International Journal of Engineering Trends and Technology
ISSN: 2231–5381 / https://doi.org/10.14445/22315381/IJETT-V73I5P124

Volume 73 Issue 5, 277-296, May 2025

Original Article

Durability Studies on the Effect of Low Carbon Quaternary Binder - Composite Cement with Alccofine

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Received: 14 February 2025 Revised: 02 May 2025 Accepted: 26 May 2025 Published: 31 May 2025

Abstract - *In the current construction practices, new materials are developed and used as admixtures in the concrete. Alccofine is one such admixture that has been added to the concrete to improve its compressive strength and durability properties. Composite cement is also a new material, which is a blended cement made with the addition of Supplementary Cementitious Materials (SCMs), such as fly ash and Ground Granulated Blast Furnace Slag (GGBS). The studies on the combined effects of composite cement and alccofine are limited. Hence, this study fills this gap by investigating the combined effects of partial additional (10%) Alccofine in the composite cement on the durability properties of the concrete. It was observed that the inclusion of Alccofine into the Composite Cement (COC) concrete significantly enhances the concrete resistance to acid, sulphate, and chloride attacks. The Alccofine improves the concrete's microstructure, reducing permeability and inhibiting harmful ion ingress into composite cement concrete. Additionally, it was found that the depth of water penetration and Rapid Chloride Permeability Test (RCPT) values were considerably lower in COC + 10% Alccofine mixes, indicating improved durability. Furthermore, higher-grade concrete with Alccofine demonstrated better carbonation resistance, with significantly reduced carbonation depths compared to lower-grade concrete.*

Keywords - *Ordinary Portland Cement (OPC), Composite Cement (COC), Alccofine, Durability properties, Carbonation depth.*

1. Introduction

One of the most often utilized construction materials in commercial, residential, and infrastructure projects is concrete. However, a significant concern in the construction industry is the durability of concrete structures, especially when they are exposed to aggressive environments. Durability is the capacity of the concrete to resist the impact of weathering, chemical attacks, and other environmental conditions without causing significant degradation over time. Carbonation is a process in which atmospheric carbon dioxide (CO_2) combines with Ca $(OH)_2$ in the matrix of cement to reduce the alkalinity of the concrete, which is one of the primary mechanisms for degradation in concrete [1], [2]. This reduction in alkalinity within the concrete leads to the depassivation of steel embedded in the concrete, prompting corrosion and ultimately affecting the structural integrity [3], [4], [5]. As a result, it reduces the strength and durability of the concrete, thereby increasing the risk of severe structural failure. This reduction in strength and durability of the concrete can be mitigated through the incorporation of SCMs or mineral admixtures into the concrete. The utilization of these mineral admixtures appears to be a promising solution for the durability and sustainability of reinforced concrete [6]. The alkali-aggregate reaction, sulphate ion attacks, and chloride ions attacks can reduce the strength of the concrete and make it less durable. By incorporating SCMs like GGBS, fly ash, metakaolin, etc., into the cement matrix, the strength and durability of the concrete can be improved [7]. Among the various SCMs, the FA and GGBS are the most commonly used SCMs because of their pozzolanic properties. After reacting with portlandite, the GGBS and fly ash can form an additional C-S-H gel. Fly ash is a commonly available pozzolans extracted from the combustion of powdered coal. Improved workability, lower water demand, and improved strength are the significant advantages of using fly ash in concrete [8]. Upon reaction with water, the oxides of SiO_2, CaO, MgO, Al_2O_3, and MgO present in the GGBS will induce a hydration process [9]. The strength and durability of the concrete can be enhanced with a denser microstructure when the appropriate amount of GGBS is included in the concrete [10]. The rate at which fly ash added to concrete gained strength was slower compared to OPC concrete, which is a major disadvantage of utilizing fly ash in concrete [6], [11], [12], [13]. Portland Composite Cement (PCC) has been introduced by cement manufacturing companies in Indonesia as a means to mitigate the rising cost of cement production. Composite cement has been developed as per IS: 16415-2015 standards [14]. The PCC is comparable to CEM type II/A-M cement, comprised of 80% OPC clinker with 20% SCMs like silica fume, GGBS, gypsum, fly ash, etc. Generally, the PCC available in the market was made with cement clinker (OPC), containing 80% OPC clinker with 20% GGBS and 20% fly ash. The hydration reaction of the composite cement is influenced by the combustion of cement with fly ash in accordance with BS: 3892 (part-1) or GGBS in accordance with BS: 6699 are generally slower than the OPC in accordance with BS: 12-1996, resulting in a low rise in temperature [15], [16], [17]. It was reported that composite cement is appropriate for salt scaling in terms of concrete deterioration [18]. The two primary mechanisms that cause corrosion to reinforced structures are carbonation and chloride ion ingress [19]. The primary cause of degradation in a concrete structure is corrosion of the steel reinforcement [20]. Concrete carbonation is a complex chemical and physical process. Villain et al. (2007) detailed the chemical reactions involved in the carbonation. Cabon starts at the concrete surface by the penetration of CO_2 [21]. After diffusion of the ash onto the concrete, the CO_2 dissolves in the pore solution before reacting with OH^- to form CO_3^{2-}. As a result, the pH of the concrete pore solution decreases. The calcium carbonate ($CaCO_3$) precipitates when $Ca(OH)_2$ solubility reaches the pH of 12.5, as shown in equ (1-3).

The concentrations of these components depend on various factors, such as humidity, the presence of other solutes in the pore water, the concentration of ambient CO2, and the pH of the pore water solution (Goñi et al., 2002). When concrete was exposed to 50–70% relative humidity, a high rate of carbonation was observed [22]. Based on Henry's law, the concentration of CO_2 in the pore air and pore water are intimately correlated. Higher CO_2 concentrations allow for more calcium to react to generate calcium carbonate because more CO_2 molecules can dissolve and dissociate at the carbonation front in a given amount of time. The calcium from the components of the hardened cement pastes dissolves into the water more quickly as a result of this reaction. As a result, the carbonation front progresses more quickly, and the calcium supply, which may react, is depleted faster [23].

$$CO_2 + 2OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (1)$$

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^- \quad (2)$$

$$CO_2 + Ca(OH)_2 \downarrow 2OH^- \leftrightarrow Ca^{2+} + CO_3^{2-} + H_2O \leftrightarrow CaCO_3 \downarrow + H_2O \quad (3)$$

Bakharev et al. (2001) found that the carbonation depth increases for the Alkali-Activated Slag (AAS) concrete specimen than the OPC concrete specimen when the concrete was exposed to accelerated carbonation with 10%-20% CO_2 and 70% relative humidity for 120 days [24]. The findings also demonstrated that the strength cutback and carbonation depth of AAS concrete samples were still higher than those of the OPC samples. Behfarnia and Rostami (2017) found that the carbonation depth progressively reduces with increasing compressive strength [25].

To improve the durability properties of the concrete, the cement with the inclusion of SCMs has gained attention among researchers. Among various SCMs, alccofine has risen as a high-performance material. Alccofine is a slag-derived ultrafine material recognized for its high pozzolanic activity and fine particle size. These properties enable it to fill voids in the concrete matrix and promote the formation of C-S-H gel. Alccofine densifies the microstructure and durability and thus increases the mechanical properties of the concrete. The durability properties of the concrete were studied by Prithiviraj et al. (2022) by replacing different percentages of alccofine for cement, ranging from 0% to 60% [26]. They found that replacing cement with 30% alccofine offers better durability properties, which possess better chemical resistance because of reduced permeability and better formation of C-S-H gel through improved hydration. Jagadeesan and Gokul (2023) reported that replacing cement by 20% significantly increases compressive strength by 20.38% due to the enhanced pozzolanic reactions of alccofine [27].

Additionally, it was found that the cement replaced with 20% alccofine decreased chloride ion penetration and water absorption by 12.60% and 20.63%, respectively. Reddy et al. (2024) reported that the inclusion of 25% of alccofine into the concrete reduces the water absorption rate by 2.6% as compared to conventional concrete [28]. It was concluded that the inclusion of alccofine shows significant enhancement in the properties of the concrete due to enhanced hydrated products. The formation of additional hydrated gel results in denser microstructure and improved durability properties of the concrete. Andrade & Bujak (2013) reported that the addition of ultra-fine slag-based concrete was found to be more chloride resistant; however, it had less resistance to carbonation as compared to OPC [29]. Teng et al. (2013) reported that due to their increased specific surface area, ultra-fine slag materials increase both the hydration rate and the pozzolanic reaction [30]. Sivakumar et al. (2015) reported that the addition of Alccofine significantly decreases the permeability of the concrete [31].

The chloride penetration into the concrete is impeded by the reduced permeability. This indicates a significant enhancement in the durability aspect of the concrete. Reddy et al. (2020) examined the durability properties of the M25 and M40 grade concrete with partial replacement of OPC with alccofine at replacement levels of 0%, 5%, 10%, and 15% [32]. They discovered that 15% alccofine replacement offers maximum resistance to acid penetration for the M25 and M40 grades. They concluded that high SiO_2 content in alccofine reacts with $Ca(OH)_2$ to form an impermeable C-S-H gel that improves durability by reducing acid penetration. Sharma et al. (2016) conducted a durability test on the high-strength concrete made with alccofine SCMs to cement and waste foundry sand partial replacement to fine aggregate in the Portland Pozzolana Cement (PPC) concrete [33]. The results of the alkalinity test revealed that the concrete was sufficiently protected from the carbonation effect, and the probability of corrosion was reduced at 15% replacement levels. The durability properties of the concrete made with partial replacement of cement containing 5%, 10%, 15%, and 20% alccofine were investigated by Gayathri et al. (2016) [34].

In comparison to the control mix, they found that the mix containing 15% alccofine had the lowest coulombs passing value, demonstrating the highest resistance to acid penetration and the lowest weight and strength loss. Sagar and Sivakumar (2020) examined the water absorption and porosity properties of high-strength concrete made with fly ash and alccofine as a partial replacement for cement [35]. It was concluded that the concrete made with 20% fly ash and 10% alccofine possesses less water absorption due to the formation of a dense matrix with low pore concentration. Similarly, Kavyateja et al. (2020) examined the durability properties of SCC concrete made with fly ash and alccofine as a partial replacement for cement [36]. It was concluded that the concrete made with 20% fly ash and 10% alccofine has shown high resistance to acid attack, chloride penetration, and electrical resistivity.

Balamuralikrishnan and Saravanan (2019) reported that concrete made of 40% cement replacement with 30% GGBS and 10% alccofine showed high resistance to chloride, acid, and sulphate attack [37]. Additionally, it has a lower pass rate of the columns compared to the control concrete. In addition to this, many studies have reported the mechanical properties of OPC concrete using alccofine in ternary and quaternary mix [38], [39], [40], [41], [42]. Zhuguo and Sha (2018) investigated the carbonation resistance of geopolymer concrete made with blast-furnace slag (BFS) and fly ash [43]. They found that, when the specimen was cured at room temperature, the carbonation resistance was lesser than the concrete cast from OPC. Furthermore, high-strength concrete typically has a higher resistance to carbonation. Andrade (2020) demonstrated that the carbonation rate increases with the increases in GGBS content [44]. Singh & Singh (2016) reported that high-performance concrete with ground granulated blast-furnace slag (GGBFS) exhibits superior carbonation resistance compared to high-performance concrete (HPC) with fly ash (FA) due to its denser matrix and lower calcium hydroxide (CH) concentration [45]. Despite numerous studies highlighting the advantages of using alccofine in the concrete as SCMs, particularly for increasing durability properties. Many studies have concentrated on investigating the effect of using alccofine as SCMs in concrete, but its effects, when used in combination with Composite Cement (COC), have received less attention among researchers. Surprisingly, the impact of the utilization of alccofine on the carbonation resistance of the concrete was still not yet examined. This provided an opportunity to explore the impact of using alccofine as a supplementary material in composite cement concrete concerning its durability properties. The proposed study aims to examine the effect of 10% replacement levels of alccofine on the durability properties and carbonation of the COC and compare them with those of OPC concrete.

2. Research Significance

This study is significant because it aims to fill the research gap in understanding the durability properties of concrete by replacing composite cement with 10% of alccofine. While earlier studies extensively explored the alccofine effects in OPC concrete, limited consideration is given by researchers in exploring the properties of the concrete replacing composite cement with 10% alccofine, especially in regards to the durability properties and carbonation resistance. By examining the impact of replacing composite cement with 10% of alccofine, this study seeks to provide insights into optimizing material efficiency without compromising performance, which is particularly relevant in cost-sensitive and sustainability-focused construction methods. Furthermore, this study will provide a valuable comparison between OPC and COC concrete, contributing to a broader understanding of the effect of alccofine inclusion on the durability of various concrete types. i.e., OPC and COC, as well as concrete grades, i.e., M25, M40, and M60.

3. Materials & Methodology

3.1. Materials

3.1.1. Ordinary Portland Cement (OPC)

The OPC 53 grade cement used in this study conforms to IS: 12269-1987 standards [46]. The physical properties of the OPC are presented in Table 1. The cement has a high fineness of 309 kg/m$^{3, \text{which}}$ helps promote better hydration and strength development [47]. The initial and final setting time of OPC was 50 and 460 minutes, which ensured sufficient workability and curing. The compressive strength of the PC was 35.4 MPa, 45.7 MPa, and 62.4 MPa at 7, 14, and 28 days, respectively, indicating its high early strength and making it suitable for high-strength concrete applications.

Table 1. Physical properties of the OPC

Properties	Fineness (m^2/kg)	Normal Consistency (%)	Setting Time		Compressive Strength (MPa)		
			Initial (minutes)	Final (minutes)	7 days	14 days	28 days
Values	309	28	50	460	35.4	45.7	62.4

Table 2. Chemical composition of OPC

Components	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O_3	K_2O	Chloride	LOI
%	22.02	60.84	5.59	5.12	1.22	1.92	0.29	0.67	0.07	2.03

The chemical composition of OPC is presented in Table 2, which demonstrates a crucial role in its performance. The high CaO (60.84%) and SiO_2 (22.02%) content help in C-S-H gel formation, thus contributing to the strength development of concrete.

The presence of Al_2O_3 (5.59%) and Fe_2O_3 (5.12%) support early strength, while MgO (1.22%) and SO_3 (1.92%) regulate expansion [48].

3.1.2. Composite Cement (COC)

The composite cement from the Chettinad brand is composed of 60% OPC clinker, 20% fly ash, and 20% GGBS, as per IS: 16415-2015 standards [14]. Table 3 presents the physical properties of the composite cement. The fineness of 332 m^3/kg indicates the improved particle distribution, which contributes to the hydration process [49].

The compressive strength of 20.9 MPa, 31 MPa, and 42.6 MPa at 3, 7, and 28 days demonstrate moderate strength gain, which is a typical characteristic of composite cement.

The chemical composition of the composite cement, as outlined in Table 4, shows that the composite cement contains 32.81% SiO2 and 41,785 CaO, which helps in C-S-H gel formation.

Table 3. Physical properties of COC

Properties	Fineness (m^2/kg)	Normal consistency (%)	Setting time		Compressive strength (MPa)		
			Initial (min)	Final (min)	7 days	14 days	28 days
Results	332	32	75	535	20.9	31	42.6

Table 4. Chemical composition of COC

Composition	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	Chloride	LOI
%	32.81	41.78	11.63	5.31	2.74	2.37	0.29	0.69	0.01	2.21

The presence of 11.63% of Al_2O_3 improves early strength development [48], while the presence of 2.74% of MgO and 2.37% of SO_3 helps in preventing sulfate attacks. The presence of a low amount of Na_2O (0.29%) and K_2O (0.69%) content minimizes the risk of alkali-silica reactions. The presence of 2.21% LOI indicates low impurity levels, ensuring durability and quality in concrete applications.

3.1.3. Alccofine

Alccofine is a byproduct of the iron ore industry. The calcium silicate content of the alccofine 1200 series is higher than the alccofine 1100 series. The fine, micro-fine, and ultra-fine particle sizes of the alccofine are denoted by the 1201, 1202, and 1203 series. The most widely available alccofine on the market are Alccofine-1206, Alccofine-1203, and Alccofine-1101. In this study, alccofine 1203 was used as a partial replacement (10%) to the composite cement as it conforms to IS 16715-2018 [50].

The fineness of the alccofine-1203 was 12000 cm2/gm. Table 5 provides the chemical composition of alccofine. The chemical composition of the alccofine demonstrates its suitability to be utilized as SCMs in the concrete, meeting the specifications of IS: 16715-2018. The amount of MnO (1.27%) and MgO (5.8%) are found to be within the permissible limits, which ensures material stability.

The presence of low levels of sulphide sulphur (0.48%) and SO_3 (0.12%) lessens the risk of sulphate attack. The presence of a low chloride content level (0.012%) helps prevent reinforcement corrosion. With a glass content of 85% and a low moisture content of 0.1%, it guarantees improved strength and durability when mixed with concrete.

Table 5. Chemical composition of alccofine

Composition	%	Requirements as IS 16715-2018
MnO	1.27	5.5 Max
MgO	5.8	17 Max
Sulphide Sulphur	0.48	2.0 Max
SO_3	0.12	3.0 Max
Insoluble residue	0.63	3.0 Max
Chloride content	1.012	0.1 Max
LOI	0.1	3.0 Max
$(CaO+MgO+1/3Al_2O_3)/(SiO_2+2/3Al_2O_3)$	1.28	1.0 Min
$(CaO+MgO+1/3Al_2O_3)/SiO_2$	1.76	1.0 Min
Glass content	>85	85 Min
Moisture content	0.1	1 Max

3.1.4. Fine Aggregate

M-sand, locally sourced, is utilized as a fine aggregate in the concrete. The M-sand particles were passed through a sieve of 4.75 mm and retained in 150 µm, which falls under grading zone -II as per (IS 383 : 2016 [51]. The M-sand has a specific gravity of 2.71, water absorption of 0.67%, and fineness modulus of 2.57.

3.1.5. Coarse Aggregate

According to IS:383-1970, a coarse aggregate with a maximum particle size of 12.5 mm was utilized [51]. The coarse aggregate has a specific gravity of 2.7, water absorption of 0.62%, and fineness modulus of 7.2.

3.1.6. Superplasticizer

The commercially available Poly Caboxylate Ether (PCE) based superplasticizer called Master Glenium ACE30, a product from the BASF chemical company, was utilized as a superplasticizer for concrete production. The specific gravity and solid content of the superplasticizer were found to be 1.82 and 25%, respectively.

3.2. Mix Proportioning

By considering the ratio of fine aggregate and coarse aggregate and the ratio of binder to total aggregate in accordance with IS: 10262-2019, the mix proportioning for concrete was made to achieve the target strength [52]. Initially, 27 trail mixes were formulated for each M25, M40, and M60 grade of concrete with partial replacement of cement by alccofine at 5%, 10%, and 15%.

Finally, 9 optimized mixes with 10% replacement of alccofine for M25, M40, and M60 grades of concrete were selected with the consideration of target strength as presented in Table 6.

Table 6. Mix proportioning

Description	OPC 53			COC			COC +10% ALC		
	M25	M40	M60	M25	M40	M60	M25	M40	M60
Cement (kg/m^3)	300	410	500	-	-	-	-	-	-
Composite cement (COC) (kg/m^3)	-	-	-	330	450	550	297	405	495
Alccofine (kg/m^3)	-	-	-	-	-	-	33	45	55
M-Sand (kg/m^3)	857	847	809	831	314	765	831	814	765
Coarse Aggregate (kg/m^3)	1085	1002	958	1044	963	905	1044	963	905
w/c	0.55	0.39	0.33	0.51	0.36	0.30	0.51	0.36	0.3
Super Plasticizer (%)	0.35	0.5	0.55	0.5	0.5	0.7	0.7	1	1.1

Based on the optimized mix ratio, the concrete was made using cement, alccofine, coarse aggregate, fine aggregate, superplasticizer, and water. The coarse and fine aggregates were initially added to the mixer and mixed for a duration of 2 minutes. Then, the necessary quantities of cement, COC, and alccofine were incorporated into the mixture and blended for an additional 2 minutes, depending on the concrete mix type. For instance, just cement for OPC 53 concrete mix, cement along with composite cement for COC concrete mix, and composite cement with alccofine for COC+10% alccofine concrete mix. Then, the water, along with the superplasticizer, is added to it and mixed for 4 minutes. Then, the freshly mixed concrete was tested to measure its workability utilizing a slump cone test as per IS: 456-2000 guidelines [53]. Then, the test specimen was made for each test as required.

3.3. Experimental Investigation

This study primarily focused on investigating the partial replacement of COC by 10% of alccofine on the durability properties of COC concrete. The impact of alccofine on the durability properties of COC has been analyzed using a series of tests, including acid attack, sulfate attack, chloride attack, water permeability test, rapid chloride permeability test, drying shrinkage, and carbonation test.

3.3.1. Acid Attack

As per ASTM C267, this test aimed to determine the reduction in weight and compressive strength when exposed to acid solutions. This test was done using a 100mm size cube sample after 28-day curing. The cube specimen was weighted and immersed into the acid solutions. The acid solution used was a 3% concentration of H_2SO_4 solution. After 30, 60, 90, 120, 150, and 180 days of immersion of the cube sample in the acid solution, the specimen was removed, surface cleaned, and weighed to determine the weight loss. Similarly, the samples were tested for compression using UTM to determine the loss in compressive strength.

3.3.2. Sulphate Attack

According to ASTM C267, this test is meant to decide the decline in weight and compressive strength of the OPC53, COC, and COC+10% ALC when exposed to sulphate solutions. This test was performed using a 100mm size cube sample after 28 days of curing. The cube sample was weighted and immersed into the solution containing 5% concentration of $MgSO_4$. After 30, 60, 90, 120, 150, and 180 days of immersion of cube samples into the sulphate solution, the samples were taken out and surface cleaned and weighted to measure the loss in weight. Similarly, the samples were tested for compression using UTM to determine the loss in compressive strength.

3.3.3. Chloride Attack

As per ASTM C267, this test intended to choose the reduction in weight and compressive strength of the OPC53, COC, and COC+10% ALC when presented to sulfate arrangements. After 28 days of curing, the 100 mm size cube sample was weighed and immersed into a 5% concentration of NaCl solution. After 30, 60, 90, 120, 150, and 180 days of immersion of the shape test in the sulfate arrangement, the samples were removed, surface cleaned, and weighed to measure the loss in weight. The samples were also subjected to UTM for compression testing to ascertain the loss in compressive strength.

3.3.4. Water Permeability Test

The water permeability characteristics of OPC53, COC, and COC+10% ALC concrete were measured as per IS 3085 (1965). After 28 days of curing, the specimen was kept under vacuum to guarantee that no air pockets were present in the specimen. The concrete specimen was then placed in the testing cell of the permeability test apparatus. The specimen was properly sealed in the cell to prevent the leakage of water around the specimen. Connect the cell to a water reservoir and pressure system. Then, a constant water pressure was applied to the sample for a specific period as per IS 3085 (1965) [54].

The amount of water that penetrates through the sample over the testing period was measured. Record the total volume of water passed, the testing period, and applied pressure. Equation 4 was used to measure the permeability coefficient based on the collected data and the dimension of the specimen.

$$K = \frac{Q}{AT\frac{H}{L}} \quad (4)$$

Where K is the coefficient of permeability (cm/sec); Q is the amount of water percolating over the entire test period; A is the area of specimen face; T is time; $\frac{H}{L}$ is the ratio of pressure head to the thickness of the specimen.

3.3.5. Rapid Chloride Penetration Test (RCPT)

The cylindrical specimen of size 100 mm x 200 mm was utilized to measure the chloride penetration capacity of OPC53, COC, and COC+10% ALC concrete as per ASTM C1202 guidelines [55]. After 28 days of curing, the cylindrical specimen was cut into size of 50 mm thickness. Each of these specimens was coated with epoxy resin and subjected to RCPT testing. The test setup involves two containers filled with 3% NaCl and 0.3 M NaOH exposed to a 60 V DC charge.

Over the period of six hours, the current was measured every 30 minutes. Three specimens were tested to measure the average RCPT value of each concrete mix. The assessment of the RCPT rating depends on the coulombs of charge passed versus the penetration of chloride ions, as referenced to ASTM C1202 standards, as presented in Table 7.

Table 7. Level of chloride ion penetration as per ASTM C1202

Charge passed (Coulombs)	Level of chloride ion penetration
>4000	High
2000-4000	Moderate
1000-2000	Low
100-1000	Very Low
<100	Negligible

3.3.6. Drying Shrinkage

The drying shrinkage of the OPC53, COC, and COC+10% ALC concrete samples was measured as per ASTM C157/C157M by measuring the length change of the concrete specimen over time [56]. The prism specimen of size 285 mm x75 mm x 75 mm was cast and allowed to moist curing for 24 hours and then placed in the lime-saturated water for 48 hours. The initial length of the specimen was measured, and then the specimen was exposed to a controlled environment (50% relative humidity; 23 ± 2°C). The length measurement was taken at 28 days. The drying shrinkage is measured as the percentage change in length as compared to the initial length of the specimen using equation (5);

$$Drying\ shrinkage = \frac{\Delta L}{L} \quad (5)$$

ΔL is the change in length; L is the original length.

3.3.7. Carbonation Test

The carbonation depth of the OPC53, COC, and COC+10% ALC concrete samples were measured in accordance with IS 516 (Part- 5/Sec 3): 2021 and ASTM C856 standards [57], [58]. The prism specimens of size 100mm x100mm x 500 mm were cast and covered with plastic sheets and kept at 23°C for 24 hours. After curing, the prism is cut into five equal sections of 100 mm each, which will be used for testing at various time intervals. These samples are then placed in a carbonation chamber maintained at a relative humidity of 6%, a temperature of 25℃, and a carbon dioxide concentration of 3%.

The samples are exposed to this controlled environment for various duration, such as 30, 60, 90, and 120 days, to observe the carbonation depth over time. At each specified interval, one section is removed from the carbonation chamber, and the cube is split in half to expose a fresh, uncarbonated surface. To detect carbonation, an indicator solution of phenolphthalein is sprayed onto the exposed surface. A phenolphthalein 1% ethanol solution consisting of 1 gm of phenolphthalein with 90 ml of ethanol diluted in 100 ml of water was used as the indicator [59]. The depth of the colorless phenolphthalein zone, extracted from the three-average points, immediately after spraying the indicator and after 24 hours.

4. Results and Discussions

4.1. Acid Resistance of OPC53, COC and COC+10% ALC Concrete Mixes

The acid attack test results, as presented in Table 8, show a clear trend of reduced weight loss in the concrete with the addition of alccofine (COC + 10% ALC) into the composite cement (COC) when compared to the OPC concrete mix. This finding was found to be aligned with various earlier studies [37], [60], [61] that replacing a portion of cement with any SCMs in concrete significantly reduces weight loss when exposed to acid attack. It was observed that the weight loss for all the mix was relatively low at 30 days and increased over time. The 25 OPC 53 mix possesses a weight loss of 3.23%, while the 25 COC+10% ALC mix possesses a weight loss of 3.02%. The advantages of adding alccofine to the composite cement become more pronounced as the exposure period increases to 60, 90, 120, 150, and 180 days. By 180 days, the weight loss for the 25 OPC 53 mix was found to be 11.63%, whereas the weight loss for the 25 COC+10% ALC sample was found to be 7.36%. This same weight loss trend was also observed for the 40 OPC 53 and 60 OPC 53 mix; the inclusion of alccofine significantly reduces the weight loss. The 40 COC + 1% ALC mix has a weight loss of 6.58% at 180 days, compared to 11.12% for 40 OPC 53. The 60 COC + 1% ALC mix shows a weight loss of 6.01% at 180 days, compared to 10.56% for 60 OPC 53. On comparing the results with various existing studies, the alccofine was found to be effective against the acid attack [37], [60], [61]. Balamuralikrishnan and Saravanan (2019) discovered that the replacement of OPC with 30% of GGBS results in 3.23% weight loss at 28 days [37]. However, in this study, the replacement of COC with 10% alccofine results causes only 3.02% weight loss even at 30 days. Rao & Rao (2020) showed that replacing OPC with 30% of GGBS results in a 3.14% weight loss at 28 days. Deep & Jabez (2017) showed that replacing OPC with 10% of GGBS and 5% of fly ash results in a 3.69% reduction in weight loss at 28 days. However, in this study, replacing COC with 10% alccofine results in just 3.02% weight loss even at 30 days. This reduction in weight loss by alccofine when added to composite cement was due to its finer particles and high pozzolanic activity, which improves the microstructure. A dense matrix is when it reacts with calcium hydroxide to form additional calcium silicate hydrate (C-S-SH) [62]. This improved density diminishes the permeability of the concrete, thereby making it more resistant to acid attack and reducing the rate of weight loss.

Table 8. Weight loss of various concrete against acid attack

Days	25 OPC 53	25 COC	25 COC + 10% ALC	40 OPC 53	40 COC	40 COC + 10% ALC	60 OPC 53	60 COC	60 COC + 10% ALC
0	0	0	0	0	0	0	0	0	0
30	3.23	3.12	3.02	3.19	3.13	3.09	3.02	2.98	2.8
60	5.12	4.68	4.15	4.9	4.38	4.13	4.46	4.04	3.97
90	7.64	7.2	5.85	7.15	5.81	5.29	6.98	5.45	4.78
120	9.72	7.65	6.28	9.26	6.24	5.5	8.8	5.63	4.92
150	10.96	8.11	6.82	10.55	6.81	5.96	9.97	5.82	5.38
180	11.63	8.61	7.36	11.12	7.24	6.58	10.56	6.19	6.01

The acid attack test results, as presented in Table 9, show a clear trend of reduced compressive strength loss in the concrete mix containing alccofine (COC + 10% ALC), especially when used in combination with composite cement (COC) when compared to OPC concrete mix.

When the exposure duration is extended to 60, 90, 120, 150, and 180 days, the benefits of using alccofine in the composite cement become more noticeable. 25-grade concrete mix made with OPC showed the highest strength loss of 40.23% at 180 days, indicating its vulnerability to acid attack due to its less dense mix and higher porosity.

On the other hand, utilization of COC reduced the strength loss to 37.66%, and the composite cements typically contain Supplementary Cementitious Materials (SCMs) like fly ash and GGBS that improve durability. When 10% Alccofine was added to COC, the strength loss was further reduced to 34.22%, demonstrating Alccofine's role in reducing porosity and refining the microstructure.

This same trend is also observed for the 40-grade concrete mix, which exhibits 38.11% strength loss for the concrete made with OPC and 35.20% strength loss for the concrete made with COC. However, only 33.09% strength loss for the concrete made with COC with 10% replacement of alccofine. This might be due to the formation of a dense matrix and C-S-H gel, thus hindering the ingress. It was also demonstrated that the higher-grade concrete (60) exhibits less strength loss than the low-grade concrete (25).

60-grade concrete mix made with OPC showed a strength loss of 37.33% at 180 days and, reduced to 34.85% for COC and further reduced to 32.59% on 10% replacement of COC with alccofine. This clearly indicates the role of Alccofine in improving acid resistance, especially in concrete of a higher grade. By accelerating the pozzolanic reaction that lowers calcium hydroxide, which is susceptible to acid attack, and refining the microstructure of concrete, alccofine plays a critical role in increasing the resistance to acid attack [26].

The combination of composite cement and alccofine consistently resulted in the lowest compressive strength loss, highlighting its effectiveness in improving concrete durability, especially in aggressive environments. However, all the conventional mixes (25 OPC 53, 40 OPC 53, and 60 OPC 53) show high weight loss because they are more sensitive to H_2SO_4 solution compared to others. This is because of the formation of calcium chlorides, especially water-soluble salts, as a result of H_2SO_4 reacting with water.

Table 9. Strength loss of various concrete against acid attack

Days	25 OPC 53	25 COC	25 COC + 10% ALC	40 OPC 53	40 COC	40 COC + 10% ALC	60 OPC 53	60 COC	60 COC + 10% ALC
0	0	0	0	0	0	0	0	0	0
30	9.99	9.51	8.26	9.23	8.8	8.08	8.25	7.65	7.01
60	14.86	12.59	10.97	13.5	11.81	10.86	12.16	9.89	9.22
90	25.98	24.25	21.05	23.06	20.61	19.19	20.26	17.99	15.07
120	31.26	29.61	27.02	29.98	27.93	26.82	26.78	24.21	22.19
150	36.64	36.02	32.56	35.56	33.29	32.28	36.03	33.99	30.25
180	40.23	37.66	34.22	38.11	35.2	33.09	37.73	34.85	32.59

4.2. Sulphate Resistance of OPC53, COC and COC+10% ALC Concrete Mixes

The outcomes of the sulfate attack test were presented in Table 10, which indicates that weight loss increased gradually in all cement mixes, with mixes including Alccofine demonstrating better resistance to sulphate attack. At 180 days, 25 OPC exhibits the highest weight loss of 0.353%, indicating its vulnerability to sulphate attack. This might be attributed to the formation of a less dense microstructure of lower-grade concrete, which facilitates the penetration of sulphate ions and causes matrix degradation. On the other hand, 25 COC poses a weight loss of 0.406%, even higher than the 25 OPC mix. This could be because the elements in the composite cement are less resistant to sulphate attack.

However, the addition of 10% Alccofine to 25 COC resulted in a weight loss of 0.385%, which is found to be less than the 25 COC mix. This demonstrates better sulphate resistance through microstructure refinement and reduced permeability. 40 OPC concrete shows better performance than Grade 25, which shows a weight loss of 0.342%.

However, 40 COC exhibits a slightly higher weight loss of 0.395%, suggesting that composite cement by itself does not provide a significant enhancement over OPC in terms of sulphate attack resistance at this grade. The weight loss is reduced to 0.372% when 10% Alccofine is added in 40 COC, demonstrating the beneficial effect of Alccofine in boosting sulphate resistance. Alccofine fills microvoids, reduces sulphate ingress, and contributes to the formation of additional C-S-H, which strengthens the concrete matrix. 60 OPC possesses the best performance among the other OPC grade concrete, with a weight loss of 0.331% after 180 days.

This illustrates how the lower water-to-cement ratio and denser microstructure of higher-grade concrete, such as Grade 60, provide superior resistance to sulphate attack. Conversely, 60 COC exhibits a marginal rise in weight loss to 0.386%, continuing the pattern observed in lower grades, where composite cement alone may not provide significant improvements in resisting sulphate attack. But, 60 COC + 10% Alccofine shows the least amount of weight loss of 0.361% after 180 days. This result emphasizes that the synergistic effects of a denser matrix and improved microstructural characteristics provided by the inclusion of Alccofine result in superior sulphate resistance when high-grade concrete is combined with composite cement. Therefore, it was concluded that the inclusion of 10% alccofine into the composite cement significantly improves resistance to sulphate attack, as demonstrated by the lower weight loss compared to OPC and COC mixes. This justifies the use of Alccofine as a beneficial additive for improving the durability performance of the concrete exposed to sulphate-rich environments.

Table 10. Weight loss of various concrete against sulphate attack

Days	25 OPC 53	25 COC	25 COC + 10% ALC	40 OPC 53	40 COC	40 COC + 10% ALC	60 OPC 53	60 COC	60 COC + 10% ALC
0	0	0	0	0	0	0	0	0	0
30	0.024	0.036	0.03	0.022	0.032	0.028	0.02	0.03	0.026
60	0.048	0.064	0.056	0.04	0.06	0.052	0.036	0.056	0.048
90	0.112	0.145	0.128	0.104	0.138	0.12	0.094	0.132	0.106
120	0.186	0.22	0.194	0.172	0.216	0.18	0.165	0.204	0.172
150	0.278	0.324	0.304	0.272	0.318	0.297	0.268	0.307	0.288
180	0.353	0.406	0.385	0.342	0.395	0.372	0.331	0.386	0.361

The sulphate attack test results on compressive strength, as presented in Table 11, show a clear trend of reduced weight loss in the concrete mix containing alccofine (COC + 10% ALC), especially when used in combination with composite cement (COC), when compared to OPC concrete mix. The advantages of adding alccofine to the composite cement become more pronounced as the exposure period increases to 60, 90, 120, 150, and 180 days. 25 OPC53 concrete mix shows the highest strength loss of 19.23% at 180 days. This is because lower-grade concrete has more porosity and less density, which allows sulphate ions to penetrate and weaken the matrix. The 25 COC mix performs marginally better, with a strength loss of 15.12% at 180 days, sulfate attack still has a major impact on it. However, the incorporation of 10% Alccofine into the COC mix (COC + 10% ALC) results in a reduction of strength loss of 13.08% at 180 days, which indicates that Alccofine is crucial for improving the durability, microstructure refinement, and permeability of the concrete. This same trend was also observed for the 40-grade concrete. 40 OPC 53 experiences a strength loss of 18.7%, which is marginally better than Grade 25 OPC.

This improvement is due to the formation of the dense matrix, which helped improve performance by reducing the penetration of sulphate ions. The COC mix exhibits a minor improvement with a strength loss of 14.77%. The COC + 10% Alccofine mix further minimizes strength loss to 12.56%, demonstrating the advantageous effects of Alccofine. 60-grade concrete exhibits the best resistance to sulfate attack.

At 180 days, the 60 OPC 53 mix had a strength loss of 18.12%. COC mix exhibits comparable performance with a strength loss of 14.06%. However, the COC + 10% Alccofine mix exhibits less strength loss of 12.2%. Comparing the alccofine-based mixtures to the conventional mix (i.e., 25 OPC 53, 25 OPC 53, and 25 OPC 53), the strength loss was less.The reduced strength loss in alccofine added to the concrete mix was mainly due to the fact that the pozzolanic reactions involving calcium hydroxide made it unavailable to react with sulphate to ettringite as well as reduced permeability, which prevented the ingress of harmful sulphate ions into the concrete. In general, the mineral admixture can lessen the sulphate attack effect. (Juenger and Siddique 2015; Ramezanianpour and Hooton 2013).

Since there were no additional fillers, the conventional mix had more permeability, which allowed more sulphate ions to enter and contribute to the higher strength loss. It was concluded that replacing cement with alccofine partially helps in reducing the loss of strength when exposed to sulphate attack. Parmar et al. (2014) also discovered that replacing cement with alccofine partially reduced the strength loss of the concrete against sulphate attack, which was about 11.37% at 56 days [64]. However, in this study, replacing cement with alccofine partially, especially at 10%, results in only 4.82 % weight loss even at 60 days.

Table 11. Strength loss of various concrete against sulphate attack

Days	25 OPC 53	25 COC	25 COC + 10% ALC	40 OPC 53	40 COC	40 COC + 10% ALC	60 OPC 53	60 COC	60 COC + 10% ALC
0	0	0	0	0	0	0	0	0	0
30	2.54	2.08	1.88	2.44	1.98	1.82	2.38	1.81	1.75
60	5.45	5.06	4.82	5.36	4.87	4.64	5.06	4.56	4.51
90	8.07	7.23	6.72	7.8	7.14	6.51	7.07	6.9	6.15
120	12.38	10.78	9.85	12.09	10.58	9.59	11.83	10.23	9.27
150	16.74	13.93	12.07	16.58	13.72	11.78	15.95	13.37	11.66
180	19.23	15.12	13.08	18.7	14.77	12.56	18.12	14.06	12.2

4.3. Chloride Resistance of OPC53, COC and COC + 10% ALC Concrete Mixes

The chloride attack test results on weight loss, as presented in Table 12, offer valuable insights about the various cement types (OPC, COC, and COC + 10% Alccofine) and concrete grades (25, 40, and 60) to chloride ion penetration. The advantages of adding alccofine to the composite cement become more pronounced as the exposure period increases to 60, 90, 120, 150, and 180 days. At 180 days, 25 OPC mix exhibits a weight loss of 4.01%, suggesting that lower-grade concrete made with ordinary Portland cement is susceptible to chloride attack. This is because of its less dense microstructure and increased porosity, which allow chloride ions penetration and deteriorate the matrix. The COC mix shows a weight loss of 4.86%, which is found to be higher than the 25 OPC53 mix.

This indicates that the composite cement alone may not enhance chloride resistance significantly in 25-grade concrete. However, the COC + 10% Alccofine mix performs better, which shows a weight loss of 3.55%. The chloride resistance of Grade 25 concrete is increased by the addition of Alccofine, which also refines the microstructure, lowers permeability and aids in limiting chloride ion penetration. For Grade 40 concrete, the OPC mix experiences a weight loss of 3.86% after 180 days, showing improved resistance compared to Grade 25 due to the denser microstructure and lower water-cement ratio. The COC mix in Grade 40 shows a slightly higher weight loss of 4.8%, which follows a similar trend observed in Grade 25. However, the COC + 10% Alccofine mix reduces the weight loss to 3.73%, demonstrating the beneficial impact of Alccofine in enhancing chloride resistance.

It was observed that the ability of alccofine to refine the concrete matrix, fill microvoids, and reduce chloride penetration makes this mix more durable than both OPC and COC alone [65]. At 180 days, 40 OPC mix exhibits a weight loss of 3.71%. The 40 OPC mix shows a weight loss of 3.71%, which is the lowest among the OPC mixes across all grades. This is due to the high density and lower water-cement ratio of Grade 60 concrete, which limits the ingress of chloride ions, which is found to be higher than the 60 OPC53 mix. This indicates that the composite cement alone may not enhance chloride resistance in 60-grade concrete. However, the COC +

10% Alccofine mix performs better, which shows a weight loss of 3.55%. The chloride resistance of Grade 25 concrete is increased by the addition of Alccofine, which also refines the microstructure, lowers permeability and aids in limiting chloride ion penetration. The inclusion of Alccofine proves to be crucial in reducing weight loss and improving the overall performance of the concrete, especially in high-grade concretes like Grade 60, where the combination of high-density concrete and Alccofine provides superior chloride resistance.

Table 12. Weight loss of various concrete against chloride attack

Days	25 OPC 53	25 COC	25 COC + 10% ALC	40 OPC 53	40 COC	40 COC + 10% ALC	60 OPC 53	60 COC	60 COC + 10% ALC
0	0	0	0	0	0	0	0	0	0
30	1.76	2.01	1.56	1.49	1.86	1.39	1.39	1.7	1.2
60	2.26	2.76	2.18	2.27	2.6	2.1	1.98	2.42	1.66
90	2.76	3.29	2.7	2.76	3.1	2.7	2.54	2.98	2.21
120	3.38	3.98	3.29	3.51	3.82	3.4	3.38	3.7	2.99
150	3.76	4.45	3.4	3.7	4.41	3.61	3.53	4.2	3.29
180	4.01	4.86	3.55	3.86	4.8	3.73	3.71	4.68	3.54

Table 13. Strength loss of various concrete against chloride attack

Days	25 OPC 53	25 COC	25 COC + 10% ALC	40 OPC 53	40 COC	40 COC + 10% ALC	60 OPC 53	60 COC	60 COC + 10% ALC
0	0	0	0	0	0	0	0	0	0
30	9.25	10.28	8.11	8.06	8.98	7.29	7.98	8.11	7.26
60	12.99	15.03	11.31	11.26	13.86	10.97	10.68	12.01	9.06
90	14.59	16.35	13.28	13.56	15.23	11.35	11.23	13.73	10.37
120	17.63	19.21	15.97	17.68	18.09	15.29	14.35	16.93	13.29
150	23.1	25.68	21.69	21.19	23.91	20.23	19.53	22.79	17.99
180	27.51	30.86	25.39	25.29	29.68	24.09	24.13	28.87	23.71

The results of the chloride attack on compressive strength loss, as presented in Table 13 provide a comprehensive view of how different grades of concrete (25, 40, and 60) and cement types (OPC, COC, and COC + 10% Alccofine) react to chloride exposure over time. At 180 days, the OPC mix in Grade 25 concrete exhibits a strength loss of 27.51%, showing a high degree of vulnerability to chloride attack. Because of Grade 25 OPC's less compact microstructure and relatively large porosity, chloride ions can enter the concrete and damage it. Grade 25's COC mix exhibits an even worse strength loss of 30.86%, indicating that resistance to chloride-induced strength degradation cannot be increased only by composite cement.

However, the COC + 10% Alccofine mix shows a lesser strength loss of 25.39%, indicating that by enhancing the microstructure and lowering permeability, the inclusion of Alccofine helps lessen the adverse effects of chloride attack. When compared to Grade 25, Grade 40 concrete exhibits superior resistance to chloride attack. After 180 days, the OPC mix exhibits a strength loss of 25.29%, which is better than the lower-grade concrete but indicates a decrease in compressive strength owing to chloride exposure. Although Grade 40 OPC's denser matrix helps to prevent chloride infiltration, the concrete still deteriorates noticeably. The COC mix in Grade 40 exhibits a larger strength loss of 29.68%, which is consistent with the trend that composite cement is not more effective than OPC at fending off strength loss caused by chloride. With a strength loss of 24.09% after 180 days, the COC + 10% Alccofine mix performs better, demonstrating how Alccofine greatly improves chloride resistance by minimizing ion penetration and improving the microstructure. At 180 days, the 60 OPC mix loses less strength than both Grade 25 and 40 OPC concretes strength loss of 24.13%. Grade 60 concrete's high micro-density microstructure offers superior defense against chloride intrusion, preventing structural deterioration. Even in higher-grade concrete, the COC mix in Grade 60 exhibits a strength loss of 28.87%, demonstrating that composite cement alone is insufficient to resist chloride attack.

The mix of COC and 10% Alccofine exhibits the least amount of strength loss at 23.71%, indicating that the combination of Alccofine and high-grade concrete provides better resistance to strength loss caused by chloride attack. It was concluded that the inclusion of alccofine at 10% of cement helps in reducing the strength loss against sulphate attack. Parmar et al. (2014) found that the strength loss of the concrete made with alccofine in the OPC against chloride attack was 16.73% at 56 days [64]. However, in this study, replacing composite cement with 10% alccofine resulted in only 11.31 % weight loss, even at 60 days. This comparison shows that Alccofine minimizes strength loss in composite cement more effectively than in OPC because of its increased pozzolanic activity. When added to composite cement, alccofine reacts with the higher amount of calcium hydroxide produced by supplementary cementitious materials (SCMs), forming additional C-S-H gel that strengthens the concrete matrix. This leads to a denser structure with reduced porosity, providing better protection against sulfate and chloride attacks, which results in less strength loss compared to OPC-based concrete.

4.4. Water Penetration Resistance of OPC53, COC and COC + 10% ALC Concrete Mixes

Figure 1 presents the water penetration test results of the different grades of concrete (25, 40, and 60) made with various types of cement (OPC and COC). The water penetration test measures the resistance of the concrete to water ingress and its long-term durability. The low water penetration depth denotes the better durability performance of the concrete. The 25 OPC 53 mix has a water penetration depth of 10.8 mm at 28 days, which is reduced to 9.7 mm at 56 days.

This decline in water penetration depth is expected as the concrete continues to cure, gaining strength and reducing its porosity. The 25 COC mix, which contains 100% composite cement, has a water penetration depth of 9 mm at 28 days, which is reduced to 8.2 mm at 56 days. The presence of fly and GGBS in the composite cement makes the denser matrix and prevents water infiltration. The COC + 10% Alccofine mix, which contains composite cement with 10% replacement of alccofine, has a water penetration depth of 7.5 mm at 28 days, which is reduced to 6.5 mm at 56 days. The 40 OPC 53 mix exhibits a penetration depth of 8 mm at 28 days, reducing to 6.5 mm at 56 days, demonstrating better water resistance than Grade 25 OPC. The water penetration depth of the 40 COC mix, which is made entirely of composite cement, is 6 mm at 28 days and drops to 5.2 mm at 56 days. The water penetration depth of the COC + 10% Alccofine mix, which comprises composite cement with 10% replacement for alccofine, is 4.5 mm at 28 days and 3.8 mm at 56 days. The addition of Alccofine refined the microstructure and reduced the permeability of the concrete. Alccofine, as a micro-fine material, aids in the refinement of the pore structure, lowers permeability and increases the resistance to water penetration. These results align with other studies indicating that adding SCMs like alccofine can significantly improve the water penetration resistance of the concrete by filling microvoids and reducing pore connectivity. Patankar et al. (2018) found that the OPC concrete mix with the inclusion of 15% alccofine shows a water penetration depth of 8.63mm [66].

However, in this study, the inclusion of 10% of alccofine COC concrete mix shows a water penetration depth of 6.5 mm. On comparing the obtained results with existing studies, it was observed that alccofine is highly efficient in water penetration depth of concrete, especially composite cement concrete [66]. The 60 OPC 65 mix exhibits a water penetration depth of 6 mm and 4.5 mm at 28 and 56 days.

The COC mixes exhibit reduced water penetration depth of 5 mm and 4.4 mm at 28 and 56 days as compared to OPC, indicating better water resistance compared to OPC. The best performance is seen in the COC + 10% Alccofine mix, where water penetration depths are 4.2 mm and 3.6 mm at 28 and 56 days. Alccofine fills in microvoids and contributes to a more refined microstructure, improving impermeability [67], [68].

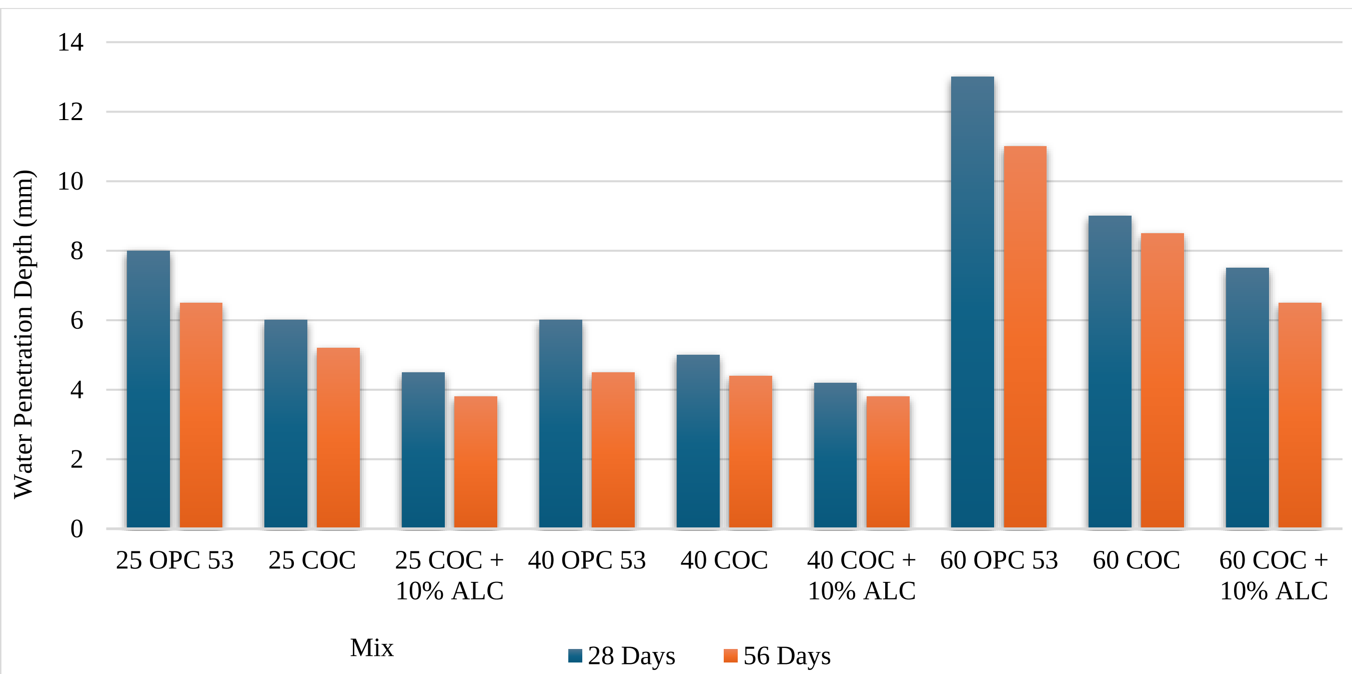


Fig. 1 Water penetration depth of various concrete mix

4.5. Chloride Penetration Resistance of OPC53, COC and COC + 10% ALC Concrete Mixes

The chloride resistance of the concrete was determined by measuring the charge that passes through the concrete sample in coulombs using the RCPT test as per ASMTC1202 guidelines. The RCPT test results of the OPC53, COC, and COC + 10% ALC concrete mixes are presented in Table 14. The RCPT results for 25-grade concrete demonstrate a clear improvement in chloride resistance over time for all mixes. At 28 days, the 25 OPC 53 mix has 969 coulombs, which indicates “Very Low” chloride ion penetrability. After 90 days, this value drops to 285.1 coulombs, indicating a denser microstructure with prolonged curing.

However, the initial permeability suggests that this mix is comparatively more vulnerable to chloride ingress at early stages. On the other hand, the 25 COC mix possesses lower initial values, starting at 945 coulombs at 28 days and dropping to 225.9 coulombs by 90 days. This shows enhanced resistance to chloride, perhaps as a result of the composite cement added, which contains fly ash and GGBS, which refine the pore structure. With noticeably lower values of 680 coulombs at 28 days and 220 coulombs at 90 days, the 25 COC + 10% Alccofine combination shows the best performance, falling into the “Very Low” category. The ultra-fine particles of Alccofine increase the density of the concrete and shorten the pathways for chloride penetration.

There is a clear distinction between the OPC and COC-based mixes in Grade 40 concrete. The 40 OPC 53 mix falls within the “High” chloride penetrability category due to its extremely high early RCPT values, which peak at 3541 coulombs at 28 days. While this value drops significantly to 310 coulombs at 90 days, suggesting that the concrete becomes more resistant over time, the initial high permeability raises concerns regarding its durability in chloride-exposed environments. However, the 40 COC mix performs significantly better, with RCPT values falling into the “Very Low” penetrability category at 28 days, 56 days, and 90 days (602 coulombs, 335 coulombs, and 277.6 coulombs, respectively). This increased resistance is probably the result of the composite cement added to the COC mixture. Even better results are obtained with the 40 COC + 10% Alccofine mix, with values that are continuously below 500 coulombs at all stages and as low as 244.1 coulombs at 90 days.

This mix benefits from both the SCMs and the additional refinement provided by Alccofine, making it highly durable in aggressive chloride environments. The Grade 60 concrete results reveal similar trends, with the 60 OPC 53 mix starting with very high RCPT values, indicating poor early-stage resistance to chloride ions. At 28 days, the mix records 3322 coulombs, which falls within the “High” penetrability category. Although the values decrease to 1757 coulombs at 90 days, placing it in the “Low” category, the initial high permeability suggests that high-strength OPC concrete is prone to micro-cracking or inadequate early-stage refinement. The 60 COC mix shows much better performance, with values of 586 coulombs at 28 days, 446 coulombs at 56 days, and 343 coulombs at 90 days, all within the “very low” penetrability range. The inclusion of SCMs in this mix contributes to its improved chloride resistance. The best performance was observed for the 60 COC + 10% Alccofine mix, where the RCPT values are consistently low, such as 482 coulombs at 28 days, 268 coulombs at 56 days, and 245 coulombs at 90 days.

It was found that adding Alccofine into the Composite cement considerably lowers the permeability of chloride ions in all concrete grades, improving long-term durability. The “very low” permeability values in the COC + 10% alccofine mixes for all grades demonstrate the effectiveness of alccofine in increasing resistance to chloride ion penetration. Although grade 40 and 60 OPC concretes have more permeability at initial days, they perform far better over time.

The addition of COC and Alccofine accelerates this improvement and results in more durable concrete. It was noted that with OPC replaced with composite cement along with partial replacement (10%) of inclusion of alccofine into the concrete at 90 days, the RCPT values were reduced from 1757 to 245, i.e., the chloride penetration changes from “low” to “very low” category. The addition of alccofine to composite cement enhanced the overall homogeneity of concrete, which leads to improved pore microstructure, and this reduces the RCPT values [69].

Similar results on the addition of alccofine into cement resulted in a reduction of chloride penetration have been reported in the various existing studies. i.e., Kavyateja et al. (2020) reported that the inclusion of 10% of alccofine along with fly ash into the concrete reduction in RCPT values from 1235 to 104 indicates a shift in chloride penetration from the “low” to the “very low” category [70]. Parmar et al. (2014) achieved RCPT values of 477 at 56 days with the utilization of 15% of alccofine into the OPC concrete, which indicates the chloride penetration of the “very low” category [64]. Sivakumar et al. (2015) observed that the replacement of OPC cement by 10% of alccofine caused an increase in RCPT values and reported that an RCPT value of 2840 was obtained at 28 days of testing, which indicates the chloride penetration falls into “moderate” category [31].

With the addition of 10% of alccofine and 30% of GGBS into the OPC concrete, Balamuralikrishnan & Saravanan (2019) obtained RCPT values of 204.6 at 28 days, indicating “very low” category chloride penetration [37]. On comparing the obtained results with existing studies [31], [37], [64], [70], it was demonstrated that alccofine is a highly efficient Supplementary Cementitious Materials (SCMs) for reducing chloride ion penetration of the composite cement concrete without the need for additional SCMs like fly ash, GGBS, etc.

Table 14. RCPT test results

Mix ID	RCPT (coulombs)		
	28 Days	56 Days	90 Days
25 OPC 53	969	650	285.1
25 COC	945	580	225.9
25 COC + 10% ALC	680	420	220
40 OPC 53	3541	3375	310
40 COC	602	335	277.6
40 COC + 10% ALC	465	312.8	244.1
60 OPC 53	3322	3072	1757
60 COC	586	446	343
60 COC + 10% ALC	482	268	245

4.6. Drying Shrinkage of OPC, COC, and COC + 10% ALC Concrete Mixes

Figure 2 presents the drying shrinkage test result of the different grades of concrete (25, 40, and 60) made with various types of cement (OPC, COC, and COC + 10% Alccofine) at 28 days. In compliance with ASTM C157/C157M, the drying shrinkage of the various concrete samples was assessed on day 28 to determine the percentage change in the length of the concrete specimens after being subjected to a controlled environment [56]. The drying shrinkage measurements for Grade 25 concrete show that adding Alccofine aids in reducing shrinkage.

The 25 COC mix has a slightly lower value of 0.050% than the 25 OPC 53 mix, which is related to the inclusion of SCMs, which decrease the porosity of the matrix and increase the overall stability. The combination of 10% Alccofine and 25 COC has the least shrinkage, which was 0.046%, indicating the advantage of using Alccofine. With its finer particles, Alccofine reduces pore size and increases particle packing density, which lowers shrinkage and enhances the microstructure of the concrete. The drying shrinkage results for Grade 40 concrete show a similar trend to those for Grade 25 concrete. With a lower drying shrinkage value of 0.036% than Grade 25 OPC, the 40 OPC 53 mix is expected, given its higher grade and lower water content. The 40 COC mix exhibits even less shrinkage, at 0.032%, indicating the effectiveness of SCMs in controlling shrinkage. The best performance is observed in the 40 COC + 10% Alccofine mix, which has the lowest shrinkage value of 0.029%. 10% Alccofine is an excellent option for minimizing shrinkage in higher-grade concretes because it refines the microstructure and lowers internal stresses brought on by moisture loss, further enhancing the concrete's resistance to shrinkage.

For Grade 60 concrete, which has the highest strength, the drying shrinkage values are significantly lower than the lower grades. A shrinkage value of 0.026% is recorded for the 60 OPC 53 mix, indicating the better stability of high-strength concrete. Because SCMs help to densify the matrix and lessen the effects of drying, the 60 COC mix further reduces shrinkage to 0.020%. The 60 COC + 10% Alccofine mix demonstrates the best performance, with a drying shrinkage value of 0.018%. The results of reduction in drying shrinkage with the addition of SCM like alccofine, etc., were supported by many earlier studies. Wang et al. (2022) reported that the drying shrinkage is only reduced by 5.5% when 10% of fly ash is as replacement by OPC cement [71]. According to Babu et al. (2018), there is only a 3.6% decrease in drying shrinkage when 30% of fly ash and China clay are replaced with OPC cement [72]. Saluja et al. (2019) found adding GGBS to concrete causes more drying shrinkage than the control concrete mix [73]. Liu et al. (2022) found that the replacement of OPC with 30% GGBS results in 20% less drying shrinkage than the control concrete mix [74]. However, in this study, the replacement of composite cement with 10% alccofine causes an 8% reduction in drying shrinkage, which outperforms many other SCMs like fly ash and GGBS at similar replacement levels.

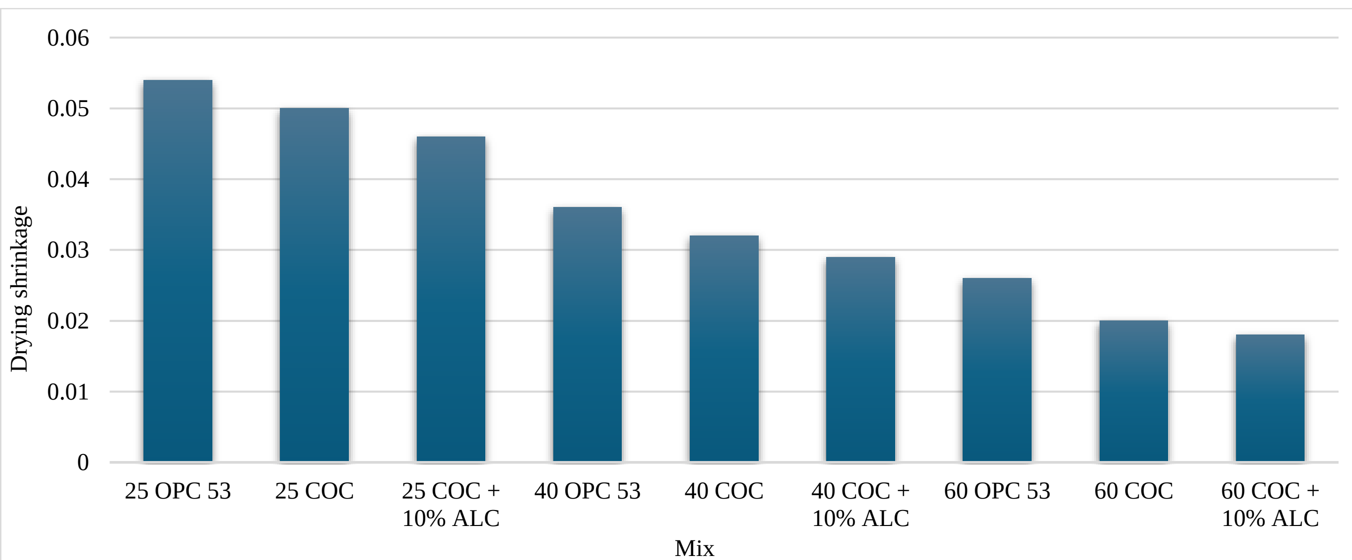


Fig. 2 Drying shrinkage of various concrete

This demonstrates the superior efficiency of Alccofine, even at low dosages. The finer particles of alccofine are essential for improving particle packing and lowering free water content, which minimizes drying shrinkage. The reduction in drying shrinkage across all grades with the incorporation of COC and 10% Alccofine is supported by the understanding that SCMs and Alccofine reduces the porosity and permeability of the concrete mix. The enhanced particle packing and microstructure refinement from alccofine result in less water evaporation and results in less shrinkage.

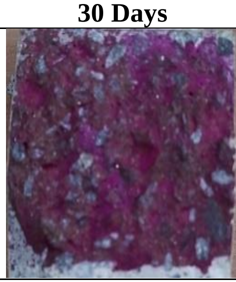
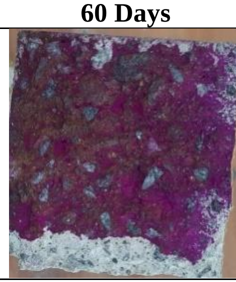
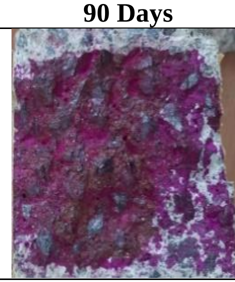
4.7. Carbonation Resistance of OPC, COC, and COC + 10% ALC Concrete Mixes

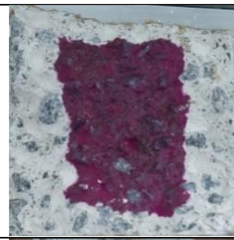
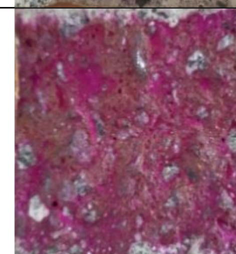
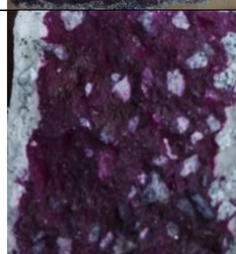
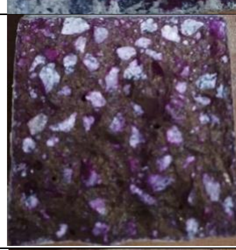
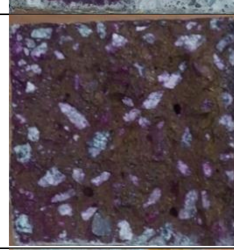
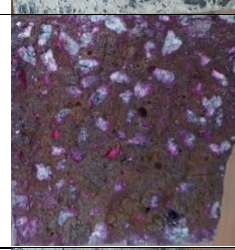
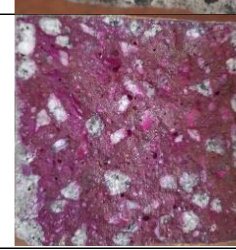
Carbonation depth is a significant factor in assessing the durability of the concrete since it directly relates to the decline of pH in the concrete because of the reaction of the carbon dioxide with the calcium hydroxide, which may cause corrosion of reinforcement. The results of carbonation depth over 30, 60, 90, and 120 days of the OPC, COC, COC+10% ALC specimen of 25, 40, and 60 grades are presented in Figure 3 and Table 15. The carbonation progresses slowly over the testing period for all the concrete grades. For 25 OPC 53 concrete mix, the partial carbonation (Pc) reached a depth of 2mm at 30 and increased to 7 mm at 120 days. For 25 COC concrete mixes, the full carbonation (fc) reached a depth of 20mm at 30 days and increased to 32 mm at 120 days. The inclusion of 10% alccofine into the COC mix shows the full carbonation (fc) depth of 25mm and 36mm by 30 and 120 days, as observed for the 25 COC+10% ALC mix. This same carbonation depth trend is observed for 40-grade concrete also. The partial carbonation (Pc) depth of 40 OPC 53 concrete mix was 1 mm at 30 days and raised to 3 mm after 120 days. The full carbonation (fc) depth of 40 COC concrete mix was 18 mm at 30 days, and it rose to 25 mm at 120 days.

As with the 40 COC+10% ALC mix, the addition of 10% alccofine to the CC mix causes a full carbonation (fc) depth of 15 mm and 24 mm by 30 and 120 days. The 60 OPC 53 concrete mix shows a full carbonation (fc) depth of 1 mm, which increased to 3 mm at 120 days. The 60 COC concrete mix shows a full carbonation (fc) depth of 12 mm at 30 days and increased to 17mm at 120 days. The addition of 10% alccofine to the COC mix yields a full carbonation (fc) depth of 10 mm and 15 mm by 30 and 120 days for the 60 COC+10% ALC mix. When compared to COC and COC + 10% ALC mixtures, OPC concrete shows noticeably lower carbonation depths in all concrete grades (25, 40, and 60). This lower carbonation depth is due to the fact that OPC concrete mixtures have a larger amount of calcium hydroxide ($Ca(OH)_2$). A significant amount of calcium hydroxide ($Ca(OH)_2$) is produced during the hydration of Portland cement. This compound functions as a buffer by reacting with atmospheric CO_2 to generate calcium carbonate [75], [76]. The presence of $Ca(OH)_2$ prevents the pH from dropping rapidly, thereby reducing carbonation depth. Furthermore, the slower rate of carbonation in OPC concrete is caused by the absence of SCMs [20]. The higher carbonation depth for COC and COC + 10% ALC mixes as compared to OPC mixes for all concrete grades (25, 40, and 60) is due to the presence of SCMs like fly ash and GGBS in the composite cement, which consumes $Ca(OH)_2$ through pozzolanic reactions, producing C-S-H that improves the strength. However, the decrease in $Ca(OH)_2$ leaves less material to buffer carbonation, making the concrete more vulnerable to CO_2 penetration, thus results in higher carbonation depth [77].

Despite the positive effects of alccofine on reducing permeability and enhancing microstructure, the accelerated consumption of $Ca(OH)_2$ leaves the concrete less protected against CO_2 ingress, leading to higher carbonation depth. However, the carbonation depth of the COC+10% ALC mix was somewhat lesser than the COC mix. Alccofine is a pozzolanic material that consumes $Ca(OH)_2$, but it also improves the microstructure of the concrete, lowering permeability, and together, these two actions result in a stronger resistance to carbonation than COC without alccofine, though not as effectively as OPC.

The carbonation depth of the 60 OPC 53 grade mix was about 50% and 57.14% less than the carbonation depth of the 25 OPC 53 grade mix at 30 and 120 days. The carbonation depth of 60 COC mix was about 40% and 46.88% less than the carbonation depth of 25 COC mix at 30 and 120 days. The carbonation depth of 60 COC + 10% ALC mix was about 60% and 58.33% less than the carbonation depth of 25 COC + 10% ALC mix at 30 and 120 days. This indicates that high-strength concrete or high-grade concrete results in less carbonation depth or high carbonation resistance. This finding was aligned with the findings of Zhuguo & Sha (2018), Chen et al. (2018), and Elsalamawy et al. (2019), who found that concrete with higher strength has higher carbonation resistance [43], [78], [63].

Mix	**30 Days**	**60 Days**	**90 Days**	**120 Days**
25 OPC 53				

25 COC				
25 COC + 10% ALC				
40 OPC 53				
40 COC				
40 COC + 10% ALC				
60 OPC 53				
60 COC				

60 COC + 10% ALC

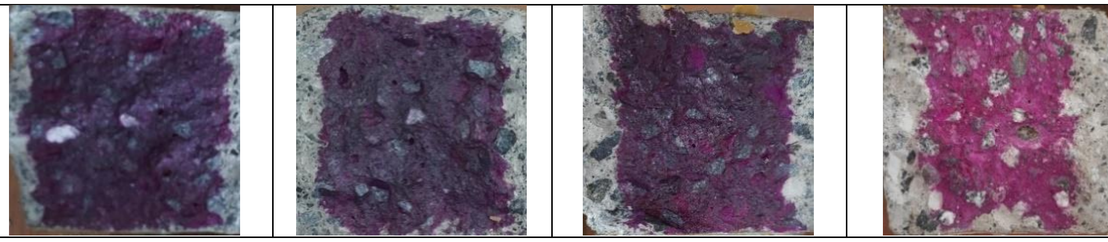


Fig. 3 Accelerated carbonation of various concrete

Table 15. Carbonation depth measurement of specimens at 30, 60, 90 and 120 days of accelerated curing

Mix	30 Days	60 Days	90 Days	120 Days
25 OPC 53	Pc: 2mm	Pc:4mm	Pc:5mm	Pc:7mm
25 COC	Fc:20mm	Fc:25mm	Fc:30mm	Fc:32mm
25 COC + 10% ALC	Fc:25mm	Fc:27mm	Fc:33mm	Fc:36mm
40 OPC 53	Pc: 1mm	Pc:2mm	Pc:3mm	Pc:3mm
40 COC	Fc: 18mm	Fc:20mm	Fc:22mm	Fc:25mm
40 COC + 10% ALC	Fc: 15mm	Fc:18mm	Fc:20mm	Fc:24mm
60 OPC 53	Fc:1mm	Fc:2mm	Fc:2mm	Fc:3mm
60 COC	Fc:12mm	Fc:13mm	Fc:14mm	Fc:17mm
60 COC + 10% ALC	Fc:10mm	Fc:12mm	Fc:13mm	Fc:15mm

Fc: Full carbonation (concrete colour); Pc: partial carbonation (light purple red colour).

5. Conclusion

This study primarily examined the influence of partial replacement (10%) of alccofine into composite cement concrete and compared it with OPC concrete. The various conclusions as observed from the outcomes of this study were as follows;

- The resistance of composite cement (COC) concrete to acid attack was greatly increased by the addition of 10% Alccofine. After 180 days, the weight loss in the 25 COC + 10% ALC mix was 34.22%, which was less than the 36.64% weight loss for the 25 OPC 53. Similarly, strength loss in 25 COC + 10% ALC was 7.36 %, while it was 11.633 % in 25 OPC 53. This improvement in acid resistance of composite cement (COC) concrete was due to the formation of a dense matrix and C-S-H gel, thus hindering the ingress of acid.
- The inclusion of alccofine improved the concrete's resistance to sulphates. At 180 days, there was a weight loss of 0.385% and a strength loss of 13.08% in the 25 COC + 10% ALC combination and a weight loss of 0.353% and 19.23% in the 25 OPC 53 mix. Compared to the 18.12% for 60 OPC 53, the strength loss in the 60 COC + 10% ALC mix was 12.2%, which is a far better result. The strength loss in alccofine-added concrete mixes was reduced due to the pozzolanic process that uses calcium hydroxide, making it unavailable to react with sulphate forming ettringite and lowering permeability to prevent the ingress of harmful sulphate ions into the concrete.
- The resistance of composite cement (COC) concrete to chloride attack was greatly increased by the addition of 10% Alccofine. After 180 days, weight reduction was 3.55% for the 25 COC + 10% ALC mix and 4.01% for the 25 OPC 53 mix. Strength loss was 25.39% in 25 COC + 10% ALC, a much less percentage than the 30.86% strength loss in 25 OPC 53.
- Alccofine, as a micro-fine material, aids in the refinements of pore structures, thereby minimizing the permeability of the concrete and increasing the resistance to water penetration.
- The replacement of OPC with composite cement, combined with 10% Alccofine in concrete, reduced RCPT values from 1757 to 245 at 90 days, shifting chloride penetration from "low" to "very low." This improvement is attributed to Alccofine enhancing concrete homogeneity and refining its pore structure, thereby reducing RCPT values.
- The partial replacement (10%) of alccofine in the composite cement concrete has a significant effect on the carbonation depth of the concrete. It was observed that higher-grade concrete (e.g., 60 grade) has significantly lower carbonation depths, indicating that higher-strength concrete provides better resistance to carbonation.

This study concluded that the addition of alccofine has a significant impact on the durability properties of composite cement concrete. Advanced microstructural studies employing methods like Scanning Electron Microscopy (SEM) images, Mercury Intrusion Porosimetry (MIP), and X-ray Diffraction (XRD) may be conducted in the future to better understand the hydration processes, micro-cracking behavior, and pore structure of concrete containing composite cement and alccofine.

Data Availability Statement

Data will be made available on reasonable request

Disclosure Statement
Concerning the writing and publishing of this research paper, the authors reported no conflicts.

Acknowledgments
We would like to acknowledge the Centre for Advanced Concrete Research – Civil (CACR-Civil), SRM Institute of Science and Technology, Kattankulathur, for their equipment support in carrying out the research.

Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contribution
B Suresh: Conceptualization, Methodology, Writing-Original Draft, Visualization; P R Kannan Rajkumar: Supervision, Resources, Writing-Review & Editing, Validation.

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