

EVALUATING THE IMPACT OF SILICA FUME AND WASTE MARBLE DUST/POWDER ON CONCRETE DURABILITY CHARACTERISTICS

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Abstract

Two of concrete's weaknesses share a single origin. Ordinary Portland cement (OPC) is carbon-intensive to produce and the calcium hydroxide left behind by its hydration is the phase most readily dissolved when concrete meets acids or sulfates. This study tests whether both can be addressed at once by combining silica fume (SF), which consumes calcium hydroxide pozzolanically with waste marble powder (WMP), which densifies the matrix physically in a single mix. A full factorial of sixteen mixes crossed four SF levels (0, 5, 10 and 15% of cement mass) with four WMP levels (0, 10, 20 and 30% of fine-aggregate mass) at a fixed 1:2:4 proportion and a water-to-binder ratio of 0.60, using materials locally sourced in Sindh, Pakistan. Slump was measured on every fresh mix. A total of 128 cubes of 100 mm were cured with water for 28 days and then immersed for a further 28 days in 5% sulfuric acid (ASTM C267) solution, after which residual compressive strength was determined. All replacements produced a monotonic reduction in slump from 85 mm for the control to 40 mm for SF15WMP30. However, all mixes retained cohesiveness and were placeable. The maximum residual strength after acid exposure (+22.116 MPa with +5.18% relative to the control mix on the exposed control or in acid exposure) was recorded for SF10WMP10, while the weakest mix SF15WMP30 experienced a loss of 11.78% in acid after 28 days of immersion time. Performance was degraded beyond 10% of either material. Acid was the more aggressive medium throughout. On its own, marble powder contains carbonate which is acid soluble, this can limit the benefit of marble under acid attack. Recommended as the optimal combination: SF10WMP10.

1. INTRODUCTION

Concrete carries two liabilities that are usually addressed separately. The first is the carbon of its

binder. Global cement output has passed 4.2 billion tonnes a year, and clinker manufacture

releases between 0.9 and 1.0 tonnes of CO₂ for every tonne produced, arising partly from fuel combustion and partly from the calcination of limestone itself [1]. Cement and concrete together account for an estimated 5 to 8% of global anthropogenic CO₂ emissions, a share that has grown rather than contracted over the past decade [2], [3]. The second liability is chemical and it is built into the hardened material.

When the calcium silicate phases of OPC hydrate, they yield calcium silicate hydrate (C-S-H), which carries almost all of the strength and cohesion together with a substantial quantity of calcium hydroxide (Ca (OH)₂ or CH). C-S-H is durable; CH is not durable. It is comparatively soluble, chemically reactive and the first hydration product consumed when concrete meets with acids [4]. Sewers, water-treatment works, marine structures and foundations in sulfate-bearing soils deteriorate not simply because concrete is porous but because a soluble phase sits inside the pore network waiting to be attacked [5]. Permeability governs how quickly aggressive ions arrive; calcium hydroxide governs what they find when they get there.

SCMs work both ways within the same reaction, amorphous silica further reacts with CH to precipitate additional C-S-H and eliminate this vulnerable phase [5]– [7]. Consequences found in the SCM literature are consistent: lower heat of hydration and CH content; increased fineness, capillary pores small enough to be considered effectively [8]– [12]. The trade-off is reactivity, since most SCMs react more slowly than clinker, so early-age strength is often exchanged for later-age durability [13]. The SCMs that have been most closely studied in Pakistan are agricultural and industrial residues like rice husk ash [14], [15].

The most reactive of the SCMs in widespread use is silica fume. It is recovered from the exhaust fumes of smelting silicon and ferrosilicon as a very fine (0.1 μm – One hundred times finer than cement) black or brown powder consisting almost entirely (85 to 98%) SiO₂ [16], so it also acts simultaneously like pozzolanic material in addition to being ultrafine filler. He reported that compressive, tensile and flexural strength gained

along with reductions in porosity over a large body of work [17]; the best balance in performance is often achieved at replacement levels between 5 to 15% as higher dosages come with sacrifice towards workability while also sometimes leading to increased drying shrinkage. He directly distinguished these two mechanisms by contrasting silica fume against equally fine quartz powder [18]: the latter produced only a filler effect, but because of its pozzolanic properties also refined and decreased permeability in addition to a filler effect. The durability benefit is therefore chemical first and physical second. Moderate contents of silica fume under wet-dry sulfate cycling delay the coarse pore structure growth and accompanying strength loss [19].

High volume of fine waste produced from marble cutting and polishing mainly gets discarded instead of being utilized [20]– [22]. Pakistan contains marble resources of the order 160 million tonnes and a stone-processing industry located on few districts, so this powder is very locally available where concrete production happens [23]. Chemically it is almost inert: mainly calcium carbonate, low in silica and alumina and non-pozzolanic [24]– [26]. Its role is one of particle packing, similar to that played by filler (limestone powder) in low water/cement concrete and flowable mortars [27], [28].

Reported optima cluster but do not coincide. He found strength optimised near 10 to 15% replacement and declining beyond 15%, as the non-pozzolanic powder began to dilute the binding medium and disturb the grading [29]. They recorded improving workability with strength maintained at moderate replacement [30] and he reached broadly similar conclusions [31]. They draw the more useful distinction: marble dust contributes more durability than mechanical performance, because packing and pore refinement are the only mechanisms available to a filler [32].

Work on the two materials together is more recent and less settled. He tested sixteen binary, ternary and quaternary mixes and found that 10% silica fume markedly improved resistance to 5% sulfuric acid with a mix containing 20% marble powder

and 10% silica fume matching the controlled mix or reference mix while using roughly 30% less cement. He reported to enhance density, compressive strength and acid resistance for high-performance concrete containing silica fume, ground blast-furnace slag and marble powder [33],[34]. He found bond strength to corroded reinforcement improved by 27% at adding 10% silica fume with 5% marble powder [35]. The reported optima nonetheless disagree: He stated to place them at 7.5% silica fume with 15% marble powder [36]. He utilized at 10% and 10% with steel fibre [37], and reported at 15% marble powder [38], [39]. He stated to add that raising SCM content lowers workability, dry density, water absorption and carbonation depth together, so a gain in one property is rarely free.

Two differences explain most of that spread. The first is the role assigned to the marble powder: cement replacement in some studies and sand replacement in others, which changes the binder content and the aggregate grading in opposite directions. The second and the most important the response is being optimised. Most of this work optimises compressive strength, and a mix optimised for strength is not necessarily optimised for chemical durability. Where the combination has been evaluated for durability rather than strength, the exposure has usually been chloride ingress or reinforcement corrosion rather than acid and sulfate attack [41].

The deterioration mechanisms themselves make the case for combining the two materials. Sulfuric acid attacks calcium hydroxide first and then

decalcifies C-S-H, producing gypsum, softening and surface scaling [42], [43]. Sulfate ions react with the hydration products to form expansive ettringite and gypsum, causing expansion, cracking and spalling [19]. Both processes begin at the same two features: available calcium hydroxide and an open pore structure. Silica fume addresses both. Marble powder addresses only the second, and under acid its carbonate content is itself consumable. Whether the combination is genuinely complementary, and where its useful limit lies, has not been established under a controlled factorial judged on durability criteria [44].

This study addresses that question. Sixteen mixes cross four silica-fume levels with four waste marble powder levels, with silica fume replacing cement and marble powder replacing fine aggregate. Hence, the dual role rather than the more common arrangement in which both replace cement. The responses are workability, residual compressive strength after 28 days immersion in 5% sulfuric acid. This acid exposure was chosen because industrial effluent, sulfate bearing soils and coastal groundwater are the dominant aggressive conditions for concrete in Sindh. The objectives are to quantify the effect of each material and of their combination on workability and on resistance to acid, and to identify the replacement combination performing best across exposure. Table 1 summarises the studies against which the present work is positioned.

Table 1. Position of the present study within previous work on silica fume and waste marble powder.

Study	Materials and replacement	Focus	Principal finding
Munir et al. [23]	SF (cement) + marble powder up to 15% (sand); 16 mixes	Mechanical and acid resistance	10% SF markedly improved resistance to 5% H ₂ SO ₄ ; 20% MWP with 10% SF matched the control using ~30% less cement
Singh et al. [29]	Marble dust 0–50% (cement and sand)	Mechanical	Strength optimised near 10–15%; declines beyond 15%

Study	Materials and replacement	Focus	Principal finding
Ashish [38], [39]	15% marble powder (sand) + SF or metakaolin	Durability	Both SCMs improved durability, metakaolin slightly more; no adverse setting effects
Chandramouli et al. [36]	SF 5/7.5/12.5% (cement) + MP 5–25% (fine agg.)	Compressive and split tensile strength	Optimum at 7.5% SF with 15% MP
Abbas et al. [33]	SF + GBFS at 8% of cement + MP 5/10/15% (fine agg.)	Physical and mechanical properties	Improved density and compressive strength over plain OPC concrete
Ghalehnovi et al. [35]	SF 10% + MWP 5/10% (cement)	Bond strength, corrosion	Bond strength raised 27% with 10% SF and 5% MWP
Pattanayak et al. [37]	SF 0/10/15% + MP 0/10/15% + 1.5% steel fibre	Fresh and hardened properties	Compressive strength optimised at 10% MP with 10% SF
Bheel et al. [40]	SF, RHA and MDP as binary and ternary SCM	Workability and durability	Increasing SCM content lowered workability, water absorption and carbonation depth together
Abbas et al. [34]	Marble waste (fine agg.) + GGBS in HPC	Acid attack	Improved acid resistance with marble-waste replacement
Present study	SF 0/5/10/15% (cement) + WMP 0/10/20/30% (fine agg.); 16 mixes	Acid durability	Durability-led factorial of the dual SF-WMP system with materials sourced in Sindh

2. Materials and Methods

2.1 Experimental design

The programme is a full 4×4 factorial with two independent variables. Silica fume replaced cement at 0, 5, 10 and 15% by mass, and waste marble powder replaced fine aggregate at 0, 10, 20 and 30% by mass. The sixteen resulting mixes comprise one control, three containing silica fume

alone, three containing marble powder alone, and nine containing both, which allows the individual and combined effects to be separated on a common basis. The dependent variables are slump on the fresh mix and residual compressive strength after chemical exposure.

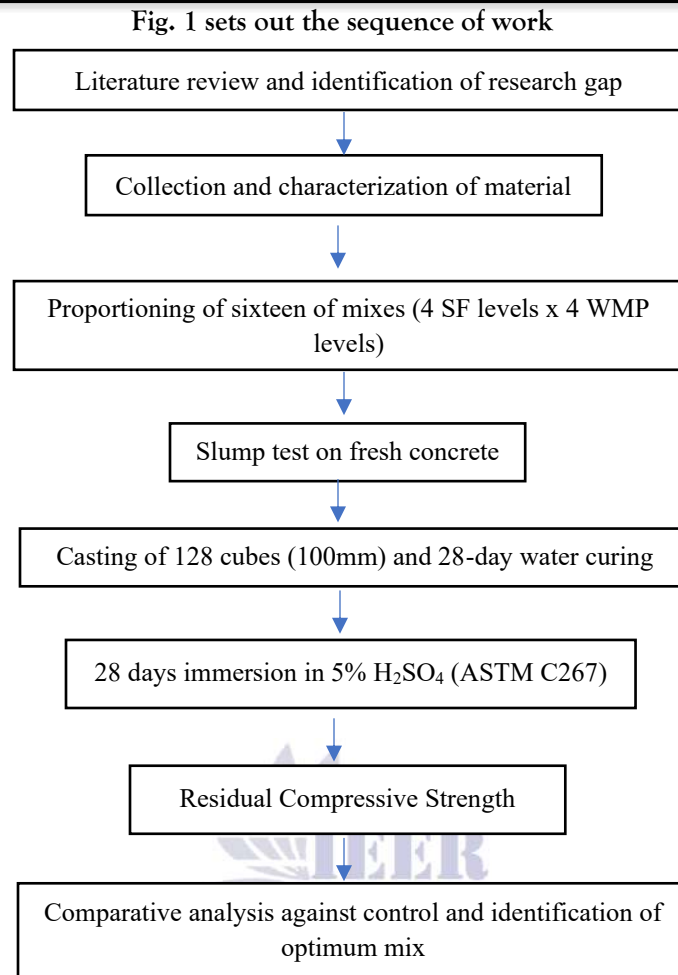


Fig. 1. Sequence of the experimental programme.

2.2 Materials

Cement. Ordinary Portland cement (DG Elephant) conforming to ASTM C150 Type I was obtained in sealed bags from a single consignment

and stored dry, so that no batch-to-batch variation entered the programme. Its measured physical properties and typical oxide composition are given in Table 2.

Table 2. Physical properties and oxide composition of the OPC. Physical values were measured; oxide contents are the typical ranges for ASTM C150 Type I cement and were not determined for this consignment.

Physical property	Method	Result	Requirement	Oxide	Typical content (%)
Specific gravity	ASTM C188	3.11	3.10–3.16	CaO	60–67
Standard consistency (%)	ASTM C187	30	26–33	SiO ₂	17–25

Physical property	Method	Result	Requirement	Oxide	Typical content (%)
Initial setting time (min)	ASTM C191	87	≥ 45	Al_2O_3	3–8
Final setting time (min)	ASTM C191	359	≤ 375	Fe_2O_3	0.5–6
Fineness, residue on No. 100 (%)	ASTM C184	6	≤ 10	MgO	0.1–4
—	—	—	—	SO_3	1.5–3.5
—	—	—	—	$\text{Na}_2\text{O} + \text{K}_2\text{O}$	0.2–1.3
—	—	—	—	Loss on ignition	≤ 3.0

Aggregates. Natural sand from Bholari passing the 4.75 mm sieve was used as fine aggregate, and crushed stone from Khairpur Ubhan Shah, passing 19 mm and retained on 4.75 mm, as coarse aggregate. Both were washed with potable water, air-dried and free of silt, clay and organic matter. Grading was determined to ASTM C136 and specific gravity and absorption to ASTM C128 and C127 (Table 3, Fig. 2). Although the

fineness modulus of 3.34 is just above the C33 band of 2.3 to 3.1, it satisfies the ASTM C33 grading envelope at every sieve; therefore, the fine aggregate is at the coarser edge of specification (Fig. Very low absorption ($< 2\%$) for both aggregates still means solid, sound and non-porous particles, in this matters because the skeleton of aggregate is common to all sixteen mixes – it should not affect differences in chemical resistance.

Table 3. Physical properties of the aggregates.

Property	Method	Fine aggregate	Coarse aggregate	Permissible limit
Specific gravity	ASTM C128 / C127	2.68	2.50	2.4–2.8
Water absorption (%)	ASTM C128 / C127	1.00	1.91	≤ 2
Fineness modulus	ASTM C136	3.34	2.78	2.3–3.1 (fine agg.)
Maximum size (mm)	ASTM C136	4.75	19.05	—

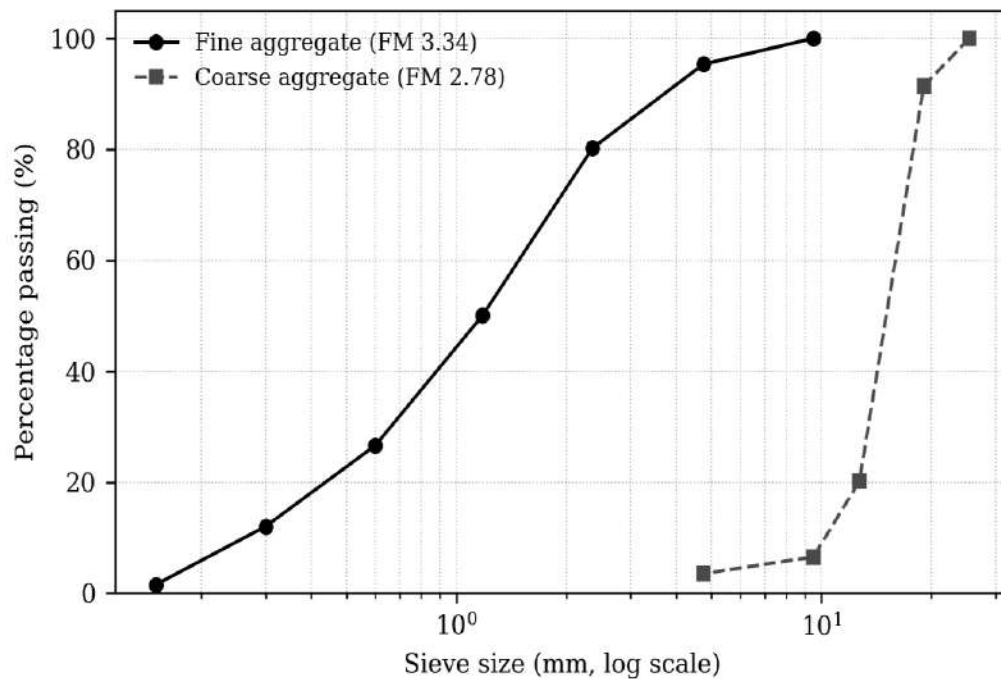


Fig. 2. Particle size distribution of the fine and coarse aggregate.

Silica fume. Densified silica fume (SikaFume-92D), recovered from ferrosilicon exhaust gases and conforming to ASTM C1240, was supplied by Brisk Engineering Services, Karachi, and stored in sealed containers to prevent moisture uptake before batching. Manufacturer's specifications are listed in Table 4.

Waste marble powder. Marble powder was collected from cutting and polishing units in the Khairpur district, oven-dried and passed through

the 4.75 mm sieve to remove oversize particles. It is predominantly calcium carbonate and essentially non-pozzolanitic, so its contribution is expected to be one of filling and particle packing rather than chemical reaction. The oxide composition in Table 4 is indicative of marble waste reported in the literature [20], [24]; X-ray fluorescence analysis was not performed on the material used here, and the composition should be read accordingly.

Table 4. Characteristics of the silica fume (manufacturer's specification) and indicative oxide composition of the waste marble powder.

Silica fume property	Specification	WMP oxide	Indicative content (%)
SiO ₂ content	> 85%	SiO ₂	< 5
Alkalis as Na ₂ O	< 1.5%	CaO	≈ 40 (CaCO ₃ ≈ 95+)
Loss on ignition	< 4%	Al ₂ O ₃	< 1
Moisture content	< 3%	Fe ₂ O ₃	< 1
Specific surface area	> 15 m ² /g	MgO	1–5
Bulk density (densified)	> 500 kg/m ³	Loss on ignition	High (carbonate)

Silica fume property	Specification	WMP oxide	Indicative content (%)
Standards	ASTM C1240, IS 15388	—	—

Chemicals and water.

To prepare the exposure solutions, sulfuric acid (assay 98%), The sulfuric acid of laboratory grade was purchased from a chemical supplier of Sindh Chemicals in Sukkur. Mixing and Curing was carried out with Potable water of pH 6.5 to 8.5, free from oils and dissolved organic matter.

2.3 Mix proportions

Each mix used the same water-to-binder ratio of 0.60, with a mass-based nominal ratio of 1:2:4, and no chemical admixture was added. The skeleton

and the water content were fixed so that any differences between mixes would be a result of replacements alone rather than decreases in mix richness or free water. Quantities for the control mix and full set of mixes are explained in (Table 5) and (Table 6) respectively. The nomenclature of the mix identifiers is performed based on SFxWMPy, where x and y are the silica-fume percentage (SF% with respect to mass cement) and marble-powder percentage (MP% w. r. t. to fine-aggregate mass) respectively; thus, SF10WMP10 denotes 10% each of both phases.

Table 5. Quantities of materials for the standard/control/targeted mix.

Material	Proportion by mass	Quantity (kg/m ³)
Cement (binder)	1	320
Fine aggregate	2	640
Coarse aggregate	4	1280
Water	0.60 (w/b)	192

Table 6. Composition of the sixteen mixes. Cement and silica fume are based on total binder mass; fine aggregate and waste marble powder are based on total fine-aggregate mass. Coarse aggregate and w/b of 0.60 were constant throughout.

No.	Mix ID	Cement (%)	SF (%)	Fine agg. (%)	WMP (%)	Category
1	Control	100	0	100	0	Reference
2	SF5	95	5	100	0	Silica fume only
3	SF10	90	10	100	0	Silica fume only
4	SF15	85	15	100	0	Silica fume only
5	WMP10	100	0	90	10	Marble powder only
6	WMP20	100	0	80	20	Marble powder only
7	WMP30	100	0	70	30	Marble powder only
8	SF5WMP10	95	5	90	10	Combined
9	SF5WMP20	95	5	80	20	Combined

No.	Mix ID	Cement (%)	SF (%)	Fine agg. (%)	WMP (%)	Category
10	SF5WMP30	95	5	70	30	Combined
11	SF10WMP10	90	10	90	10	Combined
12	SF10WMP20	90	10	80	20	Combined
13	SF10WMP30	90	10	70	30	Combined
14	SF15WMP10	85	15	90	10	Combined
15	SF15WMP20	85	15	80	20	Combined
16	SF15WMP30	85	15	70	30	Combined

2.4 Specimen preparation and curing

All ingredients of mixes were measured by mass on a calibrated balance. For the silica fume, it was then dry blended into the cement before using, while for the marble powder, it was dry blended in with the fine aggregate and introduced to mix fractions so that very fine materials were more dispersed than clumped. After, coarse aggregate was added into batches, the dry mix turned until uniform, and water introduced slowly to homogeneity.

The cube moulds (100 mm) were cleaned, sealed and tightly oiled before casting. Concrete was poured in three stages followed by 25 blows of a tamping rod to remove entrapped air, and the top surface of each layer levelled prior to adding a succeeding layer.

Cube moulds of 100 mm were cleaned, sealed and lightly oiled before casting. Concrete was placed in three layers with 25 strokes of a tamping rod per layer to expel entrapped air, and the top surface was struck off level. Fresh samples were left in the laboratory at ambient temperature for 24 hours before demoulding, labelling and curing these for 28 days in potable water. For each mix casted 8 cubes and divided equally four cubes were cast for acid exposure and four for sulfate exposure, resulting in 128 specimens. So, casting was spread out over October and November 2025.

2.5 Test methods

Workability. Slump was measured on every fresh mix immediately after mixing and before casting, following ASTM C143 and BS EN 12350-2, with

the cone filled in three rodded layers on a clean, level, non-absorbent base.

Acid resistance. Acid exposure followed ASTM C267. After 28 days of water curing, specimens were removed, surface-dried, cleaned and weighed, then immersed for 28 days in a 5% sulfuric acid solution. The solution was checked periodically with a Lovibond pH meter through the exposure period. On removal, specimens were air-dried for 24 hours and loose deteriorated material was brushed off before testing.

Compressive strength. Residual compressive strength was determined on a universal testing machine in accordance with BS EN 12390-3, as the maximum load at failure divided by the loaded cross-sectional area. Reported values are the mean of the four specimens tested for each mix and exposure.

2.6 Analysis

Slump and residual strength for each mix are expressed relative to the control mix subjected to the same exposure, as

$$\text{Change (\%)} = [(V_{\text{mix}} - V_{\text{control}}) / V_{\text{control}}] \times 100 \quad (1)$$

Because both the mix and the control were exposed to the same solution for the same period, the comparison isolates the relative benefit or penalty of the replacements. It does not quantify absolute strength loss due to exposure, since the unexposed 28-day strength of each mix was not determined. Main effects of silica fume and of marble powder, and the interaction between them, were read from the 4×4 response surface. Individual cube results were not retained

separately, so no formal analysis of variance was undertaken.

3. Results and Discussion

3.1 Workability

The control mix gave a slump of 85 mm, in the medium range used for general construction. Every replacement reduced it, and the reduction grew with dosage in both directions (Table 7, Fig. 3).

Table 7. Slump and change relative to the control mix.

Mix ID	Slump (mm)	Change (%)
Control	85	—
SF5	72	−15.29
SF10	65	−23.53
SF15	58	−31.76
WMP10	70	−17.65
WMP20	64	−24.71
WMP30	55	−35.29
SF5WMP10	65	−23.53
SF5WMP20	59	−30.59
SF5WMP30	54	−36.47
SF10WMP10	58	−31.76
SF10WMP20	53	−37.65
SF10WMP30	48	−43.53
SF15WMP10	54	−36.47
SF15WMP20	48	−43.53
SF15WMP30	40	−52.94

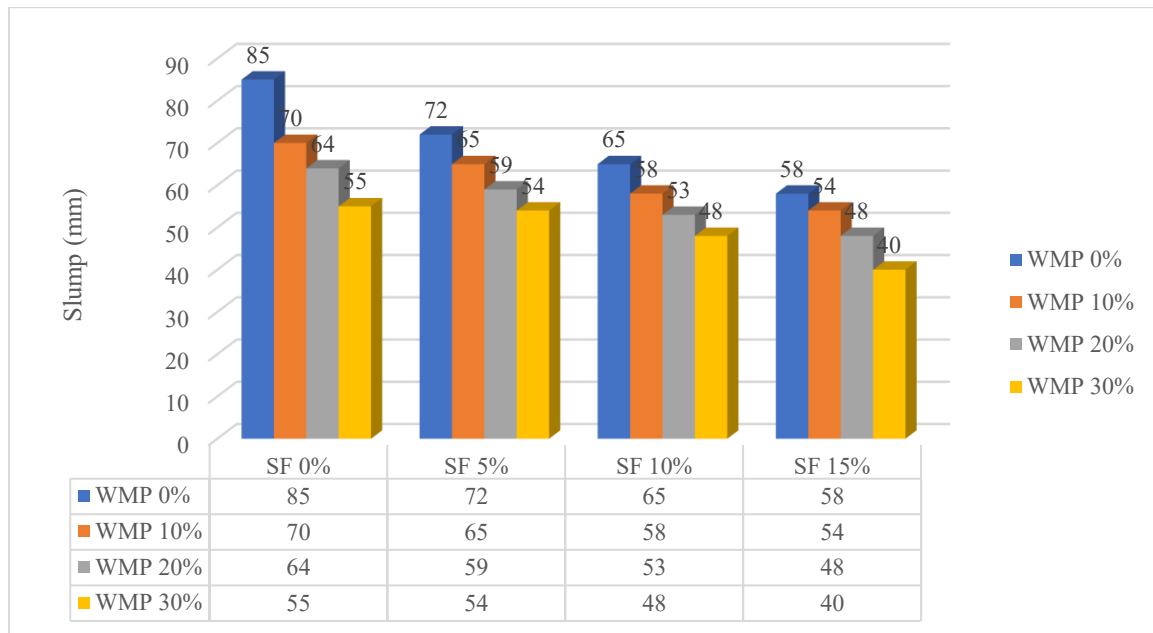


Fig. 3. Slump of the sixteen mixes, grouped by silica-fume level.

With 5%, 10% and 15% of silica fume alone fall the slump to 72, 65 and 58 mm. This behaviour is easily explained: silica fume, with a specific surface area over $15 \text{ m}^2/\text{g}$, adsorbs an in proportionate fraction of the mix water onto particle surfaces, leaving little free water to lubricate the paste at a constant water binder ratio. At equal replacement, marble powder behaved similarly and a bit more forcefully by providing 70, 64 and 55 mm at each of the three dosages (10, 20 and 30%), because this filler replaces well-graded sand with more finer particles, which increases the area covered for whole fine fraction.

The penalty was proportional not additive. Multiplying the individual slump retentions of SF15 (0.682) and WMP30 (0.647) predicts 37.5 mm for SF15WMP30 against the 40 mm measured, whereas summing the absolute losses would predict 28 mm. The same is true across the factorial: measured depressions were always a few millimeters above what the proportional prediction allowed. Water demand is therefore shared to some degree; the fine particles are competing for the same water rather than each removing an independent share of it.

No mix segregated or was unplaceable. All attained nominally cohesive and reasonably compacted under the laboratory rodding, including SF15WMP30 at 40 mm. In field placement, both materials above 10% will require a water-reducing admixture instead of simple added water in order not to increase the water-to-binder ratio which would be counterproductive because the purpose of these replacements is precisely that pore refinement.

This result is not in agreement with Filali and Nasser [30], who observed the improvement in workability due to replacement of sand by marble powder. The most likely hypothesis is a mixture of fineness and free water: at a relatively high water to binder ratio of 0.60 without admixture, the additional surface area predominates, the effect whereas in mixes where the powder is finer and better dispersed in which packing can release water therefore increases flow. The overall monotonic reduction observed here is also consistent with that of Bheel et al. [40] and Abhilash et al. [17].

3.2 Acid resistance

The result of control mix was 21.027 MPa after 28 days in 5% sulfuric acid. Results sorted by silica-fume level (Table 8, Fig. 4).

Table 8. Residual compressive strength after 28 days immersion in 5% sulfuric acid (ASTM C267).

Mix ID	Residual strength (MPa)	Change (%)	Outcome
Control	21.027	—	Reference
SF5	21.300	+1.30	Improved
SF10	22.041	+4.82	Improved
SF15	20.150	−4.17	Reduced
WMP10	21.150	+0.58	Improved
WMP20	20.500	−2.51	Reduced
WMP30	19.600	−6.79	Reduced
SF5WMP10	21.389	+1.72	Improved
SF5WMP20	20.750	−1.32	Reduced
SF5WMP30	20.185	−4.00	Reduced
SF10WMP10	22.116	+5.18	Optimum
SF10WMP20	21.466	+2.09	Improved
SF10WMP30	20.455	−2.72	Reduced
SF15WMP10	20.236	−3.76	Reduced
SF15WMP20	19.610	−6.74	Reduced
SF15WMP30	18.550	−11.78	Reduced

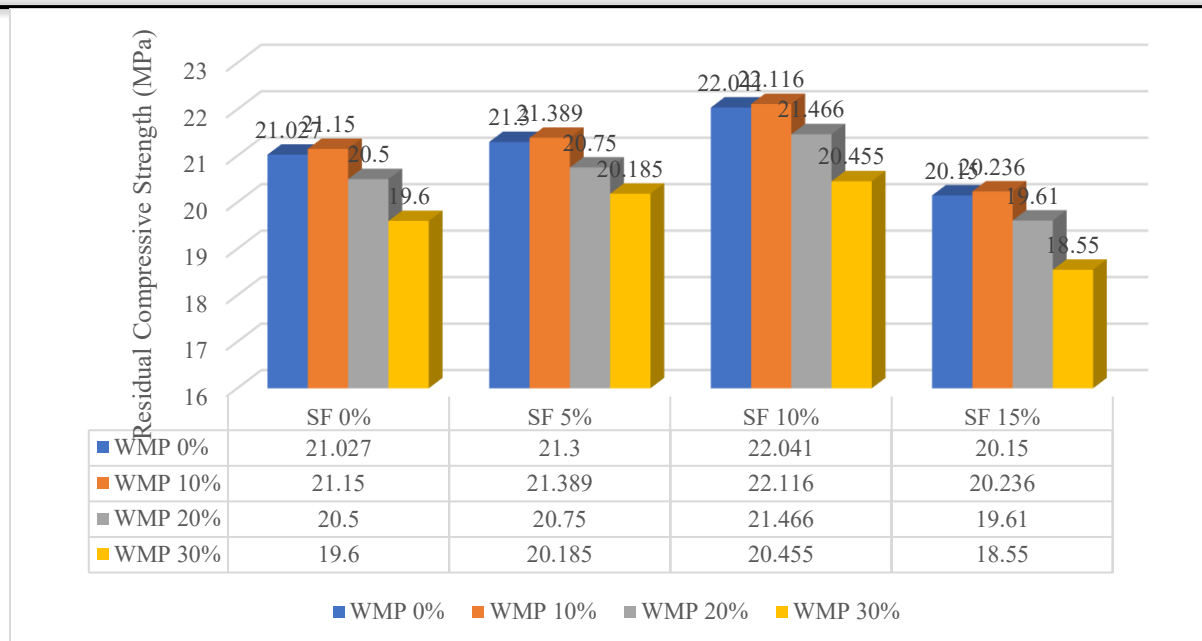


Fig. 4. Residual compressive strength after acid exposure, grouped by silica-fume level. Note the truncated vertical axis.

Silica fume enhanced acid resistance up to 10%: 21.300 MPa at 5% (+1.30%) and 22.041 MPa at 10% (+4.82%). At 15% it fell below the control, to 20.150 MPa (−4.17%). The enhancement occurs because the pozzolanic reaction helps removing some of the calcium hydroxide that firstly sulfuric acid attacks and the finer pore structure slow down further ingress of acidic compounds into concrete. This is the same mechanism and the same 10% optimum that Munir et al. [23] identified under 5% H₂SO₄. The reversal at 15% is not evidence against the mechanism. It reflects three competing effects: dilution of the clinker that supplies calcium hydroxide in the first place, silica that remains unreacted at 28 days and acts as weak filler, and poorer compaction in a mix whose slump already dropped down to 58 mm.

Marble powder performed as its chemistry expects. Only WMP10 was significantly better than the targeted mix (21.150 MPa, +0.58%) and then performance dropped progressively to 19.600 MPa at 30% (−6.79%). Calcium carbonate is soluble in sulfuric acid, so each increment of

marble powder adds acid-consumable material to the matrix and the packing benefit is offset by an enlarged reaction front. The strongest major limitation of the dual system is quite clear: under acid attack, at the best marble powder is nearly too neutral.

Overall, SF10WMP10 was the strongest mix at 22.116 MPa (+5.18%), just shading out SF10 alone. This margin of 0.075 MPa, or 0.36%, should not be overstated based on neither mean value alone nor replicate scatter; on the acid evidence alone, SF10 and SF10WMP10 are not clearly distinguishable. The lowest strength was recorded with SF15WMP30 of 18.550 MPa (−11.78%), the most diluted mix by clinker, the highest content of carbonate minerals and the worst workability in the programme.

3.4 Comparison of the two exposures and the optimum mix

Table.9 maps the percentage change in residual strength across the factorial for both media. Three findings follow.

Table.9 Change in residual compressive strength relative to the exposed control, across the sixteen mixes. The optimum SF10WMP10 cell is outlined.

Mix	Control Mix	WMP 10%	WMP 20%	WMP 30%
Control Mix	---	+0.58	-2.51	-6.79
SF 5%	+1.30	+1.72	-1.32	-4.00
SF 10%	+4.82	+5.18	+2.09	-2.72
SF 15%	-4.17	-3.76	-6.74	-11.78

First, the optimum is the same in both media, at 10% silica fume with 10% marble powder, even though the exposures reward the two materials differently. Under acid the gain comes almost entirely from the silica fume. That the same cell wins in both is a stronger result in exposure, because it means the mix does not have to be re-optimised for the exposure a structure will actually meet useful where a foundation sits in sulfate-bearing soil and is periodically wetted by industrial effluent.

Second, the combination is complementary rather than synergistic. The synergistic SF10WMP10 at 10% weighted contributions mean that it performed better than either a single material or media used alone, but the observed gain was marginally lower than the predicted sum of the independent effects: +5.18% against +5.40% in acid. Hence, the interaction is semi negative. The mechanism is in fact different mode of chemical

consumption of calcium hydroxide on one side, challenge with physical densification on another side but at these two dosage materials are partly competing for the same constrained resource (i.e. the pore volume that each is trying to occupy). This is an overstatement of how the data support these things; a complementary and with diminishing return read would be more on target. Third, acid was constantly the more destructive medium. Every mix kept less strength and decreasing consecutively in acid attacks and least result of acid attacks was obtained at SF15WMP30 as represented in Table 10. Two things drive the difference. Both calcium hydroxide and C-S-H are attacked by sulfuric acid directly; Sulfuric attack requires ionic ingress before expansive products can form. And the marble powder is chemically vulnerable in one medium and inert in the other, which widens the gap at high marble-powder contents specifically.

Table 10. Performance of the optimum mix relative to the control.

Response	Control	SF10WMP10	Change
Slump (mm)	85	58	-31.76%
Residual strength after acid exposure (MPa)	21.027	22.116	+5.18%

The practical case for SF10WMP10 is based on the combinations of results in Table 10 rather than pure gain in durability which is a real but relatively small number. The mix therefore is 32 kg lower in cement per m³, at a cement content of 320 kg/m³, i.e. ~29 to 32 kg of CO₂ per cubic metre based on the emissions factors if all the cement were assumed to be clinker as in [1], and diverts from disposal (not landfill) 64 kg of marble waste per cubic metre. The workability cost is a 27 mm loss

of slump set against the matter without water-reducing admixture. There was no life cycle assessment, and the number above refers to only avoided clinker; the burdens of processing and transporting silica fume which is provided commercially rather than recovered locally, are not included and would reduce the net benefit.

3.5 Limitations

Six constraints bound these conclusions. The programme used a single mix proportion and a single water-to-binder ratio, so the position of the optimum at richer or leaner mixes is unknown. Exposure was 28 days of continuous immersion; cyclic wetting and drying, which is more severe and more representative of service, was not examined, and neither was any longer-term progression of deterioration. Only residual strength after exposure was measured, so absolute strength loss cannot be quantified and the comparison is relative among exposed mixes. The mechanisms invoked here – consumption of calcium hydroxide and refinement of the pore network – are inferred from the strength results and from the published literature rather than demonstrated directly, since no X-ray diffraction, scanning electron microscopy or porosimetry was performed. The oxide composition of the marble powder is indicative rather than measured. Finally, results are reported as means without replicate scatter, which matters most where differences between mixes are under 1%, as they are between SF10 and SF10WMP10 under acid.

4. Conclusions

A total of sixteen concrete mixes incorporating the partial cement replacement with silica fume and the partial fine-aggregate replacement with waste marble powder were investigated for workability properties and residual compressive strength at 28 days in 5% sulfuric acid solution. In support of these results, the following conclusions can be drawn:

- 1) Both replacements diminish workability, and the reductions interact multiplicatively rather than additively. For Slump, 85 mm for control mix to 40 mm for SF15WMP30, a loss of 53%. Any mix no more than 10% of either material was useful, but beyond that a water-reducing admixture would be necessary at the job rather than just adding water; no mix segregated or proved unplaceable.
- 2) Silica fume progresses acid resistance up to 10% replacement and impairs it at 15%. SF10 retained 22.041 MPa (+4.82%) and SF15 only 20.150 MPa (−4.17%), the reversal being attributable to

clinker dilution, unreacted silica acting as weak filler, and reduced compaction at low slump.

- 3) Waste marble powder assists under sulfate stress and is almost neutral under acid. WMP10 alone provided more sulfate but less acid than +5.24% and 0.58%, respectively, and higher levels were toxic in both media. Its carbonate content, which is inert in sodium sulfate, is itself dissolved by sulfuric acid.
- 4) SF10WMP10 in acid exposures, maintaining 22.116 MPa in acid (+5.18%) and considered as an optimum mix.
- 5) The two materials are complementary to each other without any synergy. Combined gain < sum of the individual gains in both media, pointing to a weakly negative interaction: chemical (from silica fume) vs physical advantage (from marble powder; pores compete with each other at these dosages).
- 6) At the age of exposure, acid attack was the more aggressive medium throughout, with residual strengths lower in every mix and penalties at high replacement level.

Wherever concrete is going to contact the sulfates bearing soils, coastal groundwater or industrial effluent basically found all over Sindh, 10% of silica fume with 10% of waste marble powder is suggested as practice. It is not a good idea to exceed 10% of either material on these results. The emissions reductions are slight in between 5 and 6%, and the bigger advantage of the mix is that it provides them using 10% less cement while disposing of a quarrying by-product.

The case would be materially strengthened by the addition of four extensions. X-ray diffraction to detect residual $\text{Ca}(\text{OH})_2$, scanning electron microscopy and mercury-intrusion porosimetry would interrogate the mechanisms presented here directly rather than through inferential means. How the estimated resistance ranking changes as the substrate deteriorates over longer durations with wet and dry cycling needs to be tested. The factorial would appear to extend across the water-to-binder ratios and there would be the optimum in between mixes of high or low richness. And chloride infiltration, the mechanism that determines service life of coastal reinforced

concrete, has not underwent any testing for these combinations.

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Conflict of Interest

The authors declare no conflict of interest.

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