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Studies on the concrete with composite cement and alccofine: from use of OPC towards low-carbon quaternary binder

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Abstract

In recent days, there is an increased interest in using alternative materials in cement to produce concrete with improved properties. Supplementary cementitious materials (SCMs), which are the alternative materials used in the production of cement, are mainly industrial wastes like fly ash (FA), ground-granulated blast furnace slag (GGBS) and silica fume, giving rise to sustainable construction practices. Numerous investigations have been performed on the utilisation of alternate materials in the production of cement that is used in concrete, and an enhancement in the performance of concrete has been reported. Composite cement, a novel material, finds application in construction in which a certain percentage of cement clinker is replaced by GGBS, FA and silica fume during its production. The drawback of the composite cement containing GGBS and FA is that it attains a lower strength at earlier ages. Alccofine, an ultrafine slag-based material collected as a residue from the iron industry, has also been utilised as an SCM in the production of cement. In this study, the effect of a partial replacement of composite cement (COC) with alccofine is examined. It was observed that 10% replacement of COC by alccofine increases the maximum compressive strength (CS), modulus of elasticity (MOE), split tensile strength (STS) and flexural strength (FS) of concrete, respectively, by 12.67%, 16.95%, 11.4% and 21.42% at 28 days. The formation of closely packed structure due to the finer particles of alccofine contributes to an improvement in the strength of concrete.

Keywords Supplementary cementitious materials (SCMs) \cdot Composite cement (COC) \cdot Alccofine \cdot Mechanical properties \cdot Microstructural characterisation

Introduction

Cement manufacturing is an energy-intensive and resourceexhausting process that releases a large amount of greenhouse gases into atmosphere. It was reported that around 2.8 tonnes of raw material, including fuel and other materials, are needed to produce 1 tonne of Portland cement (PC) [1, 2]. Moreover, the production of 1 tonne of PC releases 1 tonne of greenhouse gases as a result of decarbonisation of limestone [3, 4]. The cement industry faces a number of challenges including scarcity of raw materials, leading to lower availability of concrete in construction [5, 6]. As of now, efforts have been made to promote the utilisation of pozzolans as a replacement for PC in concrete. The

pozzolans are either artificial or natural materials with silica in the reactive formation. ASTM C618 describes pozzolana as a siliceous or aluminous material that possess little or no cementitious value, but it will automatically react with calcium hydroxide in the chemical form in the presence of moisture at ambient temperature to develop hydrated cementitious properties [7]. The reaction of pozzolanic material with lime is known as "pozzolanic reaction," which is usually slow at ordinary temperature. The utilisation of pozzolanic material as a blended component of cement production results in huge energy savings and lowers the amount of solid wastes needed [8, 9]. The use of different kinds of waste materials like fly ash (FA) [10], clay brick wastes [11] and metakaolin [12] as pozzolans in concrete results in better chemical resistance, high strength and better durability. Among various industrial waste materials, fly ash (FA) and ground-granulated blast furnace slag (GGBS) are the commonly used pozzolanic materials because of their pozzolanic properties. The amount of fly ash and GGBS generated from industries are increasing on a daily basis, necessitating

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their disposal. GGBS and FA form an additional C-S-H gel after the reaction with portlandite, whose structure is similar to hydrated cement. FA is one of the most widely used pozzolans obtained as a by-product from the combustion of powdered coal. Among the significant advantages of using FA are better workability, decreased water needs and increased strength properties [13]. The major drawbacks of using FA are that its replacement percentage with cement is lower and early strength gain is minimum [14]. The low strength gain is due to the formation of Ca(OH)₂ during the cement hydration process [15], whereas GGBS obtained from steel industry as a by-product can be replaced with cement up to 70% [16]. The oxides of SiO₂, CaO, Al₂O₃ and MgO present in GGBS undergo hydration upon reaction with water [17]. Due to its denser microstructure, using an optimum amount of GGBS, the durability and strength characteristics of concrete can be improved [18]. However, the carbon footprint is higher than when FA alone is used as more processing time is needed for GGBS, which consumes more energy [19].

Alccofine is an ultrafine slag-based material which possesses high strength and durability characteristics than other SCMs used in the construction industry [20]. It is the most refined material obtained from steel industry as a waste material. The particle size distribution is one of a kind due to the granulation process. The individual particle size in alcoofine is up to 6 µm. The particles of alccofine are very finer than cement, rice husk and FA, which leads to enhanced hydraulic properties, pozzolanic reactivity and packing density of paste [21, 22]. Two commercially available forms of alccofine are 1101 and 1203 [23] with specific surface area greater than 12,000 cm^2/g and with specific gravity in the range of 2.8–2.9 [24, 25]. SiO₂ plays a major role in enhancing the strength properties [26]. Alcoofine is inert in nature, but once it is combined with cement, it possesses greater binding properties. This property leads to a significant improvement in strength and durability properties of concrete [27, 28]. Due to pozzolanic reaction, alcoofine modifies the interfacial transition zone (ITZ), thus reducing porosity. Balamuralikrishnan and Saravanan [29] replaced cement with alccofine at 0%, 5%, 10%, 15% and 20% to examine its impact on the compressive strength (CS) of cement mortar and reported that replacement of cement with 10% of alcofine increases the CS by 18.73%. Srinath et al. [30] stated that replacement of cement with 15% of alccofine leads to 40.71%, 41.5% and 125% increase in CS, split tensile strength (STS) and flexural strength (FS), respectively. Rajesh Kumar et al. [31] noted that the replacement of cement with 10% of alcofine increases the FS by 27.6%. Venkatesan et al. [32] reported that replacement of cement with 10% alcofine increases the CS by 20.52%. Gautam and Sood [33] found that the replacement of cement with

10% alcoofine increases the FS by 25.5%. Srinivasan [34]. on the other hand, found FS to increase by 22% on replacing cement with 10% alccofine. Harish et al. [35] tested the mechanical properties of concrete in which cement was replaced by 5-20% of alcoofine and concluded that the addition of alccofine in concrete yielded promising results as compared to conventional concrete. Chakravarthy and Raj [36] observed that the replacement of cement with 16% of alcofine increases the CS by 60.95%. Even highperformance concrete is more durable with the addition of alcoofine along with other SCMs [37]. Due to microfiller effect and pozzolanic reaction of GGBS, the cement paste has a lower number of pores [38]. It was also noted that concrete developed with 88.3% alccofine and 16.3% FA possessed substantial CS and FS [39]. From the previous studies, it was demonstrated that 8-12% of alccofine as a replacement for cement produces higher strength in the relevant concrete grades [40]. Thus, cement in concrete can be partially replaced with alcofine, FA and GGBS. The addition of alccofine with GGBS improves the workability of concrete because of its high fineness and glassy surface characteristics and low calcium silicate chemical composition [41]. Kavitha and Kala [41] replaced cement with 5-20% of alccofine in combination with 30% of GGBS in concrete and noted that CS and STS increase by 17.7% and 107%, respectively, for the combination of 10% alccofine with 30% GGBS. Kavyateja et al. [42] replaced cement with 5-15% of alcoofine combined with 25% of FA in concrete and reported that the CS and STS are increased by 17.49% and 39.25%, respectively, for the combination of 10% of alccofine with 25% of FA. Soni et al. [39] reported that the CS and FS increase by 6% and 1.76% when cement is replaced by 16% FA and 8% of alccofine. Ansari et al. [43] studied the behaviour of concrete by partially replacing cement with alcofine in combination with FA for the M30 grade concrete. They found that the strength of concrete is improved on replacement up to 15%. Reddy et al. [44] replaced cement with



Fig. 1 XRD of cement

Table 1 Physical properties of OPC

Description	Fineness (m ² /kg)	Normal consistency (%)	Setting time		Compressive strength (MPa)		
			Initial (min)	Final (min)	3 days	7 days	28 days
Results	309	28	50	460	35.4	45.7	62.4



Fig. 2 SEM images and EDX of OPC

Table 2 Chemical composition of OPC Image: Composition	Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	LOI
	%	21.31	5.71	5.55	61.20	1.35	2.17	0.59	0.12	2

Table 3 Physical properties of COC

Description	Fineness (m ² /kg) Normal co	Normal consistency (%)		Setting time				Compressive strength (MPa)			
						Fina	Final (min)		7 d	ays	28 days	
Values	332	32	32		75		535		31		42.6	
Table 4 Chem	ical composition	Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	LOI	
01000		%	31.93	11.49	5.78	42.66	2.59	2.73	0.50	0.10	2.22	

5–20% of alccofine in combination with 5–20% of FA in concrete and achieved a maximum CS of 52 MPa for the combination of 20% of FA with 20% of alccofine. Similarly, Sambangi et al. [45] replaced cement with 5–20% of alccofine in combination of 5–20% of FA in concrete and achieved a maximum CS of 62.74 MPa for the combination of 15% of FA with 15% of alccofine. Reddy and Ramadoss [46] developed ultra-high-performance concrete (UHPC) using alccofine with GGBS and found that UHPC attains 80% of the characteristic CS within 7 days itself.

Upadhyay and Jamnu [47] also reported that the strength gain of the concrete produced from alccofine and FA was excellent between 3 and 7 days, whereas strength gain between 7 and 28 days was comparatively lower. Saiya et al. [48] compared the performance of FA–alccofine concrete mix and GGBS–alccofine concrete mix and concluded that the FA–alccofine mix has better flowability than the GGBS–alccofine mix, whereas FA–alccofine mix possesses better CS than the GGBS–alccofine mix. Hence, it is essential to optimise the mix that produces better

mechanical properties with better flow properties. So, an attempt has been made to replace alcoofine in composite cement (COC) concrete in various proportions. COC is prepared using waste materials such as FA, slag and silica fume. COC is the cement in which a proportion of the cement clinker is replaced by industrial waste materials such as FA and slag. These industrial waste materials react with the hydration products of the cement forming additional hydrates, which contribute to the development of strength in concrete [49–51]. The hydration reaction of the composite cement based on the combination of cement with FA conforms to BS:3892 (Part-I) [52] or GGBS conforms to BS: 6699 [53] and is generally slower than the cement that conforms to BS:12-1996 [54], which results in a low rise in temperature. COC is developed accordance with Indian standards IS-16415-2015 [55], which



Fig. 3 SEM images and EDX of COC

Table 5 Chemical composition of ALC Image: Chemical composition	Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	LOI
	%	35.30	21.4	1.20	32.20	8.20	1.7



Fig. 4 SEM and EDX of ALC

of alccofine



pertain to COC. COC is the combination of 35-65% of OPC, 12-35% of FA and 20-50% of GGBS [56]. COC is one of the recent innovations in construction material research. Therefore, only a limited number of reports are available on the properties of COC concrete using alccofine as an SCM [57]. On the other hand, the utilisation of alcoofine is limited due to lack of proper code for its utilisation. For example, the Indian Standard (IS) concrete design mix guidelines IS-10262:2019 [58] recommends the use of GGBS, FA and silica fume as a partial replacement for cement but does not advocate the usage of the ultrafiner materials like alccofine [59, 60]. The aim of this study is to examine the mechanical properties and undertake the microstructural characterisation of COC concrete in which COC is partially replaced by alccofine. This study will prove highly beneficial to the construction industry. Alccofine's potential as a game changer in concrete is undeniable. The use of alccofine marks a stride towards sustainability, as industrial waste materials are used in construction. Embracing industrial waste materials like alcoofine in COC leads to stronger, greener structures, which reduce carbon footprint.



Materials and methodology

The current study examines the effect of SCMs such as alccofine on the mechanical properties and microstructure of COC. Comprehensive experimental tests such as slump cone, CS, STS, FS and modulus of elasticity (MOE) test have been conducted to examine the effect of SCM (alccofine) on the mechanical properties of COC.

Materials

Ordinary Portland cement (OPC)

The cement utilised was Coromandel King OPC 53 grade, which conforms to IS:12,269–1987 [61]. The characteristic composition of the Ordinary Portland cement was determined using XRD analysis, and the XRD images are shown in Fig. 1. The presence of alite, belite, aluminate periclase and calcite can be observed at peaks of 56.385°, 32.514°, 34.281° and 29.350°, respectively. The physical properties are given in Table 1, and the chemical composition of OPC as determined for EDX analysis is displayed in Fig. 2 and Table 2.

Composite cement (COC)

The Chettinad composite cement containing 60% OPC clinker, 20% GGBS and 20% fly ash according to IS-16415:2015 [55] is used in this study. The physical properties of this cement are given in Table 3. The chemical compositions and the amount of COC are listed in Table 4 with reference to the peak positions and intensities ascertained from the EDX pattern. The chemical composition of COC as determined for EDX analysis is displayed in Fig. 3.

Alccofine

Alccofine is the slag residue produced from the iron ore industries in India. Alccofine 1100 series has a low amount of calcium silicate, whereas alccofine 1200 series has a high amount of calcium silicate. The fine, microfine and ultrafine particle sizes of alcoofine are represented as 1201, 1202. and 1203 in alccofine 1200 series. Alccofine-1101, Alccofine-1203 and Alccofine-1206 are the most commercially available alcoofine compositions in the market [62]. Alccofine-1203 used in this study as a partial replacement material for composite cement conforms to ASTM-C989-99 [63]. Because of the granulation process, Alccofine-1203 contains ultrafine particles with a fineness of 12,000cm²/gm with a unique chemistry. The chemical compositions of the alccofine with reference to the peak positions and intensities as determined from the EDX pattern are given in Table 5. Alccofine interacts synergistically with ground-granulated blast furnace slag (GGBS) and fly ash, both of which are supplementary cementitious materials in the composite cement. These materials undergo pozzolanic reactions themselves, reacting with calcium hydroxide and contributing to the formation of additional C-S-H gel during hydration process. Alccofine presence intensifies these reactions, augmenting the overall pozzolanic activity and enhancing the durability and strength of the concrete. The chemical composition of composite cement (COC) suggests a favourable environment for C-S-H (calcium silicate hydrate) formation, particularly



Fig. 7 Modulus of elasticity test setup

Description	OPC 5	3	COC			COC + 10% ALC				
	M25	M40	M60	M25	M40	M60	M25	M40	M60	
Cement (kg/m ³)	300	410	500	_	_	_	_	_	_	
Composite cement (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	814	765	831	814	765	
Coarse Aggregate (kg/m ³)	1085	1002	958	1044	963	905	1044	963	905	
W/C ratio	0.55	0.39	0.33	0.51	0.36	0.30	0.51	0.36	0.3	
Superplasticizer (%)	0.35	0.5	0.55	0.5	0.5	0.7	0.70	1	1.1	

Table 6Optimised mix for OPC53, COC and COC + 10% ALC

due to the high CaO content (42.66%). Both Al_2O_3 (11.49%) and SiO₂ (31.93%) contribute to C-S-H formation. The presence of ground-granulated blast furnace slag (GGBS) and fly ash acts as supplementary cementitious materials (SCMs). They participate in hydration reactions, consuming CaO and forming additional C-S-H gel. Alccofine, though primarily considered an inert filler, possesses some pozzolanic activity. It can react with CaO released during hydration to form additional C-S-H gel, contributing further to strength and durability. The SEM image of alcoofine as shown in Fig. 4 indicates that the particles are irregular in shape and have sharp edges. The particle size distribution of alcoofine is presented in Fig. 5. The graph shows that the majority of the particles are between 1 and 10 µm in diameter. This indicates that alcoofine is a very fine material, which could contribute to providing beneficial effects on the properties of concrete.

Fine aggregates

The fine aggregate used is locally available manufactured sand, which passes through sieve of 4.75 mm, conforming to grading zone II of IS: 383–1970 [64] with water absorption of 0.67%, specific gravity of 2.71 and fineness modulus of 2.57. Figure 6 presents the gradation curve of fine aggregate.

Coarse aggregates

The coarse aggregate with maximum size of 12.5 mm, conforming to IS: 383–1970 [64], was used. Its fineness modulus was 7.2, specific gravity 2.7 and water absorption 0.62%.

Superplasticizer

The commercially available SP is based on the copolymer of acrylic acid and polyethylene glycol (PEG) referred to as polycarboxylate ether (PCE). A commercially available SP known as Master Glenium ACE 30 from BASF chemical company is used as the chemical admixture. The admixture has a specific gravity of 1.82 and solid content of 25% and was added to concrete.

Mix proportioning

The concrete mixture was designed aiming for the target strength using the conceptual proportioning strategy by keeping the binder to total aggregate and fine to coarse aggregate ratio proportioned as per IS:10,262–2019 [58]. A total of nine trial mixes were developed for the M20, M40 and M60 grade concrete mixes by replacing COC by 5%, 10% and 15% of alccofine. Finally, three optimised mixes with 10% of alccofine were selected for M20, M40 and M60 grade concrete mixes, respectively, which offer between workability and mechanical properties as presented in Table 6. The workability and mechanical properties of these optimised mix are compared with the OPC and COC mixes.

Initially, the coarse aggregate and fine aggregate were fed into the mixer and mixed for 2 min. Then, the required amount of cement was introduced into the mixture and mixed for 2 min in the dry condition. Then, the water and accelerator mix were added in the mixer containing cement, coarse and fine aggregate and mixed for the period of 4 min.



Experimental investigation

The primary aim of this study is to examine the effect of the partial replacement (10%) of composite cement by alccofine. In order to achieve the objective of this study, various tests (slump cone test, CS test, elastic modulus test, STS and FS test) were conducted. Three samples are tested to compute the average CS value for each concrete mix.

Workability

The prepared fresh concrete was tested to determine the workability properties using slump cone, and the slump value was noted. The slump cone test was performed using the apparatus called slump cone with height of 300 mm, with top diameter and bottom diameter of 100 m and 200 mm as per IS-1199:1959 [65] standards.

Compressive strength test

The CS test was conducted as per IS: 516–1959 with a 100-mm cube [66]. After 24 h of curing, the specimens were demoulded and cured in water. After 28 days of water curing, the specimens were tested for its properties. The test was done by loading the test specimen using the compressive testing machine (CTM) of 1000 kN capacity having a least count of 1 kN.

Modulus of elasticity

As per IS:5816–1959 [67], cylindrical specimens of 100 mm diameter and 200 mm height were cast and tested to determine the modulus of elasticity. All the specimens were demoulded after 24 h of moist curing and then introduced into the water tank for curing. After 28 days of curing, the specimens were tested for its properties. The test was done as per IS:516-1959 [66] standards using the universal testing machine (UTM) of 1000 kN capacity having a least count of 1 kN as shown in Fig. 7.

Split tensile strength test

In order to study the tensile strength, cylinder specimens of height 200 mm and diameter 100 mm were cast for testing. All the specimens were demoulded after 24 h and then immersed in water for curing. After 28 days of curing, the specimens were tested for its properties. The test was done as per IS: 5816-1959 [68] standards using the universal testing machine (UTM) of 1000 kN capacity having a least count of 1 kN.

Flexural strength test

A prism specimen of size 100 mm \times 100 mm \times 500 mm specimen was cast for testing FS or modulus of rupture. All the specimens were demoulded after 24 h of moist curing and then introduced into water tank for curing. After 28 days of curing, the specimens were tested for its properties. The test was done as per IS:516-1959 [66] standards using the



universal testing machine (UTM) of 1000 kN capacity having a least count of 1 kN.

Results and discussion

Workability

The slump flow value of the M25, M40 and M60 COC concrete mixes was 5.55-12.5% higher than the slump flow value of the M25, M40 and M60 OPC concrete mixes. The slump flow value of the M25, M40 and M60 COC + 10%ALC concrete mix was 5.25–12.5% higher than the slump flow value of the M25, M40 and M60 COC concrete mixes. For the M25 mix, there was no change in the slump flow value when OPC was replaced with COC and COC + 10%ALC. Generally, the addition of FA into concrete increases the slump value due to the spherical shape of the FA particles. This shape causes the ball bearing effect, resulting in the improvement in slump value of the concrete. However, the combined addition of FA and GGBS as COC in the concrete mix does not lower the slump value. This may be due to the elongated shape of the GGBS particles and also high surface area of GGBS, thus requiring more water for wetting. However, the amount of the superplasticiser was increased to 0.5 kg/m³ without affecting the mechanical properties. Similarly, the addition of ALC into the COC reduces the slump flow value. However, the amount of the superplasticiser was increased to 0.7 kg/m³ without affecting the mechanical properties. Figure 8 presents the slump flow of the OPC 53, COC and COC + 10% ALC for M25, M40 and M60 grades of concrete.

For the M40 mix, there was an improvement in the slump flow value when OPC was replaced with COC and COC + 10% ALC. The slump flow value of the COC of M40 grade concrete is 5.55% higher than the OPC mix. The slump flow value of COC with 10% ALC mix of M40 grade concrete is 5.25% higher than the COC mix. The partial replacement of COC by alccofine produces a high volume of paste due to its lower density, and this high volume of paste reduces the friction between binder-aggregate interface, improves the cohesiveness and plasticity and thus prompts increased workability. For the M60 mix, there was an improvement in the slump flow value when OPC was replaced by COC. For the M60 mix, there was a reduction in slump flow value when COC was replaced with 10% ALC, though the addition of 1.1 kg/m³ of superplasticiser does not lead to any improvement in the slump flow value. The slump flow value of the COC with 10% ALC mix of M60 grade concrete is 6.25% lower than the OPC mix. This may be because of high water absorption, surface area and fineness of alccofine materials. A higher amount of alccofine will absorb more water due to its finer particle size and also as a result of its increased surface area [69].

Compressive strength

It was observed that the replacement of OPC by COC cement in concrete increases the CS by 5.30%, 3.93% and 1.96%, respectively, for M25, M40 and M60 grade concretes. Also, it was observed that the partial replacement of COC cement with 10% of ALC increases the CS by 9.02%, 12.46% and 6.42% for M20, M40 and M60 grade concretes,



Fig. 10 Elastic modulus of different grades of concrete respectively. For the M25 grade concrete, the replacement of OPC with COC cement in concrete increases the CS by 5.30% and the partial replacement of COC cement with 10% of ALC increases the CS by 9.02%. For the M40 grade concrete, the replacement of OPC with COC cement in concrete increases the CS by 3.93%, while the partial replacement of COC cement with 10% of ALC increases the CS by 12.46%. For the M60 grade concrete, the replacement of OPC with COC cement in concrete increases the CS by 1.96%, whereas the partial replacement of COC cement with 10% of ALC increases the CS by 6.42%. Figure 9 shows the variation of CS of OPC 53 concrete, COC concrete and COC+10% ALC concrete at 28 days of curing.

It was concluded that the addition of 10% alcofine into the composite cement (60% of OPC + 20% GGBS + 20%FA) increases the CS. Reddy and Ramadoss [46] also achieved an improvement in the CS of concrete with the addition of alccofine into the concrete mix containing FA and GGBS. They achieved a 6.69% improvement in CS on the addition of alccofine of 160 kg/m³; in this study, a maximum of 9.2% improvement in CS was achieved with the addition of 45 k/m^3 of alcoofine. This improvement in CS is due to the homogeneity of the concrete matrix, where materials with the same chemical composition display a stronger bonding. The higher production of CSH gel also contributes to an improvement in CS. The chemical composition of COC offers a favourable environment for C-S-H formation, especially due to the presence of high CO_2 content (42.66%) along with Al₂O₃ (11.49%) and SiO₂ (31.93%). GGBS and FA in the COC participate in the hydration reactions, consuming CaO and forming additional C-S-H gel. Alccofine,

though primarily considered an inert filler, possesses some pozzolanic activity. It can react with CaO released during hydration to form additional C-S-H gel, contributing further to strength and durability. Srinath and Patnaikuni [70] reported that the replacement of cement with 10% alccofine can increase the CS by 8%. However, in this study, more than 8% improvement in CS was achieved when composite cement (60% of OPC + 20% GGBS + 20%FA) was replaced by 10% alccofine. However, some studies reported that the addition of high amount of alccofine decreases the CS. Kavyateja et al. [42] realised a reduction in CS on the addition of 15% alccofine into the concrete mix containing 72% OPC and 15% FA. The decrease in strength with the addition of alccofine beyond 10% is due to the increased water demand by alccofine, which prompts a reduction in the pore bonding strength [71]. Reddy and Meena [72] obtained a reduction in CS on the addition of 8% of alcoofine into the concrete mix containing 72% of OPC with 20% of GGBS. In line with the outcomes of Reddy and Meena [72], a partial replacement of COC with alccofine is more beneficial than the replacement of OPC with a combined addition alccofine and GGBS in concrete. Reddy et al. [73] obtained the maximum CS of 55.21 N/mm² for M40 grade concrete when OPC cement was partially replaced by 15% alccofine. Oureshi et al. [74] noted a maximum CS of 59.56 N/mm² on the partial replacement of OPC cement by 18% FA and 12% alccofine. In this study, the maximum CS of 61.32 N/mm² was achieved for M40 grade concrete on the partial replacement of COC cement by only 10% alccofine at 28 days. This demonstrates the beneficial effect of mechanical properties on partially replacing COC cement with alccofine in concrete for construction applications.



Fig. 11 Split tensile strength of different grades of concrete



Fig. 12 Flexural strength of different grades of concrete

Modulus of elasticity (MOE)

The replacement of OPC with COC cement in concrete results in an increase of MOE by 2.15%, 5.05% and 4.8% for M25, M40 and M60 grade concretes, respectively. Similarly, the partial replacement of COC cement with 10% of ALC results in the increase of the MOE by 8.33%, 16.95% and 9.67% for M20, M40 and M60 grade concretes, respectively. For M25 grade concrete, the replacement of OPC with COC cement in concrete increases the MOE by 2.15%, whereas the partial replacement of COC cement with 10% of ALC increases the MOE by 8.33%. For the M40 grade concrete, the replacement of OPC with COC cement in concrete increases the MOE by 5.05%, while a partial replacement of COC cement with 10% of ALC increases the MOE by 16.95%. For the M60 grade concrete, the replacement of OPC with COC cement in concrete increases the MOE by 4.8%, whereas the partial replacement of COC cement with 10% of ALC increases the MOE by 9.67%. Figure 10 shows the variation of MOE of OPC 53 concrete, COC concrete and COC + 10% ALC concrete at 28 days of curing.

The alccofine particles are much finer than the other cementitious materials like fly ash, GGBS and cement. Hence, the voids that are formed in the concrete between the FA, GGBS and cement are filled by the alccofine particles, resulting in a closely packed structure. During testing, the load transfer from one grain to another as a result of strain increases eventually at the rate of stress, thereby contributing to an improvement of elastic modulus.

Split tensile strength

It was observed that the replacement of OPC with COC cement in the concrete increases the STS by 1.56%, 2.59% and 3.7% for M25, M40 and M60 grade concretes, respectively. Also, it was observed that the partial replacement of COC cement with 10% ALC increases the STS by 1.9%. 11.4% and 3.45% for M20, M40 and M60 grade concretes, respectively. For the M25 grade concrete, the replacement of OPC with COC cement in the concrete increases the STS by 1.56%, while a partial replacement of COC cement with 10% of ALC increases the STS by 1.9%. For the M40 grade concrete, the replacement of OPC with COC cement in concrete increases the STS by 2.59%, while a partial replacement of COC cement with 10% of ALC increases the STS by 11.4%. For the M60 grade concrete, that replacement of OPC with COC cement in the concrete increases the STS by 3.7%, whereas a partial replacement of COC cement with 10% of ALC increases the STS by 3.45%. Figure 11 shows the variation of STS of OPC 53 concrete, COC concrete and COC + 10% ALC concrete at 28 days of curing.

The improvement in tensile strength might be due to the improved properties of the concrete matrix and strong interphase bond between the binders (i.e., COC and alccofine) and aggregates [75]. Therefore, an interfacial transition zone (ITZ) plays a significant part in the improvement of STS. By utilising microparticles like FA in COC and alccofine, the ITZ becomes denser, resulting in an improvement in STS. Sagar and Sivakumar [76] achieved a 2.5% improvement in STS of concrete containing 420 kg/m³ of OPC, 120 kg/m³ of FA and 84% kg/³ of alccofine at 28 days. In this study, a 11.4% improvement in STS was achieved with the addition

Fig. 13 SEM images and EDX of M25 OPC concrete



(a)



of 45 kg/m³ of alcoofine to the concrete containing 405 kg/m³ of COC at 28 days. This demonstrates the beneficial effect of using alcoofine as a partial replacement to COC cement in concrete production with regard to STS.

Flexural strength

The replacement of the OPC with COC cement in concrete results in an increase of FS of 33.76%, 9.52% and 3.92% for M25, M40 and M60 grade concretes, respectively. Similarly, the partial replacement of COC cement with 10% of ALC results in an increase of FS by 21.42%, 13.04% and 9.43% for M20, M40 and M60 grade concretes, respectively. For the M20 grade concrete, the replacement of OPC with COC cement in the concrete increases the FS by 33.76%, whereas a partial replacement of COC cement with 10% ALC increases the FS by 21.42%. For the M40 grade concrete, the replacement of OPC with COC cement in concrete increases the FS by 9.52%, while a partial replacement of COC cement with 10% ALC increases the FS by 13.04%. For the M60 grade concrete, the replacement of OPC with COC cement in the concrete increases the FS by 3.92%, whereas a partial replacement of COC cement with 10% ALC increases the







FS by 9.43%. Figure 12 shows the variation of FS of OPC 53 concrete, COC concrete and COC + 10% ALC concrete at 28 days of curing.

This improvement in flexural strength occurs because of high specific area and high pozzolanic activity of the alccofine resulting in the high production of C–S–H gel, which helps in the formation of compact structure, thus improving the strength. Also, the various oxide compounds present in the GGBS and FA (which are present in COC) contribute to improving strength by pozzolanic or hydraulic activity [77]. Sagar and Sivakumar [76] achieved a 18% improvement in FS of the concrete containing 420 kg/m³ of OPC, 120 kg/m³ of FA and 60% kg/³ of alccofine at 28 days. In this study, a 21.42% improvement in FS was achieved with the addition of 33 kg/³ of alccofine to concrete containing 297 kg/m³ of COC at 28 days. This demonstrates the beneficial effect of using alccofine as a partial replacement to COC cement in concrete production with regard to FS. The failure of the specimen is Fig. 15 SEM images and EDX of M60 OPC concrete







associated with the sudden break of the specimen without any initial cracks.

Microstructural analysis

The surface morphology in concrete is examined using SEM images [78]. The calcium–silicate–hydrate (C–S–H) gel is a major non-crystalline phase present in the hydrated OPC that provides strength and durability to the concrete. SEM

and EDX were employed to determine the C–S–H phase in the composite sample as the hydrated sample has various other phases. Elemental analysis that is spatially resolved is possible with EDX and SEM imaging. When the electron beam strikes the sample surface, EDX identifies the emitted backscattered electrons and provides the elemental composition of the sample surface. As a result, EDX can identify the existence of elements in a scanned area. The presence of an element in the total scan area of the image is indicated by Fig. 16 SEM images and EDX of M25 COC concrete







each peak in the spectrum. To identify the C–S–H gel, three components such as oxygen (O), silica (Si) and calcium (Ca) are to be located. The C–S–H phase is represented by regions with high concentrations of Si, Ca and O. Similarly, calcium hydroxide (CH) is represented by regions with the presence of Ca and O. The SEM and EDX techniques were used to analyse the elemental composition of the OPC, COC and COC + 10% ALC powder and concrete mix using the tested samples after 28 days of curing.

The morphology of C–S–H phase formation varies from poorly crystalline fibres to clusters and rectangular

networks. When Portland cement paste is fully hydrated, it is the most important phase in a network of C–S–H clusters, amounting to 50–60% of the solids volume, which determines the properties of the paste. Figures 13a, 14 and 15a show only the clusters and reticular networks and ettringite is not observed. The formation of primary ettringite during early stages is essential and a beneficial component for the Portland cement system [79]. The formation of ettringite is typically associated with peak intensities of Al, S, Si and Ca as observed in Figs. 17b, 18 and 19b. Within a few minutes or hours of cement hydration, a needle-shaped







calcium trisulphoaluminate hydrate crystals, also known as ettringite, started to form as a result of interactions between calcium, sulphate, aluminate and hydroxyl ions. Later, the long and slender ettringite formed earlier was transformed into fibrous crystals as shown in Fig. 16a, where there are some long prismatic crystals indicating the formation of calcium hydroxide (CH) and very small fibrous crystal showing the formation of the C–S–H phase. The hexagonal plate-like structure of calcium hydroxide was found in all M25, M40 and M60 grade concretes. However, its presence was found to be higher in M60 grade. This phenomenon is primarily due to the higher cement content used in higher-grade concrete mixes. This observation is found to be in line with Srinath et al. [80], who reported that the presence of calcium hydroxide was found to be in a higher grade of concrete. SEM micrographs of the M25 OPC mix revealed wide shear cracks and interfacial cracks, whereas no cracks were observed for the M40 and M60 OPC mixes.

The SEM images and elemental peaks as obtained from the EDX analysis for COC concrete of M25, M40 and M60 Fig. 18 SEM images and EDX of M60 COC concrete





grades are presented in Figs. 16, 17 and 18. At increased magnification, the samples show distinguished microstructures with a slag content that further produces a denser matrix. The formation of CSH is evident. The EDX analysis confirms the presence of calcium of about 19.28%, 39.79% and 38.61% in the COC of M25, M40 and M60 grade concretes leads to the formation of the C–S–H gel.

The FA particles fill in the space and begin reacting with the GGBS, which improves the characteristics. Due to the presence of FA particles, the region of crack initiation on the surface of the concrete was reduced. The elements such as Na, S, and K are formed in the hydration process, which are not seen in the OPC concrete samples. This makes a more compact gel structure and improves the mechanical Fig. 19 SEM images and EDX of M25 COC + 10% ALC concrete







capabilities. For M25 and M40 concretes, stratified layerlike structures, most likely made of C–A–S–H and C–S–H gels, can be detected. For M60, hydration products in the form of denser clusters can be seen. Microcracks along with small void places are observed for some specimens. Such denser morphologies prompt improvement in mechanical and durability properties.

Figures 19, 20 and 21 show the SEM images of the COC concrete added with 10% of ALC of M25, M40 and M60 grade concretes. It was observed that the solid phase of the binders consists of C–H, primarily in the form of portlandite at the early stage of the hydration process. The SEM images showed that portlandite structures are prevalent when using concrete mix with alccofine. This may have happened as a result of the pozzolanic reaction between alccofine and

tricalcium and dicalcium silicates in cement. The formation of stratlingite was also observed from the SEM images of alccofine-mixed concrete. The formed stratlingite and portlandite crystal, which reacts with FA in the composite cement, formed a honeycomb structure called C–S–H gel at the lateral stages of the hydration process. Stratlingite has a primary composition of aluminium due to the availability of higher amount of alumina in alccofine. This is in line with Senff et al. [81]. Because of the formation of the C–S–H gel, the alccofine-added concrete mix possesses high strength than other mixes considered in this study, that is, the FS of the COC + 10% ALC concrete was around 21.42% higher than COC concrete mix. Table 7 presents the elemental compositions and the percentages of O, Ca, Si, Na, and Al based on the findings of the EDX study. These elemental atomic Fig. 20 SEM images and EDX of M40 COC + 10% ALC concrete







ratios such as CA/Si, Na/Si and Al/Si are significant factors affecting the strength and durability of the COC + ALC mixes. Table 7 displays the values of this ratio for Ca/Si, Na/ Si, and Al/Si ratios. These ratios are primarily in the narrow ranges of 1.12–1.83, 0.01–0.11 and 0.12–0.43 in the current

set of COC + 10% ALC mix. Thus, it may be concluded that the primary elements indeed appear in the COC + 10% ALC mixtures in the following order: Ca > Si > Al > Na, possibly as constituents of C–A–S–H and C–S–H gels.

Fig. 21 SEM images and EDX of M60 COC + 10% ALC concrete





Table 7	Atomic (%) of
COC + 1	10% mix using EDX
analysis	

Mix	0	Na	Mg	Al	Si	Ca	Ca/Si	Na/Si	Al/Si
M25 COC + 10%ALC	58.28	0.87	0.77	4.79	10.93	20.06	1.83	0.07	0.43
M40 COC + 10%ALC	68.74	1.26	1.53	3.60	10.74	12.74	1.18	0.11	0.33
M60 COC + 10%ALC	64.67	0.22	1.61	4.53	12.44	13.94	1.12	0.01	0.12

Conclusions

The supplementary cementitious materials (SCMs), which can partially replace cement, represent a new technological innovation in concrete manufacturing in the construction industry. This paper aimed to examine the beneficial effect of using alcofine as partial replacement to composite cement. The conclusions derived from the experimental results are as follows:

- The partial replacement of COC by alcoofine leads to an improvement in the mechanical characteristics of concrete. But due to the presence of finer alcoofine, which has a higher surface area, it absorbs higher water, leading to a decrease in the workability of concrete.
- As the percentage of alccofine used instead of cement increases, the CS of concrete increases. However, the percentage increase in strength is lower because of lesser pozzolanic nature at later ages. The maximum CS of 61.32 N/mm² was achieved for M40 grade concrete when COC cement was partially replaced by only 10% of alccofine at 28 days.
- The partial replacement of COC with 10% of alccofine to COC results in a 11.4% and 21.42% increase in STS and FS at 28 days. This improvement is due to the strong interphase bond between the binders (i.e., COC and alccofine) and aggregates. Therefore, an interfacial transition zone (ITZ) plays a significant part in the improvement of STS.
- Around 16.95% improvement in the modulus of elasticity of concrete was achieved when COC was partially replaced with 10% of alccofine. The finer particles of alccofine fill the gap formed between the COC particles and the closely packed structure formed, thus having the ability to withstand higher load.
- The microstructural characterisation of the COC with the addition of alccofine using SEM and EDX shows that the addition of alccofine can contribute to the formation of hydration products, especially stratlingite, which was formed as a result of the addition of alccofine.

This study primarily focused on determining the mechanical and microstructural properties of the concrete in which alccofine is added as a partial replacement to composite cement. However, this study has a limitation of not assessing the durability properties of concrete. In the future, the durability performance of alccofine-modified concrete would be taken up for investigation. The practical implications might involve using alccofine in concrete mix designs to create stronger and more resilient structures. Acknowledgements We acknowledge SRM Institute of Science and Technology for high-resolution scanning electron microscope (HR-SEM) facility, XRD facility at SRMIST setup with support from The Ministry of New and Renewable Energy (Project No. 31/03/2014-15/ PVSE-R&D), Government of India.

Author contributions BS contributed to conceptualization; data curation; methodology; investigation; roles/writing—original draft; and writing—review and editing. PRKR contributed to conceptualization; data curation methodology; supervision; validation; and writing review and editing.

Data availability The data that has been used are confidential.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This manuscript has not been published and is not under consideration for publication elsewhere.

Informed consent For this type of study, informed consent statement is not applicable.

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