

DURABILITY AND STRENGTH VARIATION OF CONCRETE EXPOSED TO SEAWATER: INFLUENCE OF SUPPLEMENTARY CEMENTITIOUS MATERIALS

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Abstract

This study examines the strength and durability of concrete mixes exposed to seawater. The role of SCMs as partial cement replacements is emphasised. Portland slag cement (PSC) and sulphate-resisting Portland cement (SRPC) were used as binders, each partially replaced with fly ash (FA) and silica fume (SF). Specimens were first cured in freshwater. These were then tested for mechanical properties at 7, 28, 56, and 91 days, for durability at 28 days, and for microstructural studies at 91 days. Later, the investigation assessed performance in seawater at the tidal zone of Visakhapatnam. After 28 days of freshwater curing, the specimens were transferred to the tidal zone. Strength was studied at 91, 180, and 365 days. Durability and microstructural properties were analysed at 91 days. The results showed clear differences among the mixes in per - day strength variation and long-term strength retention. PSC showed superior resistance to chloride- and sulphate-induced degradation due to slag's pozzolanic activity. SRPC, however, achieved the highest 1-year strength of about 50.9 MPa. The reduced formation of Friedel's salts resulted in a denser, more compact matrix. These factors enhanced the mechanical and durability performance. The SRPC + FA + SF mixture proved most durable, showing the lowest values for RCPT, permeability, and carbonation depth. This mix was the least permeable and ideal for sulphate - and chloride-rich environments.

Keywords: Concrete durability; Seawater exposure; PDSV; Fly ash; Silica fume; OPC; PSC; SRPC; SRR

Introduction

Marine structures exposed to wave action are particularly vulnerable to deterioration from chloride ingress, carbonation, and sulphate attack. These factors significantly reduce their service life (Zhao *et al.*, 2020; Qu *et al.*, 2021). Many case studies demonstrate that the failure of the world's

oldest structures when exposed to seawater is due to magnesium sulphate, carbonic attack, chemical attack, and concrete permeability. Similarly, breakwater case studies have failed, especially during storms, due to the enormous pressures exerted by wave action. The combined effects of

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seawater salinity, drag forces, and wave action have significantly contributed to the deterioration of plain and reinforced concrete structures (Rajendra *et al.*, 2017).

Historical studies also demonstrated that hydraulic lime concrete performs better over time. However, demands for greater early strength, easier building and more resistance to marine salts led to the development of modern supplementary cementitious materials (SCMs) (Mehta, 1991). These SCMs serve as advanced successors to traditional binders, offering refined microstructural properties and more reliable durability performance under contemporary marine exposure conditions (Panesar, 2019; Muralidharan *et al.*, 2021). Using SCMs and a water-cement ratio of 0.35-0.40 enhances the strength and durability of concrete when exposed to aggressive environments (Santhanam and Otieno, 2016).

SCMs are industrial by-products or waste materials from iron and steel production, namely ground granulated blast furnace slag (GGBFS), fly ash (FA), silica fume (SF), rice husk ash (RHA), and metakaolin (MK), which provide resistance to chemical and sulphate attacks under aggressive conditions. (Nochaiya *et al.*, 2010).

Among them, slag enhances both workability and durability, offering beneficial effects up to about 70% replacement. (Kumar, 2017). In comparison, fly ash improves workability and durability up to roughly 35% replacement, but develops strength more slowly than slag, despite ultimately achieving higher strength. (Rao & Kumar, 2023). Supplementary cementitious materials such as FA and SF can be incorporated at 5-10% cement replacement, and among these, silica fume, due to its ultrafine particle size and high reactivity, significantly improves the strength development and durability. Previous studies consistently report that the combined use of FA and SF further enhances concrete performance under aggressive environments. Their fine particle size and enhanced properties improve concrete's microstructure, reduce permeability, and enhance long-term performance in aggressive environments. Experimental studies have further validated the positive effects of SCMs on sustainable, long-term concrete. In 2007, Chalee investigated the effect of increasing the FA replacement percentage on the water-cement ratio, thereby reducing the cover depth. (Chalee *et al.*, 2010). Similarly, after seven years of marine exposure, 25-50% replacement of fly ash in concrete with a water-binder ratio of 0.45 demonstrated superior corrosion resistance and reduced chloride penetration, and after five years of exposure, 15-35% replacement of rice husk ash has improved the durability of Portland cement

concrete (Chalee *et al.*, 2013). Incorporating SCMs such as FA, and SF, and slag has attracted considerable attention in construction technology to enhance concrete longevity (Feng Naiqian *et al.*, 2009). Previous studies have confirmed that fly ash improves the workability and long-term strength. In contrast, silica fume significantly refines the pore structure because of its high pozzolanic reactivity, and slag enhances sulphate and chloride resistance (Thomas and Moffatt, 2018). Microstructural analysis has emerged as an essential tool for understanding strength and durability, and for improving value, offering valuable insights into concrete's internal structure. Looking forward, research on special cements such as SRPC, PSC, and PPC has also shown that they can enhance both strength and resistance to leaching in marine environments (Advisor *et al.*, 2000; Hussain *et al.*, 2024; Saha *et al.*, 2024). Many studies have concluded that combined FA and SF is the key partial cement replacement for enhancing concrete durability.

Therefore, this study addresses a critical research gap by evaluating the long-term performance of concrete exposed to actual tidal-zone conditions. This setting remains underexplored compared to conventional laboratory simulations using artificial seawater. Exposure to the natural tidal zone fulfils the concrete's exposure to continuous wave action, which remains a practical study of concrete in a marine environment. Furthermore, it provides one of the first comprehensive assessments of the synergistic effects of FA and SF in SRPC- and PSC-based concretes subjected to real marine exposure. By integrating mechanical, durability, and microstructural investigations, the present work offers valuable insights into the behaviour of blended cement concretes in natural tidal environments, thereby advancing marine concrete technology.

Building on this research, the present study investigates concrete performance with three distinct types of cement blended with fly ash and silica fume to enhance their performance in marine environments. To evaluate the short-term and long-term behaviour, the proposed mixes were first cured in freshwater for 7, 28, 56, and 91 days. In the second phase, the proposed mixes were initially cured in freshwater for 28 days, followed by natural seawater exposure in the tidal zone of Visakhapatnam to evaluate their mechanical and durability properties for 91, 180 and 365 days. After exposure to seawater, the optimised mixes were further analysed for durability and microstructural characteristics, providing insights into the concrete's homogeneity, microcracking, and

microhardness. The performance of concrete can be fully evaluated through mechanical, durability, and microstructural studies, which provide clear justification for its deterioration. Scanning Electron Microscopy (SEM) analysis was conducted on specimens cured in freshwater for 91 days to assess their intrinsic structural properties before seawater exposure. The outcomes provide insights into the practical application of blended cement systems for enhancing the durability of marine concrete structures.

Importance and Purpose of the Research

With the rapid expansion of ports and harbours, there is a critical demand for sustainable concrete solutions to ensure long-term service in highly aggressive marine environments. The continuous exposure of marine structures to chloride- and sulphate-rich environments poses persistent durability challenges, necessitating concretes with reduced permeability and enhanced resistance to chloride and sulphate-induced deterioration. This study addresses these challenges by employing blended cements, such as PSC and SRPC, which are further enhanced with supplementary cementitious materials (FA and SF) to improve mechanical and durability performance. The investigation not only evaluates strength and durability characteristics but also integrates microstructural analyses of concretes exposed to tidal zone conditions, thereby providing comprehensive insights into the suitability of these materials for resilient and sustainable marine infrastructure.”

The objective of this investigation is to examine the mechanical properties, particularly the compressive strength, of specimens cured with freshwater, as well as PDSV and SRR for concrete specimens exposed to seawater. It also aims to study the durability of concrete in terms of RCPT and permeability for mixes exposed to seawater, and to assess their water absorption capacity prior to seawater exposure. To support the durability studies related to seawater exposure, carbonation tests were conducted, and to establish a clear correlation between strength and durability, microstructural analyses were performed on specific mixes selected under performance criteria from the seawater-exposed samples.

Materials and Methodology

Materials

Cement

Ordinary Portland cement (IS 269:2015; specific gravity 3.15), Portland slag cement (IS 455:2015; 3.10), and sulphate-resisting Portland cement (IS 12330:1988; 3.15) were used to investigate the performance of blended cements in marine concrete compared with standard OPC 53. Table 1. lists the oxide compositions of cementitious materials. Figure 1 illustrates the particle size distribution (PSD) of cement. The results indicated that 90% of particles were finer than 56.12 μm for PSC, 76.2 μm for OPC, and 85 μm for SRPC, reflecting differences in fineness that may influence hydration kinetics and microstructural development. Figure 2, Figure 4 and Figure 6 explains the SEM images of respective cements, whereas Figure 3, Figure 5 and Figure 7 describes the Electron Dispersive X-ray Spectrum (EDS) analysis of OPC, PSC and SRPC, respectively.

Table 1. Oxides of selected cement constituents

Oxides	OPC53	PSC	SRPC
CaO	63.33	48.01	62.2
SiO ₂	21.27	28.53	21.58
Fe ₂ O ₃	4.06	2.55	4.76
Al ₂ O ₃	5.51	11.03	3.94
MgO	1.21	4.78	2.75
SO ₃	2.10	2.31	2.23

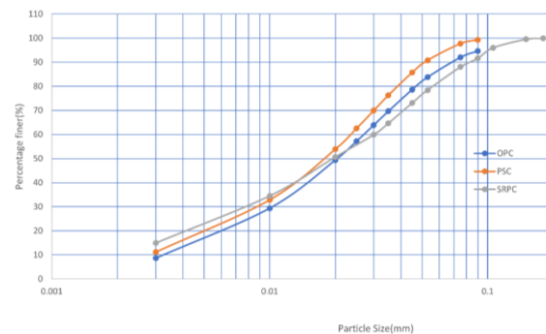


Figure 1. Particle size distribution for three different cements: OPC 53, PSC and SRPC

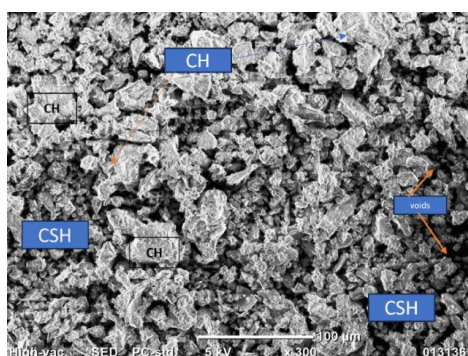


Figure 2. Microscopic analysis of Ordinary Portland Cement particles

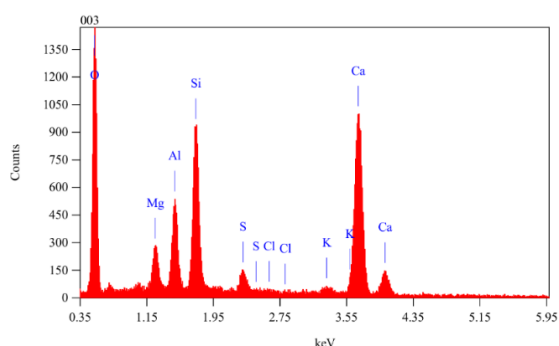


Figure 3. EDS analysis of ordinary Portland cement particles

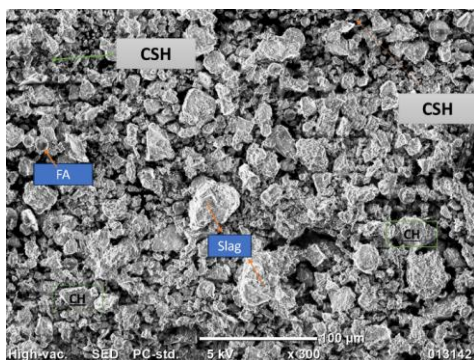


Figure 4. Microscopic analysis of Portland slag cement particles

Fly ash and silica fume.

FA conforming to IS 3812:2003 was procured from NTPC Visakhapatnam (specific gravity 2.11), while SF was sourced from Elkem (specific gravity 2.20). Combining FA and SF in ternary blended systems reduces chloride ingress, refines the pore structure, mitigates the alkali-silica reaction (ASR), and enhances sustainability by reducing cement use.

Aggregates

The coarse aggregate consisted of crushed stone in 20 mm and 10 mm fractions, blended in a 60:40 ratio (specific gravity 2.65). Natural river sand conforming to the Zone III requirements of IS 383:2016 (specific gravity 2.65) was used as the fine aggregate. To maintain workability with reduced water content, a high-range water-reducing admixture (HRWRA), CONPLAST SP430 (IS 12203:1999; specific gravity 1.18), was incorporated.

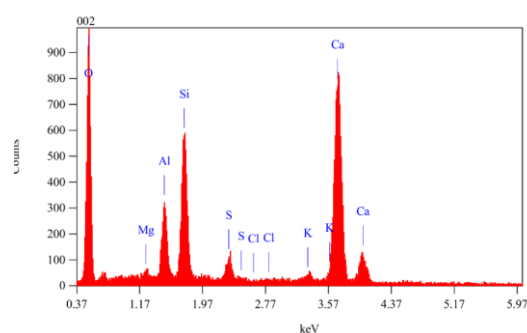


Figure 5. EDS of Portland slag cement particles

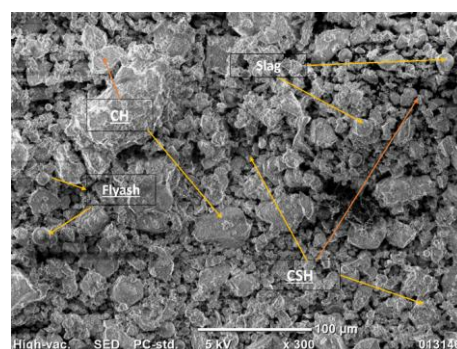


Figure 6. Microscopic analysis of sulphate-resistant Portland cement particles

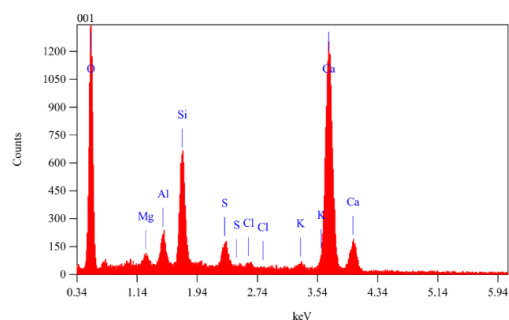


Figure 7. EDS analysis of SRPC particles

SEM micrographs demonstrated that OPC exhibited a dense matrix characterised by well-formed calcium silicate hydrate (C–S–H) and portlandite crystals. In contrast, PSC displays a more refined pore structure attributable to slag hydration products, whereas SRPC presents a compact matrix with fewer ettringite formations, indicating its sulphate resistance. The corresponding EDS spectra confirmed the predominance of oxygen (O) and calcium (Ca) across all mixtures, reflecting the presence of C–S–H and portlandite. OPC is noted for higher silicon (Si) and aluminium (Al) contents, whereas PSC exhibits reduced Al with additional magnesium (Mg) and sulphur (S) derived from slag (Patil *et al.*, 2018). SRPC showed the lowest Al content, consistent with its reduced tricalcium aluminate (C₃A) content, which is known to enhance sulphate attack. Minor peaks of potassium (K), chlorine (Cl), and S in PSC and SRPC are attributed to the supplementary materials. The integrated microstructural and compositional evidence suggests that PSC enhances durability in aggressive marine environments, whereas SRPC is designed explicitly for sulphate-rich conditions. (Huang *et al.*, 2019).

Mix detailing

The mix design adhered to IS 10262:2019, utilising a constant binder content of 450 kg/m³, water content of 162 L, and high-range water-reducing admixture at 0.7%. A water-binder ratio (w/b) of 0.36 was studied in the present study. The cement was partially replaced by 30% FA and 5% SF. The Conventional concrete using OPC 53, PSC, and SRPC with 0.36 was labelled as O0.36, P0.36, and S0.36, respectively. The fly ash mixture with a w/b ratio of 0.36 was identified as O0.36F, P0.36F, and S0.36F, respectively, while the mix with FA + SF was designated as O0.36FS, P0.36FS, and S0.36FS, respectively. Table 2 presents the ingredients used in the concrete design, expressed in kg.

Methodology

The experimental program aimed to assess the mechanical properties, durability, and microstructural features of three types of cement: OPC, PSC, and SRPC. The research involved comparative testing in a controlled laboratory setting, under natural marine and sulphate-rich conditions. The methodology included material characterisation, concrete mix design, specimen preparation, curing processes, and testing procedures, in accordance with the relevant Indian Standards.

Initially, specimens were tested up to 91 days to evaluate the strength development of mixes partially replaced with FA and SF. In the subsequent stage, all specimens were first cured in freshwater for 28 days and then transferred to the tidal zone for marine exposure. These specimens were then exposed to seawater for 91, 180, and 365 days to assess their long-term mechanical and durability performance. Figure 8 represents the exposure of concrete specimens at the tidal zone in the marine environment.



Figure 8. Exposing concrete specimens in a marine environment

Table 2. Representation of the Mix proportions

Sl. No	Mix	Materials(kgs)							
		W/C	Cement	FA	SF	Water	SP	CA	FA
1	O0.36	0.36	450	135	0	162	2.25	787	577.2
2	O0.36F	0.36	315	135	0	162	2.25	763.1	559.69
3	O0.36FS	0.36	292.5	135	22.5	162	2.25	759.4	556.98
4	P0.36	0.36	450	0	0	162	2.25	785.5	576.11
5	P0.36F	0.36	315	135	0	162	2.25	762	558.8
6	P0.36FS	0.36	292.5	135	22.5	162	2.25	758.5	556.3
7	S0.36	0.36	450	0	0	162	2.25	788.7	578.48
8	S0.36F	0.36	315	135	0	162	2.25	764.3	560.54
9	S0.36FS	0.36	292.5	135	22.5	162	2.25	758.3	556.22

Tests performed on concrete specimens

Compressive and split tensile strength test

Compressive strength evaluations were carried out in accordance with IS 516:2013 standards, using concrete cubes measuring 150 mm × 150 mm × 150 mm on a 300 T universal testing machine. The cube shape ensures uniform stress distribution, enabling precise measurement of the concrete's load-bearing capacity. The specimens underwent two curing processes: (i) immersion in fresh water for 7, 28, 56, and 91 days, and (ii) exposure to tidal zone conditions for 91, 180, and 365 days after 28 days of curing in freshwater. Long-term exposure to tidal conditions provides insights into the mechanisms of strength degradation in harsh marine environments, establishing a direct link between mechanical performance and durability indicators such as permeability, chloride penetration, and microstructural changes. Similarly, concrete cylinders with a diameter of 150 mm and a height of 300 mm, as per IS 5816-1999, were tested for split tensile strength. Daily strength variations and retention ratios were analysed to evaluate the strength results for concrete exposed to seawater.

Strength Retention Ratio (SRR)

The relative compressive strength was evaluated by comparing samples immersed in natural seawater within the tidal zone for 91, 180, and 365 days with that of unexposed samples measured at 28 days. This is expressed as the percentage ratio of the strength of the exposed samples at a given age to the unexposed strength at 28 days.

Per-day strength variations (PDSV)

The per-day strength variation of the concrete mixes was analysed to investigate the rate and pattern of strength development over time under seawater exposure. Compressive strength tests were conducted at specified intervals, including 28, 91, 180, and 365 days, following standard procedures (IS 516:1959). For each mix, the average daily strength gain was calculated as the increase in compressive strength between two consecutive testing ages divided by the number of days in that period. Mathematically, the per-day strength increment was determined as follows:

$$(\text{PDSV}) = \frac{f_c(t_2) - f_c(t_1)}{t_2 - t_1}$$

Where $f_c(t_1)$ and $f_c(t_2)$ are the compressive strengths of the respective ages and t_1 and t_2 are the respective times. The per-day strength data were plotted to visualise the temporal evolution of

strength for each mix and to identify differences in early-age and long-term performance. This approach enables a more detailed understanding of hydration kinetics, the effects of supplementary cementitious materials, and the influence of blended cements on strength development under aggressive marine conditions.

Durability studies

Concrete specimens were tested using the Rapid Chloride Permeability Test (RCPT) and the coefficient of permeability (K) to evaluate concrete durability after 28 days of freshwater curing to study the permeability of the proposed concrete mixes. Additional carbonation studies were conducted on a concrete sample obtained from a specimen exposed to a marine environment for 91 days.

Coefficient of Permeability (K)

The permeability of concrete was measured in accordance with IS 3085 (1965). The concrete specimens, with a diameter of 100 mm and a thickness of 50 mm, were sealed tightly and then inserted into a cylinder attached to the apparatus. The tubes were filled with water, and the results and observations were recorded accordingly. The coefficient of permeability (K) was calculated as follows:

$$k = \frac{Q}{A \times T \times \frac{H}{L}}$$

Where Q is the discharge, A is the area of the specimen, H is the head of the water, L is the length of the specimen, and T is the time.

Rapid chloride permeability test (RCPT)

The test was conducted on concrete specimens measuring 100 mm in diameter and 50 mm thick. The current was passed through the cylinder by placing it in the apparatus. The samples were oven-dried and impregnated with epoxy to preserve their pore structure. According to ASTM C1202, a charge exceeding 4000 is considered high, whereas a charge of less than 100 is considered low. The test was performed on 28-day-cured concrete immersed in freshwater to assess the concrete's permeability.

Carbonation depth

Carbonation occurs when atmospheric carbon dioxide reacts with wet cement compounds to form calcium carbonate, thereby reducing the concrete's alkalinity. Adding SCMs to concrete reduced the carbonation depth. This study examined the depth of carbonation in concrete exposed to natural

seawater. The inner core was used, and the phenothiazine indicator was used to measure depth under a microscope. In this case, the concrete exposed to natural seawater for 91 days determines the carbonation depth.

Microstructural studies

This study performed SEM and EDS analyses on three different cement types to examine particle morphology and its impact on concrete performance. Additionally, the microstructures of the optimised mixes derived from durability studies were examined after freshwater curing and 91 days of seawater exposure.

SEM

The morphology of the particles in the ingredients was examined under a microscope. The samples were oven-dried and impregnated with epoxy to preserve their pore structure. Secondary electron (SE) and backscattered electron (BSE) imaging modes, which are techniques in scanning electron microscopy, facilitate the examination of hydration product morphology and the distribution of unhydrated particles. Analysis of the micrographs revealed the formation of calcium silicate hydrate (C-S-H) gel, the presence of calcium hydroxide [$\text{Ca}(\text{OH})_2$], the extent of voids, and products of the pozzolanic (silica-alumina-containing mineral additive) reaction. The findings establish a correlation between the microstructural refinement and durability performance.

EDS

Energy-dispersive X-ray Spectroscopy (EDS or EDX) is a widely used analytical technique for elemental analysis or chemical characterisation of materials, primarily solids. EDS analysis and SEM imaging were performed at accelerating voltages of 15-20 kV. Spectra were collected from specific regions of interest, focusing on areas rich in C-S-H gel, calcium hydroxide (CH), unhydrated FA, and SF particles. The distributions of elements such as Ca, Si, Al, and other trace elements were identified to confirm pozzolanic activity and to refine the hydration products. EDS was used in conjunction with SEM to examine the elemental composition of blended concrete mixes. It provides semi-quantitative data on the chemical makeup of the hydration products and unreacted particles. This information helps to correlate the microstructural features with the durability performance of concrete.

Results and discussion

Compressive strength

Freshwater

Figure 9 illustrates the development of compressive strength in concrete cured in freshwater for more than 91 days. A comparative analysis of mixtures incorporating OPC, PSC, and SRPC identified distinct trends in the compressive strength development. The S0.36FS with consistent development showed a strength of 56.3 MPa at 91 days, owing to the enhanced effect of FA+SF. The OPC mixture (O0.36) demonstrated the highest overall strength, achieving 61.23 MPa at 91 days, with consistent growth beyond 28 days. Conversely, PSC mixtures exhibited comparatively lower strength gains, with P0.36 reaching only 51.43 MPa at 91 days. The P0.36F and P0.36FS mixes further indicate that slag-based binders are less effective than the other systems. The SRPC mixtures displayed balanced performance, with S0.36 recording a high early strength of 42.51 MPa at 7 days and maintaining steady growth to 54.22 MPa at 91 days. Furthermore, SRPC mixtures (S0.36F and S0.36FS) demonstrated significant later age strength development, reaching 53.03 and 56.3 MPa, respectively, narrowing the OPC gap. Overall, OPC remains superior in terms of peak strength. At the same time, SRPC emerges as a competitive alternative with more balanced and consistent strength development across curing ages, whereas PSC lags in both early and long-term performance.

Splitting tensile strength

The split tensile strength tests (Figure 10) show that the OPC-based mixtures generally performed better at early ages. This is due to the high clinker content and quick hydration of C_3S . Conversely, PSC and SRPC mixtures with SCMs exhibited lower strength at 7 days, primarily when FA was used as a substitute. These declining results indicate slower pozzolanic activation and a reduced supply of early calcium hydroxide. By 28 days, all mixtures had gained strength, with combinations of FA+SF surpassing those with only FA. This performance of concrete demonstrates the synergistic effects of filler and pozzolanic activity, which improve the pore structure and bond strength at the aggregate-paste interface. PSC mixtures exhibited moderate recovery, reducing the performance gap with OPC. However, S0.36FS showed notable improvements

at later ages, likely due to continued hydration of C₂S and delayed pozzolanic reactions.

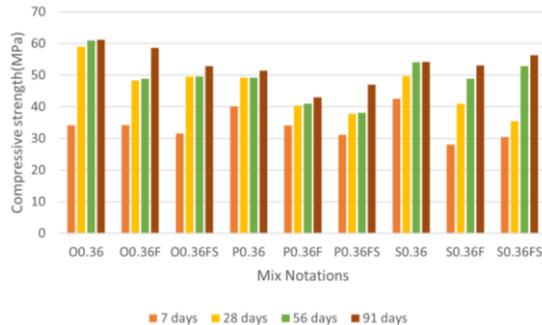


Figure 9. Compressive strength of concrete cured in fresh water

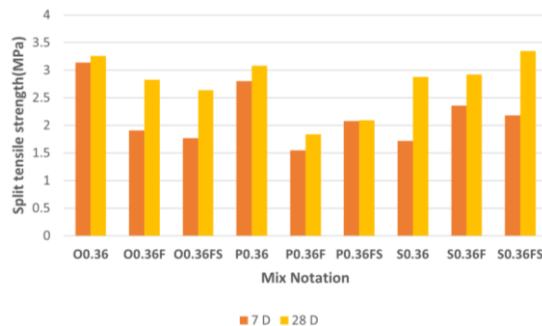


Figure 10. Tensile Strength variation of concrete cured in freshwater

Per-day Compressive strength Variation analysis for concrete exposed to natural seawater

Figure 11 shows the PDSV analysis of concrete exposed to seawater, and Table 3 presents

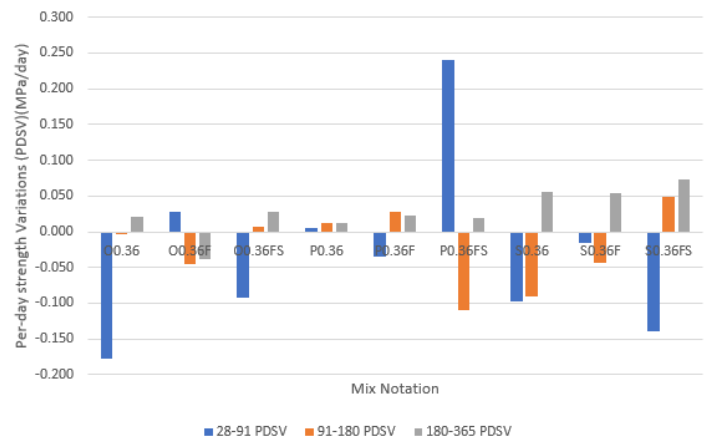


Figure 11. Histograms of OPC, PSC and SRPC mixes per day compressive strength variations in seawater

the per-day strength variations at 28-91, 91-180, and 180-365 for the compressive strength of seawater-exposed concrete. The OPC mixes exhibited significant early deterioration when exposed to seawater, as reflected by a negative PDSV in the 28-91-day period and a noticeable drop in compressive strength. The PSC mixes demonstrated the most stable natural resistance to seawater, maintaining a nearly constant strength throughout the exposure period. SRPC consistently achieved the highest long-term strengths, with SO.36 reaching 50.97 MPa after 365 days, making SRPC the most suitable binder for marine environments. FA significantly boosted early-age strength in OPC-based mixes but declined beyond 180 days due to delayed pozzolanic reactions. In the PSC and SRPC mixes, FA helped maintain moderate strength development, although its effect was less pronounced. The combination of FA and SF delivered optimal performance in seawater-exposed concrete. (OPC+FA+SF) and (SRPC+FA+SF) achieved 49.03 MPa and 50.96 MPa, respectively, at 365 days, demonstrating excellent durability and resistance to salt-induced deterioration. Most mixes showed negative PDSV values during the 28-91-day period, indicating early degradation upon first exposure to seawater. Between 91 and 180 days, some mixes exhibited further strength losses (e.g., OPC and PSC+FA), while others showed moderate gains due to ongoing pozzolanic reactions. After 180 days, nearly all mixes had stabilised, and several achieved average strength recoveries by 365 days, highlighting the beneficial long-term effects of SCMs.

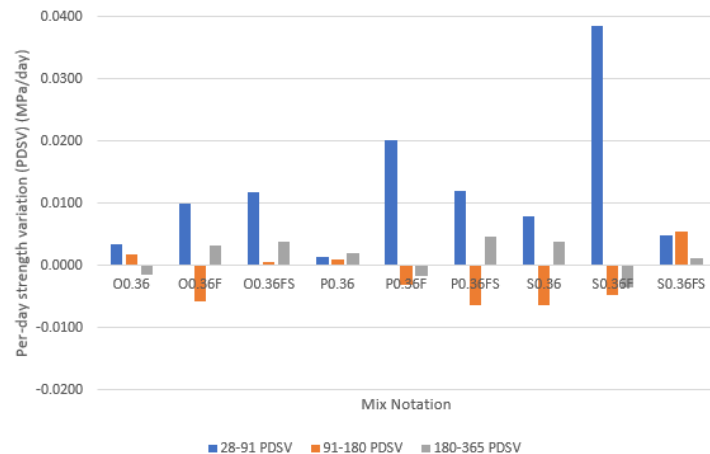


Figure 12. Histograms of OPC, PSC and SRPC mixes per day, showing split tensile strength variations in seawater

Table 3. Per-day compressive strength variation of concrete mixes in seawater

Concrete Mix	28-91 PDSV	91-180 PDSV	180-365 PDSV
O0.36	-0.177	-0.003	0.020
O0.36F	0.027	-0.046	-0.039
O0.36FS	-0.093	0.007	0.027
P0.36	0.006	0.012	0.013
P0.36F	-0.035	0.028	0.022
P0.36FS	0.239	-0.109	0.019
S0.36	-0.098	-0.091	0.055
S0.36F	-0.016	-0.044	0.054
S0.36FS	-0.139	0.049	0.074

Table 4. Per-day split tensile strength variation of concrete mixes in seawater

Mix Notations	28-91 PDSV	91-180 PDSV	180-365 PDSV
O0.36	0.0033	0.0018	-0.0014
O0.36F	0.0100	-0.0058	0.0031
O0.36FS	0.0117	0.0006	0.0038
P0.36	0.0014	0.0009	0.0020
P0.36F	0.0202	-0.0031	-0.0017
P0.36FS	0.0119	-0.0063	0.0047
S0.36	0.0079	-0.0063	0.0038
S0.36F	0.0386	-0.0047	-0.0036
S0.36FS	0.0049	0.0054	0.0012

The PDSV analysis of the split tensile strength of seawater-exposed concrete is illustrated in Figure 12, and Table 4 represents the per-day strength variations for 28-91, 91-180, and 180-365 days for the split tensile strength of seawater-exposed concrete. The per-day strength variation (PDSV) analysis provided valuable insights into the tensile strength development of the mixes under seawater exposure. During the early age period (28-91 days), most mixes recorded positive PDSV values, indicating strength gain. Among them, S0.36F showed the most significant increase

(~0.039), followed by P0.36F (~0.020), indicating rapid pozzolanic activity at this stage. In the intermediate age (91-180 days), however, several mixes, including O0.36F, P0.36FS, S0.36, and S0.36F, showed negative PDSV values, signifying a decline in strength. Only S0.36FS and O0.36FS sustained moderate positive increments, suggesting that the combined action of fly ash and silica fume imparted improved resistance against seawater-induced deterioration. Over the long term (180-365 days), all mixes showed positive PDSV values, confirming continued tensile-strength development under aggressive exposure. Notably, the FS mixes (O0.36FS, P0.36FS, and S0.36FS) demonstrated steady improvements, underscoring the beneficial role of supplementary cementitious materials in refining the pore structure and sustaining long-term strength. Overall, the results reveal that while SCM mixes with FA and SF may exhibit delayed early-age strength gains, they significantly enhance long-term tensile performance, making them more suitable for marine environments.

Strength Retention Ratio for Seawater-Exposed Concrete

The strength retention rate (SRR) trends in Figure 13 illustrate the apparent influence of binder type and supplementary cementitious materials (SCMs) on the long-term durability of seawater exposure. The control OPC mix (O0.36) consistently showed lower SRR values (<1.0) at all ages, whereas the addition of fly ash (O0.36F) improved the retention to approximately 1.0 by 365 days. The O0.36FS further boosted the performance, exceeding 1.1 at one year, confirming the synergistic effect of FA and SF. In contrast, PSC-based mixes demonstrated better retention,

with steady growth in P0.36 (reaching ~1.1) and more significant improvements in P0.36F and P0.36FS, the latter reaching the highest SRR (~1.5) at 365 days. SRC mixes showed intermediate behaviour, with S0.36FS reaching ~1.2 at one year, indicating the positive role of SCMs, although less effective than PSC-based systems. Overall, the results highlight that PSC and SRPC ternary blends with FA and SF offer the highest resistance to strength loss in harsh marine environments, underlining their suitability for durable port and coastal infrastructures.

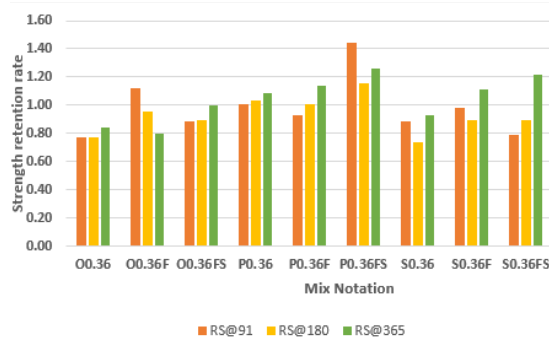


Figure 13. Evaluation of compressive strength based on strength retention rate

Splitting Tensile strength

Figure 14 illustrates the variation in strength retention for the proposed mixes over 91, 180, and 365 days of exposure. The control OPC mix (O0.36) showed a stable but limited SRR (~1.0), whereas O0.36F provided only a marginal improvement. In contrast, the O0.36FS achieved superior long-term retention (>1.3 at 365 days) owing to the synergistic effects of FA and SF. The control PSC mix (P0.36) exhibited gradual SRR improvement with age (~1.0 to >1.2), whereas P0.36F and P0.36FS achieved higher retention (>1.4), demonstrating the durability benefits of slag combined with FA and SF. The S0.36 exhibited a fluctuating SRR (~1.0-1.2), whereas S0.36F achieved significant gains (~2.0 at 91 days, >1.8 at 365 days), highlighting FA's substantial durability benefits. The S0.36FS also improved retention (>1.2), although less effectively than FA alone due to SF's slower reactivity. Across all systems, OPC showed modest improvements with FA and notable gains with the FA-SF blend. PSC demonstrated consistent enhancement with both FA and SF, and SRPC showed the most remarkable durability improvement with FA incorporation, while the ternary FA-SF blend provided moderate, though less pronounced, benefits owing to SF's slower

reactivity. When concrete is exposed to the tidal zone, chloride ions from seawater penetrate the surface layers, potentially increasing permeability and reducing strength due to microstructural deterioration. However, the continued development of strength observed even after prolonged seawater exposure indicates that the concrete matrix remains relatively impermeable. This demonstrates the densification of the microstructure and the refinement of pores due to ongoing hydration and pozzolanic reactions, which collectively enhance the concrete's durability under marine conditions.

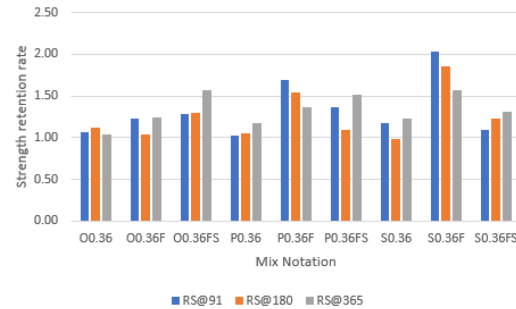


Figure 14. Evaluation of strength retention rate for split tensile strength analysis

Durability studies

Rapid chloride permeability test

The charge passed in coulombs is shown in the Figure 15. Highlight the significant influence of supplementary cementitious materials (SCMs) on chloride ion penetration resistance. The control OPC mix (O0.36) exhibited a charge passed of 567.9 coulombs, while its FA- and FA+SF-modified counterparts (O0.36F and O0.36FS) showed reduced values of 453.6 and 359.1 coulombs, respectively, indicating improved resistance. Similarly, the PSC mix (P0.36) recorded 453.6 coulombs, which increased slightly in the FA- and FS-blended mixes (P0.36F: 582.3; P0.36FS: 595.8), suggesting that the effect of SCMs in PSC systems is less pronounced at this stage. By contrast, the SRPC mix (S0.36) exhibited the highest charge passed (1268.1 coulombs), indicating a high permeability to chloride ions. However, the incorporation of fly ash (S0.36F: 386.1) and especially the combined FA+SF system (S0.36FS: 209.7) markedly reduced permeability, demonstrating the strong synergistic effect of SCMs in refining the pore structure and blocking chloride ingress.

Overall, the results confirm that OPC and PSC systems benefit moderately from SCM incorporation. However, the effect is most

significant in SRPC mixes, where FA and SF substantially mitigate the otherwise high chloride permeability. According to ASTM C1202 classification, most SCM-modified mixes fall into the *low-to-very-low* permeability category, highlighting their suitability for marine and chloride-exposed environments.

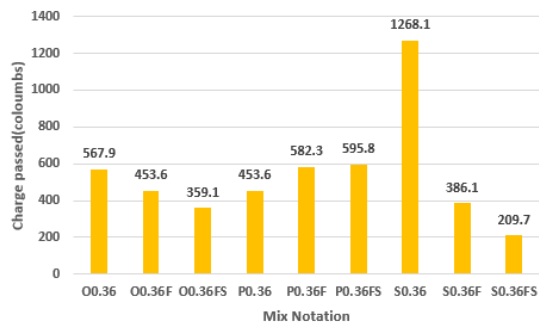


Figure 15. Comparison of charges passed for 28-day cured concrete

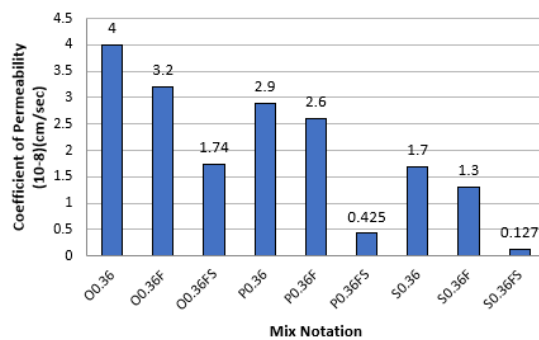


Figure 16. Coefficient of Permeability results for concrete cured for 28 days

Coefficient of Permeability (K)

The coefficient of permeability results are shown in Figure 16, which demonstrates an apparent reduction in permeability with the incorporation of supplementary cementitious materials (SCMs). The control OPC mix (O0.36) exhibited the highest permeability coefficient of 4×10^{-8} , indicating a relatively porous microstructure. The addition of fly ash (O0.36F: 3.2×10^{-8}) and especially the combined fly ash + silica fume system (O0.36FS: 1.74×10^{-8}) significantly reduced permeability, confirming the role of SCMs in refining the pore structure. A similar trend was observed in PSC-based mixes, where permeability decreased from 2.9×10^{-8} (P0.36) to 2.6×10^{-8} (P0.36F), with the most substantial improvement in P0.36FS (0.425×10^{-8}). In SRPC mixes, the base

mix (S0.36) recorded 1.7×10^{-8} , which further reduced to 1.3×10^{-8} with fly ash (S0.36F) and reached the lowest value of 0.127×10^{-8} in the FS blend (S0.36FS).

These results clearly establish that SCM incorporation-particularly the synergistic effect of fly ash and silica fume-markedly lowers permeability, thereby enhancing resistance to fluid transport and chloride ingress. The drastic reduction in the S0.36FS mix demonstrates the superior densification and pore refinement achieved through combined pozzolanic reactions, leading to a highly impermeable matrix.

Carbonation depth

The carbonation depths for O0.36FS, P0.36FS and S0.36FS are shown in Figure 17, Figure 18, and Figure 19, respectively. The incorporation of fly ash significantly improves the anti-permeability of the concrete composite, thereby reducing the ingress of atmospheric CO₂. Silica fume further enhances carbonation resistance due to its finer particle size compared to fly ash. Optimised concrete mixes containing three different cement types, combined with fly ash and silica fume, were tested for carbonation depth after exposure to natural seawater. After 91 days, O0.36FS recorded the carbonation depth of 3.13 mm, P0.36FS showed 1.02 mm, and S0.36FS exhibited only 498 μ m. The superior performance of S0.36FS was attributed to sulphate-resistant cement, which has a refined pore structure and low tricalcium aluminate content. S0.36FS demonstrated exceptional performance in minimising the carbonation depth. (Rao & Meena, 2017). In the present study, three types of cements were employed to evaluate carbonation resistance under marine exposure conditions. Among the investigated mixes, S0.36FS exhibited the lowest carbonation depth of 498 μ m, which was notably lower than that of O0.36FS and P0.36FS. The superior performance of the SRPC-based mix can be attributed to its lower C₃A content and reduced calcium hydroxide availability, which collectively limit the carbonation reaction. Furthermore, the inclusion of fly ash (FA) and silica fume (SF) enhanced the pozzolanic reaction, leading to the consumption of portlandite and the formation of additional C-S-H and C-A-S-H phases. These secondary hydration products refined the pore structure and reduced the connectivity of capillary pores, thereby impeding CO₂ ingress during the early stages of seawater exposure. Consequently, the synergistic effect of SRPC with FA and SF resulted in a densified microstructure and improved resistance to carbonation compared with OPC- and PSC-based systems

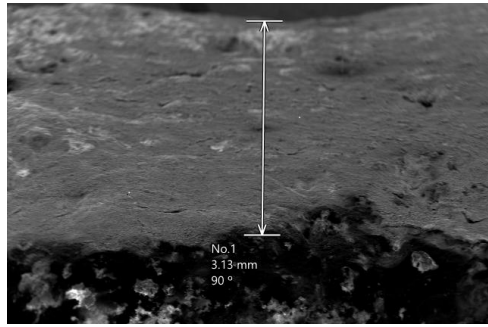


Figure 17. Carbonation depth of O0.36FS concrete exposed to seawater

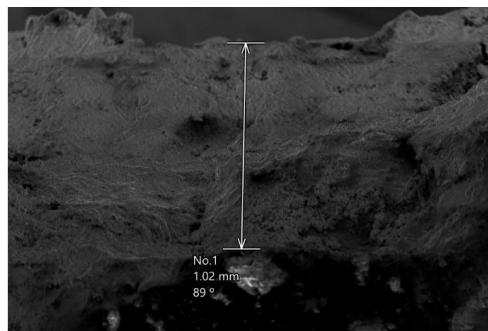


Figure 18. Carbonation depth of P0.36FS concrete exposed to seawater for 91 days

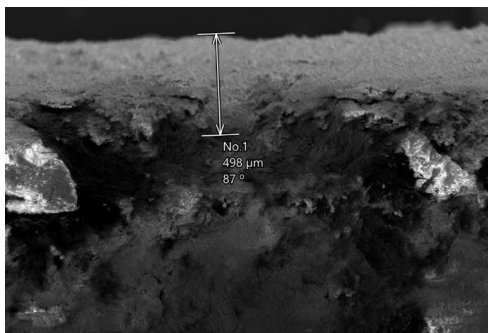


Figure 19. Carbonation depth of S0.36FS concrete exposed to seawater for 91 days

Correlation of strength and durability indices for the concrete

The durability performance of the investigated concretes, evaluated through the strength retention rate (SRR), permeability, and rapid chloride permeability test (RCPT), as illustrated in Figure 20. The results revealed a consistent trend highlighting the superiority of the combined effect with FA+SF. The OPC controls exhibited the lowest durability, with relatively poor SRR (<1.0), higher permeability ($>4 \times 10^{-8}$ cm/s), and moderate

chloride penetrability (~ 600 coulombs), confirming their vulnerability to seawater exposure. The PSC and SRPC controls showed mild improvement, but significant enhancements were observed with the addition of SCMs. Inclusion of FA achieved noticeable reductions in permeability and chloride transport, along with modest SRR gains, while ternary mixes incorporating both FA and SF consistently outperformed all others. In particular, PSC- and SRC-based mixes (P0.36FS and S0.36FS) achieved the lowest permeability ($<1 \times 10^{-8}$ cm/s), very low charge passed (<300 coulombs), and the highest SRR (~ 1.4 – 1.5 at 365 days). The strong correlation between reduced transport properties, lower chloride ingress, and higher long-term strength retention underscores the microstructural refinement imparted by SCMs. Overall, ternary blended systems, especially PSC+FA+SF and SRC+FA+SF, have emerged as the most durable concretes, offering superior resistance to seawater-induced deterioration, making them the most reliable choice for marine and coastal infrastructure.

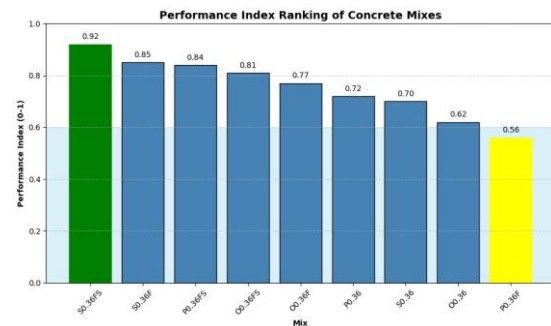


Figure 20. Performance indices of the concrete exposed to the marine environment

Microstructural studies

Scanning electron microscopy (SEM)

Analysis of the O0.36FS, P0.36FS, and S0.36FS mixtures, which were either cured in freshwater for 91 days or exposed to seawater after 28 days of freshwater curing, highlighted significant microstructural variations, as shown in Figure 21, Figure 22, and Figure 23, respectively. In the O0.36FS mix, exposure to seawater led to moderately refined matrices with micro voids, whereas the P0.36FS mix displayed larger voids and notable C–S–H formation. The extension of fly ash reduced the CH content, improving long-term stability. The S0.36FS mix exhibited dense C–S–H networks with unhydrated fly ash particles, indicating an ongoing pozzolanic activity. The combination of fly ash and silica fume resulted

in tightly packed hydration products, creating a compact microstructure with low permeability. Overall, specimens exposed to seawater developed denser and more interlocked C-S-H structures than those cured in freshwater, with SRPC-based blends exhibiting enhanced durability in marine environments. (Gürabi *et al.*, 2024).

Energy Dispersive X-ray Spectroscopy (EDS)

EDS was used alongside SEM to analyse the elemental composition of the blended Mixes. EDS

yielded semi-quantitative data on the chemical composition of the hydration products and unreacted particles. This information facilitates the correlation between the microstructural characteristics and durability performance of concrete. Figure 24, Figure 25, and Figure 26, respectively, illustrate these for the O0.36FS, P0.36FS, and S0.36FS concrete mixes.

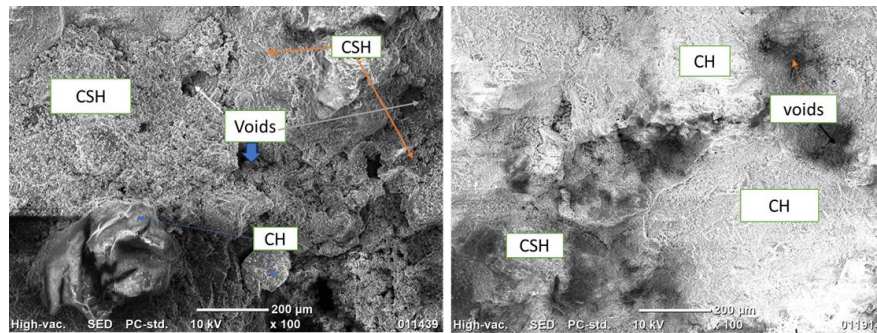


Figure 21. Morphological studies on O0.36FS concrete cured for 91 days in fresh water(left) and seawater(right)

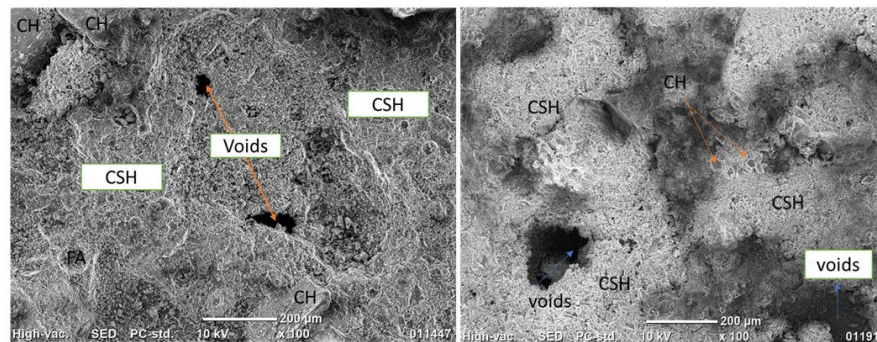


Figure 22. Morphological studies on P0.36FS concrete cured for 91 days in fresh water(left) and seawater(right)

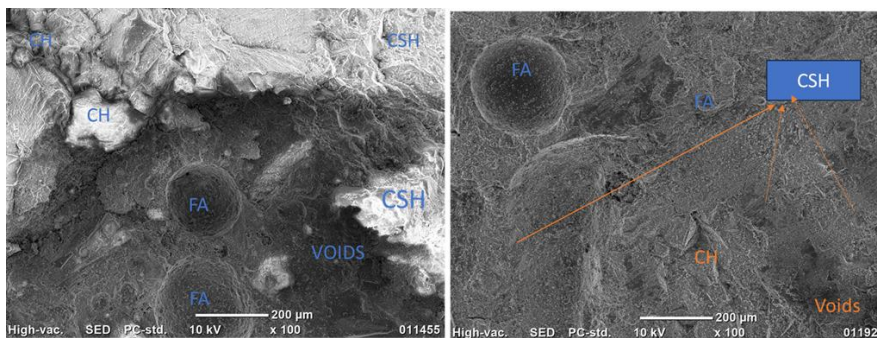


Figure 23. Morphological studies on S0.36FS concrete cured for 91 days in fresh water(left) and seawater(right)

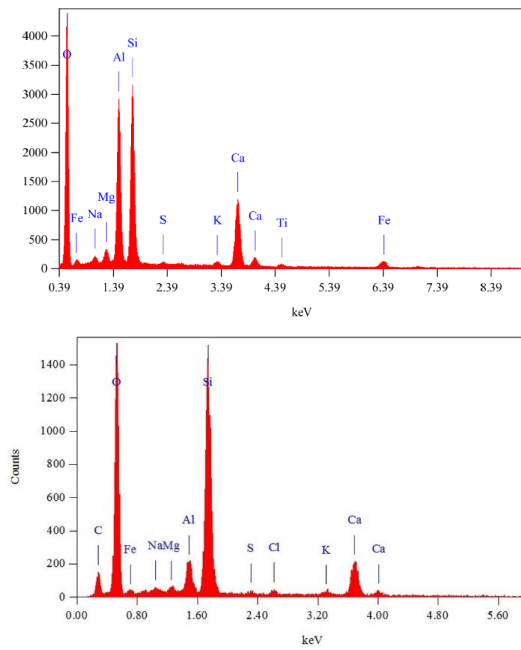


Figure 24. EDS analysis of O0.36FS concrete cured in fresh water(top) and seawater(bottom)

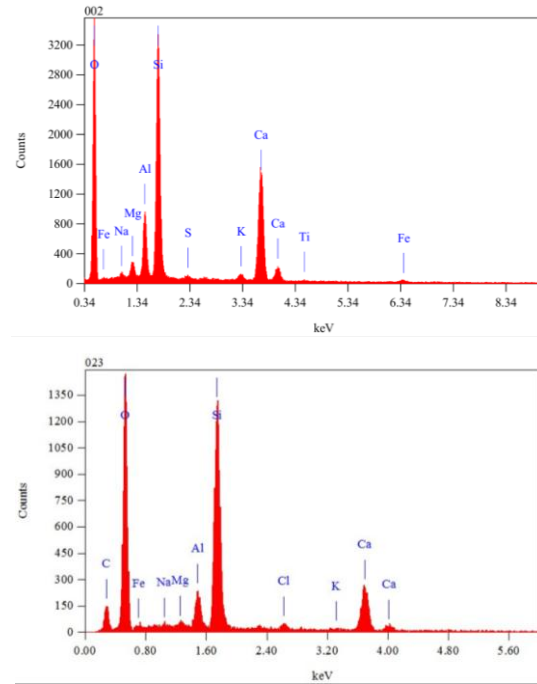


Figure 26. EDS analysis of S0.36FS concrete exposed to fresh water(top) and seawater(bottom) for 91 days

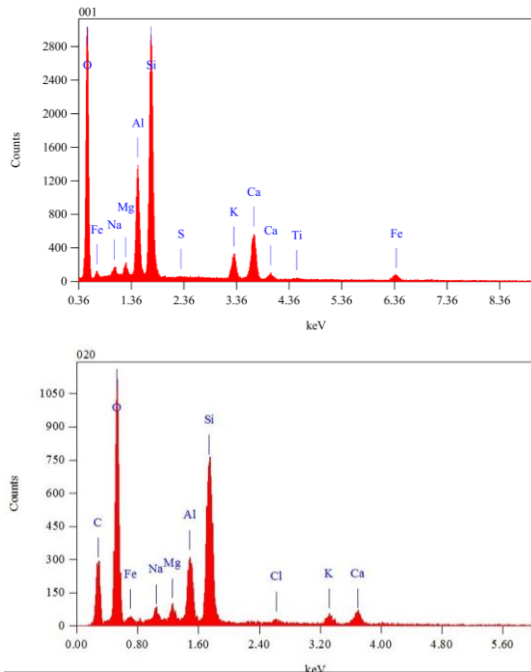


Figure 25. EDS analysis for P0.36FS concrete cured in fresh water(top) and seawater(bottom) for 91 days

EDS analysis of concrete exposed to freshwater and seawater is illustrated by Figure 24, Figure 25 and Figure 26. The comparative study of concrete mixes for EDS revealed higher chloride ion concentrations in seawater-exposed concrete than in freshwater-cured concrete. A reduction in calcium (Ca), silicate (Si), and aluminate (Al) peaks is observed in the EDS graphs. This study demonstrates the penetration of chloride ions into concrete exposed to seawater. Among the three mixes, S0.36FS showed lower chloride ion levels than O0.36FS and P0.36FS. The presence of slag, FA, and SF in P0.36FS contributed to better performance than that of O0.36FS.(Muralidharan *et al.*, 2005)The chloride-binding capacity of FA and SF, and the sulphate resistance of S0.36FS, contributed to S0.36FS's superior performance, highlighting its balanced results across all tests conducted in the current study.(Wang *et al.*, 2024). Correlating the SEM images of the cement particles with the SEM images of concrete made of those cements, the highly dense compact microstructure of the SRPC cement added better performance of

concrete, even in seawater, even after 91 days of exposure. The presence of FA and SF has a positive effect on SRPC, leading to a compact microstructure

Conclusions

This study evaluated the variation in compressive strength and durability of nine concrete mixes exposed to seawater for 365 days. As detailed, the study was conducted in two distinct phases, and the conclusions from these discussions are presented here.

Observations from freshwater cured concrete indicated that OPC achieved the highest early and peak strengths, while SRPC showed balanced gains in FA + SF mixes, further narrowing the gap with OPC. PSC lagged in both early- and long-term performance, highlighting the combined effect of FA+SF on improving later-age strength. PDSV analysis revealed that OPC mixes deteriorated rapidly in seawater, highlighting poor durability, while PSC maintained the most stable resistance, and SRPC achieved the highest long-term strengths. SCMs, particularly FA + SF, mitigated early degradation and enhanced recovery after 180 days, with SRPC +FA + SF showing strong overall performance. SRR trends indicated that OPC had the lowest retention, though improved by FA and FA+SF, while PSC with FA+SF achieved the highest SRR (~1.5), confirming superior durability. In comparison, PDSV underscored OPC's early vulnerability and the resilience of PSC and SRPC. At the same time, the SRR highlighted the long-term advantage of the PSC+FA+SF mix, making it the most durable option for marine environments. Durability indicators from RCPT, permeability, SRR, PDSV, and carbonation depth demonstrated that the superiority of FA+SF and SRPC-based FA+SF mixes was achieved by achieving the lowest chloride ingress (<300 C) and permeability ($<1 \times 10^{-8}$ cm/s), while also sustaining the highest strengths. The carbonation resistance was most substantial in SRPC with FA + SF, with a depth of only 498 μm after 91 days. Overall, PSC+FA+SF and SRPC+FA+SF provided the most durable balance, combining transport, strength retention, and carbonation resistance, making them best suited for marine environments. SEM and EDS analyses confirmed that the combined effect of FA and SF, particularly S0.36FS, resulted in dense C–S–H networks, reduced CH, and the lowest chloride penetration, validating the durability trends observed in the macro-level tests. Consistent with this, PDSV and SRR highlighted superior strength retention in PSC- and SRPC-based FA+SF mixes,

while RCPT and permeability results confirmed their very low chloride ions and fluid transport. Carbonation depth measurements further support these findings, with S0.36FS achieving the least ingress (498 μm), aligning microstructural compactness with long-term durability. The agreement between the microstructural evidence and the durability indices collectively established PSC+FA+SF and SRPC+FA+SF as the most reliable concrete mixes for sulphate- and chloride-rich environments.

This study demonstrates that combining SCMs with special cements provides a durable, high-performance solution for infrastructure in harsh tidal zones, shaping material selection standards in coastal construction projects.

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