

## **An Experimental Study on Durability Properties of Reactive Powder Concrete Containing Silica Fume and Fly Ash as Supplementary Cementitious Materials**

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## ORIGINAL STUDY

# An Experimental Study on Durability Properties of Reactive Powder Concrete Containing Silica Fume and Fly Ash as Supplementary Cementitious Materials

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## Abstract

The paper reports on the influence of using silica fume (SF) and fly ash (FA) as supplementary cementitious materials (SCMs) on the durability properties of reactive powder concrete (RPC), focusing on sorptivity, ultrasonic pulse velocity (UPV), and carbonation depth. The study also compares the performance of RPC with high-strength concrete (HSC) to assess the relative benefits of RPC. A total of 19 mixtures, including 17 RPC and 2 HSC mixtures, were evaluated. Parameters such as the volume of binder content (45, 50, 55, and 60 %), water–binder ratios (20, 25, and 30 %), and SCM proportions (0, 10, 20, and 30 %) were varied; these parameters were examined experimentally to evaluate their effect on durability. Results showed that increasing the binder volume ratio from 40 to 60 % reduces water absorption by up to 60 %, with SF mixtures outperforming FA mixtures in water resistance. The sorptivity and water absorption are increased by 78 and 46.6 %, respectively, when the water-to-binder ratio is increased from 20 to 30 % for FA mixtures, whereas for SF mixtures, the optimal performance occurs at a 25 % water-to-binder ratio. The highest reduction in water absorption and sorptivity occurred at a 20 % SCM replacement for SF. UPV increased with higher binder content and SCM replacement with SF mixtures showing superior results. Further, RPC with SF exhibits minimal resistance to CO<sub>2</sub> penetration. In comparison to HSC, RPC with SF demonstrates significantly lower sorptivity, up to 63.4 %, 8.12 % higher UPV, and minimal carbonation depth, while HSC shows a 62.5 % greater carbonation depth compared with RPC with FA.

**Keywords:** Carbonation, High-strength concrete (HSC), Reactive powder concrete (RPC), Sorptivity, Supplementary cementitious materials (SCMs), Ultrasonic

## 1. Introduction

### 1.1. Research background

Reactive powder concrete (RPC) has gained considerable attention in recent years due to its ultra-high strength, low porosity, and enhanced durability characteristics. Developed in the early 1990s by Richard and Cheyrezy (1994), RPC is distinguished by its low porosity and high density, achieved through a unique blend of fine powders and minimal water content (Richard and Cheyrezy, 1995). This composition not only enhances compressive strength but also significantly

improves resistance to environmental factors. These unique properties of RPC make it suitable for specialized applications where superior performance is essential, such as in high-load-bearing structures, marine environments, and infrastructure exposed to aggressive conditions.

However, understanding the durability and long-term performance of RPC remains critical. The first durability studies of these innovative concretes were performed by Andrade and Sanjuán (1994), in which corrosion assessment, mercury intrusion porosimetry, and air permeability test results, among others, showed the high durability of this building material.

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To evaluate the durability of RPC, several important tests are conducted to measure its long-term performance like sorptivity, ultrasonic pulse velocity (UPV), and carbonation depth. RPC has emerged as a highly durable material, marked by its ultra-high strength, low permeability, and resistance to environmental degradation.

This unique performance has led researchers to focus on its water transport properties, which are crucial for predicting durability, particularly in aggressive environments. As water ingress largely mediates concrete deterioration, sorptivity or the rate at which water is absorbed by capillary action has become an essential parameter for assessing concrete's long-term resilience. It was found that the sorptivity test was a simple and rapid way to quantify the material quality that describes the propensity to absorb and transport water through capillarity. It was also discovered to have a clear correlation with permeability. When there is no head of water present, it assesses an unsaturated concrete's capacity for water penetration by absorption. Therefore, reducing sorptivity is crucial to lowering the amount of sulfate or chloride that enters concrete.

The sorptivity, or capillary suction, depends on the liquid's viscosity, density, and surface tension as well as the porous solid's pore structure (radius, tortuosity, and capillary continuity). It is expressed as the water absorption rate. [Abdellatif et al. \(2023a\)](#), explored the effects of replacing cement with industrial wastes [silica fume (SF), Ground Granulated Blast Furnace Slag (GGBS), fly ash (FA)] and metakaolin (MK) on ultra-high-performance concrete (UHPC) properties, showing that concrete with 30 % FA achieved low chloride ion permeation (55 C) and sorptivity ( $8.9 \times 10^{-4} \text{ mm/s}^{0.5}$ ), while mixtures with 50 % GGBS and 25 % MK had the lowest performance. The study highlighted the potential of industrial waste and MK for producing sustainable UHPC with reduced environmental impact. [Alkaysi et al. \(2016\)](#), found that RPC's dense matrix contributes to its very low water absorption and internal integrity, making it highly resistant to freeze–thaw cycles and chloride ion penetration. The study also showed that increasing SF content improves RPC's frost resistance and chloride resistance by enhancing its microstructure.

Similarly, [Xu et al. \(2022\)](#) reported that a combination of steam curing and SF significantly reduced RPC porosity, which directly lowered sorptivity and increased impact resistance due to a denser microstructure and better energy absorption facilitated by steel fibers. Further studies by [Ge et al. \(2023\)](#) evaluated the effects of alternative binder components, including FA, slag, and SF, on RPC's mechanical and

sorption properties. Their results indicated that SF replacement at optimal levels achieved high strength and reduced water absorption, while also promoting economic and environmental benefits. [Tahwia et al. \(2021\)](#) studied UHPC with cement replacements by CEM III, FA, and Granulated Blast Furnace Slag (GBFS), finding that up to 50 % FA improved resistance to sulfate attack and chloride penetration. SEM and Energy Dispersive X-ray Spectroscopy (EDX) analyses showed a dense microstructure, highlighting FA's potential to enhance the sustainability and durability of UHPC while maintaining ultra-high-performance characteristics.

[Elawady et al. \(2014\)](#) specifically examined the relationship between SF content and sorptivity in RPC, showing that increasing cement content and partial SF replacement reduced sorptivity by up to 68.3 %, thus enhancing durability under various curing conditions. In addition to SF, other pozzolanic materials have been explored for RPC applications. [Alharbi et al. \(2021\)](#) investigated MK as a partial SF replacement in RPC, finding that MK-SF blends improved strength and durability, particularly under autoclave curing. Their research further indicated that while nanomaterials were tested for enhancing compressive strength and durability, they offered limited benefits compared with those recorded in traditional concrete. In addition to RPC, other high-performance concretes have been studied for sorptivity and related durability characteristics.

A study by [Leung et al. \(2016\)](#) investigated the effect of FA and SF on sorptivity in self-compacting concrete (SCC), finding that both additives significantly reduced surface water absorption. Particularly, a combination of FA and SF reduced sorptivity more effectively than FA alone, with notable improvements as the proportion of these additives increased. [Abdellatif et al. \(2023b\)](#) investigated the optimization of sustainable UHPC with Ultra-Fine Fly Ash (UFFA), MK, and steel fibres, showing improved mechanical properties and microstructure. SEM and X-ray Diffraction (XRD) analyses revealed a denser microstructure with optimal UFFA content, and economic and environmental evaluations highlighted significant reductions in cost and carbon emissions, particularly with UFFA.

[Paktiawal and Alam \(2021\)](#) evaluated the use of basalt and glass fibers in high-strength concrete (HSC), noting that basalt fibers yielded a lower coefficient of sorptivity and reduced void content compared with glass fibers, further improving the concrete's durability. In addition to sorptivity, nondestructive testing methods such as UPV have become essential for assessing RPC's internal quality and durability without damaging the material.

UPV testing is particularly advantageous because it provides quick, reliable insights into the structural integrity of concrete, making it widely used for examining both new and existing structures. Research has shown that UPV values correlate well with the elastic properties of concrete, such as transition time, damping, and frequency, making it an ideal technique for examining hardening and hardened cementitious materials.

The research by [Nematzadeh and Poorhosein \(2017\)](#) explored the application of UPV in RPC reinforced with steel and polyvinyl alcohol fibers, finding that RPC specimens containing steel fibers exhibited the highest UPV values and mechanical properties. Furthermore, heat treatment was shown to positively influence RPC's density, UPV, dynamic modulus, and compressive strength, although it had minimal impact on the shear modulus and static modulus of elasticity.

[Khelil et al. \(2023\)](#) examined the effect of incorporating dune sand (DS) as a partial substitute for river sand in RPC mixes. This research aimed to determine how DS substitution influences mechanical properties, water absorption, and UPV. The findings showed significant improvements in compressive strength, with increases of up to 104.4 % in fiber-less mixes and 83.9 % in fiber-reinforced RPC at higher DS substitution levels. In addition, the study highlighted the crucial role of fiber reinforcement, as fibers counteracted the flexural strength reductions observed in high DS-content concretes. Enhanced UPV results and reduced porosity in DS-containing mixes suggest that DS promotes a denser matrix, improving RPC's durability.

[Sonkusare et al. \(2021\)](#) investigated the RPC behavior in relation to destructive and nondestructive tests. Regression analysis was used in this paper to establish a linear relationship between wavelength and material compactness. An  $R^2$  score between 0.8 and 0.99 indicates a strong association and a homogeneous material. Carbonation, or the reaction between concrete's alkaline components and atmospheric carbon dioxide ( $\text{CO}_2$ ), represents another essential test for assessing RPC durability. This reaction lowers the pH of the pore solution, reducing the concrete's alkalinity and potentially weakening its protective layer, which can expose steel reinforcement to corrosion.

[Liu et al. \(2009\)](#) found that under controlled conditions (20 %  $\text{CO}_2$  concentration, 20 °C, 70 % RH), the carbonation depth of RPC and fiber-reinforced RPC (FRPC) was nearly zero, suggesting long-term resistance to carbonation under natural conditions. Similarly, [Ahmad et al. \(2022\)](#) observed that the addition of SF to natural pozzolan-based concrete

improved durability without significantly increasing shrinkage, even though carbonation depth increased slightly. This increased depth, however, remained within safe levels, below the cover thickness typically provided over reinforcement, thus reducing the risk of corrosion. In addition, the use of industrial by-products such as FA, SF, and ground granulated blast-furnace slag in high-performance concrete has shown promising results for durability. [Tahwia et al. \(2024\)](#) studied the effect of hybrid micro and macro polypropylene fibers on the durability of high-performance concrete (HPC). Hybrid fibers improved compressive and flexural strength, with significant residual strength after exposure to temperatures up to 800 °C. SEM analysis showed that the fibers enhanced the microstructure, preventing capillary cracks and improving concrete durability.

[Liu et al. \(2021\)](#) demonstrated that these materials enhance concrete's resistance to chloride penetration and sulfate attack. [Anwar and Emarah \(2020\)](#) further investigated concrete's resistance to carbonation and chloride ingress in ternary blends of by-products with ordinary Portland cement, finding that such mixes significantly improved durability and chloride resistance compared with conventional concrete. Together, sorptivity, UPV, and carbonation testing offer a multifaceted approach to understanding RPC's durability. Each test contributes unique insights into the material's resilience against water absorption, internal structural integrity, and resistance to chemical deterioration, all of which are essential for high-performance concrete applications in demanding environments.

## 2. Research significance

While much has been studied regarding the durability properties of RPC, few studies have explored the comparative effects of different supplementary cementitious materials (SCMs), such as SF and FA, on RPC's long-term performance under varying mix conditions. This study aims to fill this gap by separately investigating the impact of SF and FA on the durability properties of RPC, focusing on key parameters such as sorptivity, UPV, and carbonation depth.

Key parameters influencing the durability of RPC include the volume of binder content ratio (60, 55, 50, and 45 %), water to binder ratio (20, 25, and 30 %), the type of SCMs (SF and FA), and the proportions of SCMs (0, 10, 20, and 30 %). Each of these factors plays a crucial role in determining the microstructural characteristics of RPC, which in turn affects its performance in real-world applications. By comprehensively investigating the interaction

between these parameters and durability outcomes, this study aims to enhance the understanding of RPC as a sustainable and high-performance building material.

### 3. Experimental programs

#### 3.1. Materials

In this study, cement, SF, FA, quartz sand, quartz powder, water, and superplasticizer were the components used to produce locally made RPC mixtures.

##### 3.1.1. Cement

Ordinary Portland cement CEM I 42.5, which was used in this experiment, was supplied by the Suez Company. Cement's physical and chemical properties comply with the Egyptian Standard Specification (ES 4756-1, 2022).

##### 3.1.2. Silica fume and fly ash

SF and FA type F used in this investigation were produced in Egypt by Sika Company. Their characteristics are shown in Table 1 based on manufacturing data.

##### 3.1.3. Quartz sand and quartz powder

The quartz sand and quartz powder used in this study were supplied by El-Hashem for the Minerals and Quartz Materials Company in Egypt. The quartz sand had a specific gravity of 2.65 and particle sizes smaller than 2.36 mm, while the quartz powder had a specific gravity of 2.65 and a mean particle size of 10–15  $\mu\text{m}$ .

##### 3.1.4. Aggregate

A HSC mixture was applied in this study to examine the durability properties as a comparative mixture to RPC. Coarse aggregate was used in the preparation of HSC, in contrast to RPC. Crushed-grade hard dolomite of up to 3/4" (1.9 cm) in size was incorporated into the concrete mixture. The general shape of crushed dolomite was angular and subangular; with a consistently rough surface free of undesired particulates. The HSC mixes included, also, natural silica sand as a fine aggregate. It was

almost unadulterated and pure. A 4.75 cm sieve was used to first filter out any bigger particles from the sand. The fineness modulus of the used sand is 3. The properties of coarse aggregate and fine aggregate are presented in Table 2.

##### 3.1.5. Water

Pure drinking water, free of impurities, has been used for mixing and curing. The water included no organic compounds, contaminants, silt, oils, sugars, or acidic substances.

##### 3.1.6. Superplasticizer

Sika ViscoCrete-3425, manufactured by the Sika Company in Egypt, was used for both HSC and RPC. Sika ViscoCrete-3425 is a third-generation superplasticizer. It satisfies ASTM-C 494 Types G and F and BS EN 934 Part 2: 2001 specifications for superplasticizers.

##### 3.1.7. Mixture proportion

To achieve the goals of the current study, a total of 19 mixtures, including 17 RPC and two HSC mixtures, were prepared, tested, and analyzed. RPC mixtures consist of two groups, one for SF and the other for FA; similarly, two mixtures of HSC were prepared, one with SF and the other with FA, to enable direct comparison between the RPC group and its relative HSC group. Table 3 displays the proportions of the HSC mixture, and Table 4 displays the proportions of the RPC mixture. The impact of mix proportions on the durability properties of RPC was studied by varying the volume of binder content (60, 55, 50, and 45 %), the water-to-binder (W/B) ratio (20, 25, and 30 %), and the SCM (SF or FA) proportions (0, 10, 20, and 30 %). A high range water reducer was consistently maintained at 2 % of the binder content across all mix proportions, and the ratio of quartz powder to quartz sand was set at 0.2. The abbreviations of mixture ID in Table 4 indicate the volume of binder content, the W/B ratio, and the proportions and type of cement substitution used. For instance, a specimen with a 60 % binder volume, a 0.25 W/B ratio, and 20 % SF as a supplementary material is denoted as 0.60BC-0.25W-0.20SF. This naming convention allows for a clear understanding of the mixture composition and facilitates comparisons between different mixtures.

Table 1. Characteristics of silica fume and fly ash.

	FA	SF
Composition	Alumina silicate	A latently hydraulic blend of active ingredients
Colour	Light gray colour	Grey color
Specific density	$\approx 2.13$	$\approx 2.20$
Bulk density	300 kg/m <sup>3</sup>	320 kg/m <sup>3</sup>

Table 2. Properties of coarse and fine aggregates.

	Coarse aggregate	Fine aggregate
Specific weight	2.7	2.73
Volume weight kg/m <sup>3</sup>	1670	1620
Percent of water absorption	1.2	0.43



Table 3. High-strength concrete mixture proportion.

Group	Mix No.	ID	W/B	Cement (kg/m <sup>3</sup> )	SF/C %	FA/C %	Coarse Aggregate (kg/m <sup>3</sup> )	Fine Aggregate (kg/m <sup>3</sup> )	Superplasticizer/Binder%
HSC	10	HSC-SF	0.3	475	10	0	1290	485	2
	20	HSC-FA	0.3	475	0	10	1290	485	2

Table 4. Reactive powder concrete mixture proportion.

Group	Mix No.	ID	W/B	Vol. percent of Binder Content (C + SF or FA + W) %	Cement (kg/m <sup>3</sup> )	SF/Binder %	FA/Binder %	Volume percent of Quartz (QS + QP) %	QP/QS %	Superplasticizer/Binder %
G1-SF	01	0.60BC-0.25W-0.20SF	0.25	60	782.6	20	0	40	20	2
	02	0.55BC-0.25W-0.20SF	0.25	55	717.4	20	0	45	20	2
	03	0.50BC-0.25W-0.20SF	0.25	50	652.2	20	0	50	20	2
	04	0.45BC-0.25W-0.20SF	0.25	45	586.9	20	0	55	20	2
	05	0.60BC-0.25W-0.00SF	0.25	60	1024	0	0	40	20	2
	06	0.60BC-0.25W-0.10SF	0.25	60	900.5	10	0	40	20	2
	07	0.60BC-0.25W-0.30SF	0.25	60	669.8	30	0	40	20	2
	08	0.60BC-0.20W-0.20SF	0.2	60	852	20	0	40	20	2
	09	0.60BC-0.30W-0.20SF	0.3	60	723.6	20	0	40	20	2
	11	0.60BC-0.25W-0.20FA	0.25	60	782.6	0	20	40	20	2
	12	0.55BC-0.25W-0.20FA	0.25	55	717.4	0	20	45	20	2
	13	0.50BC-0.25W-0.20FA	0.25	50	652.2	0	20	50	20	2
	14	0.45BC-0.25W-0.20FA	0.25	45	586.9	0	20	55	20	2
G2-FA	15	0.60BC-0.25W-0.00FA	0.25	60	1024	0	0	40	20	2
	16	0.60BC-0.25W-0.10FA	0.25	60	900.5	0	10	40	20	2
	17	0.60BC-0.25W-0.30FA	0.25	60	669.8	0	30	40	20	2
	18	0.60BC-0.20W-0.20FA	0.2	60	852	0	20	40	20	2
	19	0.60BC-0.30W-0.20FA	0.3	60	723.6	0	20	40	20	2

Due to their 0 % additional content (plain RPC mixture without SF or FA), mixtures number 5 and 15 are identical. The absolute volume theory was used to determine the unknown component of each in the mixture.

### 3.2. Mixing, placing, and curing procedures

A 120 l capacity mixer, operating at ~50 revolutions/min, was used for the mixing procedure. After carefully weighing the components, cement, and sand were combined to create a homogeneous mixture. Subsequently, FA or SF was first added to the drum and mixed. The water and superplasticizer were then mixed together. The dry ingredients in the mixer were combined with the water and a superplasticizer, and the mixture was blended until it achieved the appropriate consistency for casting. The mixing time varied depending on the specific components used. The specimen molds were meticulously cleaned, properly assembled, and checked for dimensional accuracy before use. Before placing, the molds were lightly coated with oil to ensure easy removal of specimens. The casting process involved three layers for each specimen. After compaction, any excess concrete was removed.

The specimens were demolded 24 h later and then subjected to standard curing in water at ~25 °C. To ensure consistent curing, all specimens were placed in the same curing tanks. They were removed from water after 28 days.

### 3.3. Testing methods

#### 3.3.1. Sorptivity test

The purpose of this test is to determine how quickly hydraulic cement concrete absorbs water or its sorptivity. With only one surface of the specimen exposed to water, it achieves this by measuring the mass increase caused by water absorption over time. To guarantee constant moisture conditions within its capillary pore system, the specimen is conditioned in a standard relative humidity environment before testing. The specimen, as specified in Ref (ASTM C1585-13, 2013), is a cylinder with a diameter of 100 mm and a height of 50 mm.

Before testing, the specimens were placed in an oven at a temperature of 50 °C for 3 days. After this drying period, the mass of each specimen was measured before sealing the side surfaces. This mass serves as the baseline for absorption measurements. All surfaces, except one circular face,

were sealed with a waterproof material to prevent evaporation and side absorption. Each specimen was then placed on a nonabsorbent platform with the unsealed surface facing down, in contact with water at a depth of approximately 1–3 mm. The specimen mass was measured at specific intervals of 1, 5, 10, 20, 30, and 60 min and then every hour up to 6 h for initial sorptivity phase. For the secondary sorptivity phase, the mass was measured once daily for up to 5 days. Figs. 1 and 2 illustrate the sorptivity test setup and the specimens during testing, respectively.

The sorptivity coefficient ( $S$ ) and absorption were calculated as in equations (1) and (2), respectively.

$$S = I / \sqrt{t} \quad (1)$$

$$I = \frac{m}{a * d} \quad (2)$$

where  $S$  is the sorptivity coefficient ( $\text{mm/s}^{1/2}$ );  $t$  is time(s);  $I$  is the absorption (mm);  $m$  is the change in specimen mass at the time of measurement, (g);  $a$  is the exposed area of the specimen ( $\text{mm}^2$ ); and  $d$  is the density of water ( $\text{g/mm}^3$ ).

### 3.3.2. Ultrasonic pulse velocity test

The UPV test is a widely used nondestructive method for evaluating the quality, uniformity, and structural integrity of concrete and other construction materials. By measuring the speed of ultrasonic pulses transmitted through a material, the UPV test

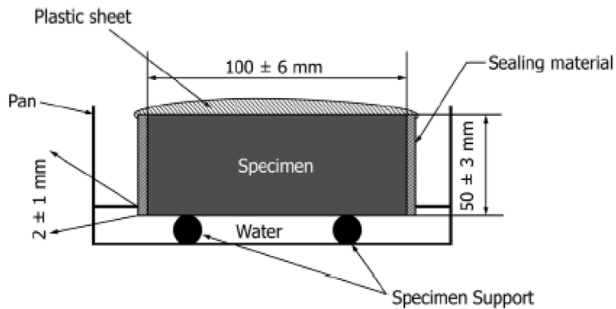


Fig. 1. Schematic diagram of typical sorptivity test setup.



Fig. 2. Concrete specimens during sorptivity test.

provides insight into key characteristics such as density, homogeneity, and the presence of internal defects such as cracks, voids, or other forms of deterioration. Due to its noninvasive nature, the UPV test has become an essential tool in quality control, structural assessment, and durability evaluation of concrete structures. The test was performed on three prism specimens ( $150 \times 150 \times 150 \text{ mm}$ ) in accordance with Ref (ASTM C597, 2022).

The UPV test was conducted using a PUNDIT apparatus, which includes a pulse generator, a pair of transducers (transmitter and receiver), an amplifier, a time-measuring circuit, a time display unit, and connecting cables. To ensure accuracy, any dust, debris, or loose particles were removed from the specimen surfaces as they could interfere with the results. To improve contact and reduce signal loss, a thin coating of couplant (solid Vaseline) was put between the transducers and the concrete surface. A cylindrical Perspex bar with a predetermined pulse transfer duration was used to calibrate the apparatus before any measurements were made. Figs. 3 and 4 illustrate the UPV test setup and the calibration of the device, respectively.

The pulse transmission velocity was calculated using (3) the equation

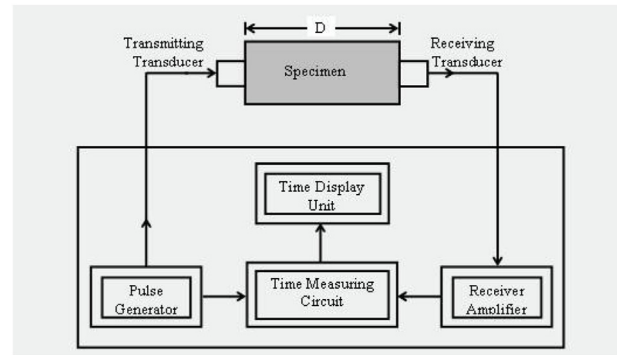


Fig. 3. Schematic of ultrasonic pulse velocity apparatus.



Fig. 4. Calibration of the test device.

$$V = \frac{L}{T} \quad (3)$$

where  $L$  is the distance between the transducer faces which is length of the specimen in mm;  $T$  is the transmission time reading of ultrasonic pulses in the concrete specimen through the mentioned device in terms of microseconds, and  $V$  is the velocity expressed in m/s.

### 3.3.3. Carbonation test

Carbonation occurs when carbon dioxide from the atmosphere diffuses through the porous concrete cover. Also, the pH may drop to about 8 or 9, which is the point at which the protective oxide layer on reinforcement steel becomes unstable. There are two steps in this process: first, airborne carbon dioxide ( $\text{CO}_2$ ) combines with water in the pores of the concrete to generate carbonic acid ( $\text{H}_2\text{CO}_3$ ). The calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ] in the concrete then interacts with this carbonic acid to form calcium carbonate ( $\text{CaCO}_3$ ). Consequently, the pore solution's pH falls from its usual range of 12.5–13.5 to ~8 to 9, disrupting the protective layer surrounding the steel reinforcement and starting the corrosion process.

Three prepared cylindrical specimens (150 mm in diameter and 100 mm in height) for each mixture stored in a rain-sheltered environment at 20 °C and 50 % relative humidity for 2 years were subjected to tests for natural carbonation. One percent phenolphthalein solution in ethanol will serve as the pH indicator solution. To make this, 1 g of powdered phenolphthalein was dissolved in 100 ml of ethanol and 30 ml of deionized water according to the method proposed by (IS-516(Part 5/Sec. 3), 2021). Fig. 5 shows how the specimens were split. As soon as the concrete split, any dust or loose particles were removed from the surface, and the freshly exposed



Fig. 5. Splitting of carbonation test specimens.

concrete sample was ready for a carbonation test. The split face was sprayed with a pH indicator solution. While the carbonated regions remain colorless, the uncarbonated regions exhibit a dark pink tint. The carbonation depth was measured on the freshly broken exposed face.

## 4. Results and discussion

### 4.1. Sorptivity test result

All mixtures show an increase in water absorbed along with the measured times. To determine the impact of the factors taken into consideration in this study, comparisons between the results of various mixes were made.

#### 4.1.1. Effect of volume ratio of binder content

Fig. 6 illustrates the effect of different volume ratios of binder on the water absorption in RPC over time, considering the two groups (SF and FA), each of which consisting of four mixtures with volume binder content ratios of 45, 50, 55, and 60 %. In this case, the total W/B ratio and the supplemental material ratio remained constant. The mixture with the maximum binder volume ratio (60 %) consistently shows the lowest water absorption values across time for both SF and FA mixtures, underscoring the beneficial impact of a higher binder volume on the water resistance properties of RPC. Increasing the volume of binder ratio from 45 to 60 % reduces water absorption by up to 60 % for both additives. This indicates that a higher binder volume ratio, meaning more binder in the mixture, reduces water absorption and improves water resistance in RPC.

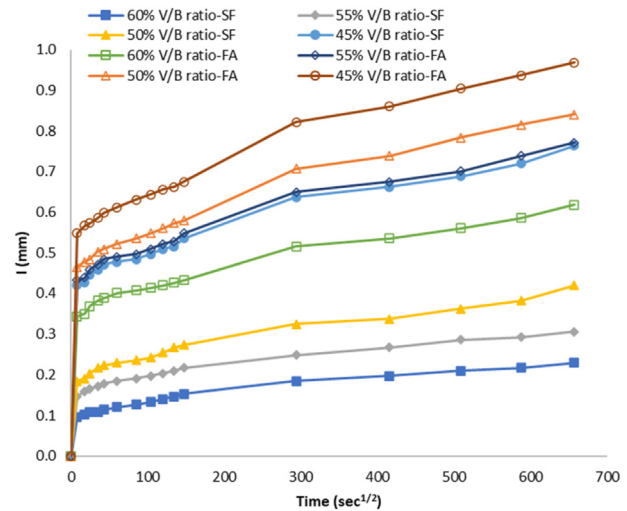


Fig. 6. Effect of volume ratio of binder content on water absorption of reactive powder concrete (water-to-binder = 0.25 and SF or FA = 20 % of binder).



The figure also shows that, for any given volume of binder ratio, the use of SF results in significantly lower water absorption compared with FA, indicating that SF is more effective in enhancing water resistance in RPC. In fact, FA mixtures exhibit up to 67 % higher water absorption than comparable mixtures incorporating SF.

Fig. 7 depicts the relationship between sorptivity (both initial and secondary) and volume of binder content ratio in RPC, with two types of additives, SF and FA. The initial sorptivity curves for SF and FA mixtures decline as the binder component ratio rises from 45 to 60 %. FA has consistently higher initial sorptivity than SF across all binder content levels, indicating that FA mixes allow more initial water ingress. The difference becomes more pronounced at higher binder contents. Secondary sorptivity values are consistently lower than the initial sorptivity for both SF and FA, which aligns with the behavior of RPC as it stabilizes over time. Similar to the initial sorptivity, secondary sorptivity also decreases as the binder volume increases. For SF mixtures as the volume of binder content increased from 45 to 60 %, the initial and secondary sorptivity decreased by 47.36 and 61.53 %, respectively. For FA mixtures as the volume of binder content increased from 45 to 60 %, the initial and secondary sorptivity decreased by 31.8 and 32.1 %, respectively. The sorptivity reduction rate is more gradual in FA compared with SF, which indicates that the effect of binder volume is more pronounced with SF. FA also has higher secondary sorptivity than SF at all binder contents, with the difference becoming very significant at 55 and 60 % binder content levels. This suggests that SF is more effective in creating a dense matrix that resists long-term water absorption.

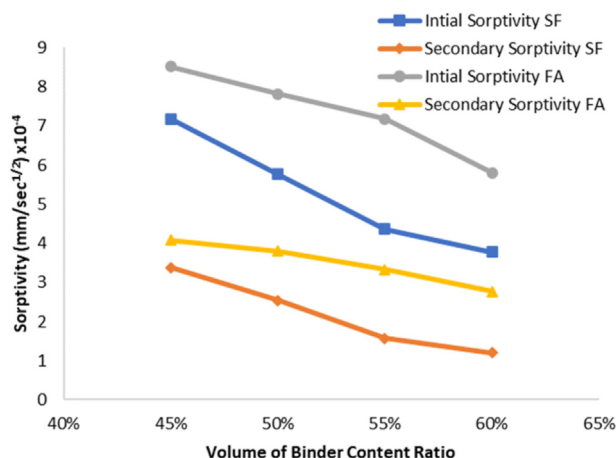


Fig. 7. Effect of volume of binder content ratio on sorptivity of reactive powder concrete (water-to-binder = 0.25 and SF or FA = 20 % of binder).

#### 4.1.2. Effect of water–binder ratio

The effect of the W/B ratio on water absorption in RPC, where the W/B ratio varies at 20, 25, and 30 %, using two different SCMs: SF and FA, is shown in Fig. 8. In this case, the total volume of binder content and the supplementary material ratio were kept constant. As shown in Fig. 8 for the mixture containing SF, it is observed that increasing the water-to-binder ratio results in higher water absorption, which is well known. However, the lowest water absorption value was achieved with a W/B ratio of 25 % rather than 20 %. This can be illustrated as the hydrated material's structure was negatively impacted by the unhydrated cement and silica in a low W/B ratio of 20 % making the mixture more permeable to water than a mixture with a W/B ratio of 25 %. For the mixture containing FA, the increase in the W/B ratio led to an increase in water absorption, increasing the W/B ratio from 20 to 30 %, which results in ~46.6 % increase in water absorption. For both supplementary materials, the 30 % water-to-binder ratio shows the steepest curve, meaning water absorption increases most quickly with time. Water absorption for FA mixtures is consistently higher than SF mixtures at each W/B ratio, indicating that FA leads to a more absorbent concrete mix.

Fig. 9 distinguishes between initial and secondary sorptivity for mixtures with W/B content ratios of 20, 25, and 30 %, respectively, with two types of SCMs, SF and FA. For silica fume mixtures, the initial and secondary sorptivity decreases slightly when the W/B ratio increases from 20 to 25 % by about 10 and 14 %, respectively, and then increases again at 30 % by 41 % and by 56.6 %, respectively. This unexpected dip at 25 % suggests that the SF mix achieves

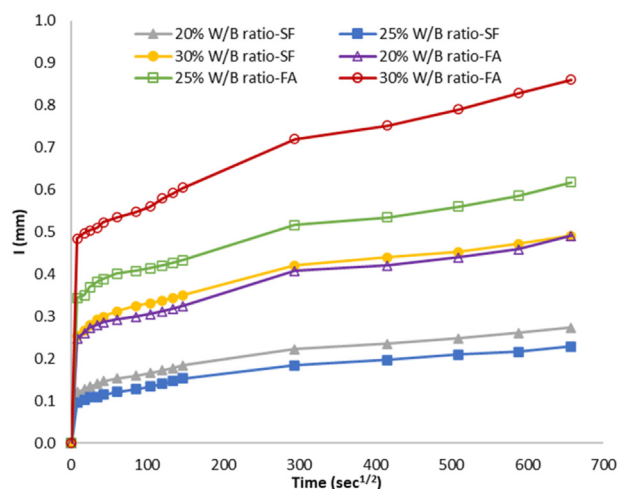


Fig. 8. Effect of water–binder ratio on water absorption of reactive powder concrete (VB = 60 % and SF or FA = 20 % of binder).

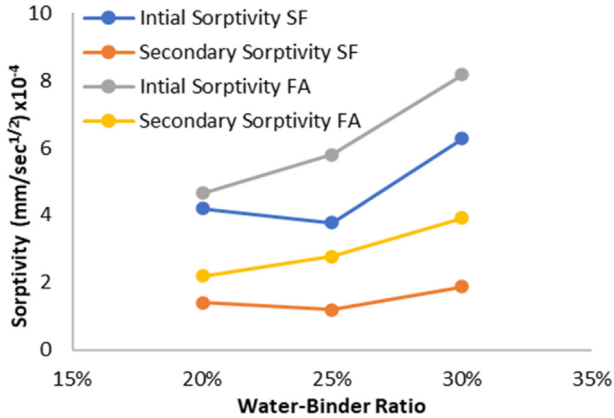


Fig. 9. Effect of water–binder ratios on sorptivity of reactive powder concrete (VB = 60 % and SF or FA = 20 % of binder).

lower initial absorption at this specific W/B ratio than 20 % W/B ratio. This is demonstrated by the fact that the unhydrated cement and silica, present in a mixture with a low W/B ratio of 20 %, negatively affected the structure of the hydrated material.

The initial and secondary sorptivity for FA mixtures consistently increases as the W/B ratio increases from 20 to 30 % by 75.3 and 78 %, respectively, indicating a straightforward relationship where a higher water content leads to increased initial sorptivity. FA mixes have higher sorptivity values than SF mixes at all W/B ratios, for both initial and secondary sorptivity. This means that FA mixes generally allow for more water absorption than SF mixes.

#### 4.1.3. Effect of supplementary cementitious material (SCM) type and ratio

RPC water absorption results for the two groups (SF and FA) are displayed in Fig. 10. Each group has four supplementary cementitious material ratios of 0, 10, 20, and 30 % over time. In this instance, the W/B ratio and the total volume of the binder material remained unchanged. The mixture without cement replacement exhibits the greatest water absorption over time, reaching around 0.72 mm, as shown in Fig. 10. It is observed that for SF mixes, the water absorption of RPC initially declines and then rises as the replacement ratio increases. The lowest water absorption was achieved at a replacement ratio of 20 %. As the SF ratio increased, from 0 to 20 %, the water absorption decreased by 68.45 % which aligns with the findings of Ge et al. (2023), who reported a similar trend. In their study, the water absorption of RPC paste was found to decrease by 73.2 % when SF replacement was set at 25 %, compared with RPC made with pure cement. However, when the SF replacement ratio goes from 20 to 30 %, water

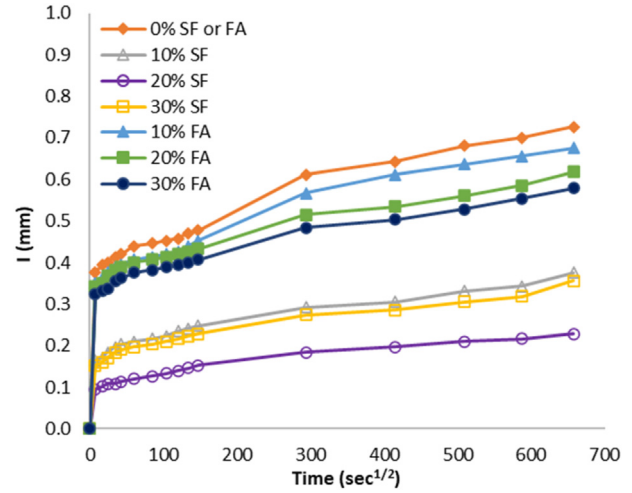


Fig. 10. Effect of supplementary cementitious material ratio on water absorption of reactive powder concrete (VB = 60 % and water-to-binder = 0.25).

absorption rises. When the FA ratio was increased from 0 to 30 %, the water absorption of the FA-containing mixture decreased by 14.6 %. With each increase in the ratio of cementitious material, SF outperforms FA in lowering water absorption, indicating superior performance in enhancing RPC's resistance to water penetration.

The impact of the ratio of FA to SF as SCMs on the sorptivity of RPC is depicted in Fig. 11. Sorptivity is measured at both initial and secondary stages. For SF mixes, both initial and secondary sorptivity of RPC initially declines and then rises as the replacement ratio increases. At a 20 % replacement ratio, the lowest initial and secondary sorptivity values were obtained. When the replacement ratio

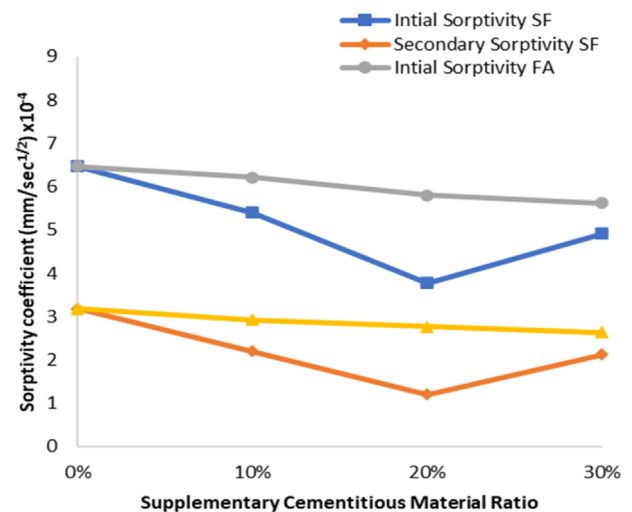


Fig. 11. Effect of supplementary cementitious material ratio on sorptivity of reactive powder concrete (VB = 60 % and water-to-binder = 0.25).

increased from 0 to 20 %, the sorptivity dropped by 41.6 % and 62.2 % for initial and secondary sorptivity, respectively. When the SF replacement ratio increased from 20 to 30 %, RPC's sorptivity rises. For FA mixes, the initial sorptivity also decreases with increasing FA ratio, which is consistent with the findings of Abdellatif et al. (2023a), but to a lesser extent compared with SF. As the FA ratio rises from 0 to 30 %, the initial sorptivity decreases by 13 %. Also, when the FA ratio rises from 0 to 30 %, secondary sorptivity reduces by 17 %. While FA offers some sorptivity reduction it is not as effective as SF, especially in lowering initial sorptivity. Silica fume exhibits a higher reduction in both initial and secondary sorptivity, improving RPC's resistance to water absorption.

#### 4.1.4. Effect of silica fume and fly ash on sorptivity for RPC and HSC

Mixture No. 06 (0.60 BC-0.25 W-0.10 SF) from the first group, which used SF as the SCM, and mixture No. 16 (0.60 BC-0.25 W-0.10 FA) from the second group, which used FA, will be chosen to compare the durability properties of RPC and HSC. The 10 % additional cementitious ratio used in HSC combinations is likewise included in both blends. Fig. 12 illustrates how the impact of FA and SF on water absorption of RPC and HSC. The best performance in lowering water absorption is shown by the 0.60BC-0.25W-0.10SF (RPC with SF) mixture, which also indicates a greater resistance to water ingress. The 0.60BC-0.25W-0.10FA (RPC with FA) mixture also exhibits good resistance, although it is less

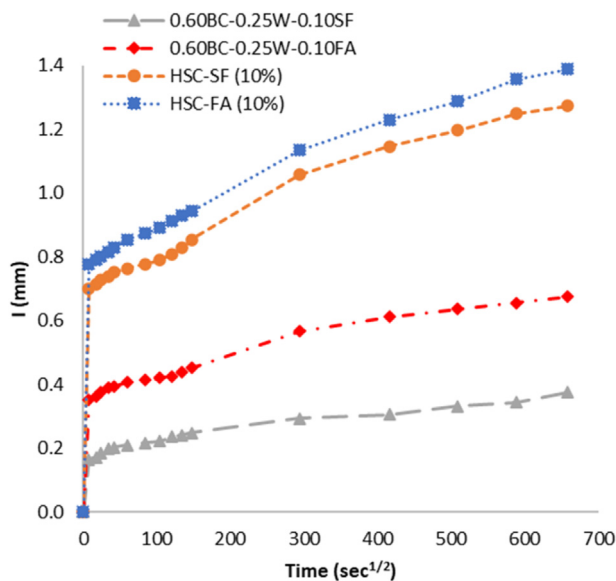


Fig. 12. Comparison of water absorption results for reactive powder concrete and high-strength concrete.

effective than the SF mix. Higher water absorption is seen in both HSC mixes (SF and FA), but HSC-FA has the largest absorption of all of them, suggesting less resistance to water penetration than RPC.

First, a comparison was made between the mixtures containing SF as cement replacement, as shown in Fig. 13. The initial and secondary sorptivity of RPC were  $5.4 \times 10^{-4}$  and  $2.2 \times 10^{-4}$  mm/s<sup>1/2</sup>, respectively, compared with  $9.64 \times 10^{-4}$  and  $6.01 \times 10^{-4}$  mm/s<sup>1/2</sup> for HSC. The initial and secondary sorptivity for RPC is lower than that of HSC by 44 and 63.4 %, respectively. Also, as shown in Fig. 13, when FA is used as a cement replacement the initial and secondary sorptivity for RPC is lower than that of HSC by 46.3 and 58.8 %, respectively.

#### 4.2. Ultrasonic pulse velocity test result

The quality of RPC can be effectively evaluated using UPV testing, with assessment criteria derived from various codes and research studies. Notably, the standards set by IS 13311: Part 1 (1992), as presented in Table 5, provide widely accepted quality classifications, grounded in both empirical research and expert consensus.

The UPV values for RPC mixtures incorporating SF as a SCM range from 4.97 to 4.63 km/s, which is

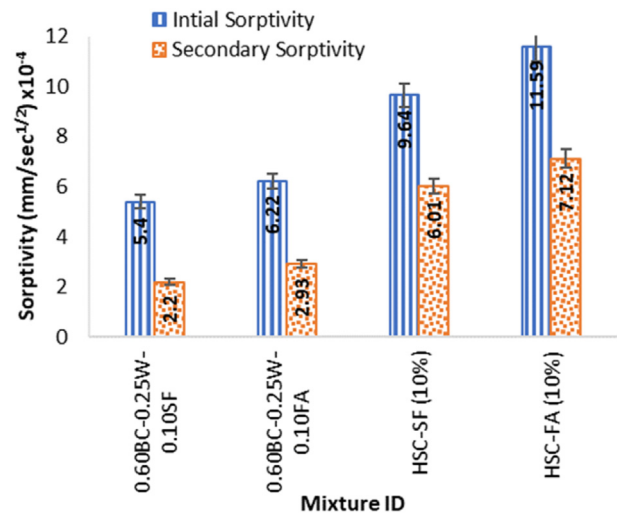


Fig. 13. Comparison of the results of Sorptivity of reactive powder concrete and high-strength concrete.

Table 5. Classification of concrete quality considering the UPV values adopted by IS 13311: Part 1 (1992).

UPV Values V Km/sec	Concrete Quality
Greater than 4.5	Excellent
Between 4.5 and 3.5	Good
Between 3.5 and 3	Medium
Less than 3	Doubtful

close to the range reported by (Nematzadeh and Poorhosein, 2017), where the UPV of RPC containing various types and contents of fibers varied between 4.60 and 4.72 km/s. These values classify the mixtures as ‘excellent’ in terms of both quality and physical integrity, based on the established classification thresholds. For RPC mixtures containing FA, nearly all mixtures achieve an ‘excellent’ rating, with the exception of only one mixture which has 45 % by volume of the binder content with 0.25 W/B ratio, and containing 20 % FA as a SCM. In contrast both HSC mixtures are rated as ‘good’ in terms of concrete quality, indicating lower quality in comparison to RPC mixtures.

Comparisons between the outcomes of different mixes were done to examine the effects of the three parameters on the RPC mixtures.

#### 4.3. Effect of volume of binder content ratio

The binder content ratio represents the proportion of binder by volume in the mixture. As shown in Fig. 14, both SF and FA mixtures show an upward trend in UPV as the binder content ratio increases from 45 to 60 %. This indicates that a higher binder content generally leads to better compaction and reduced porosity in RPC, which enhances UPV.

In SF mixtures, increasing the binder content from 45 to 50 % raises the UPV by 3.53 %, indicating a notable improvement in matrix compactness and integrity. From 50 to 55 %, the UPV increases by 2.29 %, showing that while more binder still enhances the structure, the rate of improvement slows down. Between 55 and 60 %, the UPV increase is just 0.99 %, suggesting that the matrix is nearing optimal density, with additional binder leading to diminishing returns. In FA mixtures, the UPV starts lower at 45 % binder content (4491.02 m/s) but gradually

risks with increasing binder content. From 45 to 50 %, the UPV increase is just 1.52 %, noticeably lower than in SF mixtures. Between 50 and 55 %, the UPV increase is slightly higher at 1.54 %, and from 55 to 60 %, it reaches 2.21 %, indicating that while FA benefits from higher binder content, the improvement occurs at a slower rate than with SF. The UPV values for SF mixtures are consistently higher than those for FA at each binder content ratio. This suggests that SF is more effective than FA in enhancing the density and cohesion of the concrete. The superior effect of SF in increasing UPV can be attributed to its finer particle size and higher pozzolanic activity, which improve the concrete microstructure by filling voids more effectively. Thus, a denser, more cohesive matrix with better transmission of ultrasonic waves is produced.

##### 4.3.1. Effect of water–binder ratio

Fig. 15 shows how the W/B ratio affects the UPV in RPC mixtures containing either SF or FA. At a low W/B ratio of 20 %, the UPV is 4950.50 m/s, indicating a dense and well-compacted matrix. Increasing the W/B ratio to 25 % slightly improves the UPV by 0.33 %, reaching 4966.89 m/s. However, the lowest UPV was achieved with a W/B ratio of 25 %, not 20 %. At 30 % W/B ratio, the UPV drops sharply by 6.79 %, down to 4629.63 m/s, indicating a substantial increase in porosity and a decrease in matrix integrity. For FA mixtures, the UPV at 20 % W/B ratio is 4777.07 m/s, lower than SF, but still indicating a relatively dense matrix. At 25 % W/B ratio, the UPV decreases slightly by 0.94 %, indicating that FA mixtures are more sensitive to increased water content. At 30 % W/B ratio, the UPV drops by 3.94 %, reaching 4545.45 m/s. This decline is less pronounced than for SF, suggesting that FA mixtures may retain structural integrity slightly better at

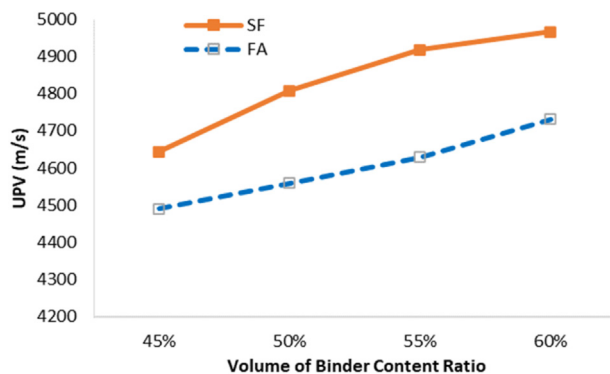


Fig. 14. Effect of volume of binder content ratio on the UPV of reactive powder concrete (water-to-binder = 0.25 and SF or FA = 20 % of binder).

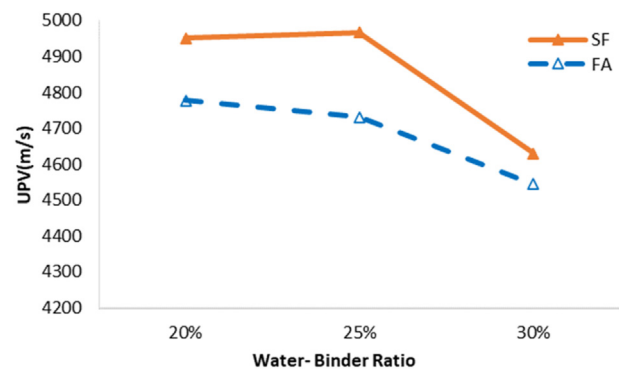


Fig. 15. Effect of water–binder ratio on UPV of reactive powder concrete (VB = 60 % and SF or FA = 20 % of binder).



higher W/B ratios, though the overall UPV remains lower than SF.

Reduced W/B ratios correlate with elevated UPV values for both SF and FA mixtures, with SF mixtures consistently exhibiting superior performance. Nevertheless, SF demonstrates a more substantial decline in UPV at elevated W/B ratios, likely attributable to its finer particle size and higher pozzolanic reactivity, making it more susceptible to excess water and accelerating microstructural degradation. While FA is less reactive, it also experiences a notable drop in UPV at higher W/B ratios, though not as sharply as SF.

#### 4.4. Effect of supplementary cementitious material (SCM) type and ratio

Both SF and FA mixtures show an increase in UPV as the SCM ratio rises from 0 to 20 % as shown in Fig. 16, indicating that adding SCMs improve matrix density and cohesion. This is likely due to the pozzolanic activity of SF and FA, which enhances the matrix microstructure as well as the contribution of SCM fine particles in filling the voids, thereby creating a more cohesive and denser matrix. For SF mixtures, UPV reaches its highest point at a 20 % SCM ratio, suggesting that this level of SF addition optimally improves the RPC's matrix structure. Beyond 20 %, at a 30 % SF ratio, UPV decreases, which may indicate that excessive SF starts to reduce cohesion. In FA mixtures, UPV also increases with higher SCM ratios, but at a slower rate and without a peak within the tested range. This steady, moderate improvement suggests that while FA improves matrix density, it is less effective than SF. FA mixtures continue to benefit from additional SCM, but the UPV remains consistently lower than that of SF mixtures, reflecting a less cohesive and dense structure.

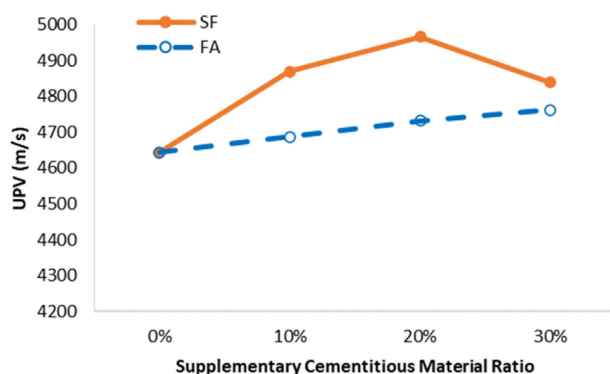


Fig. 16. Effect of supplementary cementitious material ratio on UPV of reactive powder concrete (VB = 60 % and water-to-binder = 0.25).

#### 4.4.1. Effect of silica fume and fly ash on UPV for RPC and HSC

Fig. 17 illustrates the impact of adding 10 % FA and 10 % SF on the UPV through each of HSC and RPC. RPC with 10 % SF has a UPV of 4870.13 m/s, which is 8.12 % higher than HSC with 10 % SF (4504.50 m/s). This difference indicates that RPC benefits more from SF's properties, achieving higher compactness and structural integrity. The RPC mix design likely allows SF to maximize its pozzolanic reaction, filling voids and strengthening the matrix to a greater extent than in HSC. RPC with 10 % FA has a UPV of 4687.50 m/s, which is 6.56 % higher than HSC with 10 % FA (4398.83 m/s). While FA improves the matrix in both cases, it is less effective than SF at increasing UPV, particularly in RPC. The slower reactivity and relatively larger particle size of FA contribute to a lower rate of densification compared with SF, and this is more noticeable in RPC, which requires higher density to achieve optimal performance.

#### 4.5. Carbonation test results

The natural carbonation depth was measured after 2 years for both RPC and HSC mixes, with the results presented in Table 6 and Fig. 18. The findings showed that for mixtures containing SF as a SCM, there was almost complete absence of carbonation in RPC mixtures, while HSC exhibited a carbonation depth of 8 mm. This lack of carbonation in RPC highlights its superior ability to resist CO<sub>2</sub> penetration, providing better protection for embedded reinforcement. The near-zero carbonation depth observed in this study aligns with the findings of Liu et al. (2009) on RPC's resistance to CO<sub>2</sub> penetration under conditions of carbon dioxide concentration of 20 %, 20 °C, and RH of 70 %.

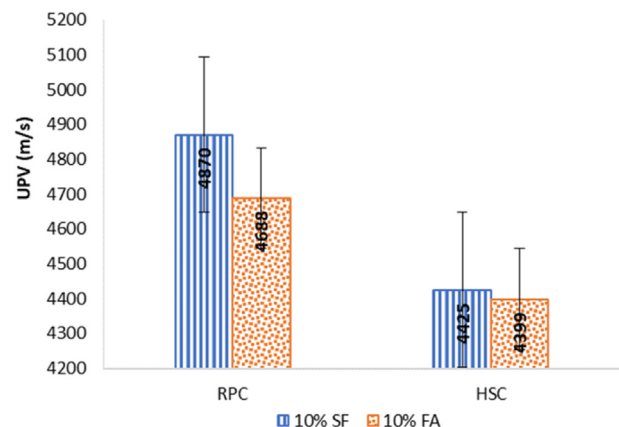


Fig. 17. Comparison of the UPV test results for reactive powder concrete and high-strength concrete.

Table 6. Natural carbonation depth for all mixtures.

Mix No.	ID	Natural carbonation depth after two years (mm)
01	0.60BC-0.25W-0.20SF	≈0
02	0.55BC-0.25W-0.20SF	≈0
03	0.50BC-0.25W-0.20SF	≈0
04	0.45BC-0.25W-0.20SF	≈0
G1-SF 05	0.60BC-0.25W-0.00SF	4
06	0.60BC-0.25W-0.10SF	≈0
07	0.60BC-0.25W-0.30SF	≈0
08	0.60BC-0.20W-0.20SF	≈0
09	0.60BC-0.30W-0.20SF	≈0
10	HSC-SF	8
11	0.60BC-0.25W-0.20FA	≈0
12	0.55BC-0.25W-0.20FA	≈0
13	0.50BC-0.25W-0.20FA	≈0
14	0.45BC-0.25W-0.20FA	1
G2-FA 15	0.60BC-0.25W-0.00FA	4
16	0.60BC-0.25W-0.10FA	≈0
17	0.60BC-0.25W-0.30FA	≈0
18	0.60BC-0.20W-0.20FA	≈0
19	0.60BC-0.30W-0.20FA	1
20	HSC-FA	13



Fig. 18. Two years natural carbonation depth results of mixtures.

Although HSC exhibits high strength, its microstructure is not as cohesive and dense as that of RPC. The relatively lower density and higher permeability of HSC allow  $\text{CO}_2$  to penetrate more easily, resulting in a carbonation depth of 8 mm after 2 years.

For mixtures incorporating FA as an SCM, most RPC mixtures showed almost no carbonation, except for mixtures No. 14 and No. 19, which had a binder content of 45 % by volume and a water-to-cement ratio of 0.30, respectively. These two

mixtures exhibited a carbonation depth of 1 mm, which can be explained by their higher porosity. The increased water-to-cement ratio and decreased binder content in these mixtures led to a more porous structure, allowing  $\text{CO}_2$  to penetrate more readily. In contrast, the HSC mixture containing FA showed a carbonation depth of 13 mm, which is significantly higher. This indicates that, despite the inclusion of FA, the overall microstructure of HSC remains more susceptible to carbonation compared with RPC, emphasizing the importance of microstructural refinement.

In RPC mixtures, the highest carbonation depth was observed when no SCMs were used, with a carbonation depth of 4 mm, suggesting the beneficial effect of supplementary materials in improving the carbonation resistance of RPC. In contrast, the highest carbonation depth in HSC mixtures was 13 mm. This indicates that the carbonation in HSC is ~3.25 times greater than in RPC, which aligns with the results of [Sanjuán and Andrade \(2021\)](#) who calculated the carbonation rate of RPC from accelerated tests and found that it is more than four times less in the RPC than in the C80 concrete.

The results of this study clearly show that RPC has much better carbonation resistance than HSC over a 2-year period. However, to truly confirm these findings and understand their relevance in real-world situations, it is important to explore how these materials perform over longer periods and in tougher environmental conditions. Future studies should focus on evaluating carbonation depths over extended periods (e.g. 5, 10, and 20 years) to provide a more robust understanding of the durability of RPC and its microstructural stability. Besides, testing the performances of RPC and HSC under a range of climate conditions (e.g., high levels of  $\text{CO}_2$  concentration and varying humidity) would also contribute to the generalizability of the results. These long-term studies are also essential to confirm the practical benefits of RPC in infrastructure applications, particularly with respect to durability and reinforcement corrosion protection.

## 5. Conclusions

This study experimentally examined the effects of the W/B ratio, the volume ratio of binder content, and the type and ratio of SCMs on the durability properties of RPC. In addition, the study evaluates the relative advantages of RPC by contrasting its performance with that of HSC. This paper's main conclusions can be summed up as follows:

- (a) Increasing the binder volume ratio from 45 to 60 % reduces water absorption by nearly 60 % for both additives. SF proved to be more effective than FA, achieving 47.36 % and 61.53 % reductions in initial and secondary sorptivity, respectively, as the volume of binder content increased from 45 % to 60 % compared with only 31.8 % and 32.1 % reductions for FA.
- (b) Sorptivity has been increased by up to 78 % and water absorption by 46.6 % when FA mixtures' W/B ratio is increased from 20 to 30 %. The optimal W/B ratio for SF mixtures is 25 %, which minimizes both water absorption and sorptivity (reductions of 10 and 14 % in initial and secondary sorptivity, respectively).
- (c) Regarding the SCM ratio, RPC without any cement replacement exhibits the highest water absorption. A replacement ratio of 20 % resulted in the lowest water absorption and sorptivity for SF, with reductions of 68.45 % and up to 62.2 %, respectively. FA's water resistance steadily improved as replacement ratios rose; at a 30 % replacement, water absorption and sorptivity decreased by just 14.6 and 17 %, respectively.
- (d) UPV increased as binder content rose from 45 to 60 %, with SF mixtures showing a significant 3.53 % improvement between 45 and 50 %. FA mixtures had slower improvements, with a 2.21 % increase between 55 % and 60 %, and SF consistently showed higher UPV.
- (e) The UPV was highest at a 20 % W/B ratio (4950.50 m/s for SF and 4777.07 m/s for FA). Increasing the W/B ratio to 30 % caused a sharp drop in UPV, particularly for SF mixtures, where a 6.79 % decline occurred.
- (f) As SCM content increased, UPV rose as well, reaching its peak at 20 % SF (best performance). FA mixtures exhibited UPV increases that were slower but more consistent, staying below those of SF mixtures, suggesting that SF had a greater effect on matrix density and cohesiveness.
- (g) RPC mixes with SF showed almost no carbonation, while RPC mixes with FA exhibited minimal carbonation. The plain RPC mix had a carbonation depth of 4 mm. SF significantly enhances RPC's resistance to carbonation.
- (h) RPC with SF shows the lowest initial and secondary sorptivity, outperforming HSC-SF (10 %) by 44 and 63.4 %, while HSC-FA (10 %) has the highest sorptivity, indicating significantly better water resistance in RPC.
- (i) The UPV of RPC with 10 % SF is 8.12 % higher than that of HSC with 10 % SF, suggesting increased structural integrity and

compactness. However, not as effective as SF, RPC with FA outperforms HSC with FA.

- (j) Compared with RPC with FA as SCM, the carbonation depth of 8 mm in HSC was 62.5 % greater. With SF, RPC revealed hardly no carbonation. This proves that RPC's denser microstructure exceeds HSC when considering long-term durability and carbonation resistance.

#### Future Work

- (a) Study the combined effects of SF and FA on RPC's durability.
- (b) Evaluate the potential of other materials like MK and slag in enhancing RPC's properties.
- (c) Investigate advanced curing techniques like autoclaving to improve RPC's durability further.
- (d) Use advanced techniques such as SEM or XRD to study the long-term evolution of RPC's microstructure.
- (e) Assess RPC's durability under industrial and aggressive environment; tests such as sulfate resistance, chloride penetration, freeze–thaw cycles, acid resistance, thermal resistance, and long-term immersion in aggressive solutions are recommended.

#### Ethics information

This study does not involve human participants or animals. All experimental procedures were conducted in accordance with ethical guidelines for materials research. No ethical approval was required.

#### Author contributions

The Corresponding author is responsible for Data collection and tools, Data analysis and interpretation, Investigation the field of the paper and writing the paper.

Third author is responsible for Conception and design of the work, Methodology, Project administration, Critical revision of the article and Final approval of the version to be published.

Second and fourth Authors are responsible for Critical revision of the article.

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#### Conflicts of interest

There are no conflicts of interest.

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