

Review

Crossover Effect in Cement-Based Materials: A Review

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Abstract: Cement-based materials (CBMs) such as pastes, mortars and concretes are the most frequently used building materials in the present construction industry. Cement hydration, along with the resulting compressive strength in these materials, is dependent on curing temperature, methods and duration. A concrete subjected to an initial higher curing temperature undergoes accelerated hydration by resulting in non-uniform scattering of the hydration products and consequently creating a great porosity at later ages. This phenomenon is called crossover effect (COE). The COE may occur even at early ages between seven to 10 days for Portland cements with various mineral compositions. Compressive strength and other mechanical properties are important for the long life of concrete structures, so any reduction in these properties is of great concern to engineers. This study aims to review existing information on COE phenomenon in CBMs and provide recommendations for future research.

Keywords: crossover effect; cementitious materials; compressive strength; accelerated curing; concrete; mortar

1. Introduction

Cement-based materials (CBMs) such as mortars and concretes are the most frequently used building materials in the construction industry [1]. Cement hydration is extremely exothermic in these materials [2]. The hydration process of cement continues for many years at a reducing rate, depending on the water quantity in mixture and appropriate curing temperature conditions [3]. For long-term durability and strength of concretes and mortars, their appropriate mixes should be placed and cured in a proper environment during early hardening by preventing water loss of evaporation from capillaries [4]. In addition, internal water loss by self-desiccation should be replaced by water from external sources [5]. The hydration process and resulting compressive strength of concrete depend on curing temperature, curing methods, curing duration and mix composition [6]. The compressive strength of concrete, along with other mechanical properties, has essential role in the design and construction of all types of concrete structures [7].

Concretes exposed to accelerated curing temperatures at the early ages gain high compression and splitting tensile strengths at early ages but low compression and splitting tensile strengths at later ages compared with those exposed to moderate normal curing temperatures. The modulus of elasticity

of concrete has the same tendency, but the variation in its value with accelerated curing temperatures is not as prominent as that of compressive strength [8]. Fall et al. [9] stated that splitting tensile strength of the CBMs is more affected by the mechanism of crossover effect (COE) than compressive strength.

Researchers [5,10] described that increasing curing temperature of CBMs, such as cement pastes, mortars and concretes, increases rate of early-age strength gain but lowers the long-term strength (see Figure 1). Garcia and Sharp [11] also reported that concrete exposed to high curing temperatures exhibits accelerated hydration and non-uniform spreading of the hydration products. Such an exposure creates less porosity at early-ages and great porosity at later-ages. It results in increased compressive strength at early-ages and reduced compressive strength at later-ages [8].

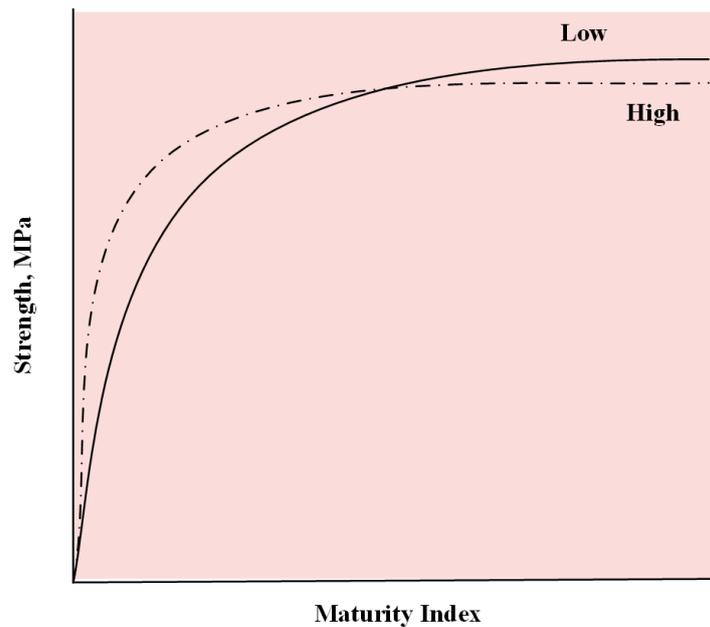


Figure 1. Crossover effect (COE) with maturity and strength at low and high temperatures.

Ogribo and Black [12] described that concrete cured at elevated temperature of 38 °C had less porosity and more compressive strength at seven days than those cured at 20 °C. However, at 28-days, the porosity of elevated temperature cured concrete increased and compressive strength decreased than that of normally cured concrete. Luz and Hooton [13] studied the effect of elevated curing temperatures up to 50 °C on supersulfated cements incorporating low and high alumina slags. They observed lower porosity and higher compressive strength due to elevated temperatures (38 °C and 50 °C) than the samples cured at normal temperature (23 °C) at the age of seven days. Ezziane et al. [14] emphasised that under elevated temperatures, cement mortars and concretes have more porous and poorer physical structures than those developed at normal room temperature. They also stated that high temperatures increase strength gain at the early ages, whereas substantial amount of the formed hydrates have insufficient time for proper arrangement at the later ages. This process results in COE, a decrease in ultimate compressive strength of CBMs.

According to the research reports [15,16], COE may occur between seven and 10 days in Portland cements of various mineralogical compositions. Weerdt et al. [17] stated that the initial fast hydration of Portland cement can produce a lesser homogenous microstructure that causes the COE in cements and concretes. Castellano et al. [18] also reported that such a process of Portland cement can decrease hydration at later ages. This decrease is due to the postponing or ending of the hydration of anhydrous cement. Moreover, the hydration products at lesser temperatures have adequate time to precipitate and diffuse homogeneously in the whole cement matrix. According to Kim et al. [8], the COE of type V Portland cement concrete is not very clear compared with that of type I Portland cement concrete because of varying rates of hydration.

The COE in CBMs due to accelerated initial and prolonged curing is of great concern to researchers because of the utmost importance of concrete structures in the present construction industry. Some researchers [15,17,19] explained that the loss in compressive strengths of CBMs at later ages is because of different initial curing temperatures. Yang et al. [19] studied the strength development of concrete due to different initial curing temperatures with ageing (see Figure 2). They found a significant difference in compressive strengths of concretes at later ages because of various initial curing temperatures. At the later ages, compressive strength of materials cured at lower initial curing temperatures were greater than those cured at higher initial curing temperatures. They termed this phenomenon as COE.

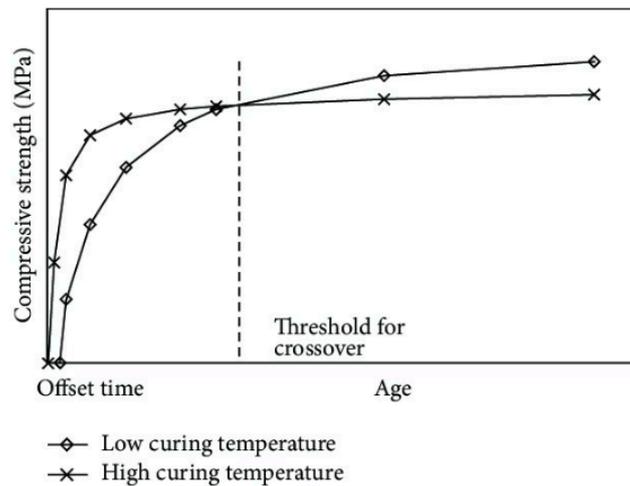


Figure 2. COE during strength development of concrete due to different initial curing temperatures. Adapted with permission from [19], Hindawi, 2015.

According to Lothenbach et al. [20], the COE in compressive strength occurs in Portland cements, but its occurrence for blended cements having slag [11,21], natural pozzolan [22] and fly ash [23] is debated. The term COE has recently been used by researchers, but information is insufficient for a detailed discussion of this phenomenon in the CBMs. However, given the importance of mechanical properties and durability of concrete for long life of concrete structures, even any small reduction in the properties greatly concerns engineers.

A comprehensive review of the existing information should be available to address the lack of knowledge on the COE. The authors believe that resources such as the ACS (American Chemical Society) Publications, Emerald, Informs, Elsevier, Springer, Taylor and Francis and the Scopus database suffice to prepare a critical review and extend the knowledge. Finally, the identified gaps will be presented as suggestions for future research. This study aims to review the existing information about the COE in CBMs and provide recommendations for future research.

2. Methods of Accelerating Strength Gain

The strength-gaining rate and hardening of CBMs such as mortars and concretes in the normal curing conditions are slow. Therefore, heat treatment is commonly used in the precast concrete industry to speed up the strength-gaining rate of these CBMs. The application of heat treatment depends on the acceleration of hydration reactions [24]. Under heat treatment application, cement fineness, Portland cement composition, types and amounts of the additives used in blended cements are the main factors to determine behaviour of cements [25]. The degree and speed of cement hydration, the consequent strength of CBMs and other mechanical properties are also directly influenced by the curing process [26].

2.1. Effect of Elevated Temperature Curing on Strength Gain

Kjellsen and Detwiler [27] found that the 28-day compressive strength of samples cast and cured at 5 °C is around 80% of that cast and cured at 21 °C to 46 °C. The later-age compressive strength will be

lower with higher casting and curing temperatures. According to Newman and Choo [28], the later-age compressive strength of heat-treated CBMs is generally lower than that of standard cured specimens. It is due to the lesser rate of reaction at lower temperatures, means that mortars and concretes should be cured for a longer time to gain the desired degree of strength. Khan and Abbas [29] reported that the fast reaction at elevated temperatures provides comparatively high early-age strengths, but long-term strength and durability are commonly decreased.

Lothenbach et al. [20] reported that cement hydration is highly affected by the temperature. The higher temperature leads the hydration towards high early-age strength. At later ages, the strength of the hydrated cements at high temperature is decreased compared with those hydrated at room temperature. Sajedi and Razak [30] stated that variations in temperature caused by either heat of hydration or changes in outer environment greatly influence mechanical properties, especially the compressive strength of concrete and mortar at the early ages. Kim et al. [8] proved by experimental results that concretes and mortars subjected to high curing temperatures gain greater early-age compressive and splitting tensile strengths but lower later-age compressive and splitting tensile strengths compared with those exposed to room curing temperatures.

Namarak et al. [31] reported that an elevated curing temperature can speed up both pozzolanic and hydration reactions and achieve greater compressive strength at the early ages. However, at later ages, mortars and concretes cured at high temperature achieve compressive strength less than that of a normal curing temperature. The similar behaviour was also stated by Ezziane et al. [14] with the reduction in compressive strength when mortars were subjected to a high curing temperature with replacement of cement by natural pozzolan.

2.2. Effect of Steam Curing on Strength Gain

In steam curing, the temperature ranges from 40 °C to 100 °C, but the temperature from 65 °C to 85 °C is commonly applied [5]. Cakir and Akoz [4] stated that the steam curing has been frequently used in prefabrication because the rate of strength gain increases by increasing range of curing temperature. Yazıcı et al. [32] observed in their study that the steam curing improved 1-day compressive strength from about 10–20 MPa of concrete mixtures containing fly ash up to 40%, 50% and 60% in replacement of ordinary Portland cement (OPC) by volume. They stated that this compressive strength is sufficient to enable formwork to be removed and significantly supports the precast concrete industry. Aldea et al. [33] emphasised that air curing at room temperature and 100% RH in a controlled chamber until 28 days is the best for improved durability of concrete. However, atmospheric pressure steam curing is better than autoclaving for fast strength development.

The researchers [34,35] investigated that steam cured concrete has less compressive strength than moist cured concrete at 28 days, indicating that ordinary concrete has lower strength gaining rate after steam curing. However, the steam curing concrete having SCMs has high rate of strength development. They also reported that the hydration rate of the cement increases rapidly at elevated curing temperatures. As a result of this fast hydration, a gel is formed around each cement particle in the cement matrix. The cement hydration rate and distribution rate of hydration products are fast, but the dissolving rate of hydration products is slow, so the gel layer becomes dense and thick progressively. The diffusion of water into this thick and dense gel layer is lessened, and the hydration of unhydrated cement particles is consequently delayed. Later-age compressive strength has lower increment. Therefore, the later strength-gaining ratio will be lower if higher temperature and longer steam curing time are used.

2.3. Effect of Autoclaving on Strength Gain

Autoclaving is high-pressure steam curing in which the temperature is from 160 °C to 220 °C, and the pressure of steam is from 6 to 10 atmospheres [4]. Autoclaving is used to accelerate strength gaining of CBMs to achieve an adequate high early-age strength [5]. Aldea et al. [33] stated that under autoclave curing conditions, addition of the slag up to 50% of cement replacement in concrete does

not affect the compressive strength, whereas 75% slag replacement decreases compressive strength. In their research, autoclave curing induced the greatest reduction in compressive strength of the tested materials because of less homogeneous scattering of hydration products in the mix. The fast initial hydration resulted in the huge capillary pore distribution [36].

2.4. Effect of Hot Water Curing on Strength Gain

According to Ozkul [37], the water acts as an insulator to conserve the heat of cement hydration in hot water curing method. Thus, the hot water curing method is more effective for rapid hardening cements (e.g., Portland cement type III) than low heat cements (e.g., pozzolan cement). Chithra and Dhinakaran [38] found that hot water curing is more effective than hot air oven curing due to the more uniform and fast distribution of temperature into the specimens in hot water curing. Their test results revealed that higher strength of concrete and mortar can be achieved from few hours of thermal curing before normal curing. Moreover, the replacement of cement with 40% of ground granulated blast furnace slag (GGBFS) under hot water curing at 60 °C produced maximum compressive and tensile strengths of concrete. Sajedi and Razak [30] reported that each specified cementitious material has an optimal temperature to achieve high early compressive strength. They found that 60 °C is the optimal temperature for the slag. Authors [8,14,39,40] also reported that a constant increase in early-age compressive strength can be achieved by enhancing curing temperature up to 60 °C.

Sajedi and Razak [41] stated that among different curing methods for mortars with or without cementitious materials, only curing in the air of all specimens cannot be recommended practically. However, they recommended curing under air in room temperature for specimens initially heated in the bath water. They also observed that heating samples in water followed by air curing and heating samples in oven followed by water curing have greater compressive strengths compared with curing in water after water heating and curing in air after oven heating, respectively. Aprianti et al. [42] also investigated that the short-time initial hot water curing is a very effective technique to achieve 1-day compressive strength for the CBMs. Their experimental results showed that the hot water curing for duration of 2.5 h considerably increases compressive strength of the mortar with 50% GGBFS. However, increasing the hot water curing duration from 2.5–5 h will not affect the gain of compressive strength.

2.5. Effect of Curing Period on Strength Gain

A minimum of seven days is recommended for moist curing for concretes containing normal Portland cement, whereas a longer curing period is required to ensure the strength contribution from pozzolanic reaction for concretes comprising slow hardening cements or mineral admixtures [43]. Sajedi and Razak [30] concluded that time period of heating is crucial for gaining high early-age strength. They reported that 20-h heating time is the optimum duration for slag used in their research. Moreover, compressive strength will increase as heating time duration increases towards the optimum, and heating of mortar more than optimum heating time will not increase the early-age strength of mortar.

Sajedi and Razak [41] concluded from their research that the duration of curing must be prolonged to 14 days when the cement has SCMs such as silica fume, fly ash and slag because of the slow hydration reactions between calcium hydroxide and SCMs. Kim et al. [8] found that for Portland cement type I concrete, the compressive strengths increases at one and three days with increasing curing temperatures from 10–50 °C. However, the seven-day compressive strength decreases up to 5.5% with increase in curing temperatures from 23–35 °C, and the 28-day compressive strength reduces up to 5% with increase in curing temperatures from 10–50 °C.

3. COE and Mechanism

CBMs exposed to elevated curing temperatures at the early ages attain higher early-age compressive strength, but a loss of ultimate strength may occur at later ages because of the unsuitable arrangement of hydrates during fast hydration. This phenomenon is called COE [44–46]. The scanning electron microscope (SEM) images of cement paste cured at room temperature and elevated temperature of

60 °C at the ages of three and 28 days were studied by Teixeira et al. [47] as shown in Figures 3 and 4, respectively. From the images, they observed more uniformly distributed hydration products in the cement pastes cured at room temperature than in the cement pastes cured at 60 °C. The observed that cement paste cured at room temperature had porous microstructure with uniformly distributed capillary pores at early age of three days. This porous microstructure densified due to curing at elevated temperature and an increase in compressive strength of cement paste was observed. A dense rim of hydration product, generally composed of calcium silicate hydrate (C-S-H), was formed around cement particles cured at elevated temperature of 60 °C at the ages of three and 28 days. The concluded that increase in heterogeneous phases in microstructure of cement paste cured at elevated temperature might be the reason of compressive strength reduction at the age of 28 days.

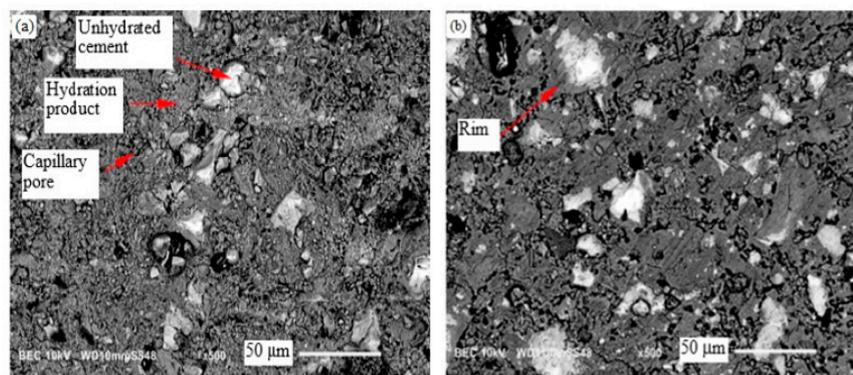


Figure 3. SEM images of cement (ordinary Portland cement (OPC)) paste at the age of three days, (a) cured at room temperature, and (b) cured at 60 °C. Adapted with permission from [47], MDPI, 2016.

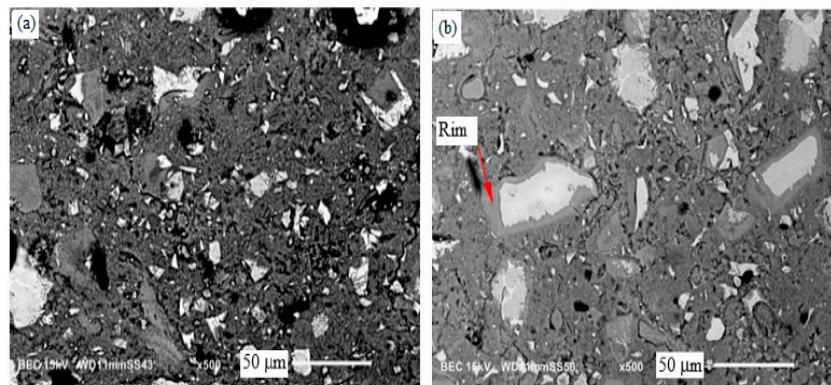


Figure 4. SEM images of cement (OPC) paste at the age of 28-days, (a) cured at room temperature, and (b) cured at 60 °C. Adapted with permission from [47], MDPI, 2016.

According to the research reports [18,48], the detection of COE depends on the range of temperature, duration of testing, type of cement used, proportions of the mineral additions and mineralogical composition of the cement used. Reports from the researchers [49,50] showed that an elevated temperature speeds up the binder hydration process and increases the quantity of formed hydration products (for example calcium-silicate-hydrate). Moreover, accelerated curing temperature increases strength gain at initial ages by faster precipitation of hydration products and refining pore structure of CBMs. According to several reports [49,51–54] COE is caused by harder and thicker formation of hydrated shells, low porosity hydration products round cement grains, slow diffusion of hydration products in secondary cement hydration reaction and non-uniform scattering of reaction products in pores of the hardening cement paste at elevated temperature. Kim et al. [55] reported that COE can appear even after seven days. Kjellsen et al. [56] reported that the non-uniform distribution of hydration products results in porosity of bulk cement paste. Additionally, speedy temperature increase

during early ages can increase inside stresses that surpass tensile strength of immature concrete, leading to increased porosity, cracking and decreased potential strength.

According to the reports [11,49,52], the rate of hydration and concrete strength increase rapidly by increasing early curing temperature, but porosity increases and micro cracks appear because of non-homogeneous distribution of hydration products and variance in coefficients of thermal expansion of the concrete's ingredients, which finally leads to reduced compressive strength at the later ages. Aldea et al. [33] stated that the hydration products do not have sufficient time for their uniform distribution within the pores of hardening CBMs at elevated temperature. Consequently, hydrated shells with low porosity are formed near the cement particles by ending further hydration. This non-uniform scattering of the hydration products causes large capillary pores by decreasing later-age compressive strength. Mindess and Young [57] also reported that steam curing makes the COE by causing great reduction in compressive strength because of less homogeneous scattering of hydration products in the paste due to fast initial hydration.

Researchers [41,58] reported that the major cause of the strength reduction at later ages is the shortage of the inner water present in samples to complete hydration. In a common water to cement ratio, internal water is present and sufficient for hydration for the duration of 1–28 days. However, after 28 days, this amount of water may be reduced and become insufficient for further hydration, which will result in strength loss at later ages. Reports by the authors [27,49,50] stated that the lesser hydration reaction of anhydrous cement is also due to delaying effect of the shell on distribution of hydrates in the secondary cement hydration reaction.

4. Effect of Different Types of Portland Cements on COE Phenomenon

According to Neville [26], all Portland cements have the same constituents. However, types of Portland cement differ only because of the differences in the proportions of these constituents. Constituents of C_3S and C_2S form 70–80% of all Portland cements. Strunge et al. [59] stated that Portland cements with high alite (C_3S) and tricalcium aluminate (C_3A) contents such as Portland cement type III develop high early-age strength along with high early heat. Cements with low alite (C_3S) and tricalcium aluminate (C_3A) contents such as Portland cement types IV and V have slow strength and heat development. Alkali oxides (Na_2O and K_2O) of Portland cement also increase the compressive strength to the period of seven days but reduce it at the later ages.

All types of Portland cements as well as blended cements can be used in concretes cured by steam curing at atmospheric pressure or by the accelerating heat methods [60]. According to Mehta and Monteiro [43], Portland cement type III has higher fineness and hydrates more quickly compared with other Portland cement types at ordinary temperature. Therefore, concretes containing Portland cement type III will have a higher strength at any given water to cement ratio and early ages of hydration as one, three and seven days. Popovics [61] described that the early-age strengths can be intensely increased during heat curing using cements with SO_3 contents somewhat higher than usual. Portland cement type IV is used for minimum rate and quantity of heat generated from hydration. It gives strength at lower rate compared with other types of Portland cements. Portland cement type V gains strength more slowly than Portland cement type I.

5. Effect of Cementitious Materials on COE Phenomenon for Prolonged Curing

5.1. Ordinary Portland Cement (OPC)

Sajedi and Razak [41] used various mixes of OPC mortars with different curing conditions in their research. They observed COE in compressive strengths of tested mortars at 56 and 90 days when temperature of water curing was 60 °C for a period of 20 h. They used specific names for their mortar mixes and curing regimes. The detail of mix names, curing conditions, proportions of the mortars and range of COE detected are given in Table 1. The age at which COE occurred and the percentage of COE were determined from the graphical representation of their obtained results.

Table 1. Mix proportions of ordinary Portland cement (OPC) mortars in one batch, curing conditions and crossover effect (COE) records.

Number	Name of Mix	Curing Condition	Age at Which COE Occurred	COE (%)
1	OM-WH-ac	Water bath heated followed by air curing under room temperature	90 days	7.14
2	OM-WH-wc	Curing at water bath heated and then water curing	90 days	5.13
3	OM-OH-ac	Oven heated curing and then air curing under room temperature	56 days	4.30
4	OM-OH-wc	Oven heated curing and then water curing	90 days	4.70
5	OM-G6/WH-ac	Water bath heated followed by air curing under room temperature	56 days	5.0

The major cause of the strength reduction at later ages is shortage of inner water in samples to complete hydration reaction. For 1–28 days, the internal water is present and sufficient for hydration. However, after 28 days, the water is insufficient for hydration due to consumption, which causes strength reduction in mortar specimens [62]. The loss in strength of OPC mortars also depends on fineness of cement, chemical composition of products, temperature and regime of curing. The early curing temperature has a vital effect on compressive strength and may decrease or increase it at long curing periods [41].

Garcia and Sharp [16] used two samples of OPC in their research. They observed loss in compressive strengths in the range of 4–13% of these samples at 360 days as a result of hot water curing at 40–60 °C for 24 h. Kim et al. [8] observed that concrete exposed to accelerated curing temperature at initial age gains higher initial age but lesser later-age compressive strength. They found a loss of 4.90% in compressive strength at seven days as compared to two days in Portland type V cement concrete due to hot water curing at 50 °C for 24 h.

5.2. Blast Furnace Slag, Fly Ash and Silica Fume

Sajedi and Razak [30] used different OPC-slag mortars in their research with 0%, 40% and 50% slag replacement with OPC by mass. They studied the influence of temperatures of 50 °C, 60 °C and 70 °C on compressive strengths of these mortars for up to 90 days. They found that hot water curing at a temperature of 60 °C for 20 h period is the most effective to enhance the early age strengths of all the mortars. Therefore, they selected 60 °C as the optimum temperature. They observed COE of 2.2% in OPC-slag mortar with 50% replacement of slag with OPC by mass at 56 and 28 days. This COE appeared as a result of 60 °C hot water curing for 20 h. However, they did not observe any COE in other two Portland cement slag mortars with 0% and 40% replacement of slag with OPC by mass for up to 90 days.

Bougara et al. [63] used Portland cement–slag mortars with various percentages of slag as 0%, 30% and 50% in their study. They observed a COE of about 3.7% in Portland cement slag mortar with 30% slag at 28 days when samples were initially water cured at 60 °C for 20 h. Schindler [64] suggested that the addition of higher percentages of slag as replacement with OPC in mortars tends to reduce the occurrence of COE. Verbeck [46] explained that curing at elevated temperature resulted in a non-homogeneous scattering of the hydration products in microstructure. However, at lower temperature, the hydration products have adequate time period to precipitate and diffuse more homogeneously throughout the bulk cement matrix.

Wade et al. [65] used 13 concrete mixtures to examine the effect of OPC type I and III, water to CMs ratios of 0.37, 0.41, 0.44 and 0.48 and various types and dosage of SCMs. They used class F and C fly ashes at replacement values of 20% and 30%, respectively. They used GGBFS at replacement levels of 30% and 50% and silica fume at a replacement level of 10% in a ternary mix with 20% class F fly ash.

They made three batches of each mix as cold batch (4 °C and 13 °C for 24 h), hot batch (32 °C and 41 °C for 24 h) and control batch (20 °C and 23 °C). They measured compressive strengths at 24 and 48 h and seven, 14 and 28 days. They observed that hot batches achieved strength rapidly, but they had lower later-age strengths compared with control and cold batches. The cold batches achieved strength slowly but sustained to achieve strength at later ages. They concluded that all control mixtures exhibited COE ranging from 7–12% at seven and 16 days. No COE was observed in case of Portland cement type I mixtures with 20% and 30% class F fly ash having w/b of 0.41. The COE for mixtures with 20% class C fly ash for Portland cement type I mixture with w/b ratio of 0.41 was delayed but not completely removed. The replacement of 30% class C fly ash for the type I cement mixture with 0.41 w/b ratio excellently eliminated COE. The replacement of cement up to 30% or 50% with GGBFS for cement type I mixture with 0.41 w/b ratio showed strength losses of 6–17% for hot batches in some cases. Changing the cement type I to cement type III for cement type I mixture with 0.44 w/b ratio marginally increased COE but significantly reduced the time at which crossover occurred from 16 to 4 days. The cement replacement with 20% class F fly ash and 10% silica fume for type I cement mixture with w/b ratio of 0.44 increased strength loss from 7–31% and reduced the time at which crossover take place from 16 to 5 days. The type III cement mixture with 0.37 w/b ratio had crossover of 17% which occurred within less than two days after mixing for hot batches. The ternary blended prestressed concrete mixture had crossover of 23%.

6. Effect of Cementitious Materials on COE Phenomenon Due to Different Initial Curing Temperatures

6.1. Blast Furnace Slag

Castellano et al. [15] used Portland cement (OPC) with GGBFS in their investigation. They studied the effect of curing temperature on hydration process and the phenomenon of COE. Two blast-furnace cements, BFS40 and BFS80, were made by replacement of OPC with 40% and 80% slag by mass, respectively. They found that for all test mixtures (OPC, BFS40 and BFS80) compressive strength decreased when w/b ratio increased, as shown in Figure 5A–C, respectively. All w/b ratios had 20–60 °C increase in the water curing temperature, and loss in compressive strengths was observed in OPC and BFS40 pastes at 7–365 days. Moreover, compressive strengths at early ages are lower at lower water curing temperatures for all w/b ratios.

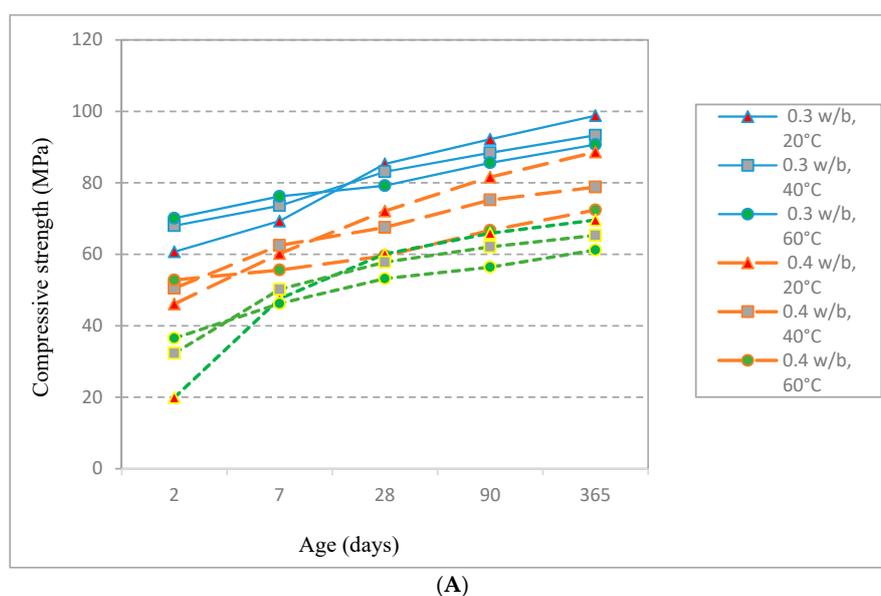


Figure 5. Cont.

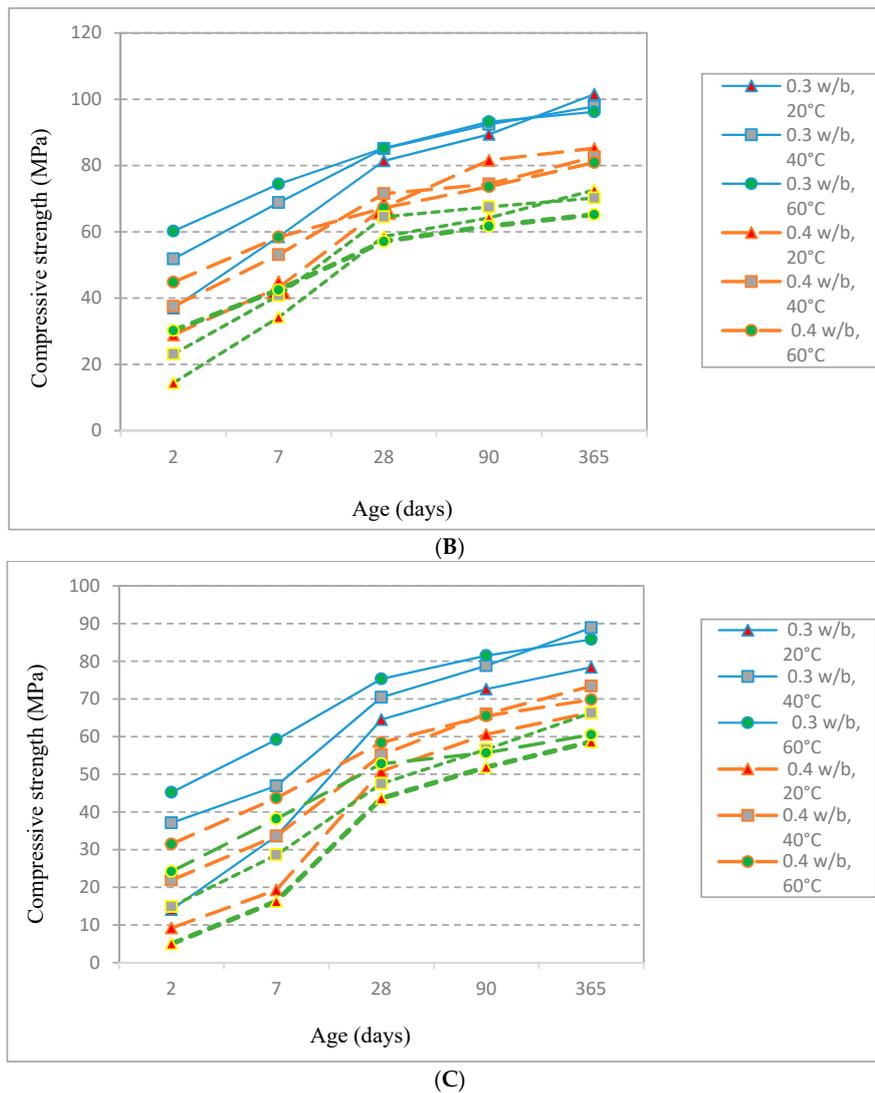


Figure 5. Compressive strength (MPa) at various water curing temperatures and ages for (A) OPC; (B) BFS40; (C) BFS80 pastes.

The losses in compressive strengths (COE %) and age of COE for OPC and BFS40 pastes were calculated from the original results provided by the researchers (Table 2). However, no COE was observed for BFS80 at all w/b ratios with 20–60 °C increase in water curing temperature up to 365 days.

Ezziane et al. [66] described the effect of increasing curing temperature from 20–60 °C on the long-term strength of OPC and two slag blended cement mortars (BFS30 and BFS50). They used 30% and 50% slag in replacement of OPC by mass. They found that the long-term strengths of slag cements are mostly greater than those of OPC for all replacement levels. Moreover, the long-term strengths of OPC and slag blended cement mortars were decreased with increasing curing temperature from 20–60 °C.

Figure 6 shows the loss in compressive strengths at later ages in OPC and slag blended cement mortars with 20–60 °C increase in water curing temperature. These losses in compressive strengths of Portland cement and slag blended cement mortars were calculated from the actual data obtained by researchers (Table 3). From the results in Table 3, it can be concluded that the amount of COE increases with age and it will be higher at later ages.

Table 2. COE records with 20–60 °C increase in water curing temperature at ages up to 365 days for ordinary Portland cement (OPC), BFS40 and BFS80 pastes.

Paste Name	w/b Ratio	Age at Which COE Occurred	COE (%)	
OPC paste	0.3	28	7.2	
		90	7.2	
		365	8.2	
	0.4	7	7.6	
		28	17.3	
		90	18.3	
		365	18.3	
	0.5	7	2.9	
		28	11.5	
90		14.4		
BFS40	0.3	365	5.2	
		0.4	28	0.1
			90	9.8
	365		5	
	0.5	28	2.6	
		90	3.9	
		365	10.2	
	BFS80	No COE was observed at all w/b ratios up to 365 days		

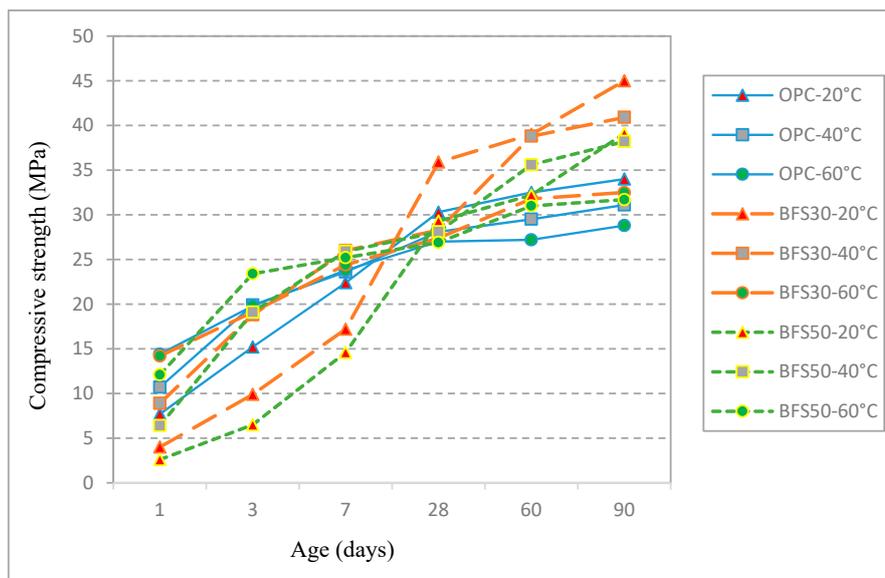


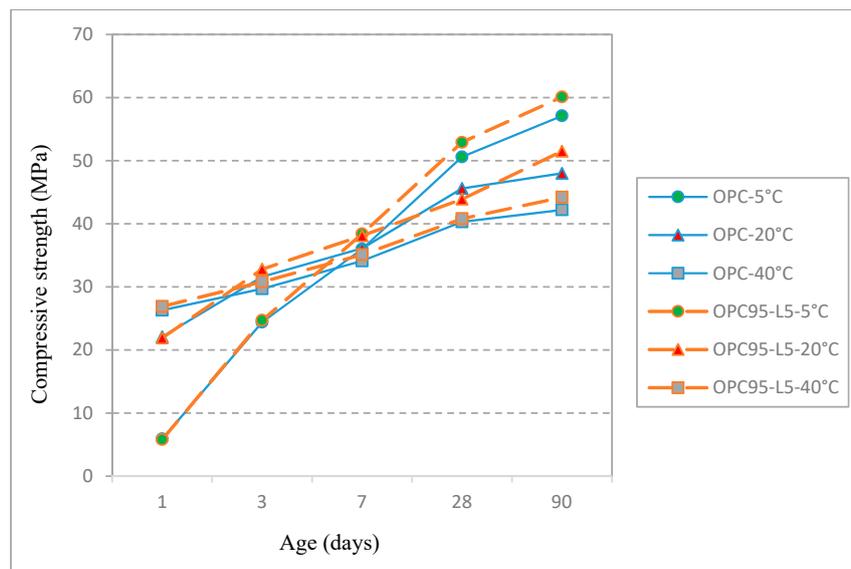
Figure 6. Compressive strength (MPa) at various water curing temperatures and ages for OPC and slag blended cement mortars (BFS30 and BFS50).

Table 3. COE records with 20–60 °C increase in water curing temperature at ages up to 90 days for OPC and slag blended cement mortars.

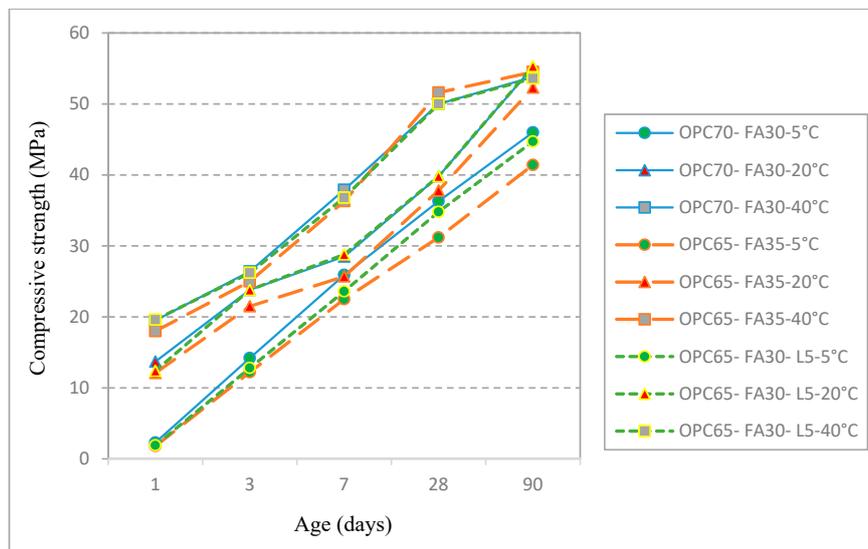
Paste Name	% Age Replacement	Age at Which COE Occurred	% Age of COE
OPC	0	28	10.9
		60	16.3
		90	15.3
BFS30	30	28	23.7
		60	18.5
		90	27.8
BFS50	50	28	18.2
		60	3.7
		90	18.9

6.2. Ternary Blended Cements

Weerdt et al. [17] used total five pastes, one OPC paste and four composite cement pastes (OPC95-L5, OPC70-FA30, OPC65-FA35 and OPC65-FA30-L5) with limestone powder (L) and fly ash (FA) in their study. They monitored the hydration of these cement pastes at three various water curing temperatures of 5 °C, 20 °C and 40 °C for a period up to 180 days. They described that loss in the compressive strength occurs at later ages because of increasing values of initial curing temperatures. Figure 7A,B display that increasing initial curing temperature from 5–40 °C resulted in loss in compressive strength of about 5.3%, 20.4% and 26.1% for OPC paste and 8.6%, 22.9% and 26.5% for composite cement paste containing OPC and lime stone powder at 7, 28 and 90 days, respectively. However, loss in compressive strengths was not observed for mixtures containing fly ash.



(A)



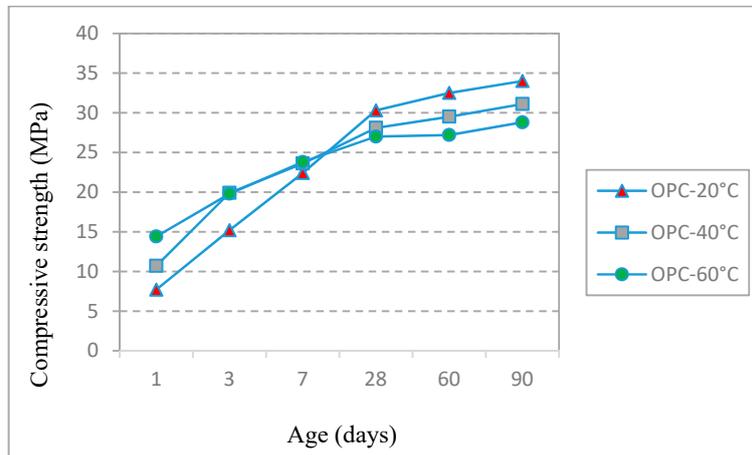
(B)

Figure 7. Compressive strengths (MPa) of (A) OPC and OPC95-L5; (B) OPC70-FA30, OPC65-FA35 and OPC65-FA30-L5 for water curing temperatures of 5 °C, 20 °C and 40 °C.

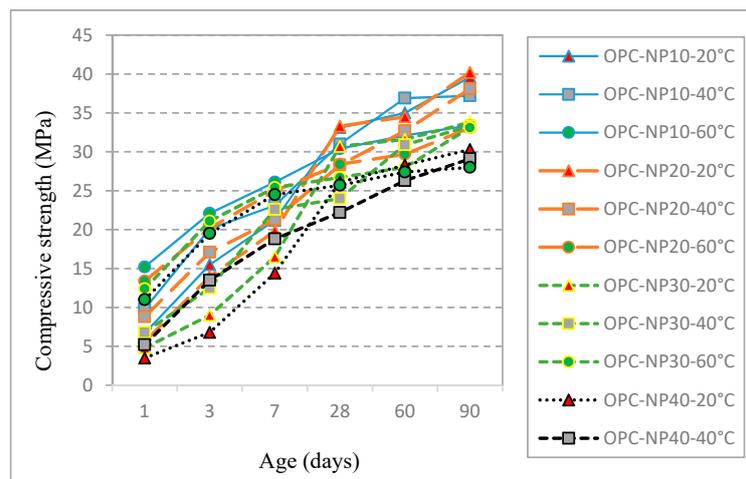
6.3. Natural Pozzolan and Limestone Powder

Ezziane et al. [66] stated the effect of increasing curing temperature from 20–60 °C on the long-term strength of OPC, natural pozzolan and limestone powder blended cement mortars. They used 100%

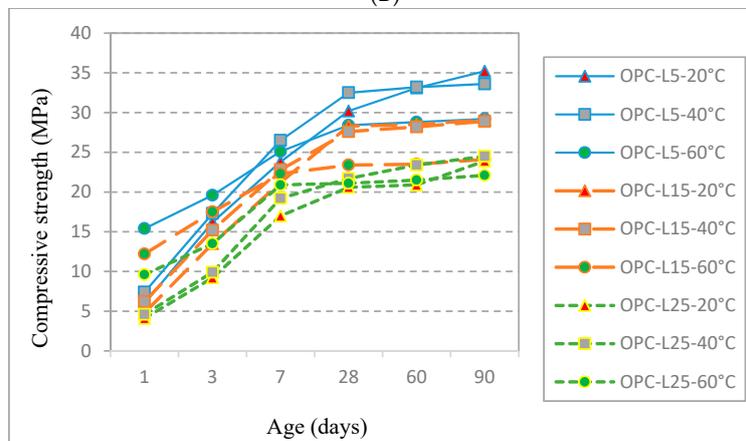
OPC, 10% (OPC-NP10), 20% (OPC-NP20), 30% (OPC-NP30) and 40% (OPC-NP40) natural pozzolan and 5% (OPC-L5), 15% (OPC-L15) and 25% (OPC-L25) limestone powder in replacement of OPC by mass. They observed that at replacement levels of 10%, 20% and 30%, the long-term strengths of pozzolan blended cement mortars decreased with increasing curing temperature from 20–60 °C and were greater than those of OPC mortar. For limestone powder blended cement mortars, the long-term strengths for 25% replacement level were less than OPC mortar and showed reduction in strength only at 90 days.



(A)



(B)



(C)

Figure 8. Compressive strength (MPa) at various water curing temperatures and ages for (A) OPC; (B) natural pozzolan blended cement; (C) limestone powder blended cement mortars.

Figure 8A–C show the loss in compressive strengths at later ages in Portland cement, natural pozzolan and limestone powder blended cement mortars with 20–60 °C increase in the water curing temperature, respectively. These losses in compressive strengths of Portland cement, natural pozzolan and limestone powder blended cement mortars are shown in Table 4.

Table 4. COE records with 20–60 °C increase in water curing temperature at ages up to 90 days for OPC, natural pozzolan and limestone powder blended cement mortars.

Paste Name	Age at Which COE Occurred	COE (%)
OPC	28	10.9
	60	16.3
	90	15.3
OPC-NP10	28	8.2
	60	8.3
	90	15.7
OPC-NP20	28	14.7
	60	13.9
	90	17.7
OPC-NP30	28	13
	60	11.4
	90	2.1
OPC-NP40	28	1.5
	60	3.2
	90	17.6
OPC-L5	28	6
	60	13
	90	17.1
OPC-L15	28	17.3
	60	17.5
	90	17.2
OPC-L25	90	7.5

7. Materials Controlling COE Phenomenon

The existing literature does not contain sufficient information about COE phenomenon in CBMs. Therefore, few materials have been mentioned to decrease or control the loss in compressive strengths at later ages at high curing temperatures. Castellano et al. [15] found that COE in compressive strength was not observed for BFS80 (by replacing Portland cement with 80% GGBS by mass) in temperature range of 20–60 °C up to 365 days.

Wang [67] stated that the compressive strength will increase by replacement of slag powder after 28 days. Moreover, slag powder will significantly increase the later-age compressive strength. Aldea et al. [33] suggested that 25% replacement of slag is optimum for the strength development with steam and normal curing. Autoclaving has no effect on the strength developed by replacing 50% slag with Portland cement, whereas 75% slag replacement with Portland cement reduces compressive strength in all types of curing methods. Normal curing methods provide higher compressive strength than the accelerated curing methods up to 50% replacement of slag with OPC.

Kim et al. [8] stated that Portland type V cement concretes do not undergo COE compared with Portland type I cement concretes up to curing temperature of 50 °C for 28 day because the rate of hydration of Portland type V cement concrete is lower than that of Portland type I cement concrete. Thus, the COE of Portland type V cement concrete is postponed. Ezziane et al. [14] used blended cement mortars with different percentages of natural pozzolan replacement with OPC. They studied their behaviour under water curing temperatures of 20 °C, 40 °C and 60 °C for up to 90 days. They detected

no COE in compressive strength of blended cement mortars at curing temperatures of 20 °C, 40 °C and 60 °C due to pozzolan in mixtures. Its presence decreases negative influence of rise in temperature. The optimal replacement rate of OPC by natural pozzolan is approximately 15% for normal room temperature curing and 20% for accelerated temperature curing of 40 °C and above.

8. Conclusions

This paper presents a detailed literature review about the COE phenomenon in CBMs due to accelerated initial curing. The basic concept and mechanism of COE, various methods of accelerating for strength gain at the early ages and reasons for strength decrease at the later ages of CBMs, effect of cementitious materials on COE and materials controlling COE have been discussed in detail. The following conclusions are drawn from this study.

- (1) Pure and blended cement products subjected to accelerated curing temperatures show faster hydration and non-homogeneous scattering of hydration products that may result in the COE of their compressive strengths.
- (2) The COE in compressive strengths of pure and blended cement products depends on the initial curing temperatures from lower to higher values and the amount of internal water present for hydration.
- (3) The detection of the COE depends on the duration of testing, loss of water loss, temperature and techniques of curing, porosity, type of cement used, proportions of mineral additions, mineralogical characteristics of mineral additions and specific surface and composition of cement used.
- (4) The COE in pure and blended cement products can appear even after 7 days onwards.
- (5) The compressive strength loss at later ages in accelerated cured specimens ranges from 2.2% to 31% at 40–60 °C for accelerated prolonged curing.
- (6) The COE due to accelerated curing can occur at curing temperature as low as 40 °C.
- (7) The COE can be controlled using slag blended cement with 80% replacement of GGBFS by OPC, 25–50% addition of slag powder in blended cement mortars, type V Portland cement concrete under an accelerated curing temperature of up to 50 °C as well as blended mortars with different percentages of natural pozzolan.

9. Recommendations for Future Studies

The COE in CBMs has a crucial role due to importance of the mechanical properties and durability of concrete for long life of concrete structures. Because of the lack of detailed investigation on COE, further studies are required to understand this phenomenon in CBMs. The following are some recommendations for better understanding of the COE phenomenon.

1. COE phenomenon was studied mainly on CBMs containing pure OPC or OPC-slag blended cements. Further studies on the CBMs incorporating other types of SCMs are required.
2. The mechanism of COE phenomenon is still unclear. A quantitative study in terms of microstructure and chemistry of materials exhibiting COE may help to understand this phenomenon.
3. The existing data of the accelerated curing is mainly for short time. While, COE may happen at later ages. In addition, the most elevated temperatures reported in the literature for curing of CBMs are in the range of 40–60 °C. Therefore, studies are required to investigate the effect of elevated temperatures more than 60 °C for long terms.

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Abbreviations

CBMs	cement-based materials
COE	crossover effect
SCMs	supplementary cementitious materials

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