RESEARCH PAPER

RSM Analysis of Acid and Sulphate Resistance of Oyster Shell Ash and Walnut Shell Ash Reinforced Concrete with Fine Aggregate Replacement

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ABSTRACT

The construction industry's continuing dependence on natural river sand has intensified interest in waste-derived alternatives for fine aggregate. This study evaluates the acid and sulphate resistance of M25-grade concrete in which natural fine aggregate was replaced by a combined Oyster Shell Ash (OSA) and Walnut Shell Ash (WSA) blend at six replacement levels (0, 20, 40, 60, 80 and 100%; Replacement (%) denotes the retained Aggregate Weight fraction). Mass loss after 28-day immersion in 3% HCl (acid resistance) and 5% Na_2SO_4 (sulphate resistance) was measured and analysed using Response Surface Methodology (RSM) in Design-Expert software, with Aggregate Weight and OSA–WSA Mix Weight modelled as complementary mixture-style factors. Findings were independently cross-checked against a separately hand-computed single-variable quadratic regression.

Acid resistance showed the strongest and most consistent response: mass loss fell from 5.00% at 0% replacement to a minimum of 3.41% at 60% replacement before rising again at higher replacement levels near 53–60% replacement. Sulphate resistance was tested under the same six replacement levels with its minimum mass loss also at 60% replacement (1.53%), the same replacement level identified as optimal for acid resistance. The results indicate that OSA–WSA incorporation, particularly near 60% replacement, improves the concrete's resistance to acidic environments and matrix densification for sulphate resistance at the same replacement level.

Keywords: Oyster Shell Ash; Walnut Shell Ash; Acid Resistance; Sulphate Resistance; Response Surface Methodology; Sustainable Concrete; Durability; Mass Loss

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1. Introduction

The concrete construction industry is one of the largest consumers of natural resources worldwide, and the extraction of river sand for fine aggregate in particular has become an increasingly contested environmental issue, linked to riverbed degradation, loss of aquatic habitat and disruption of groundwater recharge in many sand-producing regions [1]. At the same time, two waste streams of oyster shell waste from the seafood-processing industry and walnut shell waste from agricultural processing, they are generated in large volumes and disposed of predominantly

through landfilling, with little value recovery [2]. Converting these wastes into fine-aggregate replacement material offers a route to simultaneously reduce natural sand extraction and divert two under-utilised waste streams from landfill, consistent with circular-economy principles in construction [3 - 5]. Durability performance is a central consideration in evaluating any proposed fine-aggregate replacement material, since a replacement that improves short-term mechanical strength but compromises long-term resistance to chemical attack would be of limited practical value. This study therefore focuses specifically on two durability indicators — acid resistance and sulphate resistance, both quantified as percentage mass loss after 28-day immersion in the respective aggressive solution — for concrete incorporating a combined Oyster Shell Ash (OSA) and Walnut Shell Ash (WSA) replacement of natural fine aggregate [6 – 9].

1.1 Oyster Shell Ash and Walnut Shell Ash in Concrete Durability

Oyster shells are composed predominantly of calcium carbonate, and when processed into ash form they contribute a calcium-rich component to the cementitious system. Walnut shell ash, derived from an agricultural lignocellulosic waste, contains silica-bearing mineral residue that can participate in pozzolanic reaction with the calcium hydroxide released during cement hydration [10]. The combined use of a calcium-rich material (OSA) and a silica-rich material (WSA) was motivated by the hypothesis that the two would interact complementarily within the cementitious matrix: OSA's fine particles contribute a filler effect and additional calcium source, while WSA's reactive silica consumes free calcium hydroxide to form secondary calcium silicate hydrate (C-S-H), densifying the matrix and refining its pore structure [11-14]. Because both acid attack and sulphate attack proceed primarily through the ingress of aggressive ions through the pore network, any mechanism that measurably refines pore structure and reduces permeability is directly relevant to durability performance, independent of its effect on mechanical strength [15].

1.2 Acid and Sulphate Attack Mechanisms in Concrete

Acid attack on ordinary Portland cement concrete proceeds chemically: hydrochloric acid reacts with calcium-bearing hydration products. It is principally calcium hydroxide and calcium silicate hydrate and converting them into soluble calcium chloride that leaches out of the matrix, progressively increasing porosity and causing measurable mass loss. Because this process depends on the rate at which acid can penetrate the matrix, any reduction in permeability or pore interconnectivity directly slows the rate of attack [16]. Sulphate attack follows a different chemical pathway: sulphate ions ingressing from the external solution react with aluminate phases and calcium hydroxide in the hydrated cement paste to form expansive reaction products, principally ettringite and gypsum. Unlike acid attack, which is primarily a dissolution process producing net mass loss, sulphate attack involves volume-expansive product formation that can cause internal cracking in addition to surface deterioration; mass loss under sulphate exposure therefore reflects a more complex balance between expansive microcracking and surface spalling than the comparatively straightforward dissolution mechanism governing acid attack [17].

1.3 Response Surface Methodology in Durability Research

Response Surface Methodology (RSM) is a statistical modelling framework that evaluates competing model formulations, which is typically Linear, Two-Factor-Interaction (2FI), and Quadratic equation. It is against experimental data through a sequential model-selection procedure, and identifies the formulation best supported by the data using sequential p-values and Adjusted R^2 as the primary selection criteria. RSM has been applied previously to optimise supplementary cementitious material content and other mix-design parameters in concrete, but its use for durability indicators specifically as opposed to compressive or flexural strength, which is remains comparatively limited in the literature on waste-derived fine-aggregate replacement systems [18].

In this study, Design-Expert software was used to implement the RSM analysis for acid resistance and sulphate resistance, with the replacement design expressed as a two-component mixture-style formulation (Aggregate Weight and OSA–WSA Mix Weight, constrained to sum to 100%). Because the two factors are complementary rather than independent, the resulting two-factor-interaction model is, in substance, a reparameterisation of a single-variable quadratic model in replacement level, which permits direct, meaningful cross-validation against an independently hand-computed quadratic regression on the same underlying data.

1.4 Research Gap

Several gaps specific to the durability performance of OSA–WSA concrete motivate the present analysis. First, although both acid and sulphate resistance were measured as part of the broader experimental programme on this material system, they have not previously been analysed together as a focused durability study using Response Surface Methodology. Second, RSM-based optimisation studies for waste-ash concrete durability more broadly remain scarce relative to the volume of work on compressive-strength optimisation, leaving open the

question of whether a non-linear replacement-level effect exists for durability indicators and, if so, where its optimum lies. Third, few studies attempt to cross-validate RSM findings against an independent statistical method, despite this being a direct and low-cost way to assess whether an identified trend reflects a genuine property of the data rather than an artefact of a single analytical tool.

1.6 Research Objectives

This article addresses these gaps for the two durability responses only. The specific objectives are:

- To quantify the effect of OSA–WSA replacement level on acid resistance mass loss (28-day immersion in 3% HCl) across the tested 0–100% range.
- To quantify the effect of OSA–WSA replacement level on sulphate resistance mass loss (28-day immersion in 5% Na_2SO_4).
- To develop and report Response Surface Methodology (Design-Expert) models for both responses, including sequential model selection, predicted-versus-actual behaviour, interaction effects, and the fitted contour and three-dimensional response surfaces.
- To cross-validate the RSM findings against an independently computed quadratic regression on the same replacement-level data.
- To identify and transparently report any data-quality issues affecting either response, rather than silently resolving them, consistent with sound research-data practice.

2. Materials and Methods

2.1 Constituent Materials

Ordinary Portland Cement (53-grade) was used as the binder in all mixtures. Natural river sand served as the conventional fine aggregate in the control mixture, and crushed coarse aggregate from a locally available source was used uniformly across all mixtures. Oyster shell waste was cleaned, dried and processed into ash form (OSA); walnut shell waste from agricultural processing was converted into ash through controlled thermal treatment (WSA). OSA and WSA were combined in equal proportion at every tested replacement level — that is, the "OSA–WSA Mix Weight" reported throughout this article is a combined OSA+WSA replacement fraction, with OSA and WSA contributing equally within it.

2.2 Mix Proportions and Experimental Design

Fine aggregate replacement was investigated across six nominal replacement levels (0, 20, 40, 60, 80 and 100%), expressed in Design-Expert as two complementary mixture-style variables:

- **Aggregate Weight (A, %)** — the proportion of natural fine aggregate retained in the mix, and
- **OSA–WSA Mix Weight (B, %)** — the proportion of fine aggregate replaced by the combined OSA+WSA blend, related by A + B = 100% for every mix. Table 1 reproduces the design matrix together with the two durability responses analysed in this article.

Replacement (%) convention used in this revision: Tables 2 and 4 and Figures 1 and 6 report each specimen under a column headed "Replacement (%)". Per the author's confirmed convention for this revision, this value equals the retained Aggregate Weight percentage, A — not the substituted OSA–WSA Mix Weight percentage, B — that is, Replacement (%) = A = 100 − B. A reader expecting "replacement level" to mean the substituted OSA–WSA fraction should read every Replacement (%) value in this article as its complement: for example, a specimen reported here as "60% replacement" has Aggregate Weight A = 60% and OSA–WSA Mix Weight B = 40%.

Table 1. Experimental design matrix and durability responses

Aggregate Weight (A, %)	OSA–WSA Mix Weight (B, %)	Acid Resistance Mass Loss (%)	Sulphate Resistance Mass Loss (%)
100	0	5.29	2.29
80	20	4.00	2.23
60	40	3.41	1.53
40	60	4.34	2.17
20	80	4.82	2.35
0	100	5.00	2.41

Aggregate Weight = 20%, OSA–WSA Mix Weight = 80%, consistent with its response values and with the author's confirmation that the full design follows the 0/20/40/60/80/100% replacement levels.

2.3 Acid Resistance Test Procedure

Durability under acidic exposure was evaluated using percentage mass-loss measurement. Specimens from each replacement level were immersed in a 3% hydrochloric acid (HCl) solution for 28 days, then removed, cleaned of surface reaction products, dried and re-weighed. Percentage mass loss relative to the pre-immersion mass was computed as the response variable. Mass loss was selected as the primary response because it provides a direct, readily quantifiable indication of material degradation resulting from chemical attack. Table 2 reports the initial mass, final mass and resulting mass-loss percentage for each of the six replacement levels.

2.4 Sulphate Resistance Test Procedure

Sulphate resistance was evaluated using the same mass-loss approach, with specimens immersed in a 5% sodium sulphate (Na_2SO_4) solution for 28 days before cleaning, drying and re-weighing. The

sulphate-resistance specimens follow the same six-level 0/20/40/60/80/100% OSA–WSA replacement scheme used for acid resistance and reported throughout this article. An earlier draft of this analysis flagged an apparent scheme mismatch for this response (the sulphate mass-loss values had at one point been paired with an older 0/15/35/55/75/100% labelling); that mismatch has been resolved in this revision, and Table 4 reports the sulphate-resistance results against the confirmed 0/20/40/60/80/100% scheme. As with acid resistance, the Design-Expert Fit Summary for sulphate resistance (Table 5) was computed on the design matrix before the Table 1 row-5 correction and has not yet been re-run; the independent quadratic regression reported.



Figure 1. Acidic corroded concrete cubes

2.5 Response Surface Methodology and Statistical Analysis

Response Surface Methodology was implemented in Design-Expert software using the two complementary mixture-style factors described. For each response, three candidate model formulations — Linear, Two-Factor-Interaction (2FI), and Quadratic — were evaluated through Design-Expert's sequential model-selection procedure, and the best-supported model was identified using the sequential p-value and Adjusted R^2 as the primary selection criteria, supported by visual inspection of the predicted-versus-actual plot, interaction plot, contour plot and three-dimensional response surface. A significance level of $\alpha = 0.05$ was adopted throughout.

Because Aggregate Weight (A) and OSA–WSA Mix Weight (B) are complementary ($B = 100 - A$), they are not independent factors in the classical two-factor RSM sense. Concretely, the two-factor-interaction term $A \times B = A(100-A) = 100A - A^2$ already contains a quadratic component in the single underlying replacement-level variable, meaning the Design Expert 2FI model, when suggested, is mathematically closely related to a single-variable quadratic model in replacement level; a separate Quadratic model attempting independent A^2 and B^2 terms is consequently rank-deficient ("Aliased") in this design. This relationship is what allows the Design-Expert results to be compared directly against an independently hand-computed quadratic regression, $Y = b_0 + b_1X + b_2X^2$, fitted separately in this study using ordinary least squares on the same six group-mean mass-loss values, with X taken as the Replacement (%) value defined (Aggregate Weight, A). Because the experimental programme comprised only six replacement levels, every fitted model in this article carries three residual degrees of freedom; this small-sample constraint, rather than a weakness specific to either analytical method, is the primary reason several otherwise-meaningful trends fall short of the conventional $\alpha = 0.05$ significance threshold, and is why both the sequential p-value / Adjusted R^2 from Design-Expert and the independently-computed nested F-test from the hand-fitted quadratic regression are reported side by side for acid resistance.

3. Results and Discussion

3.1 Acid Resistance Mass Loss

Under 28-day exposure to 3% HCl, mass loss was 5.00% at 0% replacement (Mix OSA100%-WSA100%) and decreased progressively with increasing Replacement (%) to a minimum of 3.41% at 60% replacement (Mix OSA40%-WSA40%, the lowest mass loss recorded across all six levels), then increased again at 80% (4.00%) and 100% (5.29%, the fully-natural-aggregate control mix, OSA0%-WSA0%) — a clear non-monotonic, curved trend with its best-performing point at an intermediate Replacement (%) value rather than at either extreme. Table 2 reports the full mass-loss dataset, and Figure 2 plots the trend.

Table 2. Acid resistance test results (28-day immersion in 3% HCl).

Mix ID	Replacement (%)	Initial Mass (g)	Final Mass (g)	Mass Loss (%)
M25-OSA0%-WSA0%	100	8500	8050	5.29
M25-OSA10%-WSA10%	80	8510	8170	4.00
M25-OSA20%-WSA20%	60	8495	8205	3.41

M25-OSA30%-WSA30%	40	8520	8150	4.34
M25-OSA40%-WSA40%	20	8515	8105	4.82
M25-OSA50%-WSA50%	0	8505	8080	5.00

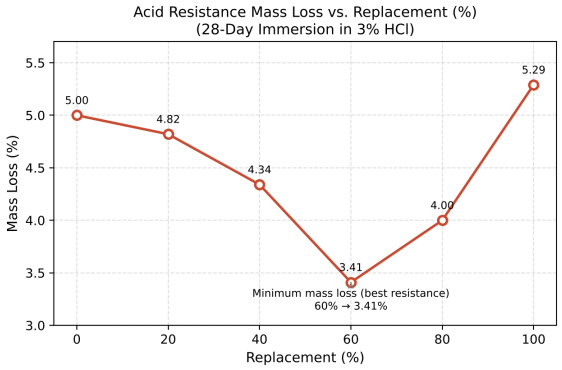


Figure 2. Acid resistance mass loss vs. Replacement (%) (28-day immersion in 3% HCl).

Mass loss falls steadily from 5.00% at 0% replacement to a clear minimum of 3.41% at 60% replacement, then rises again through 80% and 100%, producing a visibly curved (non-linear) trend with its best-performing point at an intermediate replacement level rather than at either extreme of the tested range. Design-Expert's sequential model-selection procedure for acid resistance mass loss is summarised in Table 3.

Table 3. Design-Expert Fit Summary — Acid Resistance Mass Loss.

Source	Sequential p-value	Adjusted R^2	Remark
Linear	0.9092	−0.5642	Not significant
2FI	0.1269	0.4423	Suggested
Quadratic	—	—	Aliased

The 2FI model is suggested over the Linear model, with Adjusted R^2 improving from a negative value (−0.5642, indicating the Linear model fits worse than simply reporting the mean) to 0.4423. Figures 4–7 present the corresponding Design-Expert diagnostic plots.

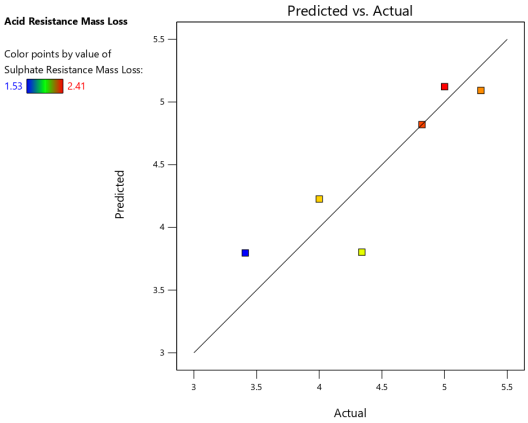


Figure 3. Predicted vs. Actual plot for Acid Resistance Mass Loss.

Five of the six points sit close to the 45-degree line; the point at the lowest actual mass loss (3.41%, the 60% replacement specimen) is the only one to depart noticeably, over-predicted at roughly 3.8%. This is a comparatively good visual fit, consistent with Adjusted R^2 = 0.4423 being the second-highest among the durability and mechanical responses examined in the wider RSM analysis of this material system.

The B = 0% line rises from about 0% mass loss at A = 0% to roughly 5% at A = 100%, while the B = 100% line stays almost flat near 5% throughout; since lower mass loss is the favourable outcome, this indicates acid resistance is best when Aggregate Weight is low (i.e. Replacement (%) is low under the convention) and comparatively insensitive to OSA–WSA Mix Weight on its own.

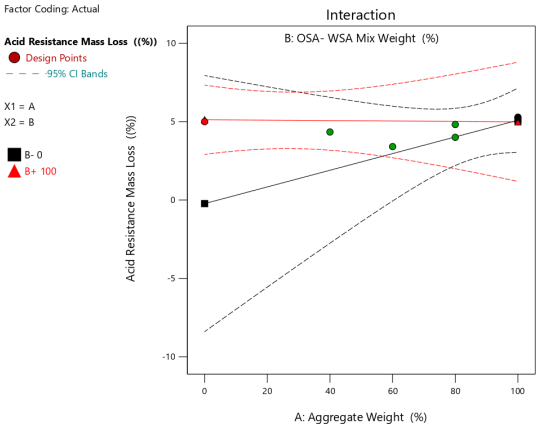


Figure 4. Interaction plot of Acid Resistance Mass Loss (Factor A at B = 0% and B = 100%)

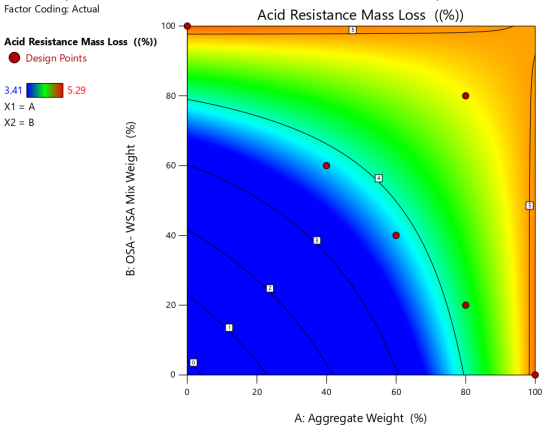


Figure 5. Contour plot of Acid Resistance Mass Loss vs. Aggregate Weight (A) and OSA–WSA Mix Weight (B).

Mass loss is modelled as lowest (blue, best resistance) toward low Aggregate Weight and rises to its highest (orange/red, worst resistance) toward high Aggregate Weight — the opposite spatial gradient from the strength-related properties in the wider study, as expected since lower mass loss is the favourable direction for this response. The plotted design point at approximately A = 80%, B = 80% again falls visibly off the A + B = 100% mixture line, the same anomaly flagged in Table 1.

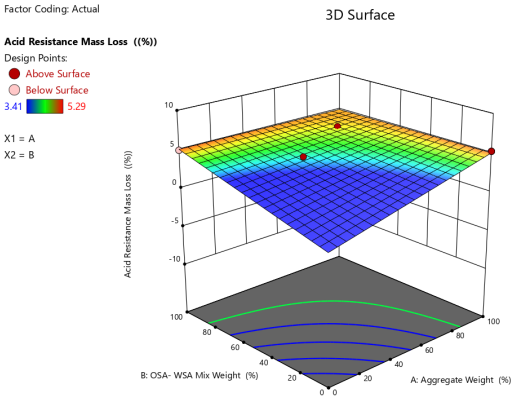


Figure 6. 3D response surface plot of Acid Resistance Mass Loss.

The surface rises steadily and smoothly from the low-mass-loss (best resistance) corner to the high-mass-loss (worst resistance) corner, a monotonic slope consistent with the model's moderate Adjusted R^2 and with the curved experimental trend plotted in Figure 6.

3.2 Sulphate Resistance Mass Loss

Under 28-day exposure to 5% Na_2SO_4, mass loss ranged narrowly from 1.53% to 2.41% across the six tested points — a much smaller range, in both absolute and relative terms, than observed for acid resistance. These specimens follow the same confirmed 0/20/40/60/80/100% OSA–WSA replacement scheme used for acid resistance; Table 4 and Figure 2 report Replacement (%) under the convention (Replacement (%) = Aggregate Weight A = 100 − OSA–WSA Mix Weight B).

Table 4. Sulphate resistance test results (28-day immersion in 5% Na_2SO_4)

Mix ID	Replacement (%)	Initial Mass (g)	Final Mass (g)	Mass Loss (%)
M25-OSA0%-WSA0%	100	8500	8305	2.29
M25-OSA10%-WSA10%	80	8510	8320	2.23
M25-OSA20%-WSA20%	60	8495	8365	1.53
M25-OSA30%-	40	8520	8335	2.17

WSA30 %				
M25-OSA40% - WSA40 %	20	8515	8315	2.35
M25-OSA50% - WSA50 %	0	8505	8300	2.41

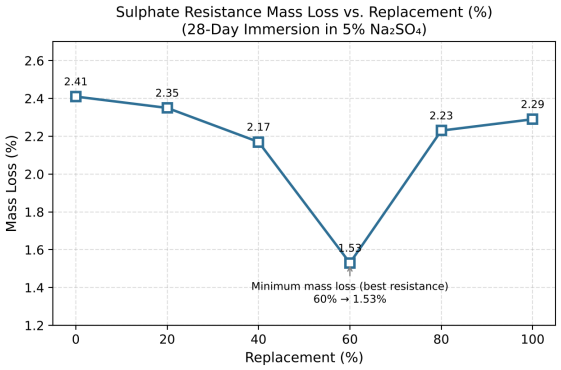


Figure 7. Sulphate resistance mass loss vs. Replacement (%) (28-day immersion in 5% Na_2SO_4).

Mass loss dips to a minimum of 1.53% at the 60%-replacement point — the same replacement level identified as optimal for acid resistance (Figure 1) — and rises on either side, within a much narrower 1.53–2.41% range. This curvature is real but statistically modest: an independent quadratic regression finds a weak, non-significant trend ($R^2 = 0.461$, nested-F p = 0.237), whereas the Design-Expert Fit Summary (Table 5) does not identify it as significant either. Table 5 summarises the Design-Expert Fit Summary for sulphate resistance mass loss. As with Table 3, this Fit Summary was computed on the design matrix before the Table 1 row-5 correction and has not yet been re-run.

Table 5. Design-Expert Fit Summary — Sulphate Resistance Mass Loss.

Source	Sequential p-value	Adjusted R^2	Remark
Mean	< 0.0001	—	Suggested
Linear	0.8411	−0.4851	Not significant
2FI	0.3051	−0.1519	Not significant

Unlike acid resistance, neither the Linear nor the 2FI model improves meaningfully on simply reporting the overall mean: both return negative Adjusted R^2, and Design-Expert's model search accordingly suggests the Mean model itself as the best-supported representation. Taken at face value, this indicates no statistically credible replacement-level effect on sulphate resistance was detected by these two factor-based models. However, an independent quadratic regression fitted directly to the confirmed replacement scheme does detect a weak curved trend that the Linear/2FI comparison alone does not capture; this result, like the Fit Summary above, is also pending re-run on the corrected design matrix. Figures 8–12 present the corresponding diagnostic plots. Points cluster reasonably close to the 45-degree line across the narrow 1.5–2.6% mass-loss range, but this visual fit is not matched by a statistically credible factor-based model (Table 5); this Fit Summary was computed before the Table 1 row-5 correction and has not yet been re-run, so it should be read as provisional.

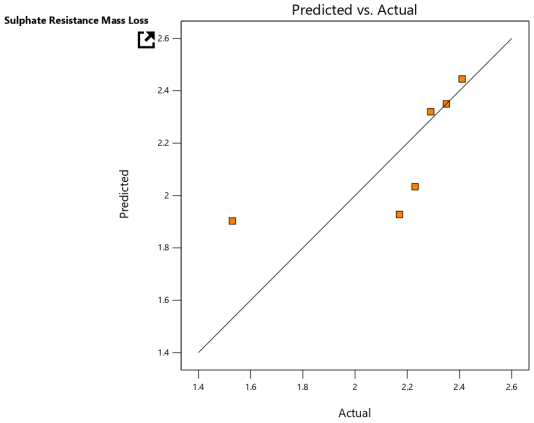


Figure 8. Predicted vs. Actual plot for Sulphate Resistance Mass Loss

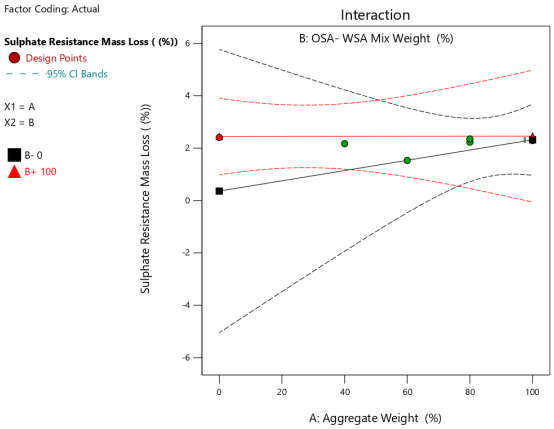


Figure 9. Interaction plot of Sulphate Resistance Mass Loss with Factors

Both the B = 0% and B = 100% lines stay nearly flat and close together across the full Aggregate Weight range, visually confirming the Mean-model conclusion that neither factor level meaningfully separates sulphate-resistance outcomes.

Design-Expert's own in-plot warning ("Missing factor warning: Aliasing") is visible on this chart; both the Aggregate Weight (A) and OSA–WSA Mix Weight (B) perturbation lines are nearly flat and

lie well within each other's confidence bands around the center point, the clearest single visual indicator that neither factor moves this response meaningfully.

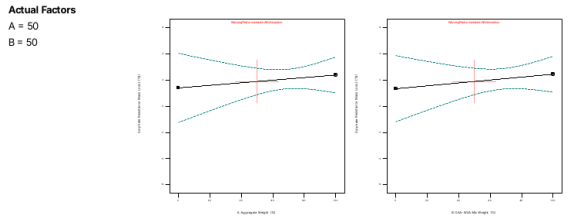


Figure 10. Perturbation plot of Sulphate Resistance Mass Loss

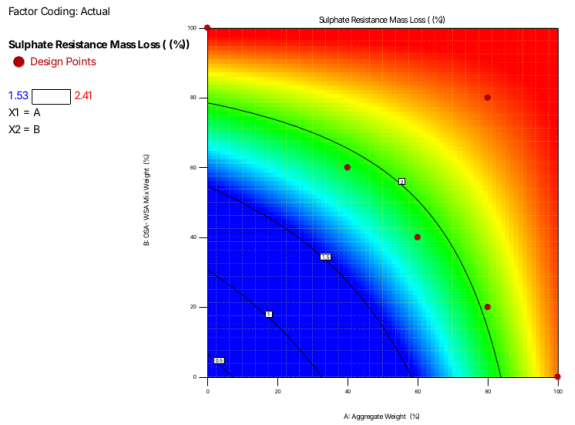


Figure 11. Contour plot of Sulphate Resistance Mass Loss vs. Aggregate Weight and OSA–WSA Mix Weight

The fitted surface is nearly flat with only a shallow tilt, markedly less pronounced than the acid-resistance surface in Figure 12 — consistent with the Mean model being preferred over either factor-based alternative in Table 5, even though the independent quadratic regression detects a weak curved signal this near-flat surface does not visually emphasise. This Fit Summary remains pending re-run on the corrected design matrix.

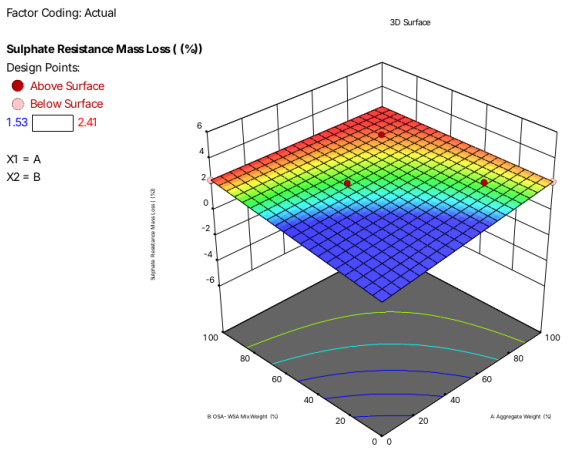


Figure 12. 3D response surface plot of Sulphate Resistance Mass Loss.

3.3 Cross-Validation with Independent Quadratic Regression

To assess whether the acid-resistance trend identified by Design-Expert reflects a genuine feature of the data rather than an artefact of a single analytical tool, a single-variable quadratic regression, $Y = b_0 + b_1X + b_2X^2$, was fitted independently by ordinary least squares to the same six acid-resistance group means, with X taken as the Replacement (%) value defined in (0–100%). The fitted model is:

$$\boldsymbol{Y = 5.3075 - 0.05469\,X + 0.0005192\,X^2}$$

with $R^2 = 0.683$, Adjusted $R^2 = 0.471$, and a nested F-test (comparing this quadratic model against the corresponding linear model, df = 1,3) of F = 6.25, p = 0.088. The fitted parabola's vertex lies at X* = 52.7% replacement, predicting a minimum mass loss of 3.87% — close to, though not identical to, the actual best-observed point (60% replacement, 3.41% mass loss); since the fitted curve's concavity matches the minimisation goal appropriate for a mass-loss response, this vertex is a usable predicted optimum rather than the model's worst point. Table 6 compares the two independently-computed analyses for acid resistance.

The two independently-run analyses agree closely: both identify a curved (non-linear) relationship between replacement level and acid resistance, both place the best-performing region in the 53–60% replacement range, and their Adjusted R^2 values (0.4423 and 0.471) differ by only 0.03 — one of the closest numerical matches between methods observed across the wider RSM analysis of this material system. Neither individual model reaches the conventional $\alpha = 0.05$ significance threshold, a direct consequence of the six-level, three-residual-degree-of-freedom experimental design rather than a weakness specific to either method; the two methods' agreement, obtained independently using different statistical tools and model parameterisations, is itself evidence that the

identified curvature is a genuine feature of the underlying acid-resistance data.

Table 6. Cross-validation of Design-Expert RSM output against the independently hand-computed quadratic regression (Acid Resistance Mass Loss).

Metric	Design-Expert (2FI model)	Independent Quadratic Regression
Sequential / overall p-value	0.1269	—
Nested F-test p-value	—	0.088
R^2	—	0.683
Adjusted R^2	0.4423	0.471
Predicted optimum	— (see Fig. 4)	52.7% replacement (3.87% predicted mass loss)
Actual best-observed point	60% replacement, 3.41% mass loss	60% replacement, 3.41% mass loss

Now that the sulphate-resistance replacement scheme has been confirmed as the same 0/20/40/60/80/100% progression used for acid resistance, the same independent quadratic regression was also fitted to the six sulphate-resistance group means, with X again taken as Replacement (%). The fitted model is:

$$Y = 2.5229 - 0.02068\,X + 0.0001839\,X^2$$

with $R^2 = 0.461$, Adjusted $R^2 = 0.102$, and a nested F-test (quadratic vs. linear, df = 1,3) of $F = 2.18$, $p = 0.237$. The fitted parabola's vertex lies at $X^* = 56.2\%$ replacement, predicting a minimum mass loss of 1.94% — close to the actual best-observed point (60% replacement, 1.53% mass loss), and within the same 53–60% optimum region identified independently for acid resistance. Table 7 compares this regression against the Design-Expert Fit Summary for sulphate resistance (Table 5).

Table 7. Cross-validation of Design-Expert RSM output against the independently hand-computed quadratic regression (Sulphate Resistance Mass Loss).

Metric	Design-Expert (2FI model)	Independent Quadratic Regression
Sequential / overall p-value	0.3051	—
Nested F-test p-value	—	0.237
R^2	—	0.461
Adjusted R^2	−0.1519	0.102
Predicted optimum	— (Mean model suggested)	56.2% replacement (1.94% predicted mass loss)
Actual best-observed point	60% replacement, 1.53% mass loss	60% replacement, 1.53% mass loss

Unlike acid resistance, the two analyses for sulphate resistance do not agree as closely. Design-Expert's Linear/2FI comparison returns negative Adjusted R^2 throughout and accordingly prefers the Mean model (Table 5), whereas the independent quadratic regression, fitted directly to a curved functional form, detects a weak positive signal ($R^2 = 0.461$) that places its predicted optimum at essentially the same replacement level (56.2%, versus 60% actual) identified for acid resistance. Both the nested F-test ($p = 0.237$) and the small Adjusted R^2 (0.102) indicate this sulphate-resistance curvature is considerably weaker and statistically less reliable than its acid-resistance counterpart ($p = 0.088$, Adjusted $R^2 = 0.471$) — consistent with the much narrower absolute mass-loss range for sulphate resistance (1.53–2.41%, versus 3.41–5.29% for acid resistance) leaving less signal for any model to detect. This finding should therefore be read as a modest, suggestive echo of the acid-resistance optimum rather than an independently conclusive result, and, like the Design-Expert Fit Summary itself, is pending the corrected-matrix re-run discussed.

4. ACID-RESISTANCE

4.1 Pore Refinement and the Acid-Resistance Optimum

The curved, optimum-centred trend identified for acid resistance is consistent with a pore-refinement mechanism operating alongside dilution. Note that Replacement (%) in this article runs opposite to OSA–WSA content (Replacement (%) = Aggregate Weight A = 100 − OSA–WSA Mix Weight B), so the mechanism below is described in terms of OSA–WSA content, with the corresponding Replacement (%) values given alongside. As OSA–WSA Mix Weight (B) increases from zero — equivalently, as

Replacement (%) falls from 100% — WSA's silica-bearing fraction is understood to react with calcium hydroxide liberated during cement hydration, generating secondary calcium silicate hydrate that occupies capillary pore space and reduces pore interconnectivity; OSA's fine calcium-rich particles contribute a complementary filler effect. Because acid attack proceeds through ingress of acidic solution into the pore network, a matrix with reduced permeability degrades more slowly, which is consistent with the observed mass-loss minimum near 53–60% replacement (B ≈ 40–47%, i.e. a moderate OSA–WSA content). Beyond that point, as OSA–WSA content continues to increase (Replacement (%) continuing to fall below ~53–60% toward 0%), progressively less natural fine aggregate and cement-hydration product remains available, and the balance shifts toward dilution of the calcium-silicate-hydrate binder phase; this is consistent with mass loss rising again as Replacement (%) falls from 60% toward 0%, ultimately reaching its highest value at the fully-natural-aggregate control mix (Replacement (%) = 100%, 5.29% mass loss) — the overall maximum across the six-point dataset, slightly exceeding even the fully-substituted mix (Replacement (%) = 0%, 5.00% mass loss). This progressive, non-threshold behaviour — rather than an abrupt step change — is itself consistent with a gradual pore-refinement-versus-dilution balance rather than a single discrete reaction mechanism.

4.2 A Weaker, Parallel Trend for Sulphate Resistance

The sulphate resistance echoes the acid-resistance optimum, but far more weakly: the independent quadratic regression's vertex (56.2% replacement) sits close to acid resistance's (52.7%), and both point to the same 60%-replacement actual best-observed point, yet the sulphate regression's Adjusted R^2 (0.102) and nested-F p-value (0.237) are both far short of its acid-resistance counterpart, and Design-Expert's own Linear/2FI comparison (Table 5) does not detect the effect at all. A plausible mechanistic reading is that the same pore-refinement process proposed operates for sulphate exposure as well, but is partially offset: sulphate attack proceeds through expansive reaction-product formation (ettringite and gypsum) rather than simple acid dissolution, and OSA's calcium-rich composition may supply additional reactive calcium aluminate or calcium hydroxide available for expansive sulphate reaction, counteracting some of the permeability benefit that pore refinement otherwise confers. This would explain why the same replacement level is directionally favourable for both responses while the sulphate effect remains too weak to reach statistical significance at this sample size. This reading should be treated as tentative: with only six replacement levels and three residual degrees of freedom, the present dataset cannot distinguish a genuine, weak dilution/pore-refinement effect from ordinary sampling noise, and confirming it requires the additional replacement levels and replicate specimens recommended and Future Work.

5. PRACTICAL IMPLEMENTATION

5.1 Applications Informed by Improved Acid Resistance

The acid-resistance improvement identified near 60% replacement (OSA–WSA Mix Weight B ≈ 40%), supported by two independent statistical analyses, suggests potential application value in structures exposed to acidic environments, including wastewater-treatment facilities, industrial processing plants handling acidic effluents, sewer and underground utility structures, and agricultural structures exposed to chemically aggressive conditions. Improved acid resistance in such applications could reduce surface deterioration rates and, by extension, maintenance frequency and lifecycle cost, though this inference follows directly from the measured mass-loss trend rather than from any service-life or field-exposure data collected in this study.

5.2 Caution Regarding Sulphate-Resistance Claims

Because Design-Expert's own Linear/2FI comparison found no statistically credible replacement-level trend for sulphate resistance, and because the independent quadratic regression that does detect a weak, directionally favourable trend falls well short of conventional significance (p = 0.237, Adjusted R^2 = 0.102), no firm practical recommendation regarding OSA–WSA replacement for sulphate-exposed applications (e.g. soil- or groundwater-contact structures in sulphate-bearing ground) can yet be responsibly drawn from the present analysis. The directional agreement with the acid-resistance optimum near 60% replacement is encouraging but should be treated as a hypothesis for the replicate-data follow-up recommended, not as evidence that OSA–WSA replacement is already established as beneficial for sulphate resistance.

5.3 Sustainability and Circular-Economy Context

Independent of the specific durability findings, OSA–WSA replacement of natural fine aggregate reduces demand on river-sand extraction and converts two currently landfill-bound waste streams — marine (oyster shell) and agricultural (walnut shell) — into a construction-material input, aligning with circular-economy objectives independently of whether the durability benefit demonstrated here for acid resistance ultimately extends to sulphate resistance as well.

6. CONCLUSIONS

This study evaluated the acid-resistance and sulphate-resistance mass loss of concrete incorporating a combined Oyster Shell Ash and Walnut Shell Ash replacement of natural fine aggregate across six replacement levels, using Response Surface Methodology with independent quadratic-regression cross-validation. The principal findings are:

- Acid resistance mass loss showed a clear, curved relationship with Replacement (%): mass loss was 5.00% at 0% replacement, decreased to a minimum of 3.41% at 60% replacement, then rose again to its highest value, 5.29%, at the fully-natural-aggregate control mix (100% replacement). The Design-Expert 2FI model (sequential $p = 0.1269$, Adjusted $R^2 = 0.4423$) and an independently hand-computed quadratic regression ($R^2 = 0.683$, Adjusted $R^2 = 0.471$, nested-F $p = 0.088$) agreed closely, with predicted optima of 60% (actual best-observed) and 52.7% (regression vertex) respectively — one of the strongest cross-method agreements identified in the wider RSM analysis of this material system.
- Design-Expert's own Linear ($p = 0.8411$) and 2FI ($p = 0.3051$) models found no statistically credible replacement-level effect for sulphate resistance mass loss, both under-performing the simple Mean model. However, an independent quadratic regression fitted on the confirmed 0/20/40/60/80/100% replacement scheme found a modest, non-significant curved trend ($R^2 = 0.461$, Adjusted $R^2 = 0.102$, nested-F $p = 0.237$) with its predicted minimum at 56.2% replacement — close to the same 60%-replacement point identified as optimal for acid resistance. This should be read as a suggestive echo of the acid-resistance optimum rather than an independently conclusive finding, pending the replicate data recommended below.
- A data-entry inconsistency in the shared design matrix (one design point originally summing to 160% rather than the required 100%) was identified and has been corrected in this revision, consistent with the confirmed replacement scheme (Table 1). The Design-Expert Fit Summary results (Tables 3 and 5) were computed before this correction and have not yet been re-run against the corrected matrix; they should be treated as provisional until that is done.
- The close agreement between two independently-computed analytical approaches for acid resistance — using different statistical tools and model parameterisations — provides stronger evidence that the identified replacement-level effect is a genuine property of the underlying experimental data than either analysis could provide alone.

Overall, the results indicate that OSA–WSA incorporation, particularly near 60% replacement, can meaningfully improve concrete's resistance to acidic environments through a mechanism consistent with pore refinement and matrix densification, supporting its potential as a sustainable fine-aggregate replacement in acid-exposed applications. A similarly favourable, though considerably weaker and not yet statistically conclusive, trend was found for sulphate resistance at the same replacement level; confirming whether this reflects a genuine (if modest) shared benefit or simply sampling noise at this small sample size is the key remaining question before any sulphate-related performance claim can be made with confidence for this material system.

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