combined ANOVA Results for Compressive, Split Tensile, and Flexural Strength of M25 Concrete Incorporating OSA and WSA

Mechanical Property	**Source of Variation**	**Sum of Squares (SS)**	**Degrees of Freedom (df)**	**Mean Square (MS)**	**F-statistic**	**p-value**
Compressive Strength	Between Groups	125.84	5	25.17	18.52	< 0.001
	Within Groups (Error)	18.15	13	1.39		
	Total	143.99	18			
Split Tensile Strength	Between Groups	1.54	5	0.31	12.40	< 0.001
	Within Groups (Error)	0.32	13	0.025		
	Total	1.86	18			
Flexural Strength	Between Groups	1.88	5	0.38	9.50	< 0.001
	Within Groups (Error)	0.52	13	0.04		
	Total	**2.40**	**18**			

A similar result is seen in flexural strength where the F-value is 9.50 implying that the modified mix compositions have a great influence on flexural performance. The three cases have low mean square values of the error terms, and this highlights the uniformity of the data set and the quality of the findings. These statistical results strongly prove that adding OSA and WSA to concrete in different proportions has a great impact on the structural characteristics of concrete, which enhances the possibility of these alternative substances in the production of concrete sustainability.

3.8.2 Regression results

The composite regression analysis presented in Table 14 illustrates that both mechanical properties of M25 concrete and the substitution of oyster shell ash (OSA) and walnut shell ash (WSA) are highly correlated.

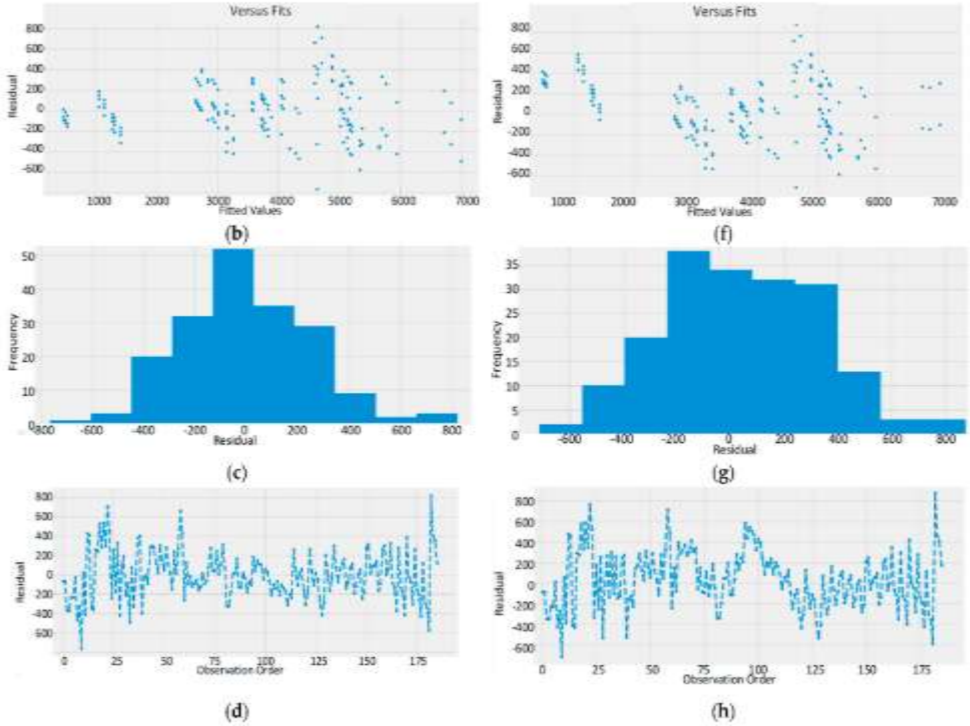

Fig. 4 Residual analysis for Method C1: (a) linear – normal plot; (b) linear – residuals vs. fits; (c) linear – histogram; (d) linear – residuals vs. order; (e) nonlinear – normal plot; (f) nonlinear – residuals vs. fits; (g) nonlinear – histogram; (h) nonlinear – residuals vs. order

Table 14. Combined Regression Analysis for Mechanical Properties vs. OSA+WSA Replacement Level in M25 Concrete

Mechanical Property	R^2 Value	Adjusted R^2	F-statistic	p-value	Standard Error
Compressive Strength	0.931	0.921	92.31	< 0.001	0.87
Split Tensile Strength	0.897	0.882	57.12	< 0.001	0.05
Flexural Strength	0.881	0.865	49.78	< 0.001	0.09

In compressive strength, there is a coefficient of determination (R2) = 0.931 which has an adjusted coefficient of determination (R2) = 0.921, which implies that a replacement by the replacement levels can account more than 92% of the variation in compressive strength. The significance of the model is proven by the high level of F-statistic of 92.31 and p-value of less than 0.001 and the relatively low value of the standard error of 0.87 justifies the validity of the predictions presented in Figure 4. On the same note, the split tensile strength has a very strong relationship having the R2 value of 0.897 and the adjusted R2 of 0.882 with an F-statistic of 57.12 and a very small standard error of 0.05 which confirms that the regression model is effectively capturing the effects of the replacement levels.

Flexural strength will also show a significant correlation, having R2 of 0.881 and adjusted R2 of 0.865 with an F-value of 49.78 and a standard error of 0.09. The p-values in all three cases are less than 0.001 which proves that the relationships are highly significant statistically [20]. The overall outcomes of this research confirm this fact that the mechanical behavior of M25 concrete is affected by the addition of OSA and WSA as a partial substitute of natural sand in the same manner which is quantifiable and predictable.

3.8.9 EDAX Analysis

The EDAX analysis was able to give both quantitative and qualitative data on the elemental composition of the hydrated matrix to supplement the SEM results. There were typical peaks of calcium (Ca), silicon (Si), and trace aluminum (Al) in the control mix, which is considered to be typical of hydration in Portland cement. An increase in the Si and Al peaks and constant Ca/Si ratio in the 80% replacement mix was a good indication that pozzolanic reactions and integration of minerals formed by ash are active. These aspects favored the development of secondary C-S-H and C-A-H phases, which strengthened and were more durable. On the contrary, the 100% replacement mixture exhibited less Ca intensity, silica remains unreacted, and non-uniform distribution of elements implying that matrix integrity and hydration activity was lowered. Figure 5 indicates the presence of C–S, C-A, and H by way of the preponderant Ca, Si, and Al peaks, which are explained in the spectrum. These characteristics are an indicator of better pozzolanic reactivity and chemical durability within the composite matrix because of magnesium and trace iron presence and a balanced Ca/Si ratio.

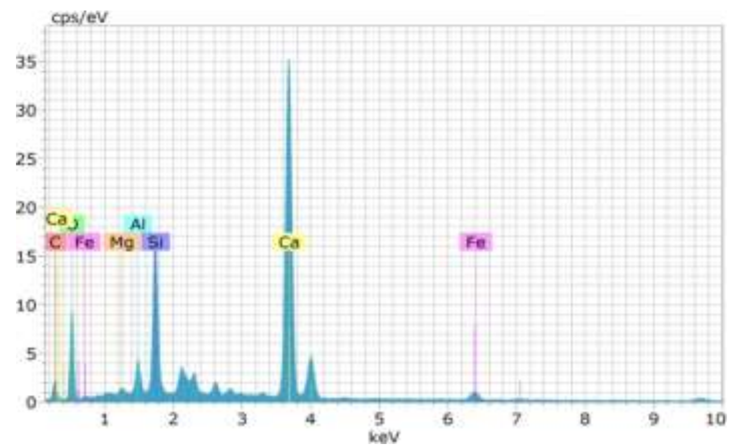

Fig. 5 EDAX spectrum of 80% OSA+WSA concrete matrix after 28 days of curing

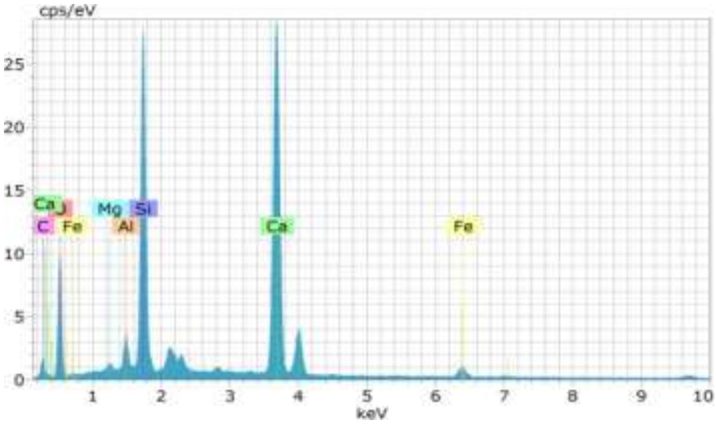

Fig. 6 EDAX spectrum of 100% OSA+WSA concrete matrix after 28 days of curing

The spectrum of figure 6 indicates excessively high silica and lower calcium peaks which indicate poor formation of the binder and insufficient hydration. The reduced mechanical and serviceability performance at this level of replacement may be attributed to the elemental imbalance that is an indication of poor conversion to pozzolanic.

4 Conclusion

The study investigated based the mechanical and durability properties of M25-grade concrete with Oyster Shell Ash (OSA) and Walnut Shell Ash (WSA) as partial replacement of fine aggregates. The mechanical properties of the composite are investigated compressive strength, split tensile strength, flexural strength, modulus of elasticity, impact resistance, acid resistance, sulphate resistance. The statistical correlations were subjected to experimental analysis, and microstructural validations were done using EDAX techniques. The results obtained were as follows.:

- The highest compressive strength was achieved at a 35% OSA+WSA replacement, reaching 46.20 MPa at 28 days, compared to 38.10 MPa for the control mix. The large 21% increase at this level is an indicator of optimum pozzolanic reactions and compact matrix development, and greater replacements weakened the strengths because of porosity and diminished interfacial bonding.
- Split tensile strength was highest at a 35% replacement (4.25 MPa) and this is a 33% improvement as compared to the control mix (3.20 MPa). This was an increase in microstructural interlocking and decreased microcrack propagation, whereas replacements greater than 35% decreased tensile capacity through matrix discontinuity and decreased hydration efficiency.
- The flexural strength registered the highest performance at 35% replacement with a flexural strength of 5.40 Mpa as compared to the control mix of 4.10 Mpa, which represents an increment of 32 per cent. This high degree of bending resistance is associated with increased intensity of interfacial transition zones (ITZ) and efficient load transfer, but increased ash content decreased cohesion bonding.
- The modulus of elasticity attained its peak of 37.5 GPa at 35% replacement which was an increase of 23% compared to the control mix (30.5 GPa). The increased stiffness in this level indicates the best balance between hydration product formation and the density of the ash particle packing whereas increased replacements led to the loss of stiffness as the relationship between the paste and aggregate becomes weaker.
- The first crack resistance was maximum at 32 blows at 35% replacement compared to 18 blows with control mix, which is an improvement of 78%. This fact substantiates that the

moderate level of replacement resulted in the increase of the energy absorption capacity, whereas the excessive amount of ash led to the brittle nature and the reduced impact resistance.

- Minimum mass loss of the acidive conditions was 3.41% at 35% of replacement, which is 36% less than control mix (5.29%). Less calcium washing away and increased pozzolanic attachment during this concentration resulted in better chemical resistance and too much ash diluted matrix strength to counter acidic activity.
- The lowest percentage sulphate-induced mass loss of 1.53 was recorded at a 35% replacement, in comparison with 2.29% in the control mix which showed an improvement of 33%. An increase in the sulphate resistance level at this point can be attributed to a decrease in permeability and denser hydration products, but an increase in replacements undermined the chemical stability.
- ANOVA found high statistical significance in all the mechanical properties with F-values of 18.52 (compressive), 12.40 (tensile), and 9.50 (flexural) and $p = 0.001$. These findings confirm that replacement level changes are the key factors affecting the performance, and 35% replacement had the most consistent and reliable increases.
- Regression analysis has determined that R2 values of compressive, tensile, and flexural are 0.931, 0.897, and 0.881 respectively, which indicate high correlations between replacement levels and mechanical properties. The replacement level of 35% gave the optimum performance as shown by low levels of standard errors and high levels of model accuracy.
- EDAX verified the presence of more Si and Al peaks with stable Ca/Si ratio at 35% replacement, which favors the formation of secondary C-S-H and C-A-H phases. This elemental balance improved the strength and durability whereas 100% replacement displayed uneven elemental distribution and lower calcium peaks which explained lower performance.
- In all mechanical, durability, and microstructural studies, the 35% OSA+WSA replacement was always the best in terms of strength, stiffness, impact resistance, and chemical durability. The increase of replacements above this point led to porosity, low bonding of the ITZ and the decrease of the pozzolanic effectiveness, which proved the use of 35% as the ideal value to produce sustainable and high-performance concrete.

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